Oxide-Semiconductor-Based Thin-Film Electronic Devices

A thesis submitted to The University of Manchester for the degree of
Doctor of Philosophy
in the Faculty of Engineering and Physical Sciences

2016

Jiawei Zhang

School of Electrical and Electronic Engineering
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Abstract

Oxide semiconductors have been envisaged to find applications in ubiquitous flexible electronics in daily life such as wearable electronic gadgets to offer novel user experiences. However, one of the bottlenecks to realise these applications is a lack of oxide-semiconductor components capable of wireless communications. As Bluetooth and Wi-Fi are the two dominant communication interfaces, fast enough front-end rectifiers must be developed to operate at their gigahertz (GHz) transmission frequencies. Furthermore, despite of significant developments of n-type oxide semiconductors in the last decade, widespread flexible electronics also requires high-performance p-type oxide semiconductors for use in complementary logic circuits. The objectives of this dissertation are to develop high quality Schottky barriers, achieve GHz speed Schottky diodes on rigid and flexible substrates, evaluate the noise properties of the Schottky diodes, develop p-type oxide semiconductor using sputtering technology, elucidate the hole transport mechanism in p-type transistors, and demonstrate their potential applications such as radio receivers, complementary inverters and ring oscillators.

First, indium gallium zinc oxide (IGZO) Schottky diodes were fabricated by using radio frequency magnetron sputtering. The oxygen content at the metal-IGZO interface was found to have a profound effect on the electrical performance. By introducing 3% O2 during the deposition of Pt or IGZO, the diodes exhibited excellent electrical properties without requiring any annealing treatment, thus allowing for the realisation of flexible IGZO Schottky diodes. The high-frequency properties of Pt-IGZO Schottky diodes on glass substrates were optimised by testing a range of IGZO thicknesses and diode active areas. The achieved highest cut-off frequency was beyond 20 GHz, which is to the best of our knowledge the fastest oxide-semiconductor device to date. On flexible substrates, the diodes also showed cut-off frequencies up to 6.3 GHz, well beyond the critical benchmark speed of 2.45 GHz for typical wireless communications. In order to assess the feasibility of using IGZO Schottky diodes in practical applications, measurements were taken to discern their low-frequency noise properties. In the as-deposited diodes, logarithmic dependence of the noise spectral density on the applied bias was observed, revealing that the dominant noise was generated in the space-charge region at low biases and in the series-resistance region at high biases, respectively. After annealing the diodes, very different noise mechanism was observed and the interface-trap-induced noise dominated the noise spectra. As one of the most promising p-type oxide semiconductors, SnO was also studied at low temperatures in this thesis. The experiment revealed that hole-transport mechanism was governed by either band conduction or variable range hopping in different temperature ranges. Finally, the potential for fully oxide-based electronics was demonstrated by an amplitude-modulation radio receiver comprising of an IGZO Schottky diode as the demodulator and a complementary ring oscillator based on IGZO and SnO transistors.
Declaration

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Acknowledgement

First and foremost, I would like to express my sincere gratitude to my supervisor, Prof. Aimin Song, for his supervision, support, and encouragement throughout my studies. He has been a great boss, and a wonderful mentor. I could never have achieved all I have without him.

Additionally, I would like to thank Dr. Leszek Majewski and Mr. Mal. McGowan for all the help with the experiments. I have learnt a lot from them about materials, electronics and vacuum systems.

Great appreciation also goes to Jidong Jin, Arun K. Singh, Linqing Zhang, and Yasaman Alimi for patiently guiding me through the experiments and the data analysis. Also to my office mates, Xiaochen Ma, Joshua Wilson, Gregory Auton, Sheida Faraji, Chun Chieh Lee, and Seonghyun Park for the great time, and all the interesting discussions. I would also like to thank our collaborators for helping me through some high-frequency characterisations and involving me with the project on the amazing p-type tin oxide. They are Dr. Qian Xin, Dr. Xijian Zhang, Yiming Wang, Hanbin Wang, He Li, Yunpeng Li, and Jia Yang. I do appreciate that.

I’m grateful to the School of Electrical and Electronic Engineering for providing me such a good opportunity to study here. I also wish to express my thanks to Dr. Geoff Baines for suggesting me presenting the dissertation in the alternative format.

Especially, I must thank one of my middle school teachers, Mrs. Shuya Huang. My life would have been different without her kind guidance.

Finally, I am heartily thankful to my parents, Yanchun Zhang and Yunxia Li, and my wife, Shaoheng Li. Their constant love and supports have always encouraged me during my study.
List of Publications

- Analysis of carrier transport and band tail states in $p$-type tin monoxide thin-film transistors by temperature dependent characteristics
  
  **J. Zhang**, X. Kong, J. Yang, Y. Li, J. Wilson, J. Liu, Q. Xin, Q. Wang, and A. Song.
  
  *Appl. Phys. Lett.* 2016. Accepted

- High performance InGaZnO-based Schottky diodes fabricated at room temperature
  
  L. Yan, Q. Xin, L. Du, **J. Zhang**, Y. Luo, Q. Wang, and A. Song.
  

- Graphene ballistic nano-rectifier with very high responsivity
  
  

- High performance Schottky diodes based on IGZO
  
  **J. Zhang**, Q. Xin, and A. Song.
  

- Room temperature processed ultrahigh-frequency indium-gallium-zinc-oxide Schottky diode
  
  **J. Zhang**, H. Wang, J. Wilson, X. Ma, J. Jin, and A. Song.
  

- Effects of annealing conditions on resistive switching characteristics of SnOx thin films
  
  

- Improving photoelectrochemical performance of highly-ordered TiO2 nanotube arrays with cosensitization of PbS and CdS quantum dots
X. Zhang, M. Zeng, J. Zhang, A. Song, and S. Lin.  
*RSC Advances*, vol. 6, pp. 8118-8126, 2016.

- Flexible indium-gallium-zinc-oxide Schottky diode operating beyond 2.45 GHz  
  J. Zhang, Y. Li, B. Zhang, H. Wang, Q. Xin, and A. Song.  
  *Nat Commun*, vol. 6, 2015.

- Low-frequency noise properties in Pt-indium gallium zinc oxide Schottky diodes  
  J. Zhang, L. Zhang, X. Ma, J. Wilson, J. Jin, L. Du, Q. Xin, and A. Song.  
Chapter 1  Introduction

1.1. Motivation
The development of flexible thin-film electronics has accelerated in the last few years, with applications ranging from thin-film solar cells to complementary electronic circuits. Metal oxide semiconductors are a popular choice for such applications because of their low cost, mechanical flexibility, high optical transparency, good reliability and low environmental impact. The total market of flexible thin-film electronics is expected to grow from £18.65 billion in 2016 to £48.05 billion in 2026 [1]. Among these, stretchable electronics, logic and memory devices, and thin-film sensors have huge growth potential [1] and will promote the development of oxide-semiconductor-based thin-film electronics [2, 3].

Since the first demonstration of flexible amorphous indium gallium zinc oxide (IGZO) thin-film transistors (TFT) in 2004 [4], amorphous oxide semiconductors have received much attention due to their superior electrical characteristics. These materials complement the traditional semiconductors not only in basic applications but also in the emerging areas such as flexible electronics, “smart” paper, and wearable technologies. The major advantages of metal oxide semiconductors include their low fabrication temperature, variable deposition methods, high uniform surface and flexibility [3]. Combining these properties with high electron mobility removes many obstacles to the use of oxide semiconductors in industry. Furthermore, due to their large band gap, metal oxide semiconductors have a high optical transmittance at visible wavelengths allowing their incorporation into optoelectronic devices such as photosensors and light emitting diodes [5].

Amorphous IGZO has already been adopted as the channel material in backplane transistors in flat-panel displays [6] where a transistor switching speed of 200 Hz is enough. In communication systems, transistors are mostly used in logic circuits which are allowed to be clocked at a low frequency. However, the front-end rectifiers in transceiver chips must always operate at the transmission frequencies such as 935 MHz to 1.88 GHz for cellular communications, around 2.4 GHz for typical IEEE 802.11b/g/n Wi-Fi channels and Bluetooth, around 1.5 GHz for GPS, 3.8 GHz for 4G LTE band and 5 GHz for 802.11a/h/j/n/ac Wi-Fi channels.
In order to achieve such high-speed operations by using metal oxide TFTs, it is necessary to reduce the device dimensions such as channel lengths and overlapping areas between source/drain and gate electrodes to the sub-micron scale [7-10]. So far, the highest frequency obtained by IGZO TFTs is just 0.384 GHz [8], which is still much lower than many of the wireless communication frequencies. To circumvent this, high-frequency Schottky diodes based on metal oxide semiconductors are required. As Schottky diodes are majority carrier devices, the absence of minority carriers contributes to a much shorter reverse recovery time compared with p-n diodes, resulting in a higher cut-off frequency [11]. However, there are only a few reports focused on IGZO Schottky diodes [5, 12-16],

Besides, lack of high-performance p-type oxide semiconductors also limits the development of fully oxide-based large-area complementary electronics [3]. Recently, tin monoxide (SnO) has emerged as a promising p-type oxide semiconductor [17]. Compared with copper dioxide, CuO₂, and organic semiconductors, SnO shows good air stability and a relative high mobility [3]. However, the on/off ratio of SnO TFTs is still quite low, which limits their potential applications. Understanding the carrier transport mechanism in SnO may help to improve the electrical characteristics.

This thesis studies IGZO based Schottky diodes, p-type SnO TFTs, oxide-semiconductor-based complementary circuits, and their potential applications. Methods to achieve high-frequency IGZO Schottky diodes with low-temperature fabrication processes are demonstrated on glass and flexible substrates. The carrier transport mechanisms in SnO TFTs have been elucidated, leading to a deeper understanding of p-type conductivity in SnO. Applications of oxide-semiconductor-based complementary circuits and Schottky diodes have also been demonstrated.

1.2. State of the Art

1.2.1. N-type Metal Oxide Semiconductors

The first metal oxide semiconductor TFT, using tin dioxide (SnO₂), was discovered in 1964 [18], and the electrical performance was evaluated in 1970 [19]. In 1968, zinc oxide, ZnO, was also used to fabricate n-type TFTs [20]. However, due to the poor electrical characteristics, there were only a few reports focused on metal-oxide semiconductors until 1990s when huge progress was made in the research of ZnO [21-24]. The mobility of
n-type ZnO was found to be more than 1000 cm$^2$V$^{-1}$s$^{-1}$ in 2004 by using metal organic vapour phase epitaxy [25] and 440 cm$^2$V$^{-1}$s$^{-1}$ in 2006 by using laser molecular-beam epitaxy [26] at room temperature (RT). Remarkably, in 2013, radio-frequency sputtered polycrystalline ZnO TFTs showed a mobility higher than 50 cm$^2$V$^{-1}$s$^{-1}$ [27]. However, it was revealed that for polycrystalline ZnO TFTs the electrical performance is not stable in the atmosphere and the mobility is limited by the grain boundaries [6, 28]. These disadvantages limited the application for oxide semiconductors until the emergence of IGZO.

In 2003, single-crystalline IGZO was firstly used as an n-type channel in transparent top-gate TFTs [29]. The IGZO layer was deposited on the (111) yttria-stabilized zirconia (YSZ) substrate by using pulsed laser deposition (PLD). The PLD deposited hafnium oxide (HfO$_2$) and indium tin oxide (ITO) were used as the gate dielectric layer and source/drain electrodes, respectively. It was reported that the first IGZO TFT achieved an outstanding field-effect mobility of around 80 cm$^2$V$^{-1}$s$^{-1}$, an on/off ratio of 10$^6$ and a turn-on voltage, $V_{on}$ of -0.5 V. However, such fabrication process required a high temperature of 1400 °C, which is not suitable for mass production. One year later, flexible transparent IGZO TFTs fabricated at RT was presented by using PLD [4]. The saturation mobility of these amorphous IGZO TFTs could reach up to 9 cm$^2$V$^{-1}$s$^{-1}$. Even after bending, the on/off ratio was still larger than 10$^3$, demonstrating that IGZO is a very promising material in flexible electronics [6].

Table 1-1. The electrical properties of different semiconductors.

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>≤ 1.0</td>
<td>50-100</td>
<td>0.1-10</td>
<td>1-100</td>
</tr>
<tr>
<td>Cost/yield</td>
<td>Low/high</td>
<td>High/low</td>
<td>Low/high</td>
<td>Low/High</td>
</tr>
<tr>
<td>Stability</td>
<td>Low</td>
<td>High</td>
<td>Low in air</td>
<td>High</td>
</tr>
<tr>
<td>Process Temp. (°C)</td>
<td>150-350</td>
<td>250-550</td>
<td>RT</td>
<td>RT-350</td>
</tr>
</tbody>
</table>

In order to optimise the performance, the chemical stoichiometry in the IGZO has been studied. The optical gap energy of IGZO increased with the content of Ga and the turn-on voltage moved to the positive value with an increasing Ga/In ratio [33]. However, the high atom ratio of Ga would cause an increase in the barrier height which may raise the contact resistance between electrodes and IGZO. An excess In can be introduced to improve the mobility and the on/off ratio [34]. The field-effect mobility highly depended on the content
of In, and the threshold voltage relied on the Ga concentration [3, 35].

As shown in Table 1-1, compared with other flexible semiconductors, IGZO has superior mobility and stability. Amorphous silicon, α-Si, can be deposited below 350 °C by using PECVD, but the low mobility, less than 1 cm²V⁻¹s⁻¹, restricts its further application [30]. Polycrystalline silicon (poly-Si) has a higher mobility and can be deposited at a relative low temperature [36]. However, due to the poor uniformity caused by the grain boundaries, the performance varies at different areas on the same sample, which makes the poly-Si unsuitable for large-area electronics such as OLEDs and high resolution LCDs [37]. Organic semiconductors have a fairly simple fabrication process. Although many studies have been carried out to improve their electrical performance, air instability, low mobility and poor uniformity are still the crucial deficiencies for organic semiconductors [32, 38].

As one of the most important features of electronics, the high-frequency performance of IGZO-based devices has also drawn much attention [7, 10, 39, 40]. In order to realise wireless communications, front-end rectifiers operating at the carrier frequency are indispensable. For TFTs, the operation speed is determined by the transit frequency, f_t. It is found that the transit frequency is related to the mobility, channel length and the overlapping area between source/drain and gate electrodes, which can be described as

\[ f_t \propto \frac{\mu}{(L_c L_{ov})} \]

where \( \mu \) is the mobility, \( L_c \) is the channel length and \( L_{ov} \) is the overlapping length [40]. Thus, in order to realise high-speed operation, the dimensions of the TFT need to be reduced. At the time of writing, the highest transit frequency of IGZO TFTs is 384 MHz on glass substrates [8] and 135 MHz on flexible substrates [40]. However, to obtain these results the channel lengths of the TFTs was reduced to the sub-micron scale (around 500 nm), which is difficult to achieve by using normal lithography processes [41]. In order to realise high-frequency rectification, Schottky diodes are proposed. It has been reported that pentacene and C60 pin diodes were able to operate up to 300 MHz [42]; pentacene Schottky diodes could work as a rectifier at 870 MHz [43]; diodes based on C60 and tungsten oxide showed a cut-off frequency of 800 MHz [44]. Due to its high mobility, IGZO Schottky diodes have already demonstrated GHz operations [14, 45]. However, all of the devices mentioned above are fabricated on glass substrates and require high-temperature treatments. Only a few flexible diodes have demonstrated so far, including polythiophene based Schottky diodes with a cut-off frequency of 14 MHz [46], polytriarylamine based devices with a cut-off frequency of 10 MHz [47], and pentacene/ZnO-based diodes with a cut-off frequency of 15 MHz [48]. Nevertheless, all
these flexible diodes still cannot reach the benchmark frequency of 2.45 GHz. Thus, flexible IGZO Schottky diodes with cut-off frequencies higher than 2.45 GHz are highly desirable.

For the use of IGZO in practical applications, the low-frequency noise properties of IGZO-based devices have to be analysed and minimized. For IGZO TFTs, most of the noise spectra show almost ideal 1/f dependency at low frequencies [49-56]. The gate dependent noise spectra follow the mobility fluctuation model, suggesting that phonon scattering is the main contributor to the LFN [51]. The Hooge’s constant extracted from IGZO TFTs was found to be around $1.0 \times 10^{-3}$, which is comparable with the value of poly-Si TFTs [57] and lower than the values of a-Si TFTs [58] and organic TFTs [59]. However, the noise properties of IGZO Schottky diodes still remain unexplored. A detailed analysis may provide a deeper insight into the quality and the electrical characteristics of the metal-IGZO interface.

As a result of the drawbacks of other flexible semiconductors mentioned above, IGZO has become one of the most promising materials for thin-film devices including TFTs and Schottky diodes. Due to its high mobility and amorphous structure, IGZO Schottky diodes have also shown the potential to be used in flexible microwave electronics.

1.2.2. P-type Metal Oxide Semiconductors

In contrast with the vast progress made in n-type oxide semiconductors, there has been limited progress on p-type metal oxides. In this section, the theory and formation of p-type oxide semiconductors are introduced.

It is easy to obtain n-type metal oxide semiconductors as carrier transport in the conduction band minimum, CBM, occurs via the large $s$ orbitals of the metal ions [60]. Hole transport in the valence band maximum, VBM, occurs in the localized O $2p$ orbitals, giving rise to hopping conduction and subsequently a relatively low hole mobility [61]. In order to obtain a better $p$-type material, it is necessary to find a metal oxide for which the VBM is formed via the hybridisation of O $2p$ and metal orbitals [62].

This conjecture led to the discovery of copper based $p$-type oxides such as CuAlO$_2$ [63], SrCu$_2$O$_2$ [64] and Cu$_2$O [65], which incorporate Cu $3d$ orbitals into their VBM [66, 67]. In 2010, the mobility of Cu$_2$O was found to be 4.3 cm$^2$V$^{-1}$s$^{-1}$ and the on/off ratio was around $10^6$ [68]. However, due to the high-temperature fabrication
processes and the large trap density, Cu$_2$O TFTs still showed quite poor electrical performance, making it difficult to use them in integrated circuits [3]. There have been only a few reports on other $p$-type binary oxide semiconductors such as NiO [69, 70] and ZnO [71] because of the poor stability and the low film quality.

Tin monoxide as a promising $p$-type oxide semiconductor has drawn much attention in recent years. The $p$-type behaviour was attributed to the Sn vacancies [72]. The VBM of SnO is composed of O 2$p$ and Sn 5$s$ hybridized orbitals, indicating the possibility of obtaining a high hole mobility [72]. However, as SnO is a metastable phase, the deposited SnO film usually contains another form of tin oxide, SnO$_2$, which is widely known to be an $n$-type semiconductor [3]. The existence of such multi-phases may lower the electrical performance of SnO TFTs.

In 2008, the first $p$-type SnO TFT was demonstrated with a field-effect mobility of 1.3 cm$^2$ V$^{-1}$ s$^{-1}$ by epitaxial growth on a (001) YSZ substrate at 575 °C [17]. Since then, $p$-type SnO was successfully obtained by using reactive thermal evaporation [73], PLD [62, 74], electron beam evaporation [75], solution process [76], RF sputtering [77-82], and DC reactive sputtering [83-85]. The highest field-effect mobility of SnO TFTs was reported to be 6.75 cm$^2$ V$^{-1}$ s$^{-1}$ by DC reactive sputtering [85]. In 2011, a CMOS like circuit was presented by using two ambipolar SnO TFTs [86]. Complementary logic gates based on IGZO and SnO TFTs have been demonstrated by using paper as the dielectric [87]. Ring oscillators based on ZnO and SnO have also been realised on glass and flexible substrates [88]. One interesting proposition put forward was to use SnO to form a $n$-type SnO$_2$ channel by annealing in air [77]. Using this method, a complementary inverter of $n$-type SnO$_2$ and $p$-type SnO could be obtained by a single step of thermal annealing with and without a capping layer [77]. However, this has not been realised so far due to the difficulties in controlling the oxidation during the annealing process. By using different dielectric layers [84] or selectively depositing another layer of oxide semiconductor [83], $n$-type SnO$_2$ and $p$-type SnO can be obtained simultaneously. However, the properties of the obtained SnO$_2$ cannot compete with IGZO and these methods also require an additional fabrication process to realise the selective oxidation. Thus, using the combination of IGZO and SnO is still regarded as one of the most promising approaches for various practical oxide-semiconductor-based electronics.

In summary, SnO shows superior performance compared with NiO [69], Cu$_2$O [65] and
p-type ZnO [71]. The advantages of SnO will prompt more studies on p-type oxide-semiconductors-based electronics.

1.3. Objectives

1.3.1. High-performance IGZO Schottky Diodes

Optimising the properties of IGZO Schottky diodes is the gateway to further practical application, including high-frequency detectors, mixers, and front-end rectifiers. These potential applications rely on the properties of Schottky barriers between the metal and the IGZO. However, due to the nature of metal oxide semiconductors, the barrier height is mainly affected by the oxygen-vacancy-induced Fermi level pinning. Moreover, in order to realise oxide-semiconductor-based flexible electronics, it is necessary to fabricate the high-performance IGZO Schottky diode at RT.

In this thesis, the following questions are addressed, aiming to realise room-temperature-processed high-performance IGZO Schottky diodes:

- How to reduce the oxygen deficiency at the metal-IGZO interface? Oxygen deficiency creates dangling bonds at the metal-oxide interface, which causes Fermi level pinning and may lower the barrier height and degenerate the Schottky junction [5].
- How to fabricate high-performance Pt-IGZO Schottky diodes at RT by RF sputtering?
- What is the trap density at the Pt-IGZO interface? The traps at the Schottky interface cause fluctuations in the barrier height. Such inhomogeneities will degenerate the rectification properties including the effective barrier height, ideality factor, reverse current, and the rectification ratio [12].
- What is the effect of thermal annealing?
- What affects the low-frequency noise (LFN) properties of IGZO Schottky diodes?

1.3.2. High-frequency IGZO Schottky Diodes

One major advantage of Schottky diodes is the excellent high-frequency performance due to the absence of minority carriers. Thus, it is desirable to realise high-speed operation on IGZO Schottky diodes. Another important feature of IGZO is its amorphous structure,
which offers the possibility of fabricating IGZO-based flexible high-frequency rectifiers.

The following questions regarding the realisation of high-frequency IGZO Schottky diodes are discussed in the thesis:

- What determines the cut-off frequency of IGZO Schottky diodes?
- How to improve the cut-off frequency?
- What are the potential applications of IGZO Schottky diodes?
- How to realise flexible IGZO Schottky diodes operating beyond 2.45 GHz?

### 1.3.3. Carrier Transport Mechanism in SnO TFTs

By using RF reactive sputtering, it is possible to deposit $p$-type SnO films. However, the different phases present in the deposited film may degrade the electrical properties. In order to further improve the performance of SnO TFTs, it is important to analyse the carrier transport mechanism, which helps understand the origin of the high off-current and the poor subthreshold swing.

In this thesis, the following questions concerning the carrier transport mechanism in SnO TFTs are discussed:

- What are the effects of oxygen content during the deposition of SnO?
- What is the carrier transport mechanism in SnO TFTs?
- What are the possible reasons for the high off-current?

### 1.3.4. Complementary Circuits

A lack of $p$-type metal oxide semiconductors prevents the realisation of complementary logic gates, thus limiting the potential applications. However, complementary circuits using $p$-type SnO and $n$-type IGZO are conceivable because SnO shows good stability and similar mobility to IGZO. In this thesis, a complementary inverter and a ring oscillator are demonstrated.

### 1.4. Thesis Outline

The thesis includes ten chapters. In Chapter 2, the background theories used in the analyses of TFT, Schottky diode, and LFN are presented. Chapter 3 gives a summary of the achievements in the thesis work. The detailed findings are presented in Chapters 4 to 9 in forms of scientific publications. Fig. 1-1 shows the underlying relations between these
chapters. The conclusions and future work are presented in Chapter 10.

In Chapter 4, the properties of high-frequency flexible Pt-IGZO Schottky diodes are discussed. Chapter 5 explains how to improve the cut-off frequency of IGZO Schottky diodes on glass substrates. As the LFN affects the resolution and sensitivity of integrated circuits, the properties of the LFN are discussed in Chapter 6. The effects of oxygen in the formation of Schottky barrier and an alternative fabrication process of high-performance Pt-IGZO Schottky diodes are presented in Chapter 7. In Chapter 8, the carrier transport mechanisms in SnO TFTs are expounded by analysis of DC characteristics in a cryostat down to 5 K. The metal-oxide-based complementary inverter and ring oscillator are demonstrated in Chapter 9. Scientific publications according to the order of chapters are listed in Table 1-2.

**Table 1-2.** Publications, manuscripts and the corresponding chapters in this thesis.

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Publications</th>
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<tbody>
<tr>
<td>5</td>
<td>Room temperature processed ultra-high frequency indium gallium zinc oxide</td>
</tr>
<tr>
<td>6</td>
<td>Low-frequency noise properties in Pt-indium gallium zinc oxide Schottky diodes</td>
</tr>
<tr>
<td>7</td>
<td>High performance Schottky diodes based on IGZO</td>
</tr>
<tr>
<td>8</td>
<td>Analysis of carrier transport and band tail states in p-type tin monoxide thin-film transistors by temperature dependent characteristics</td>
</tr>
<tr>
<td>J. Zhang, X. Kong, J. Yang, Y. Li, J. Wilson, J. Liu, Q. Xin, Q. Wang, and A. Song. Appl. Phys. Lett.-Accepted</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Ring oscillator based on complementary p-SnO and n-IGZO thin-film transistors</td>
</tr>
<tr>
<td>Manuscript</td>
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### References


P.-C. Hsu, C.-C. Wu, H. Hiramatsu, T. Kamiya, and H. Hosono, "Film Texture, Hole Transport and Field-Effect Mobility in Polycrystalline SnO Thin Films on


Chapter 2  Background Theory

The main scope of this thesis is metal-oxide-semiconductor-based electronics including Schottky diodes, TFTs, and complementary circuits. In this chapter, the background theories of Schottky diodes, TFTs, and LFNs are presented. The formation of Schottky barrier in an n-type semiconductor is illustrated using a band diagram. The current density-voltage (J-V) and capacitance-voltage (C-V) characteristics of the Schottky diode are discussed with the use of an IGZO Schottky diode as an example. The structure and the electrical performance of TFTs are discussed, including the transfer characteristics, the output characteristics, and the hysteresis. Finally, the basic theory and the measurement techniques of LFNs are presented.

2.1. Schottky Diodes

Metal-semiconductor contacts are very important for DC and microwave electronics as they are integral to many semiconductor devices such as Schottky diodes, metal-semiconductor field-effect transistors, and photodiodes [1, 2]. For an n-type semiconductor, when metal with a high work function makes contact with the semiconductor, a Schottky barrier is formed at the interface as shown in Fig. 2-1 [1]. In general, there are two different types of the contacts between metal and semiconductor, namely ohmic contacts and Schottky contacts [1]. In this section, the formation and the electrical characteristics of Schottky contacts are discussed.

Schottky diodes are well known for their low turn-on voltage and low junction capacitance.

![Fig. 2-1. Band diagram of a Schottky barrier between metal and n-type semiconductor.](image-url)
These advantages have led to the widespread use of Schottky diodes in low voltage circuits for reverse current or discharge protection and high-frequency rectification. However, very few studies have been conducted on metal oxide semiconductor Schottky diodes so far [2-7].

For an ideal $n$-type Schottky diode, the formation of the junction is shown in Fig. 2-1. In order to form the Schottky barrier, the work function of the metal should be larger than the electron affinity of the semiconductor [8]. The work function describes the minimum energy needed for moving an electron from the Fermi level to the vacuum and the electron affinity describes the energy gap between the conduction band and vacuum level. When the semiconductor gets in contact with metal, the electrons at the interface from the semiconductor will transfer into metal which causes a positively charged layer at the interface of the semiconductor. This lowers the Fermi level in the semiconductor and bends the energy band at the interface. Fig. 2-1 shows the barrier height, $\varphi_B$, and the built-in voltage, $V_{bi}$, which are caused by the band realignment. The Schottky barrier height indicates the energy an electron at the Fermi level in the metal needs to flow into the semiconductor. The built-in voltage describes the energy an electron needs to move from the conduction band minimum in the semiconductor to the metal.

In theory, the current flow through metal to semiconductor follows the thermionic emission model, as shown in Fig. 2-2(a), which can be described as
\[ I = AA^* T^2 \exp \left( -\frac{q\varphi_b}{k_B T} \right) \left[ \exp \left( \frac{q(V - IR_s)}{nk_B T} \right) - 1 \right] \]  

(2-1)

where \( A \) is the area of the active area, \( A^* \) represents the Richardson constant, \( T \) is the temperature, \( k_B \) is the Boltzmann constant, \( V \) is the applied bias, \( R_s \) is the series resistance, and \( n \) is defined as the ideality factor [1].

The depletion width can be obtained by

\[ W_D = \sqrt{\frac{2\varepsilon_s}{qN_{bg}} \left( V_{bi} - V - \frac{k_B T}{q} \right)} \]  

(2-2)

where \( \varepsilon_s \) is the dielectric permittivity, and \( N_{bg} \) is the background doping density [9]. The depletion-layer capacitance can be obtained by \( C_D = \varepsilon_s / W_D \), as shown in Fig. 2-2(b). Thus the relation between \( C_D \) and applied bias is given by:

\[ C_D^{-2} = \frac{2[V_{bi} - V - k_B T/q]}{q\varepsilon_s N_{bg}} \]  

(2-3)

If \( N_{bg} \) is constant in the depletion layer, a straight line can be obtained by plotting \( C_D^{-2} \) as a function of voltage, which is shown in Fig. 2-2(b) as the dashed line.

### 2.2. Thin-film Transistor

At present, most of the metal oxide semiconductors are used in thin-film transistors (TFTs) [10]. Due to their high mobility and low fabrication temperature, metal oxide TFTs are regarded as a potential replacement for conventional amorphous and polycrystalline silicon TFTs. In this section, the structure and operation mechanisms of TFTs are discussed.

![Fig. 2-3.](image)

(a) Schametic of a bottom-gate top-contact TFT. Cross-section image and output curve of a TFT in (b) the off-regime, (c) the linear regime, and (d) the saturation regime.
Fig. 2-4. (a) Output characteristics and (b) saturation transfer characteristics of an IGZO TFT. The thickness of the IGZO layer is 50 nm. A 30 nm-thick HfO₂ layer is used as the dielectric. Both layers were deposited via RF sputtering in Ar. The channel width and channel length are 1500 µm and 40 µm, respectively.

Fig. 2-3(a) shows a schematic of a bottom-gate top-contact TFT. Metal oxide semiconductor TFTs are usually formed by four components; source and drain contacts, a semiconductor layer, a gate dielectric layer and a gate electrode. In general, the source/drain and gate electrodes are formed by metal layers. However, metal oxide conductive layers can also be used as contacts, which is essential for transparent transistors. Generally, there are four different TFT structures which are commonly employed, namely, top-gate top-contact, top-gate bottom-contact, bottom-gate top-contact and bottom-gate bottom-contact. The operating mechanism of an standard TFT is discussed by using a diagram of a bottom-gate top-contact TFT. At the beginning, the source is connected to ground and a positive voltage is applied to drain in order to form a current from drain to source. As there is no voltage applied to gate, the semiconductor layer has a high resistance resulting in almost no current from drain to source as shown in Fig. 2-3(b). After applying a positive voltage which is larger than the threshold voltage \( V_{th} \) to the gate, carriers form a strong accumulation layer at the interface with the dielectric layer. Thus, a channel is formed. The drain current, \( I_D \), is proportional to the drain voltage, \( V_D \), since the channel resistance depends on the gate voltage, \( V_G \), as shown in Fig. 2-3(c). When the drain voltage becomes comparable with \( (V_G - V_{th}) \), the drain voltage begins to attract the electrons from channel and causes the pinch-off. The gate voltage is offset by the drain voltage and the drain current remains the same in the saturation region,
which is sketched in Fig. 2-3(d). The output curves of a typical IGZO TFT are shown in Fig. 2-4(a). In addition to output curves, a quantitative analysis of TFT can be made using the transfer characteristics ($I_D$-$V_G$). As shown in Fig. 2-4(b), the mobility ($\mu$), turn-on voltage ($V_{on}$), threshold voltage ($V_{th}$), on/off ratio and subthreshold swing ($SS$) are illustrated in the transfer curve. The standard output characterises in the linear region is expressed as

$$I_D = \frac{W}{L} C_{ox} \mu \left[ (V_G - V_{th}) V_D - \frac{V_D^2}{2} \right]$$  \hspace{1cm} (2-4)

where $W$ is the channel width, $L$ is the channel length, $C_{ox}$ represents the dielectric capacitance per unit area. When the drain voltage becomes larger than $(V_G - V_{th})$, the channel close to the drain contact is pinched off. Then the output curve can be described by

$$I_D = \frac{W}{2L} C_{ox} \mu (V_G - V_{th})^2$$  \hspace{1cm} (2-5)

When the gate voltage becomes larger than the turn-on voltage, the drain current increases exponentially with the gate voltage until reaching the linear or saturation region. This region is called the subthreshold region and is characterised by the subthreshold swing:

$$SS = (\ln 10) \frac{dV_G}{d(ln I_D)} = (\ln 10) \left( \frac{k_B T}{q} \right) \left( \frac{C_{ox} + C_{it}}{C_{ox}} \right)$$  \hspace{1cm} (2-6)

where $C_{it}$ is the trap-induced capacitance and $C_{it} = q^2 D_{it}$, where $D_{it}$ represents the interface trap density [11]. Essentially, the subthreshold swing describes gate voltage required to induce an order of magnitude increase in the drain current.

**Fig. 2-5.** (a) Typical transfer characteristics with hysteresis. (b) Illustration of the hysteresis in the TFT. The label 1 represents the electron trapping model and the label 2 indicates the ion migration model.
However, if there are a large number of traps in the bandgap, most of the carriers are
trapped in these localized states. Only a small portion of carriers can be thermally excited
into the delocalized states and contribute to the drain current [12]. This mechanism can be
described by the multiple-trapping-and-release (MTR) model [12]. In this model, the
transition between the below-threshold current and the above-threshold current is
determined by the distribution of the tail-states and deep-states in the semiconductor. The
relation between the MTR-controlled mobility, $\mu_{\text{MTR}}$, and the mobility in the delocalised
states, $\mu_0$, can be expressed as $\mu_{\text{MTR}} = \mu_0 \frac{N_c}{N_t} \exp\left(-\frac{\Delta E}{k_BT}\right)$, where $N_c$ is the density of states
at the edge of the delocalised states, $N_t$ is the density of traps, and $\Delta E$ is the energy
between the trap states and the delocalised states [13]. For some oxide semiconductors
where the conduction band is composed of large metal spherical orbitals, such as IGZO
and In$_2$O$_3$, the trap-states are relatively small compared with amorphous covalent
semiconductors. Thus, the standard TFT model can be used to describe the I-V
characteristics of IGZO TFTs [14]. In IGZO, the Hall mobility increases with carrier
concentration, which is contrary to the observed behaviour in conventional crystalline
semiconductors [15]. Thus, the carrier transport mechanism is described by percolation
conduction, which is due to the inhomogeneous conduction band minimum [16]. The
mobility dominated by percolation, $\mu_p$, equals $\mu_0 \exp\left(-\frac{\varphi_0}{k_BT}\right)$, where $\varphi_0$ is the average
height of the potential barriers, which is around 30-100 meV in IGZO [17].

In practice, the transfer curve usually shows hysteresis as illustrated in Fig. 2-5(a). There
are two types of hysteresis, namely clockwise and anti-clockwise. As shown in Fig. 2-5(b),
there are two different mechanisms of the hysteresis in TFTs, which are electron trapping
and negative/positive ion migration [18]. For the electron trapping mechanism,
accumulated electrons at the interface start to fill slow-state traps during the forward
sweep. Such slow-state traps might originate from charge trapping states at the interface on
the dielectric side [9]. In the backward sweep, the turn-on voltage shifts to positive as those
trapped electrons do not contribute the current flow and repel other free electrons in the
channel [18]. In another words, the electron trapping will cause clockwise hysteresis. For
the ion migration mechanism, the positive ions can be repelled to the semiconductor-
dielectric interface when increasing the gate voltage. Since the movement of ions is
relatively slow compared with the electrons in the channel, during the reverse sweep, the
mobile positive ions act as an extra gate voltage and shift the turn-on voltage to the left,
resulting in an anti-clockwise hysteresis [18]. However, the number of negative ions at the
The semiconductor-dielectric interface will increase with a decreasing gate voltage. Then in the forward sweep, these negative ions will cause a positive gate voltage shift and also result in an anticlockwise hysteresis [18].

2.3. Low-frequency Noise

In order to improve the resolution and sensitivity of integrated circuits, the low-frequency noise of the components needs to be carefully evaluated and minimized. The properties of low-frequency noise can be analysed from the noise power spectrum, which is the Fourier transform of the autocorrelation of the noise signal. The relation between the current noise spectral density, $S_I$, and the voltage noise spectral density, $S_V$, can be described by

$$\frac{S_I}{I^2} = \frac{S_V}{V^2} \quad (2-7)$$

In general, there are four different types of low-frequency noise existing in electronic devices, namely thermal, shot, generation-recombination (G-R) and flicker noise ($1/f$ noise). The appearances of these noise components in the current noise spectra are shown in Fig. 2-6(a). Thermal noise was firstly observed by Johnson in 1927 [19] and explained by Nyquist in 1928 [20]. This noise is generated by the thermal agitation of the carriers in the material at equilibrium, which can be expressed as $S_I = 4k_B T / R$ [20]. Shot noise was discovered by Schottky in 1918 [21], originating from the discrete nature of carriers. At low frequencies this follows the relation $S_I = 2qI$ [21]. G-R noise is generated by the fluctuations in the number of free carriers in the semiconductor due to random transitions between different states [22]. Common transitions occur between conduction band and localized trap states, and conduction band and valence band [23]. G-R noise can be...
described by

\[
\frac{S_I}{I^2} = \frac{\delta N^2}{N^2} \frac{4\tau_N}{1 + (2\pi f\tau_N)^2}
\]  

(2-8)

where \(\delta N^2\) is the variance of carrier number fluctuations which is related to the trap states in the bandgap, \(N\) is the number of free carriers, \(\tau_N\) is the carrier lifetime, and \(f\) is the frequency. In the noise spectra, the G-R noise remains the same at frequencies below \(1/\tau_N\) and then proportional to \(1/f^2\) above \(1/\tau_N\). Thus, the G-R noise can be easily identified by a plateau with a corner frequency. However, if \(\tau_N\) is probability distributed, the noise power spectrum will show a \(1/f\) dependence [24].

Flicker noise describes the noise proportional to \(1/f^\gamma\), where \(0 < \gamma < 2\) (normally equal to 1). So far, there is still no clear theory to describe such noise. In 1969, Hooge proposed a widely accepted explanation called the mobility fluctuation model [25], which can be described as

\[
\frac{S_I}{I^2} = \frac{\alpha_H}{fN}
\]  

(2-9)

where \(\alpha_H\) is a constant which describes the quality of the material. As both thermal noise and shot noise are white at low frequencies, effects of G-R noise and flicker noise are more significant and thus more important. In TFTs, another possible origin of the flicker noise is the carrier number fluctuation at the semiconductor-dielectric interface proposed in 1955 [26]. It assumes that the G-R noise can be generated by the electron trapping and release between the channel layer and the traps in the dielectric layer near the semiconductor-dielectric interface [26, 27]. By superposing the G-R noise with different carrier lifetimes, the \(1/f\) characteristics can be obtained.

The basic setup of the noise measurement is illustrated in Fig. 2-6(b). The DC component generated in the device is removed by a high-pass filter. The remaining AC part is then amplified and measured by an analog-to-digital converter (ADC). The noise spectrum can be obtained by a Fourier transform of the amplified signal. The maximum frequency of the noise spectrum is determined by the Nyquist frequency, which has a period of two sampling intervals of the ADC, \(2t_s\) [28]. However, only part of the noise spectrum is valid as the bandwidth of the amplifier, \(f_{bw}\), removes the high-frequency profile, as shown in Fig. 2-6(c). The resolution of the noise spectrum depends on the length of the input time-domain signal (time window, \(t_w\)), which is \(1/t_w\) as shown in Fig. 2-6(b). However, the
lowest valid frequency is also affected by the cut-off frequency of the high-pass filter. Besides, in order to reduce the ambient interference, the practical setup should be shielded by a metal box and adopt the star configuration to share a central ground point.

References


Chapter 3  Summary of Papers

This chapter details the experiments discussed in subsequent chapters of this thesis and summarizes their findings in a broader perspective. The techniques used to fabricate high-performance Pt-IGZO Schottky diodes are presented. The cut-off frequency of the diode is further improved. For the use of small-signal IGZO Schottky diodes in integrated circuits, the low-frequency noise properties become crucial and are evaluated in this thesis. With regards to practical application, a demonstration of the IGZO Schottky diode as a demodulator is also given.

However, in order to realise fully oxide-based complementary electronics, $p$-type oxide semiconductors with good electrical properties are required. Tin monoxide has been regarded as a promising $p$-type oxide semiconductor. In this chapter, the effects of varying oxygen content on the properties of SnO thin-films are discussed. By measuring the transfer characteristics of the SnO TFT at different temperatures, the carrier transport mechanisms in SnO films are elucidated, allowing a deeper understanding on the formation of the $p$-type conduction. Lastly, the IGZO and SnO based inverter and ring oscillator are demonstrated, highlighting the potential flexible applications that may be achieved through the use of metal oxide semiconductors.

3.1. High Performance Pt-IGZO Schottky Diodes

In order to obtain high-performance IGZO Schottky diodes, the formation of the metal-IGZO Schottky barrier needs to be studied. As IGZO is an $n$-type semiconductor with an electron affinity of around 4.5 eV [1], the Schottky contact should be made by a conductive material with a higher work function. A thin Pt film is chosen as the Schottky contact as the work function of Pt is 5.4 eV [1]. An Al film is used as the ohmic contact as it has a similar work function to IGZO [2].

Several different methods of fabricating IGZO Schottky diodes are demonstrated and explained in Chapters 4 to 7. A 50 nm-thick Pt film is deposited by using RF sputtering at 80 W in pure Ar (Devices A, B and D) and in Ar / 3 % O$_2$ mixture gas (Device C), both at a pressure of 5.0×10$^{-3}$ mbar. A gentle oxygen plasma treatment was carried out on the Pt surface of Device D at 50 W and 6.0×10$^{-2}$ mbar. The IGZO film is RF sputtered for 50 nm at 80 W in Ar (Devices A, C and D) and in Ar / 3 % O$_2$ mixture gas (Device B), again,
both at a pressure of 5.0×10⁻³ mbar. The Al contacts with a radius of 0.1 mm are deposited by thermal evaporation. All patterns are defined by using shadow masks. The detailed fabrication conditions are listed in Table 3-1. The schematic and the cross-section of the diode are shown in Fig. 3-1(a) and (b).

**Table 3-1.** Fabrication conditions and electrical properties of the Schottky diodes.

<table>
<thead>
<tr>
<th></th>
<th>Device A</th>
<th>Device B</th>
<th>Device C</th>
<th>Device D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Ar</td>
<td>Ar</td>
<td>Ar + 3% O₂</td>
<td>Ar, O₂ plasma</td>
</tr>
<tr>
<td>IGZO</td>
<td>Ar</td>
<td>Ar + 3% O₂</td>
<td>Ar</td>
<td>Ar</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>Thermally evaporated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>2.50</td>
<td>1.56</td>
<td>1.36</td>
<td>1.21</td>
</tr>
<tr>
<td>Rectification ratio at ±1 V</td>
<td>1.0×10²</td>
<td>2.0×10⁴</td>
<td>2.4×10⁶</td>
<td>5.6×10⁵</td>
</tr>
<tr>
<td>φ_b</td>
<td>0.52 eV</td>
<td>0.72 eV</td>
<td>0.92 eV</td>
<td>1.01 eV</td>
</tr>
<tr>
<td>R_{tot} at 1 V</td>
<td>0.018 Ωcm²</td>
<td>0.134 Ωcm²</td>
<td>1.192 Ωcm²</td>
<td>27.629 Ωcm²</td>
</tr>
</tbody>
</table>

According to thermionic emission theory, the barrier height, the ideality factor, the rectification ratio, and the resistance at 1 V (R_{tot}) can be obtained (shown in Table 3-1). It is found that Device A shows the lowest barrier height, the smallest rectification ratio and the highest ideality factor. The huge differences between the properties of Device A and the theoretical values indicate a poor Schottky junction. However, after introducing oxygen treatments, including deposition Pt or IGZO with O₂ and O₂ plasma oxidation, all the devices show improved performances. This suggests that the oxygen content at the Schottky interface determines the quality of the Schottky junction. One possible reason is that at the interface, IGZO might have some dangling bonds caused by oxygen deficiencies.
These dangling bonds may contribute to a high density of interface traps and thus pin the Fermi level at a lower energy level, which degrades the diode performance [3].

When depositing IGZO with 3% O₂, the excess oxygen reduces the amount of oxygen vacancies as well as the dangling bonds. Thus, for Device B, there is improved performance with respect to the barrier height and the ideality factor. However, the extra oxygen during the deposition slightly increases the resistivity of the IGZO film. As a result, it contributes to a higher series resistance. However, the rectification ratio also improved due to the higher barrier height and the low reverse current.

Alternatively, the oxygen treatment can also be applied to the Pt layer. Both Devices C and D show improved properties. The barrier height and the ideality factor are close to the ideal values. However, such treatments also cause a much higher series resistance. Besides, the oxygen plasma oxidation introduces an extra fabrication process which will increase the complexity in mass production. If depositing Pt with 3% O₂, the diode performance remains almost the same while the forward current only drops slightly.

It is noteworthy that the ideality factors for all devices are higher than 1.1. This might be due to the inhomogeneities of the barrier height. According to Tung’s model and Werner’s model, the Schottky barrier fluctuations can cause a decrease in the effective barrier height and contribute to a higher ideality factor [6, 7]. Such barrier inhomogeneities can be evaluated from the low-temperature characteristics [2].

### 3.2. High-frequency Pt-IGZO Schottky Diodes

One major advantage of the Schottky diode is that it is a majority-carrier device and the cut-off frequency mostly depends on its capacitance and resistance due to the short reverse recovery time [8, 9]. Thus it is possible for the IGZO Schottky diode to operate at a high frequency which is difficult for TFTs to reach. The small-signal equivalent diagram of the IGZO Schottky diode is shown in Fig. 3-3. The diode capacitance, $C_D$, is caused by the depletion layer at the Schottky junction. The series resistance, $R_s$, in the J-V characteristics includes the IGZO bulk resistance and the resistance from the contacts. However, at high frequencies, only when the device is fully depleted is the resistance from the contacts the sole contributor to the series resistance, labelled as $R_{es}$ in Fig. 3-3.
In order to improve the cut-off frequency of the diode, the series resistance and/or the depletion-layer capacitance can be reduced. The C-V relation is expressed as follows,

$$C_D = \frac{\varepsilon_0 \varepsilon_r}{W_D} = A \sqrt{\frac{q \varepsilon_0 \varepsilon_r N_D}{2[V_{bi} - V - (k_B T / q)]}}$$ (3-1)

The depletion-layer capacitance can be reduced by increasing the depletion width or decreasing the active area. The depletion width is related to the background doping density, dielectric constant and the built-in voltage. By introducing the oxygen treatment to the Pt contact, it is possible to increase the barrier height and hence the built-in voltage and thus reduce the capacitance. However, as discussed in Section 3.1, the oxygen treatment will contribute to a higher series resistance which will compensate the decrease in the

![Fig. 3-2.](image)

(a) Rectification properties of the Schottky diodes with different thicknesses of the IGZO layer. The inset shows the schematic and the cross-section of the diode. (b) Impedance and capacitance of the 80 nm-thick IGZO Schottky diodes with different active areas as a function of frequency.

![Fig. 3-3.](image)

Equivalent circuit of the IGZO Schottky diode with fully depleted and partially depleted IGZO. $R_{bulk}$ represents the bulk resistance of the IGZO layer. $R_{contacts}$ is the resistance from the electrodes.
capacitance and thus lower the cut-off frequency. In the practical rectifier circuit, the leakage current also affects the high-frequency performance. A high leakage current gives rise to a poor rectification ratio, contributing to a higher power conversion loss which is not suitable for front-end rectifiers. Taking these factors into account, the diode with 3% O₂ during the deposition of IGZO is the most suitable for the high-frequency applications.

It is also necessary to consider the difference between the thickness of the IGZO layer and the depletion width. If the thickness of the IGZO layer is larger than the depletion width, the difference will cause an increase in the effective series resistance as shown in Fig. 3-3. Thus, in order to reach a higher cut-off frequency, the theoretical depletion width should be always larger than the thickness of the IGZO layer. However, a thinner IGZO layer will result in a higher capacitance, which also limits the cut-off frequency. Thus we need to optimise the thickness of the IGZO layer. The rectification properties of the diodes with the IGZO thicknesses of 50 nm, 80 nm and 100 nm are evaluated as shown in Fig. 3-2(a). The rectified voltage decreases with a gradient between -22 dB/dec and -27 dB/dec dependent on the input voltage, which is slightly more pronounced than the standard rate (-20 dB/dec). This might be caused by the poor impedance matching due to the frequency dependent impedance of the IGZO Schottky diode. Although the 100 nm-thick IGZO Schottky diode exhibits the highest cut-off frequency at zero bias, in the single-stage rectifier circuit, the 100 nm-thick IGZO diode shows the worst performance among the three devices. This might be due to the increasing voltage drop across the diode, which reduces the depletion width and causes an increase in the effective series resistance. The 80 nm-thick IGZO Schottky diode shows the best overall performance. Thus we use 80-nm

![Fig. 3-4.](image)

(a) Photo of the flexible IGZO Schottky diodes on PET substrates. (b) Impedance of the flexible Schottky diode as a function of frequency.
thick IGZO as the active layer for flexible Pt-IGZO Schottky diodes.

The other way to decrease the capacitance of the diode is to reduce the active area according to Eqn. (3-1). However, when shrinking the dimensions of the diode the contact resistance becomes larger and may counteract the decrease in the capacitance. For the diodes on glass substrates, the small-signal test shows that the effective series resistance only increases slightly when decreasing the active area of the diode, as shown in Fig. 3-2(b). It is plausible that the effective series resistance depends on not only the contact resistance but also the resistance from the contact pads. In Fig. 3-4(a), the flexible IGZO Schottky diodes were fabricated on PET substrates. However, for the diodes on flexible substrates, the contact resistance dominates the effective series resistance as shown in Fig. 3-4(b). This may be due to the surface roughness of the PET film which may distort the metal-semiconductor interface and thus cause a higher contact resistance. As a result of the small-signal test, the highest cut-off frequency is found to be above 20 GHz for the Pt-IGZO Schottky diodes on glass substrates, and 6.3 GHz for the diodes on flexible substrates.

3.3. Low-frequency Noise Properties of Pt-IGZO Schottky Diodes

Schottky diodes are suitable to be used in the high-frequency circuits as front-end rectifiers, high-frequency mixers, and small-signal detectors [10, 11]. However, before Pt-IGZO Schottky diodes can be used in high-frequency applications, the low-frequency noise must be characterised as it determines the signal-to-noise ratio in high-frequency operations [12, 13].

In this experiment, a gentle oxygen plasma treatment is conducted on the Pt contact in order to create an oxygen-rich interface and improve the rectification properties of the

![Fig. 3-5. Schematic of the low-frequency noise measurement setup.](image-url)
diode. The low-frequency noise is measured by using a SR570 low-noise current amplifier and collected by an NI USB-6211 data acquisition unit. The time domain signal is then converted to the frequency domain signal in the computer. The setup is illustrated in Fig. 3-5 and the measured noise spectra are shown in Fig. 3-6(a).

For the as-deposited diode, the barrier height is 0.94 eV and the ideality factor is 1.2. The current noise spectral density, $S_I$, is found to be proportional to $I$ at low biases as shown in Fig. 3-6(b). When increasing the applied bias, $S_I$ becomes proportional to $I^2$ after a transition region. Annealing the diode in air at 100 °C for 1 h causes the performance to degrade. The barrier height drops to 0.85 eV and the ideality factor increases to 2.1. In Fig. 3-6(b), the current noise spectral density of the thermally annealed device shows a different dependency on the current. It is found that $S_I$ becomes proportional to $I^2$ from $10^{-7}$ A to $10^{-4}$ A. It indicates that the origin of the noise for the annealed diode may differ from that for the as-deposited diode.

**Table 3-2.** Current dependences of $S_I$ and $S_V$ for different models.

<table>
<thead>
<tr>
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<tr>
<td>$S_I \propto I^2$</td>
<td>$S_I \propto I$</td>
<td>$S_I \propto I^2$</td>
</tr>
<tr>
<td>$S_V \propto I^0$</td>
<td>$S_V \propto I^{-1}$</td>
<td>$S_V \propto I^2$</td>
</tr>
</tbody>
</table>

The noise can be generated from the interface, the space-charge region, or the series resistance. In the series-resistance-limited regime, the noise is governed by the mobility fluctuation model, where $S_I \propto I^2$. If the noise originates from the space-charge region, the current is limited by thermionic emission and $S_I \propto I$. The traps at the interface also generate a 1/f noise which is proportional to $I^2$. The voltage noise spectral density can be obtained by using

$$\frac{S_I}{I^2} = \frac{S_V}{V^2}$$

(3-2).

Thus the voltage noise spectral density of the Schottky diode is given by

$$S_V = S_{I, \text{space-charge}} \left(\frac{dV}{dI}\right)^2 + S_{I, \text{series-resistance}} R_s^2$$

(3-3)

where $S_{I, \text{space-charge}}$ is the current noise spectral density generated in the space-charge region, $S_{I, \text{series-resistance}}$ is the current noise spectral density caused by the series resistance, and $R_s$ is the series resistance. If the current is limited by thermionic emission, $dV/dI$ is
proportional to \(1/I\). Thus, the analysis of the noise is listed in Table 3-2.

For the as-deposited diode, the voltage noise is found to decrease at low biases and become proportional to \(I^2\) at high biases as shown in Fig. 3-6(b). This suggests that the low-frequency noise is dominated by the space-charge-induced noise in the thermionic-emission-limited regime and the resistance-induced noise in the series-resistance-limited regime [14, 16]. The Hooge’s constant is found to be \(10^{-9}\) for the thermionic-emission-limited regime, which is comparable with the value obtained from single-crystalline semiconductors such as GaAs and Si [15, 17, 18]. Such low Hooge’s constant might be due to the absence of grain boundaries and the ultra-smooth surfaces which reduce scattering centres [19]. The scattering mechanism at the interface may be dominated by the ionised impurity scattering, which is similar to that in conventional single crystalline semiconductors [20]. In amorphous oxide semiconductors, the electron scattering is also found to be much less sensitive to structural disorder compared with crystalline semiconductors [19, 20]. The Hooge’s constant is around \(10^{-5}\) in the series-resistance-limited regime. This is lower than the value obtained by the IGZO TFTs (around \(10^{-4}\)), which may be due to the absence of the scattering from the dielectric layer [21].

For the thermally annealed diode, the voltage noise remains at the same level as shown in Fig. 3-6(b), suggesting that the noise is generated at the Pt-IGZO interface. The interface trap density is estimated to be \(3.6 \times 10^{15} \text{ eV}^{-1} \text{ cm}^{-2}\), which is around 10 to 100 times higher than the value obtained in other crystalline semiconductor-oxide interfaces [22-26].
mass density of InGaZnO$_4$ is around 7 g/cm$^3$ [27], which provides an oxygen atom density of 5.37×10$^{22}$ cm$^{-3}$ and an interface density of 1.42×10$^{15}$ cm$^{-2}$. This suggests that the interface traps are generated not only in the IGZO layer, but also in the PtO$_x$ layer. As the noise is caused by the trap-induced barrier height fluctuation, the obtained trap density is also affected by the bulk trap density in the IGZO layer as the barrier height maximum is several nanometres away from the metal-semiconductor interface due to the image-force lowering [2]. The fact that the interface-trap-induced noise cannot be detected in the as-deposited diode implies that it is much smaller than the obtained current noise. Therefore, the interface trap density must be lower than 5.7×10$^{12}$ eV$^{-1}$ cm$^{-2}$. This performance is similar to Si and GaAs devices where interface trap density is around 10$^{11}$ eV$^{-1}$ cm$^{-2}$ [17, 18, 28]. Such a low noise level in the Pt-IGZO Schottky diodes indicates that they are ripe for various potential applications in small-signal electronics.

### 3.4. Potential Applications of the IGZO Schottky Diodes

As the highest rectification ratio is obtained by the diode when depositing Pt in 3 % O$_2$, this condition is adopted to fabricate the diode used as the demodulator in an amplitude-modulation (AM) radio receiver. In Chapter 7, a fully functional AM radio receiver is demonstrated. However, the rectified signal still needs to be amplified 20 times for the speaker. This suggests that in order to use the IGZO Schottky diode in flexible oxide-based electronics, complementary circuits are required.

### 3.5. P-type SnO TFTs and the Carrier Transport Mechanism

Tin monoxide is regarded as the most promising $p$-type metal oxide semiconductor. The origin for the $p$-type behaviour is believed to be the hybridized valence band maximum which is composed of O $2p$ and Sn $5s$ orbitals. Such a structure may contribute to a high hole mobility. The most widely used technique to deposit SnO is reactive RF magnetron sputtering with metallic Sn target in Ar and O$_2$ mixture gas. The oxygen content during the sputtering is crucial as it determines the extent of the oxidation. In order to optimise the fabrication conditions, it is important to investigate the effects of using different Ar/O$_2$ ratios during the deposition.
The SnO film is RF sputtered at 4.3 mTorr with the Ar/O\(_2\) ratios of 20 sccm : 0 sccm, 19 sccm : 1 sccm, 18 sccm : 2 sccm, 17 sccm : 3 sccm, 16 sccm : 4 sccm, 15 sccm : 5 sccm, 18 sccm : 3 sccm, 19 sccm : 3 sccm, 20 sccm : 3 sccm, 21 sccm : 3 sccm, 22 sccm : 3 sccm, and 23 sccm : 3 sccm. During the deposition, the substrate temperature is set to be 100 °C. The thickness of the deposited SnO film is 27 nm. The Pd source/drain contacts are deposited using e-beam evaporation. The channel length and the channel width are 60 µm and 2 mm respectively.

All devices are thermally annealed in air at 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, 250 °C, 250 °C.

**Fig. 3-7.** SEM morphologies of the 250 °C annealed SnO films with different Ar:O\(_2\) ratios of (a) 20:0, (b) 19:1, (c) 18:2, (d) 17:3, (e) 16:4, and (f) 15:5 during the depositions.

The SnO film is RF sputtered at 4.3 mTorr with the Ar/O\(_2\) ratios of 20 sccm : 0 sccm, 19 sccm : 1 sccm, 18 sccm : 2 sccm, 17 sccm : 3 sccm, 16 sccm : 4 sccm, 15 sccm : 5 sccm, 18 sccm : 3 sccm, 19 sccm : 3 sccm, 20 sccm : 3 sccm, 21 sccm : 3 sccm, 22 sccm : 3 sccm, and 23 sccm : 3 sccm. During the deposition, the substrate temperature is set to be 100 °C. The thickness of the deposited SnO film is 27 nm. The Pd source/drain contacts are deposited using e-beam evaporation. The channel length and the channel width are 60 µm and 2 mm respectively.

All devices are thermally annealed in air at 150 °C, 175 °C, 200 °C, 225 °C, 250 °C, 250 °C, 250 °C.

**Fig. 3-8.** (a) linear mobility and (b) on/off ratios of p-type SnO TFTs annealed at different temperatures with the oxygen contents from 5 % to 25 % during the deposition.
275 °C, and 300 °C for 1 h, respectively. SEM images of the surface morphologies of the SnO films after annealing are shown in Fig. 3-7. The mappings of the linear mobility and the on/off ratio obtained by transfer characteristics are shown in Fig. 3-8(a) and (b). It is found that the p-type SnO TFT can be obtained when depositing SnO with the 5 % to 25 % O₂ and annealing between 175 °C and 275 °C. The transfer and output characteristics of the SnO TFT with the Ar/O₂ ratio of 23:3 during the deposition are shown in Fig. 3-9(a) and (b). The linear dependency between $|I_D|^{1/2}$ as a function of $V_G$ at $V_D = -60$ V shown in Fig. 9(c) suggests the SnO TFT follows the ideal TFT model.

As the bandgap of SnO is around 0.7 eV, if assuming the electron mobility and the hole mobility are the same, using $\exp\left[\frac{E_g}{(2k_BT)}\right]$ yields a theoretical on/off ratio of $7.0 \times 10^5$. However, the highest on/off ratio we have obtained is slightly higher than $10^3$, which is orders of magnitudes lower than the estimation. Such a low on/off ratio may be attributed to the band-tail states and/or the deep-level states, which are difficult to analyse using conventional measurements.

Understanding the carrier transport mechanism in the SnO TFTs may help to improve the electrical performance. Thus, low-temperature measurements of the SnO TFT are carried out. Compared with the low-temperature Hall effect measurements, one major advantage of the low-temperature measurements on TFTs is that the carrier concentration can be altered by applying different gate biases [29]. Besides, the off-current at different temperatures may also reveal the properties of the bandgap in the SnO film. Detailed discussion can be found in Chapter 8.

![Fig. 3-9](image.png)

**Fig. 3-9.** (a) Typical linear transfer characteristics and (b) output characteristics of the SnO TFT with the Ar/O₂ ratio of 23:3 during the sputtering. (c) $|I_D|^{1/2}$ as a function of $V_G$ at $V_D = -60$ V. The TFT was annealed in air at 250 °C for 1h.
According to the temperature dependent transfer curves, two different temperature dependencies are found in the drain current which are shown in Fig. 3-10 (a) and (b). It is found that the hole carrier transport is dominated by the band conduction at high temperatures as $I_D \propto T^{-1}$ and the variable-range-hopping mechanism at low temperatures as $I_D \propto T^{-1/4}$ [29]. The bandgap of the SnO film is found to be around 0.6 eV. Two distinguished regions in the density of states can be found in the bandgap. The band-tail states at around 30 meV above the valance band and the deep level states at 300 meV, which have a density of around $10^{20}$ eV$^{-1}$ cm$^{-3}$ and $10^{18}$ eV$^{-1}$ cm$^{-3}$, respectively. According to the XRD analysis, the high trap density may be attributed to the interstitial Sn and O atoms. Thus, the $p$-type performance of the SnO film could be further improved by optimising the chemical stoichiometry to reduce the number of interstitial atoms.

### 3.6. Complementary metal oxide semiconductor circuits

$P$-type SnO TFTs have a huge potential in fully oxide-based complementary electronics. In order to show the possibility of using SnO TFTs in complementary circuits, inverters and ring oscillators based on $p$-type SnO and $n$-type IGZO are demonstrated.

The IGZO layer and the SnO layer are deposited on silicon-silicon dioxide substrate using RF sputtering. The channel length and the channel width of the TFTs are 60 µm and 2 mm respectively. All patterns are defined by shadow masks. The SnO film is thermally annealed in air for 1 h at 225 °C.

The gain of the inverter is found to be 6.5 at a supply voltage, $V_{DD}$, of 40 V. The threshold voltage is 17 V, which is close to the ideal value of 20 V which equals $V_{DD}/2$. By Fig. 3-10. Log($I_D$) as a function of (a) $T^{-1}$ and (b) $T^{-1/4}$ from 10 K to 300 K.
cascading 3 inverters, a three-stage ring oscillator is demonstrated shown in Fig. 3-11(a). In Fig. 3-11(b), the oscillation frequency is found to be 2.63 kHz with a supply voltage of 40 V. As the oscillation frequency of the ring oscillator depends on the geometry of the TFTs, by reducing the channel length and the total overlapping length between S/D and gate electrodes, a higher oscillation frequency can be obtained. The demonstration of the ring oscillator shows the potential of combining SnO and IGZO in large-area fully oxide-based complementary electronics.

References


Chapter 4

Flexible Indium-Gallium-Zinc-Oxide Schottky Diode Operating beyond 2.45 GHz

J. Zhang, Y. Li, B. Zhang, H. Wang, Q. Xin, and A. Song.

*Nat Commun*, vol. 6, 2015.

My contributions:

I have fabricated all the devices, performed most of the measurements excluding the EDX analyses, participated in the high-frequency measurements up to 20 GHz, analysed all the data, and prepared all the graphs.
Flexible Indium-Gallium-Zinc-Oxide Schottky Diode Operating beyond 2.45 GHz

Jiawei Zhang¹, Yunpeng Li², Binglei Zhang³, Hanbin Wang², Qian Xin², Aimin Song¹²*

¹School of Electrical and Electronic Engineering, University of Manchester, Manchester M13 9PL, United Kingdom.
²School of Physics, Shandong University, Jinan, 250100, P. R. China.

Correspondence and requests for materials should be addressed to A. S. (email: A.Song@manchester.ac.uk)

Abstract
Mechanically flexible mobile phones have been long anticipated due to the rapid development of thin-film electronics in the last couple of decades. However, to date, no such phone has been developed, largely due to a lack of flexible electronic components that are fast enough for the required wireless communications, in particular the speed-demanding front-end rectifiers. Here, Schottky diodes based on amorphous Indium-Gallium-Zinc-Oxide (IGZO) are fabricated on flexible plastic substrates. Using suitable radio-frequency mesa structures, a range of IGZO thicknesses and diode sizes have been studied. The results have revealed an unexpected dependence of the diode speed on the IGZO thickness. The findings enable the best optimised flexible diodes to reach 6.3 GHz at zero bias which is beyond the critical benchmark speed of 2.45 GHz to satisfy the principal frequency bands of smart phones such as those for cellular communication, Bluetooth, Wi-Fi and GPS.
Introduction

Since wireless radio transmissions were first achieved in the 1880s, telecommunications have evolved to the point where instant global communication is a daily reality, currently contributing more than a trillion dollars to the world economy per year\(^1\). Consumer demands for higher-performance, more fashionable mobile phones are now unprecedented. Mechanically flexible mobile phones in particular have long been envisaged in the recent rapid development of thin-film electronics. If these visions are realized, such wearable electronics could transform a range of electronic gadget concepts.

Amongst the available flexible semiconductor films, Indium-Gallium-Zinc-Oxide (IGZO) has shown perhaps the most commercial potential due to its high electron mobility and possibility of low-temperature film deposition on plastic substrates\(^2-6\). It has already seen rapid adoption as the channel material in backplane driver transistors in some newest flat-panel displays where a transistor speed of 200 Hz suffices\(^7,8\). In cellular phone communications, transistors are mostly used in logic circuits which may work at a low clock frequency. The earliest mobile phone processors were typically clocked at a few MHz\(^9\). However, the front-end rectifiers must always operate at the transmission microwave frequencies: 935 MHz to 1.88 GHz for cellular communications, around 2.4 GHz for typical IEEE 802.11b/g/n Wi-Fi channels and Bluetooth, 1.58542 and 1.2276 GHz for global satellite positioning (GPS), 3.8 GHz for highest 4G LTE band and even 5 GHz for the newest 802.11a/h/j/n/ac Wi-Fi channels.

There have been highly desirable efforts to develop high-speed Schottky diodes based on metal oxide semiconductors\(^10\), organic semiconductors\(^11-14\) and conventional semiconductors\(^15-17\). Most of these were on glass substrates, e.g., pentacene and C\(_{60}\) pin diodes working as rectifiers up to 300 MHz\(^19\); organic pentacene Schottky diodes operating up to 870 MHz\(^19\); diodes based on C\(_{60}\) and tungsten oxide showing a cut-off frequency of 800 MHz\(^20\). However, these devices required high-temperature process steps and hence could not be made on plastic substrates. Moreover, these achieve speeds are yet well below 2.45 GHz. So far, the work on flexible substrates is very limited, mainly including polythiophene-based Schottky diodes with a cut-off frequency of 14 MHz\(^11\), polytriarylamine-based devices with a cut-off frequency of 10 MHz\(^13\), and pentacene-zinc oxide-based diodes with a cut-off frequency of 15 MHz\(^14\). The frequency limitation of flexible organic diodes restricts their high-speed applications. Conventional semiconductor membranes and particles are another option for active layers in flexible diodes. By transferring single crystalline silicon\(^15\) and germanium\(^16\) membranes on flexible substrates, the diodes demonstrated frequency responses up to 30 and 10 GHz respectively. The flexible Schottky diodes based on crystalline silicon micro-particles\(^17\) also obtained a cut-off frequency of 1.6 GHz. However, due to the material and process complexity and costs, such technologies
are yet to prove commercially viable for flexible electronics. Metal-oxide semiconductors, on the other hand, have already been incorporated into flexible electronics in both academia and industry\textsuperscript{7,8,21,22}. To date, most research on metal oxide semiconductors has focused on thin-film transistors (TFTs)\textsuperscript{7,8,21-23}, and little has been reported on diodes\textsuperscript{24-30}. The recent progresses on high-speed IGZO Schottky diodes including 900 MHz in 2012\textsuperscript{25}, 1.8 GHz in 2013\textsuperscript{26} and 3 GHz in 2014\textsuperscript{27}, but these were all made on glass substrate using high-temperature annealing processes and hence not applicable to flexible substrates. To the best of our knowledge, the highest frequency obtained on plastic substrates was 27 MHz by IGZO-Cu\textsubscript{2}O diodes\textsuperscript{30}. To date, no flexible metal oxide diodes, to our knowledge, have been able to reach the benchmark speed of 2.45 GHz.

In this work, we demonstrate what to our knowledge is the first flexible IGZO Schottky diode fabricated at room temperature and operating beyond 5 GHz without any post-treatment. First, we fabricate Schottky diodes with different IGZO layer thicknesses, and analyse their current-voltage (J-V) and capacitance-voltage (C-V) characteristics. Secondly, the intrinsic and extrinsic components that determine the diode cut-off frequencies are extracted from the S-parameter measurements. Based on the relationship between series resistance and capacitance, we provide

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig1.png}
\caption{DC properties of IGZO Schottky diodes on glass substrate. (a) Structure of the IGZO Schottky diode. The device consists of a 50 nm thick Pt layer (Dark blue), an IGZO layer (red) with a thickness of 50 nm, 80 nm or 100 nm and an Al electrode (Light blue). (b) Cross-section structure of the diode. $L_d$ represents the thickness of the IGZO layer and $W_d$ is the depletion width caused by the Schottky barrier. (c) Equivalent circuit of the IGZO Schottky diode. $R_s$ is the series resistance including the bulk resistance of IGZO and the ohmic contact resistance. $R_{es}$ is the effective series resistance in the rectifier circuit which is due to the depletion width. $C_d$ is the capacitance caused by the depletion layer. (d) Band diagram of the Schottky barrier between IGZO and Pt. The barrier height can be obtained either from J-V or C-V characteristics. (e) J-V characteristics of the Schottky diodes with different IGZO thicknesses from 50 to 100 nm. (f) Solid lines represent the C-V curves, using which the built-in voltage and background carrier density can be obtained. The dashed lines show the thickness of IGZO layer which contributes to $R_{es}$ as a function of the applied voltage. (g) Capacitance of devices with different sizes and thicknesses under 0 V bias with error bars depicting standard deviation. In total we have fabricated 5 devices under each condition in each of the two rounds of fabrications. (h) Richardson plot and temperature dependency values of $\phi_{eff}$, $n$ and $n^{-1}$.}
\end{figure}
two methods to further improve the diode speed. Finally, flexible thin-film IGZO Schottky diodes with suitable RF mesas are fabricated, and a single-stage rectifier on a polyethylene terephthalate (PET) substrate is demonstrated at frequencies up to 3 GHz.

**Results**

**IGZO Schottky diodes on glass substrates.**

For the ease of fabrication and testing, we first use glass substrates to study the effects of some key parameters on the device including DC and high-frequency performance. Figure 1(a) shows the structure of the IGZO Schottky diode with a vertical design. By adopting the coplanar waveguide and mesa structure, low signal losses at high frequency can be achieved, this also serves to reduce the fringe capacitance and the possibility of breakdown. An aluminium (Al) electrode is used here as the ohmic contact because the work function of Al is only 4.2 eV and the contact resistance between Al and IGZO is known to be quite low. A platinum (Pt) electrode is chosen as the Schottky contact due to its high work function of 5.4 eV. The overlapping region between the two electrodes determines the effective area of the diode. By changing the size of Al ohmic contacts through photolithography, devices with different active areas from $20 \times 10 \mu m^2$ to $20 \times 50 \mu m^2$ are obtained. Figure 1(b) shows the cross-section schematic of the IGZO diodes. Three different IGZO thicknesses have been investigated, i.e., $L_S = 50$ nm, 80 nm and 100 nm. In Figure 1(b), $W_D$ denotes the depletion depth caused by the bending of the conduction band in the IGZO. The equivalent circuit of the diode is shown in Figure 1(c) where $R_s$ is the series resistance, comprised of the bulk resistance of the IGZO layer and the ohmic contact resistance from the Al contacts. However, in order to describe the high frequency behaviour, the effective series resistance, $R_{es}$, is introduced. It is obtained from the series resistance $R_s$ minus the resistance of the depletion region. This is because under a forward bias, the depletion capacitance is only in series with a part of the series resistance $R_s$, i.e., $R_{es}$, as shown in Figure 1(c). It is the effective series resistance $R_{es}$ that is the main factor in determining the high-frequency performance of the diode. Figure 1(d) shows the band diagram of the Pt-IGZO Schottky junction, where $\phi_b$ is the barrier height, $V_{bi}$ is the built-in voltage, and $E_C - E_F$ describes the energy gap between the conduction band and Fermi level.

In this work, the Schottky diode performance is optimised by testing different IGZO layer thicknesses and oxygen/argon ratios during the sputtering deposition process of the IGZO film. It is widely accepted that in IGZO TFTs, an excess oxygen content will degrade the film stability and mobility. For the IGZO Schottky diodes in our experiment, the thickness of IGZO is no more than 100 nm. At low voltage biases, the diode performance is limited by the Schottky junction barrier instead of the IGZO mobility. The extra oxygen during the IGZO deposition is
used to passivate the dangling bonds at the Schottky interface in order to reduce the Fermi level pinning effect\textsuperscript{30} (shown in Supplementary Fig. 1 and Supplementary Table 1). At high biases, the current is limited by the series resistance which is related to the IGZO mobility. It is found in this work that 3% oxygen during the deposition results in a good compromise with a high quality Schottky barrier and a relatively low series resistance. The J-V characteristics of the diodes with different IGZO thicknesses are shown in Figure 1(e). The diode with a 50 nm IGZO layer exhibits the highest current, while the device with a 100 nm IGZO layer shows the highest rectification ratio. Detailed analyses are summarised in Supplementary Table 2 and Supplementary Fig. 2. At an applied voltage of 1 V, the diode with a 50 nm-thick IGZO layer between the Pt and Al contacts exhibited a current density of 20 A cm\textsuperscript{-2} giving a total DC resistance of 0.05 Ω cm\textsuperscript{2}. When the IGZO layer becomes thicker, the current density drops. At an applied voltage of 1 V, the total resistance for the devices with IGZO thicknesses of 80 nm and 100 nm are 0.15 Ω cm\textsuperscript{2} and 0.26 Ω cm\textsuperscript{2} respectively. This shows that the series resistance has a sensitive dependence on the thickness of IGZO layer. Given that the effective Richardson constant of IGZO is 41 A cm\textsuperscript{2} K\textsuperscript{2} and based on the thermionic emission theory\textsuperscript{22,34,35}, the extracted barrier heights are 0.79 eV, 0.73 eV and 0.65 eV for the diodes with 100, 80, and 50 nm IGZO layer, respectively (fitting is shown in Supplementary Fig. 3). It is not clear why a thicker IGZO layer results in a higher Schottky barrier, perhaps it is due to the electrode evaporation process in vacuum\textsuperscript{22,28}. Pt-IGZO Schottky barrier is sensitive to the oxygen content at the interface\textsuperscript{30}. During the evaporation process, oxygen may escape from the IGZO layer, causing oxygen deficiency. Such defects are responsible for the Fermi level pinning, resulting in lower barrier heights and built-in voltages. Doping from the top electrode may also contribute to lowering the series resistance (shown in Supplementary Fig. 4).

The C-V characteristics of the devices with different IGZO layer thicknesses are shown in Figure 1(f). At low forward biases, the capacitance remains almost constant suggesting that the IGZO layer is fully depleted in each of the devices. Using $C = \varepsilon_0\varepsilon_r/L_S$, where $\varepsilon_0$ is the vacuum permittivity, the relative dielectric constant of IGZO, $\varepsilon_r$, is found to be 16. The dotted line represents the thickness of IGZO which contributes to the effective series resistance $R_{es}$. It shows that at around 0.7 V, the depletion width becomes negligible when compared with the thickness of the IGZO layer in all the three devices, i.e., $L_S \approx W_D$. From the $C^{-2}$ curves in Figure 1(f), the built-in voltage, $V_{bi}$, and the background charge density, $N_{bg}$ can be extracted. From the series resistance obtained from the J-V characteristics of an 80 nm-thick IGZO Schottky diode, the free carrier density is $3.33\times10^{13}$ cm\textsuperscript{-3} which is orders of magnitude lower than the background doping density, $5.01\times10^{16}$ cm\textsuperscript{-3} due to the subgap traps in IGZO\textsuperscript{12}. The energy-dispersive X-ray spectroscopy (EDX) measurement suggests that In:Ga:Zn ratio is 4.2:4.4:2.0 as shown in Supplementary Fig. 5. According to the study conducted by Olziersky \textit{et al},
al., the moderate In/Ga atom ratio of 0.95 should yield a reasonably high carrier mobility. We have therefore assumed that the mobility of IGZO is 10 cm² V⁻¹ s⁻¹ (roughly the mobility value obtained from thin-film transistors based on the similar IGZO material). Figure 1(d) shows that the barrier height can be obtained from the sum of \( V_{bi} \) and \( E_C - E_F \). Based on Supplementary Note 1, \( (E_C - E_F) \) is found to be 0.308 eV and hence the barrier height from the C-V plot is 0.864 eV. It is higher than the barrier height from J-V characteristics, which is most likely because of the imperfect uniformity of the Schottky junction. In Figure 1(g), the capacitance of the IGZO Schottky diode at 0 V bias is proportional to \( A/L_S \) where \( A \) is the area of the device. It shows that there are two ways to reduce the device capacitance, namely by shrinking the size of the device and by increasing the thickness of IGZO layer. Figure 1(h) shows the temperature dependent values of the diode derived from the J-V characteristics. The Richardson plot suggests the current transport is governed by thermionic emission since the diffusion transport is less sensitive to temperature. The large deviation at low temperatures can be explained by the barrier height fluctuation model, i.e., the barrier height follows a Gaussian distribution, \( \phi_{eff} = \phi_m - q\sigma^2/(2k_B T) \), where \( \phi_{eff} \) is the effective barrier height, \( \phi_m \) is the mean barrier height and \( \sigma \) is the standard deviation. It is found that for the diode with an IGZO thickness of 80 nm and a diameter of 1 mm, the mean barrier height is 1.40 eV with a standard deviation of 0.17 eV. Furthermore, \((n^{-1.1})\) has a linear dependency with \( T \) which implies the inhomogeneities in the barrier height. The cause of the barrier fluctuation is considered to be a consequence of IGZO grain boundaries, oxygen deficiency and different Pt crystalline orientations. A comparison of
background doping density and free carrier concentration highlights an interesting difference between IGZO and traditional covalent semiconductors, namely, not all ionized atoms in IGZO contribute free carriers; this discrepancy can be attributed to subgap traps\textsuperscript{30}. Given the direct dependency of the C-V relationship upon the background doping concentration, it is expected that the C-V barrier height shall be lower than the mean barrier height obtained by the low-temperature measurement.

**High frequency properties on glass substrates**

In order to study the high-frequency properties of the diodes, it is necessary to analyze the S-parameter of the device to extract the capacitive and resistive components of the diodes. Figure 2(a) shows a photograph of the sample and RF coplanar probe used for the high-frequency characterizations. Figure 2(b) presents that the effective series resistance $R_{\text{es}}$ and reactance of the diode at different frequencies determined from the S-parameter at zero bias. As shown in Figure 2(d), the obtained $R_{\text{es}}$ is very different from the total series resistance $R_s$ that is determined from the J-V curves. Whereas $R_s$ varies much more significantly, $R_{\text{es}}$ is virtually constant for different IGZO thicknesses. This confirms that when the IGZO layer is fully depleted, the ohmic contact resistance is considered as the sole contributor to the series resistance. Figure 2(c) shows that the capacitive components of devices remain fairly constant as a function of the frequency, and the capacitive values are in good agreement with the previous C-V measurement results.
As illustrated in Figure 1(c), the cut-off frequency of the diode should be determined by $R_{es}$ and the capacitance, $f = 1/2\pi R_{es}C_D$. Since $R_{es}$ is fairly constant in all devices with different IGZO thicknesses, the results might seemingly suggest that the diode with 100 nm thick IGZO should have the lowest capacitance and hence the best high-frequency performance. To test this, a single-stage rectifier measurement setup shown in Figure 2(e) is used, which involves a 100 nF load capacitor $C_L$ and a 1 MΩ load resistor $R_L$. The input signal is generated by Agilent E5061B ENA network analyser and the rectified DC output is measured by Agilent 34401A voltage meter. Figure 2(f) plots the dependence of the output voltage as a function of the RMS voltage of the input RF signal at 1 GHz, the result is entirely unexpected because the 100 nm diode actually exhibits the worst performance. To understand this, we refer to the setup in Figure 2(e). Upon the application of an AC signal, the diode is negatively biased during most of a period of the AC signal due to the positive DC voltage accumulated over the load capacitor. However, the capacitor is only charged during the short duration in each period when the diode is positively biased. For instance, the peak input voltage when $V_{\text{RMS}} = 1$ V is 1.41 V, at which the 80 nm diode produces a DC output of about 0.3 V, meaning the diode is forward biased at 1.1 V. At such a large forward bias, the IGZO depletion layer thickness becomes small, meaning that part of the IGZO layer shall contribute to the effective series resistance $R_{es}$. Preliminary results have indicated that $R_s$ of the 100 nm IGZO device is about 5 times that of the 50 nm diode at 1 V, and hence seriously reduced its ability to produce a large rectified output voltage despite having the lowest capacitance. We thus conclude that the hypothesis that the thicker IGZO layer the better the high-frequency performance is only valid below a critical value. Besides, the output voltage is measured across the 1 MΩ load resistor. As the IGZO thickness increases, the series resistance increases and results in a smaller voltage drop on the load resistor and a decrease in the rectified voltage. With this, we choose 80 nm as the IGZO layer thickness for the following work on flexible substrate.

Flexible Schottky diodes and GHz operations

Having optimised the diode properties on glass substrate, we have fabricated devices on Dupont flexible PET films using the same lithography steps. The devices are bendable as illustrated in Figure 3(a). The J-V characteristics are shown in Figure 3(b), which yields an ideality factor of 2.1 and a barrier height of 0.51 eV. From the C-V curve in Figure 3(c), the built-in voltage is found to be 0.45 V. As expected, compared with the diodes fabricated on glass substrates under the same condition, the performance of the flexible devices is more affected by the inhomogeneous barrier height caused by the uneven substrate surface. Figure 3(d) shows the curves of reactance and resistance versus frequency which are obtained from the S-parameters of the devices with different active areas. Since the cut-off frequency is given by the intersection of resistance and reactance curves, for the devices with an area of 200 µm², the cut-off
frequency is found to be 6.3 GHz. This is the highest achieved in our studies. The cut-off frequency of the devices with an area of 400 and 800 µm² is also higher than 5 GHz. Such zero-bias cut-off frequency is commonly regarded as the intrinsic speed of the diodes. When the diode is used in practical applications as a rectifying circuit, load resistance, impedance matching and losses from the transmissions will need to be considered.

The single stage rectifier circuit is used again to test the diode performance at high frequencies. Figure 3(e) shows the output voltage versus frequency at different input signal strengths. Figure 3(f) plots the output DC voltage as a function of the input RF signal voltage at different frequencies. When the frequency of the input signal increases, the output voltage starts to drop. Even though the output reduces with the frequency, at 2.45 GHz the rectified voltage is measured to be 0.6 V for an input RMS voltage of 1.41 V. We note that this is at the maximum output of our signal source, and the diode output can certainly increase with a stronger input signal.

**Discussion**

So far, we have demonstrated that flexible Pt-IGZO Schottky diodes exhibit an intrinsic cut-off frequency of 6.3 GHz. It is of course possible to adopt the multistage rectifier circuits to double or triple the output voltage as often used in many RFID circuits. As such, the Pt-IGZO diodes may be suitable as the front end rectifier and power supply in a variety of low-voltage operation devices.

In order to further increase the device performance, some treatments can be adopted for the IGZO Schottky diodes. As mentioned in several studies before, a post-annealing process can improve the diode barrier height and ideality factor. Fast laser annealing has been successfully demonstrated to treat IGZO TFTs on flexible substrate without heating the substrate beyond the glass transition temperature.

Considering that the diode is highly negatively biased in practical rectifier circuits, the diode breakdown voltage is an important parameter. In Supplementary Fig. 6, the diode with the same fabrication process in our experiment exhibits excellent reverse current characteristics, showing a negative breakdown voltage higher than 10 V. Also, the IGZO Schottky diodes show good air stability, and almost no degradation is observed after 30-day exposure in air as illustrated in Supplementary Fig. 7.

In the single-stage rectifier circuit, the output performance is not only related to the intrinsic cut-off frequency of the diode, but is also influenced by the quality of the load resistance and impedance matching. Due to the frequency-dependent impedance of the diode, it is impossible
to avoid the signal reflection and power loss at all frequencies. However, in most application scenarios, the circuit only operates in a certain frequency band. Thus, the system can be specifically designed to maximize power transfer and output within a fairly narrow band.

Regarding the perspectives of flexible smart phones, the mechanical flexibility may well attract customers through new user experiences, fashion and style rather than the data processing capacity. Although silicon chips currently dominate, Nokia’s early PDA, Nokia 9000 Communicator, has an i386 CPU containing around 300,000 transistors. In comparison, the recently developed IGZO-TFT-driven 14” display by Fujitsu has a 3200x1800 resolution, meaning that the display backplane driver contains millions of transistors. Furthermore, the recently developed p-type SnO with good mobility and stability has already enabled successful CMOS logic gates\(^39\). In terms of transistor speed, Yin et al. demonstrated IGZO ring oscillators at 106.5 MHz with a 0.5 \(\mu\)m channel length\(^40\). By reducing the device size to the current Silicon technology node of 14 nm, IGZO circuits can well operate at GHz frequencies.

In summary, we have reported the first flexible IGZO Schottky diodes with cut-off frequency up to 6.3 GHz. By analysing the J-V and C-V characteristics, a high-frequency model is proposed. Surprisingly the hypothesis that the thicker IGZO layer the better the high-frequency performance is found to be invalid in the experiments and our finding is discussed in terms of the series resistance and capacitance under different biases. By combining such GHz IGZO diodes with less speed-demanding TFTs, a range of flexible microwave circuits and possibly mobile phones may be constructed.

**Methods**

**Device Fabrication.** Corning 7059 glass and Dupont Melinex PET film were used as substrates in this experiment. Before the fabrication, the substrates were degreased by supersonic cleaning in deionized water, acetone and methanol, then dried with nitrogen and placed in UV/Ozone chamber for 30 min. 50 nm-thick Pt electrodes were deposited by RF sputtering at 80 W in pure argon. And subsequently IGZO (from Lesker, In:Ga:Zn=1:1:1) was sputtered at 80 W in argon with 3% oxygen at 0.5 Pa. The Al electrodes were formed by using thermal evaporation. Patterns were defined by photolithography with standard processes. All devices were fabricated and tested at RT without any thermal annealing process.

**Measurements.** The J-V characteristics were made using Agilent E5260B Semiconductor analyzer at RT in dark. Agilent E4980A LCR meter was used to measure the capacitance of IGZO Schottky diodes. The DC output of the IGZO Schottky diodes was measured by Agilent 34401A digital multi-meter. The coupling to the device was through RF probes (GGB Industries Inc.) and the AC signal was generated by Agilent E5061B network analyser. The S-parameters
were measured by Agilent PNA-X N5247A network analyser after calibration. The EDX spectroscopy was performed by an FEI Nova NanoSEM 450 scanning electron microscope with an Oxford Instrument X-MaxN Silicon Drift Detector. The measurements were performed at 20 keV with a scan area of 51 µm × 34 µm. The In L, Ga K and Zn K peaks were selected for the analyses.

References


Yin, H. *et al.* Bootstrapped ring oscillator with propagation delay time below 1.0 nsec/stage by standard 0.5µm bottom-gate amorphous Ga2O3-In2O3-ZnO TFT technology. *Int. Electron Device Meeting 2008*, 1-4 (2008).

**Acknowledgements**

We are grateful to the University of Manchester and the technical support from M. McGowan, L. Zhang, J. Jin, Y. Alimi, J. Wilson and X. Ma.

**Author Contributions**

A. S. conceived the project. J. Z. designed and fabricated the diodes and performed the DC and RF measurements. P.Y., B.Z and Q.X. performed the EDX characterisation. J. Z., Q.X. and A. S. contribute to the manuscript.

**Competing Financial Interests statement**

The authors declare no competing financial interests.
Supplementary Figures

Supplementary Figure 1. Effects of adding oxygen during IGZO sputtering. The extra oxygen during IGZO deposition provides a higher on/off ratio and a small increase in the series resistance.

Supplementary Figure 2. Barrier heights and ideality factors of the devices with different IGZO thicknesses. Error bars stand for standard deviation. We fabricated 5 devices under each condition in each of the two rounds of fabrications.
**Supplementary Figure 3. I-V characteristics of IGZO Schottky diodes.** The dash line is the fitting result with the thermionic emission model.

**Supplementary Figure 4. Background doping density as a function of depletion width with different IGZO thicknesses.** It suggests that the doping from the top electrode also contributes to the background doping density.
Supplementary Figure 5. EDX analyses of IGZO atom ratios under different sputtering conditions. The IGZO layers were deposited by RF sputter at 80 W in pure Ar and in 3% O₂ for 100 nm on glass substrates, respectively. After introducing 3% O₂ during deposition, the In/Ga ratio increased from 0.90 to 0.95.

Supplementary Figure 6. Diode behavior under large reverse biases. The result shows that the breakdown voltage is higher than -10 V. The current at 2 V is $10^3$ higher than the reverse current at -10 V.
Supplementary Figure 7. 30-day stability of the Schottky diode. The ideality factor and barrier height remain nearly unchanged. There is a slight increase in series resistance and off current.
### Supplementary Tables

#### Supplementary Table 1. Effects of oxygen during sputtering

<table>
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<tr>
<th>IGZO Sputtering Condition</th>
<th>$\phi_b$ (eV)</th>
<th>$n$</th>
<th>On/off ratio</th>
<th>$R$ at 1.5 V ($\Omega \text{ cm}^2$)</th>
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<tr>
<td>Pure argon</td>
<td>0.52</td>
<td>2.50</td>
<td>$2.3 \times 10^4$</td>
<td>0.0126</td>
</tr>
<tr>
<td>Argon with 3% oxygen</td>
<td>0.72</td>
<td>1.56</td>
<td>$9.2 \times 10^4$</td>
<td>0.0435</td>
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#### Supplementary Table 2. Properties of the diodes with different IGZO thicknesses.

<table>
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<tr>
<th>$L_s$ (nm)</th>
<th>$N_{bg}$ (cm$^{-3}$)</th>
<th>$V_{bi}$ (V)</th>
<th>$W_D$ (nm)</th>
<th>$N_C$ (cm$^{-3}$)</th>
<th>$E_C$- $E_F$ (eV)</th>
<th>$\varphi_b$ from CV (eV)</th>
<th>$\varphi_b$ from JV (eV)</th>
<th>$R_s$ ($\Omega \text{ cm}^2$)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>$9.92 \times 10^{16}$</td>
<td>0.46</td>
<td>50</td>
<td>$6.25 \times 10^{13}$</td>
<td>0.29</td>
<td>0.75</td>
<td>0.65</td>
<td>0.05</td>
<td>1.52</td>
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<tr>
<td>80</td>
<td>$5.01 \times 10^{16}$</td>
<td>0.56</td>
<td>80</td>
<td>$3.33 \times 10^{13}$</td>
<td>0.31</td>
<td>0.87</td>
<td>0.73</td>
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<td>1.45</td>
</tr>
<tr>
<td>100</td>
<td>$3.08 \times 10^{16}$</td>
<td>0.58</td>
<td>100</td>
<td>$2.92 \times 10^{13}$</td>
<td>0.32</td>
<td>0.90</td>
<td>0.79</td>
<td>0.26</td>
<td>1.21</td>
</tr>
</tbody>
</table>
Supplementary Notes

Supplementary Note 1. Properties of Schottky diodes with different IGZO thicknesses

According to the thermionic emission theory, the relation between current and voltage is expressed as:

\[ J = A^* T^2 \exp \left( - \frac{q \phi_b}{k_B T} \right) \left\{ \exp \left( \frac{q(V - J R_s)}{n k_B T} \right) \right\} \]  \hspace{1cm} (1)

where \( A^* \) is the Richardson constant which can be obtained from effective electron mass in IGZO \( m^* = 0.34 m_0 \), \( T \) is the temperature, \( \phi_b \) stands for the barrier height, \( n \) is defined as the ideality factor, and \( R_s \) represents the series resistance of the diode.

The diode capacitance is related to the built-in voltage, \( V_{bi} \), and the background carrier density, \( N_{bg} \):

\[ C_D^{-2} = \frac{2(V_{bi} - V)}{q \varepsilon_0 \varepsilon_r N_{bg}} \]  \hspace{1cm} (2)

The depletion width under different biases can be given by \( W_D = \varepsilon_0 \varepsilon_r / C_D \).

From both C-V and J-V measurements, the carrier densities remain the same order of magnitude for the devices with different IGZO thicknesses while the barrier heights increase slightly. All parameters are shown in Supplementary Table 1.

Assuming the series resistance, \( R_s \), is mainly from the bulk resistance of the IGZO layer, the free carrier density, \( N_c \), can be obtained by

\[ N_c = \frac{A}{q \mu c_L} \]  \hspace{1cm} (3)

where \( A \) is the active area of the diode and \( d \) is the thickness of the IGZO layer.

The energy gap between the conduction band and Fermi level is

\[ E_c - E_F = k_B T \ln \left( \frac{N_{de}}{N_c} \right) \]  \hspace{1cm} (4)

where \( N_{de} \) is the effective density of states in the conduction band of IGZO. \( N_{de} \) can be expressed as

\[ N_{de} = 2 \left( \frac{2 \pi m^* k_B T}{\hbar^2} \right)^{3/2} M_C \]  \hspace{1cm} (5)

where \( M_C \) is the number of equivalent minima in the conduction band. For IGZO, \( N_{de} = 5 \times 10^{18} \text{ cm}^{-3} \).
Chapter 5

Room Temperature Processed Ultra High Frequency Indium Gallium Zinc Oxide Schottky Diode

J. Zhang, H. Wang, J. Wilson, X. Ma, J. Jin, and A. Song.


My contributions:

I have fabricated all the devices, performed most of the measurements, participated in the high-frequency measurements up to 20 GHz, analysed the data, and prepared all the graphs.
Room Temperature Processed Ultrahigh-Frequency Indium–Gallium–Zinc-Oxide Schottky Diode

Jiawei Zhang, Hanbin Wang, Joshua Wilson, Xiaochen Ma, Jidong Jin, and Aimin Song, Senior Member, IEEE

Abstract—Despite being one of the most promising amorphous semiconductors, indium–gallium–zinc oxide (IGZO) has been mostly studied in transistors at low frequencies with limited effort on high-speed diodes. In this letter, the IGZO Schottky diodes with different active areas are fabricated in co-planar microwave waveguides on glass substrates at room temperature. By reducing the area of the diode, the cutoff frequency at zero bias can be improved. We are able to show that the diode with the active area of 200 $\mu$m$^2$ has an intrinsic cutoff frequency beyond 20 GHz. By connecting the diode with a load, the rectifying circuit also exhibits a cutoff frequency of 4.2 GHz with the input power of 15 dBm. Simulations based on the diode properties are performed to include intrinsic and extrinsic components, and the results agree well with the experimental data.

Index Terms—Thin film devices, IGZO, Schottky barriers.

I. INTRODUCTION

A MORPHOUS indium-gallium-zinc-oxide (a-IGZO) has emerged as a promising semiconductor for thin-film electronics and it has already been rapidly adopted in display industries for backplane driver transistors because of the advantages of high carrier mobility, large-area uniformity, and room- or low-temperature deposition processes [1], [2]. The high transparency to visible light and amorphous structure also makes IGZO suitable in potential applications of flexible electronics [3], [4]. A range of novel electronic products such as low-cost radio-frequency identification (RFID) tags and wearable electronic gadgets have drawn much attention in recent years [5]. Apart from integration of transistors for data processing, RFID and communications electronics generally require high-speed, front-end rectifiers capable of operating at wireless communication frequencies for receiving and modulation of signals with antenna. These frequency bands include 13.56 MHz for smart cards, 1.58542 and 1.2276 GHz for GPS, 2.45 to 5.8 GHz for Wi-Fi and Bluetooth, around 3.8 GHz for 4G LTE, 3.1 GHz to 10.6 GHz for wireless USBs and 10.70 GHz to 12.75 GHz for satellite television signals.

So far, much work on metal-oxide-semiconductor-based rectifiers has been using thin-film transistors (TFTs) [6]–[10]. For ZnO TFTs, due to the high carrier mobility, an operation frequency of 2.45 GHz has been achieved with an overlap of 500 nm between the source/drain and gate electrodes [10]. The highest frequency obtained by IGZO TFTs reported to date is 0.384 GHz [9]. Such a speed is still inadequate for many of the wireless communication bands. To circumvent the issues with TFTs, high-speed Schottky diodes have been explored [11]. Several studies have been made on organic and inorganic thin-film-based Schottky diodes [12]–[15], and even nanodiodes [16]. Amongst of these, C$_{60}$ and tungsten oxide diodes showed a cut-off frequency of 0.8 GHz [15], IGZO Schottky diodes worked at 16.7 GHz on glass substrates and 6.3 GHz on plastic substrates under a zero bias [4].

In this letter, IGZO Schottky diodes are fabricated in co-planar microwave waveguides on glass substrate at room temperature (RT) with different active areas. Current density-voltage (J-V) and capacitance-voltage (C-V) characteristics of the diodes were measured and analyzed. The S-parameter measurements of the 200 $\mu$m$^2$ diode showed an intrinsic cut-off frequency beyond 20 GHz. The diodes were further tested in a rectifier circuit and the results were compared with simulations.

II. EXPERIMENTS

IGZO Schottky diodes were fabricated on Corning 7059 glass substrates at RT. A 50 nm-thick Pt film was deposited by RF sputtering in Ar at 80 W as the anode. An IGZO film was deposited as the active layer using RF sputtering in Ar with 3% O$_2$ at 5 $\times$ 10$^{-3}$ mbar with an RF power of 80 W. In Ref. 4, it is found that an IGZO thickness of 80 nm produced diodes with the best overall performance. Thus in this letter, we use 80 nm as the thickness of the active layer for all devices. The atomic ratio of the IGZO target is In:Ga:Zn=1:1:1. A top Al cathode was deposited using thermal evaporation. All patterns were defined by standard photolithography processes. The diode structure and the cross-section schematic are shown in Fig. 1. The active areas of the diodes are 20 $\mu$m $\times$ 10 $\mu$m, 20 $\mu$m $\times$ 30 $\mu$m, and 20 $\mu$m $\times$ 50 $\mu$m which are determined by the overlapping area...
of the top and the bottom electrodes. A co-planar microwave waveguide structure is adopted to reduce losses at high frequencies.

J-V characteristics of the diodes were measured with an Agilent E5260B semiconductor analyzer. C-V measurements were performed with an Agilent E4980A LCR meter at 10 kHz. An Agilent PNA-X N5247A was used to obtain the impedance properties and rectification properties. The output of the single-stage rectification circuit was measured using an Agilent B2902 source/measure unit. Simulations were performed using PSpice. All measurements were conducted at RT in dark.

III. RESULTS AND DISCUSSIONS

Fig. 2(a) shows the J-V characteristics of the diodes with active areas of 200, 600, and 1000 \( \mu \text{m}^2 \). The current follows the thermionic emission model which is described by

\[ J = A^* T^2 \exp \left( \frac{q \phi_b}{k_B T} \right) \left\{ \exp \left( \frac{q (V - J R_s)}{n k_B T} \right) - 1 \right\} \tag{1} \]

where \( A^* \) is the Richardson constant of IGZO, 41 A/(cm\(^2\)·K\(^2\)), which can be obtained from effective electron mass in IGZO, \( m^* = 0.34 m_0 \), \( T \) is the temperature, \( q \) is the electron charge, \( \phi_b \) stands for the barrier height, \( n \) is defined as the ideality factor, \( k_B \) is the Boltzmann constant, and \( R_s \) represents the series resistance of the diode [17], [18]. According to the fitting shown in Fig. 2(a), the diode with the area of 200 \( \mu \text{m}^2 \) has a barrier height of 0.78 eV and an ideality factor of 1.33. The series resistance is obtained from the linear fitting at high biases and found to be 0.47 \( \Omega \cdot \text{cm}^2 \), which is mainly attributed to the bulk resistance of the IGZO layer. According to the Hall effect measurement, the mobility is found to be 3.6 cm\(^2/(\text{V} \cdot \text{s}) \) [19] which is similar to the value obtained from TFTs and diodes based on the similar IGZO material [2], [18], [20]. For the Hall effect measurement a 200 nm IGZO film was deposited on a glass substrate at 80 W in Ar and 3% O\(_2\) mixture gas. The magnetic field used in measurement is 0.512 T. Thus the free carrier density, \( N_c \), of the IGZO active layer is found to be \( 2.94 \times 10^{13} \text{ cm}^{-3} \).

The diodes with different active areas show similar barrier heights and ideality factors according to the fitting shown in Fig. 2(a). However, it is found that the diode with the smaller active area has a higher current density. It is plausible that the current path through the diode is not uniform across the active area. Similar results have also been reported in Refs. 21 and 22.

C-V characteristics of the 200 \( \mu \text{m}^2 \) diode are shown in Fig. 2(b), which can be expressed as

\[ C_D^{-2} = \frac{2 (V_{bi} - V)}{A^* q \varepsilon_0 \varepsilon_r N_{bg}} \tag{2} \]

where \( A \) is the active area of the diode, \( V_{bi} \) stands for the built-in voltage, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon_r \) is the dielectric constant of IGZO which is taken to be 13 according to the capacitance at reverse biases, and \( N_{bg} \) represents the background doping density [17], [18]. At low biases, the capacitance remains at 0.30 pF since the IGZO layer is fully depleted. When the bias increases to around 0.75 V, the depletion width becomes smaller than the thickness of the IGZO layer, resulting in a rise in the capacitance. The increase can be described by using (2), giving \( V_{bi} = 1.06 \text{ V} \) and \( N_{bg} = 4.07 \times 10^{15} \text{ cm}^{-3} \). Compared with the free carrier concentration, we find that \( N_{bg} \) is two orders of magnitude larger, which indicates that not all ionized atoms contribute to free carriers due to subgap traps [18], [23]. The energy gap between the conduction band and Fermi level is found to be 0.33 eV given by \( E_C - E_F = k_B T \ln(N_{de}/N_c) \) where \( N_{de} \) is the effective density of states of IGZO and equals to \( 5.00 \times 10^{18} \text{ cm}^{-3} \) [19]. When using the C-V method, the barrier height is calculated as the sum of \( q V_{bi} \) and \( (E_C - E_F) \), which, in this case, is 1.39 eV. As expected, this is larger than the barrier height from the J-V characteristics since the results obtained from C-V measurements are more closely related to the mean barrier height [24]. The current over the Schottky barrier highly depends on the uniformity of the barrier potential, not just the mean barrier height [24]. Such inhomogeneities may be caused by oxygen deficiency and different Pt crystalline orientations [18], [23].

According to the C-V characteristics, the equivalent circuit of the diode is obtained as shown in the inset of Fig. 3. When the voltage drop across the diode is below 0.75 V, the IGZO layer is fully depleted. Thus, the depletion-layer capacitance, \( C_D \), is parallel to the IGZO bulk resistance, \( R_{bulk} \), and series to the resistance from the contacts, \( R_c \). As long as the diode remains fully depleted, \( R_{bulk} \) would have little influence on the high frequency properties as the cut-off frequency equals \( 1/(2 \pi R_c C_D) \). Based on the information mentioned above, a PSpice model was created. The J-V and C-V simulation results of the 200 \( \mu \text{m}^2 \) diode shown in Figs. 2(a) and (b) as the dashed lines agree well with the experimental data.
has little effect on the high-speed operation, which contributes to a higher cut-off frequency [26].

To test the diode rectifying properties, the device with the active area of 200 $\mu m^2$ is connected in a circuit shown in Fig. 3. The signal source is coupled to the diode through an internal bias tee and an RF probe. The output voltage is measured at the DC node across a 10 M$\Omega$ load resistor, $R_L$. The output voltage as a function of RF frequency ranging from 10 MHz to 10 GHz is shown in Fig. 4(b). The output DC voltage at an input RF power of 15 dBm at low frequencies is around 1.5 V. Thus, the cut-off frequency is estimated to be 4.2 GHz while the output voltage drops to 1.06 V, also known as the $-3$ dB point, which is beyond most of frequency bands used in RFID and smart phones. At 10 GHz with an input power of 15 dBm, the diode is still able to provide a 0.4 V DC output. By using the PSpice model, the high frequency simulation results are also shown as the dashed lines in Fig. 4(b), which agrees well with the experimental data. As the diode showed a cut-off frequency of 4.2 GHz in the rectifier circuit, the practical transition time should be shorter than 34.6 ps.

Compared with the intrinsic cut-off frequency obtained from the S-parameters, the diode in the rectifier circuit shows a lower cut-off frequency as expected. This is partially due to the 50 $\Omega$ input resistance from the signal generator, which results in a larger series resistance compared with $R_c$ and causes an extra voltage drop from the input signal. According to the thermionic emission theory, the reverse current of the diode is limited by the barrier height and saturates at $A^*T^2\exp(-q\phi_b/k_BT) = 3.0 \times 10^{-7} A \cdot cm^{-2}$. However, as shown in Fig. 2(a), the reverse current is found to be much higher, which may be caused by the image-force lowering and the defects at the Schottky interface [24]. The high leakage current may further lower the rectified voltage and the operation frequency. Another reason is the signal reflection caused by the diode itself. Signal reflection is inevitable since the impedance of the diode is frequency dependent. Although it is impossible to match the impedances in the circuit at all frequencies, in practical applications, an optimized design can be made to reduce the reflected power by taking into account the particular diode impedance at a certain frequency. Furthermore, by adopting multi-stage rectifier circuits, it is also possible to obtain a higher DC output [27], which is applicable to RFID and distributed wireless sensor networks where low microwave powers are commonly used.

**IV. CONCLUSIONS**

A room-temperature processed IGZO Schottky diode with an intrinsic cut-off frequency beyond 20 GHz has been demonstrated. The high-speed response has also been evaluated in a practical rectifier circuit operating beyond 4.2 GHz, which satisfies most of communication frequency bands used in typical mobile phones. Such fabrication process is also compatible with the current manufacturing process of IGZO TFTs in industries. Since it has been reported that the solution processed IGZO is able to form Schottky junction [28], the realization of such high speed operation suggests
a possibility to adopt printing roll-to-roll techniques for mass production of future low-cost RFID tags and wearable electronics.

REFERENCES


Chapter 6

Low-frequency Noise Properties in Pt-Indium Gallium Zinc Oxide Schottky Diodes

J. Zhang, L. Zhang, X. Ma, J. Wilson, J. Jin, L. Du, Q. Xin, and A. Song.


My contributions:

I have fabricated all the devices, performed all the measurements, analysed the data, and prepared all the graphs.
Low-frequency noise properties in Pt-indium gallium zinc oxide Schottky diodes

Jailei Zhang,1 Lingqing Zhang,1 Xiaochen Ma,1 Joshua Wilson,1 Jidong Jin,2 Lulu Du,3 Qian Xin,3 and Aimin Song1,3,a)

1School of Electrical and Electronic Engineering, University of Manchester, Manchester M13 9PL, United Kingdom
2Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool L69 3GJ, United Kingdom
3School of Physics, Shandong University, Jinan 250100, People’s Republic of China

(Received 10 March 2015; accepted 19 August 2015; published online 2 September 2015)

The low-frequency noise properties of Pt-indium gallium zinc oxide (IGZO) Schottky diodes at different forward biases are investigated. The IGZO layer and Pt contact were deposited by RF sputtering at room temperature. The diode showed an ideality factor of 1.2 and a barrier height of 0.94 eV. The current noise spectral density exhibited 1/f behavior at low frequencies. The analysis of the current dependency of the noise spectral density revealed that for the as-deposited diode, the noise followed Luo’s mobility and diffusivity fluctuation model in the thermionic-emission-limited region and Hooge’s empirical theory in the series-resistance-limited region. A low Hooge’s constant of 1.4 × 10−5 was found in the space-charge region. In the series-resistance-limited region, the Hooge’s constant was 2.2 × 10−5. After annealing, the diode showed degradation in the electrical performance. The interface-trap-induced noise dominated the noise spectrum. By using the random walk model, the interface-trap density was obtained to be 3.6 × 1015 eV−1 cm−2. This work provides a quantitative approach to analyze the properties of Pt-IGZO interfacial layers. These low noise properties are a prerequisite to the use of IGZO Schottky diodes in switch elements in memory devices, photosensors, and mixer diodes. © 2015 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4930019]
 FIG. 1. (a) Schematic of the Pt-IGZO Schottky diodes. (b) J-V characteristics of the Schottky diode. (c) log-C curve as a function of voltage. The slope gives the built-in voltage $V_b$ and the background doping density $N_{bg}$.

Ar and 3% O$_2$ mixed gas at 80 W. Then Al contacts were deposited by thermal evaporation and defined by a shadow mask. Finally, devices were placed in 20% acetic acid for 1 h, the J-V and C-V properties were measured in the dark with an Agilent E5260B semiconductor analyzer and an Agilent E4980A LCR meter at RT, respectively. LFN was measured using a SR570 low noise current amplifier and a NI USB-6211 data acquisition module at different bias in an isolated metal box at RT.

In Fig. 1(b), it shows the J-V characteristics of a Pt-IGZO Schottky diode with a radius of 0.5 mm. The linear part in the log scale indicates the current is limited by the thermionic emission. The relation can be expressed by

$$J = A^* T^2 \exp \left( \frac{-q\phi_b}{kT} \right) \left\{ \exp \left[ \frac{q(V - J R_s)}{n kT} \right] - 1 \right\}, \quad (1)$$

where $A^*$ is the Richardson constant which equals 41 A cm$^{-2}$ K$^{-2}$, $T$ is the temperature, $k$ is Boltzmann constant, $n$ is the ideality factor which describes the uniformity of the Schottky barrier, $\phi_b$ is the barrier height, and $R_s$ is the series resistance. For the as-deposited diode, the barrier height is found to be 0.94 eV and the ideality factor is 1.2.

An ideality factor close to unity suggests that thermionic emission is the primary mechanism of transport at low voltages. Figure 1(c) shows the room temperature C-V properties of the diode at 10 kHz. The background doping density, $N_{bg}$, and the built-in voltage, $V_{bi}$, can be determined from the $C_V$-V curve by using

$$C_V^2 = \frac{2}{q \varepsilon_0 N_{bg}} \left[ V_{bi} - V - \left( \frac{kT}{q} \right) \right], \quad (2)$$

where $\varepsilon_0$ is the permittivity of IGZO and equals 1.15 \times 10^{-12} \text{ F cm}^{-1}, a value obtained from the fully depleted capacitance of the diode at negative biases. From the lineard fitting which corresponds to the bulk of IGZO, $V_{bi}$ is found to be 0.55 V and $N_{bg}$ is 8.63 \times 10^{16} \text{ cm}^{-3} for the as-deposited diode. The series resistance obtained from the J-V curve is found to be 5.4 $\Omega$ cm$^2$. The Hall measurement revealed that the IGZO film had a carrier concentration of 1.70 \times 10^{12} \text{ cm}^{-3} and a mobility of 3.6 cm$^2$ V$^{-1}$ s$^{-1}$ at RT. The energy gap between the conduction band minimum and Fermi level, $(E_c - E_F)$, is found to be 0.40 eV by using $E_c - E_F = kT \ln(N_c/n_e)$ where $N_c$ is the effective density of states. As for IGZO, the effective electron mass in the conduction band, $m^*$, equals to 0.34$m_0$ making $N_c = 5.0 \times 10^{18}$ cm$^{-3}$. Since $\varphi_b = qV_{bi} + (E_c - E_F)$, the barrier height from C-V measurements of the as-deposited diode is 0.95 eV, which is slightly higher than the barrier height from the J-V measurements. The difference is caused by image force lowering and the inhomogeneities in the barrier height. After annealing the diode at 100 °C in air for 1 h, the J-V and C-V characteristics exhibit appreciable degradation in performance. The ideality factor increases to 2.1. The barrier height obtained from the J-V characteristics drops to 0.85 eV. From the C-V curves, $N_{bg}$ increases to 1.51 \times 10^{17} \text{ cm}^{-3}$ and $V_{bi}$ is found to be 0.71 V. The decrease in barrier height and the increase in $N_{bg}$ are attributed to interface states.

The LFN properties at different forward biases are shown in Figs. 2(a) and 2(b). The bias voltage varies from 0.25 V to 1.2 V. It is clear that the current noise, $S_I$, is proportional to $1/f$ at low frequencies, which means that the LFN of IGZO Schottky diode is dominated by flicker noise. At high frequencies, the current spectral density becomes flat due to the background noise generated from current amplifiers. No G-R noise is found in the current spectral density.

In order to further analyze the noise properties, a plot of the current spectral density at 10 Hz as a function of the device currents is shown in Fig. 3(a). For the as-deposited diode, two separate regions can be discerned in the current dependencies of $S_I$. The gradient is found to be proportional to $I$ at low currents and $I^2$ at high currents. For the thermally annealed diode, the current spectral density is found to be slightly higher and proportional to $I^2$. In Fig. 3(b), it shows the current dependencies of the voltage noise, $S_V$, by using the relation $S_V/I^2 = S_I/V^2$. The thermally annealed diode still shows a higher voltage noise than the as-deposited device.

In the last few decades, the LFN properties of Schottky diodes have been widely discussed. However, to date, most of the models remain debatable and are difficult
to validate experimentally. In general, the dominant LFN comes from two separate sources, namely, series resistance and space-charge. Three theories can be used to explain the noise properties generated in the space-charge region, which are mobility and diffusivity fluctuation model,\textsuperscript{35} trapping and tunneling model,\textsuperscript{31} and random walk model.\textsuperscript{32,33} The mobility and diffusivity fluctuation model was first proposed by Kleinpenning in 1979.\textsuperscript{35} In the late 1980s, Luo et al. corrected Kleinpenning’s model and developed a widely accepted theory to describe the thermal emission limited noise,\textsuperscript{13} which is given by

\begin{equation}
S_I = \frac{2\mu l}{I} \left( \frac{v_t}{v_d} \right)^2 \frac{q^2 D_t}{kT \pi \eta W A m^*} \right)^{0.5},
\end{equation}

where $v_t$ is the electron recombination velocity, $v_d$ is the drift velocity, $m^*$ is the effective electron mass in the IGZO,\textsuperscript{26} and $\mu$ is the Hooge’s constant. It is found that the current spectral density is roughly proportional to $I$. For the trapping and tunneling model and random walk model (RWM), $S_I$ should be proportional to $I^2$. The trapping and tunneling model assumes an energetically uniform bulk trap distribution. The RWM only relates to the interface-trap density, $D_{tr}$, which can be expressed as

\begin{equation}
S_I = \frac{0.1}{I} \left( \frac{q l^2}{4 \eta} \right)^2 \frac{q^2 D_t}{kT \pi \eta W A m^*},
\end{equation}

where $W$ is the depletion width and $A$ is the active area of the diode. It suggests that the random walk of electrons in interfaces via interface states contributes to the LFN.

In the series resistance limited region, the current noise becomes dominated by the IGZO bulk resistance. According to the Hooge’s empirical equation,\textsuperscript{30} the relation is found to be

\begin{equation}
S_{I,\text{series}} = I^2 \frac{2\mu l}{v_d} \frac{D_t}{v_d Ad},
\end{equation}

where $n_{f,\text{total}}$ is the total free carrier number in the IGZO layer and $d$ is the thickness of the IGZO layer. It shows that $S_I$ is also proportional to $I^2$.

Since the interface-trap-induced noise, the trapping and tunnelling noise, and the mobility-and-diffusivity-fluctuation-induced noise are generated in the depletion region, the voltage noise, $S_V$, is related to the dynamic resistance in the depletion region which is described as $dV/dI$. The series-resistance-induced voltage noise is related to the series resistance. Then the total voltage noise can be expressed as

\begin{equation}
S_V = S_{I,\text{space-charge}} \left( \frac{dV}{dI} \right)^2 + S_{I,\text{series}} R_s^2.
\end{equation}

where $S_{I,\text{space-charge}}$ is the current noise generated in the space-charge region and $S_{I,\text{series}}$ is the current noise caused by the series resistance. When the current is limited by the barrier height, according to the thermionic emission theory, $(dV/dI)^2$ is proportional to $I^{-2}$. Thus, three different current dependencies of $S_V$ can be found referring to the trap-induced noise, mobility-and-diffusivity-fluctuation-induced noise, and $R_s$-induced noise, respectively.

For the as-deposited diode, it is found that $S_V \propto I^{-1}$ and $S_I \propto I$ at low voltages, revealing that the LFN follows the mobility and diffusivity fluctuation model. At high biases, the LFN is dominated by the series resistance because $S_V \propto I^2$ and $S_I \propto I^2$. For the thermally annealed diode, the trapped induced noise dominates the noise spectrum at low frequencies. Since the degradation in the J-V properties suggests that the current is affected by the interface traps\textsuperscript{30} and thermal annealing helps to reduce the bulk traps,\textsuperscript{1} the random walk of electrons at the interface is considered as the origin of the LFN.\textsuperscript{32} As the RWM has only been studied on conventional semiconductors, applying such model in the analysis on LFN properties of IGZO Schottky diodes has a significant contribution.

According to Eq. (3), the Hooge’s constant, $\mu$, of the as-deposited diode is found to be $1.4 \times 10^{-9}$ in the space-charge region as shown in Fig. 4, which is in the same order of magnitude as the values obtained from Si Schottky diodes ($\sim 10^{-9}$).\textsuperscript{13,14,16} Due to the amorphous structure of IGZO, such a low $\mu$ indicates the origin of scattering should be different from the crystalline semiconductors. In conventional semiconductors such as Si and GaAs, the ionized impurity scattering causes the decrease in the mobility when increasing the impurity concentration.\textsuperscript{25} For IGZO, the mobility increases with the carrier concentration which is opposite to

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the phenomenon observed in crystalline semiconductors.\textsuperscript{17} The difference is caused by the unique electron transport properties of IGZO, described by the percolation model.\textsuperscript{17-19} The carriers are scattered by the potential barriers above the mobility edge with the average height of 30–100 meV.\textsuperscript{18} Since in the space-charge region, $qV_{bh}$ is much larger than the distributed potential barriers, the electrons which are able to overcome the Schottky barrier have little interference from the disordered potential roughness. However, when the current reaches the series resistance dominated regime, according to the Hooge’s empirical equation, $\alpha I$ is found to be around $2.2 \times 10^{-5}$ as shown in Fig. 4. This suggests that the scattering of electrons by the distributed potential barriers becomes more significant in the flat band region. Compared with the $\alpha I = 10^{-3}$ obtained from IGZO TFTs,\textsuperscript{22} $\alpha I$ in the series resistance regime is two orders of magnitude lower, which implies that the remote phonon scattering from the dielectric is not negligible. In IGZO, the carrier transport occurs between the metal $s$ orbitals that compose the conduction band minimum.\textsuperscript{37} Compared with the $sp^3$ orbitals in crystalline Si, the metal $s$ orbitals make both electron transport and $\alpha I$ less sensitive to bulk defects and disordered structure.\textsuperscript{20}

After annealing, the diode shows degradation in the electrical performance and an increase in the LFN. By using Eq. (4), it is found that the interface-trap density is $3.6 \times 10^{12} \text{eV}^{-1} \text{cm}^{-2}$ as shown in Fig. 4. Since the Schottky junction is sensitive to the oxygen content at the interface,\textsuperscript{64} the O$_2$ plasma treatment on Pt and the excess O$_2$ during the deposition of IGZO are used to reduce Fermi level pinning by removing the hydroxide-induced layer and creating an oxygen-rich phase at the interface. However, according to previous studies,\textsuperscript{40-41} the thermal annealing at temperatures below 150 $^\circ$C may cause irreversible damage to Schottky interfaces. The LFN properties suggest that the thermal annealing process may cause defects in the oxygen-rich interfacial layer and create more interface traps, resulting in significant degradation in the diode performance. For other Schottky contacts with the existence of oxides, the interface-trap density is normally higher than $10^{15} \text{eV}^{-1} \text{cm}^{-2}$, which is similar to the obtained value. However, for the single-crystal Schottky diodes such as Au/n-GaAs and TiN/n-Si, the interface-trap density is found to be around $10^{12} \text{eV}^{-1} \text{cm}^{-2}$,\textsuperscript{2,12,13,15} which is as expected much smaller. As shown in Fig. 3(a), due to the oxygen-rich interface and the degraded electrical performance, the current noise of the thermally annealed diode became more than 100 times larger than that obtained from the as-deposited device. For the as-deposited diode, the LFN was dominated by the mobility-and-diffusivity-fluctuation-induced noise, making it impossible to determine the exact contribution of the interface-trap-induced noise. Nevertheless, because the interface-trap-induced noise was much smaller than the mobility-and-diffusivity-fluctuation-induced noise for the as-deposited diode, by using Eq. (4) and $S_I$ at 0.65 V, $D_I$ should be less than $5.71 \times 10^{12} \text{eV}^{-1} \text{cm}^{-2}$, in terms of which the IGZO Schottky diodes become comparable with Si or GaAs devices. It is plausible that after the thermal annealing, the interface trap density increased from around $10^{12} \text{eV}^{-1} \text{cm}^{-2}$ to $3.6 \times 10^{15} \text{eV}^{-1} \text{cm}^{-2}$.

In this letter, the LFN of Pt-IGZO Schottky diodes was measured and analyzed. At room temperature, devices showed $1/f$ noise at low frequencies. Two different current dependencies of $S_I$ were discovered. By plotting $S_I$ as a function of current, the origins of the LFN for the as-deposited diodes were found to be different from the degraded diodes. According to the experimental data, for the as-deposited diode, the Hooge’s constant was found to be $1.4 \times 10^{-9}$ in the space-charge region and $2.2 \times 10^{-5}$ in the series resistance limited region. Compared with the value obtained in IGZO TFTs, due to the absence of remote phonon scattering in the dielectric, $\alpha I$ was found to be much lower. For the thermally annealed diode, the LFN follows the RWM. The interface-trap density was found to be $3.6 \times 10^{13} \text{eV}^{-1} \text{cm}^{-2}$. Our work demonstrates the LFN measurement can determine a few material and interface physical parameters that cannot be obtained from DC measurements, including Hooge’s constant and interface-trap density. The low noise characteristics also make IGZO Schottky diodes an attractive proposition for noise sensitive applications such as microwave detectors, frequency mixers, photosensors, and memory devices.

We are grateful to the technical support by M. McGowen and I. Hawkins. This work was financed by the National Natural Science Foundation of China (Grant Nos. 11374185 and 11304180), the Natural Science Foundation of Shandong Province (ZR2013EMQ011), and an Independent Innovation Fund of Shandong University (2013TB008).

\textsuperscript{6}J. Zhang, Y. Li, B. Zhang, H. Wang, Q. Xin, and A. Song, Nat. Commun. 6, 756 (2015).
Chapter 7

High Performance Schottky Diodes Based on IGZO

J. Zhang, Q. Xin, and A. Song.


My contributions:

I have fabricated all the devices, performed all the measurements, analysed the data, and prepared all the graphs.
High performance Schottky diodes based on indium-gallium-zinc-oxide

Jiawei Zhang
School of Electrical and Electronic Engineering, University of Manchester, Manchester M13 9PL, United Kingdom

Qian Xin
School of Physics, Shandong University, Jinan 250100, People’s Republic of China

Aimin Song
School of Electrical and Electronic Engineering, University of Manchester, Manchester M13 9PL, United Kingdom

(Received 27 January 2016; accepted 15 March 2016; published 8 April 2016)

Indium-gallium-zinc-oxide (IGZO) Schottky diodes exhibit excellent performance in comparison with conventional devices used in future flexible high frequency electronics. In this work, a high performance Pt IGZO Schottky diode was presented by using a new fabrication process. An argon/oxygen mixture gas was introduced during the deposition of the Pt layer to reduce the oxygen deficiency at the Schottky interface. The diode showed a high barrier height of 0.92 eV and a low ideality factor of 1.36 from the current–voltage characteristics. Even the radius of the active area was 0.1 mm, and the diode showed a cut-off frequency of 6 MHz in the rectifier circuit. Using the diode as a demodulator, a potential application was also demonstrated in this work. © 2016 American Vacuum Society. [http://dx.doi.org/10.1116/1.4945102]

I. INTRODUCTION

Indium-gallium-zinc-oxide (IGZO) is an emerging n-type metal oxide semiconductor which has been widely used in display industries as the active material in back-panel driving units.1,2 It has been regarded as an alternative of amorphous silicon due to its relatively high mobility (~10 cm² V⁻¹ s⁻¹), good visible light transparency, high uniformity over large areas, and compatibility with low-temperature deposition techniques.3 However, most of the studies on IGZO to date have been based on thin film transistors (TFTs), which normally operated at low frequencies.4 As the operation frequencies of TFTs are limited by the mobility, the channel length, and the overlay between source/drain and gate electrodes, in order to realize gigahertz electronics by using IGZO TFTs, the scale of the active area needs to be reduced to submicron, which is difficult for photolithography processes.5 In recent years, IGZO Schottky diodes have drawn much attention due to their advantages in high speed operations.6–10 In 2015, the cut-off frequencies of IGZO Schottky diodes were improved to 16 GHz,9 which covers most of daily used frequency bands. Several potential applications have also been demonstrated in the last few years.7,11 However, due to the nature of metal oxide semiconductors, the properties of the Schottky contacts highly depend on the oxygen contents at the metal–semiconductor interfaces.12–14 Postannealing treatment is one of the methods to improve the rectification properties.6 Another method is to create an oxygen rich layer at the Schottky interface by introducing a pretreatment such as oxygen plasma etching or UV ozone oxidation on the Schottky contacts.12 For ZnO Schottky diodes, the interface properties can be improved by using oxidized noble contacts.13,14 It is found that the inclusion of oxygen during the deposition of the noble metal is able to reduce the defects caused by oxygen vacancies at the interface between metal and single crystalline ZnO.13,14 Despite the amorphous structure, it is plausible that such techniques may also be used to improve the interface properties of IGZO Schottky diodes.

In this work, we have successfully presented the high-performace Pt-IGZO Schottky diodes fabricated at room temperature (RT) by introducing oxygen during the deposition of Pt without any postannealing treatment. The properties of the diodes have been analyzed in terms of current–voltage characteristics, capacitance–voltage characteristics, and frequency response. We also demonstrated a simple crystal radio system by using the Pt-IGZO Schottky diode as the demodulator.

II. EXPERIMENT

Si-SiO₂ wafers were used as substrates in this work. The substrates were degreased by supersonic cleaning in deionized water, acetone, and methanol, then dried with nitrogen and placed in UV/ozone chamber for 30 min. Pt electrodes of 50 nm-thick were deposited by using RF sputtering at 80 W in pure Ar (devices A and B) and Ar/3% O₂ mixture gas (device C). IGZO (InₓO₂:GaₓO₃:ZnO = 1:1:2) was sputtered at 80 W for 50 nm in Ar (devices A and C) and Ar/3% O₂ mixture gas (device B). The Al top electrodes were deposited by thermal evaporation and defined by shadow masks. The current–voltage (J-V) characteristics were measured by using Agilent E5260B Semiconductor analyser at RT in dark. Agilent E4980A LCR meter was used to measure the capacitance–voltage (C-V) characteristics. The frequency response of the IGZO Schottky diodes was measured by Agilent 34401A digital multimeter, and the AC signal was generated by HP 8116A signal generator.
III. RESULTS AND DISCUSSION

The structure of the diode is shown as the inset in Fig. 1(a). The active area of the device was determined by the top Al electrode. The radius of the contact equaled 0.1 mm. In Fig. 1(a), the J-V characteristics of devices A, B, and C are shown. According to the thermionic emission theory,15 the J-V characteristics of the Schottky diode can be described as

\[
J = J_0 \exp \left\{ \frac{q(V - J R_s)}{n k_B T} \right\} - 1 \right\} = A^* T^2 \exp \left\{ - \frac{q \phi_b}{k_B T} \right\} \exp \left\{ \frac{q(V - J R_s)}{n k_B T} \right\} - 1 \right\}, \tag{1}
\]

where \(J_0\) is called the saturation current density, \(A^*\) is the Richardson constant which equals 41 A cm\(^{-2}\) K\(^{-2}\) for IGZO,\(^6\) \(k_B\) is the Boltzmann constant, \(T\) is the temperature, \(\phi_b\) represents the barrier height of the diode, \(R_s\) is the series resistance, and \(n\) is defined as the ideality factor. By fitting the J-V curves according to Eq. (1) at low biases where \(V \gg J R_s\), the barrier height, on/off ratio, and ideality factor can be obtained, which are shown in Table I. For device A, it showed a relatively low barrier height of 0.52 eV and an ideality factor of 2.50. The rectification ratio at \(\pm 1\) V was only 10\(^4\). For device B, the on/off ratio became 2.0 \(\times\) 10\(^4\), and the ideality factor dropped to 1.56. Compared with device A, device B showed a higher barrier height of 0.72 eV. When depositing Pt with 3% O\(_2\), device C exhibited a better performance compared with devices A and B. The barrier height was found to be 0.92 eV, which agreed well with the estimation if assuming the work function of Pt is 5.4 eV and the electron affinity of IGZO is 4.5 eV.\(^6\) The ideality factor was also close to unity, which suggested that the barrier height was uniform at the interface. The on/off ratio was found to be higher than 10\(^6\).

Figure 1(b) shows the C-V characteristics of devices B and C. The relation between the diode capacitance and the applied bias can be described by

\[
C^{-2} = \frac{2(V_{bi} - V)}{q \varepsilon_0 \varepsilon_r N_{bg}}, \tag{2}
\]

where \(V_{bi}\) is the built-in voltage, \(\varepsilon_0\) is the vacuum permittivity, \(\varepsilon_r\) is the relative dielectric constant of IGZO, and \(N_{bg}\) is called the background doping density. By assuming the diodes were fully depleted at \(-1\) V, the relative dielectric constant of IGZO was found to be 15 for device B and 14 for device C. The differences might be caused by the different oxygen content in the IGZO layer. By using Eq. (2), the extracted parameters are shown in Table I. It is found that for device B, the built-in voltage was 0.46 V and the background doping density was 3.50 \(\times\) 10\(^{18}\) cm\(^{-3}\). Device C showed a higher built-in voltage of 0.60 V and a background doping density of 4.05 \(\times\) 10\(^{18}\) cm\(^{-3}\).

The oxygen content at the interface is vital for metal oxide semiconductors to form high-quality Schottky junctions.\(^{10,12–14}\) Allen et al. have reported that for ZnO Schottky diodes, oxygen deficiency can induce defects at the interface and cause Fermi level pinning.\(^{13,14}\) This explains why device A, where Pt and IGZO were deposited in pure Ar, exhibited the lowest barrier height and the highest ideality factor. Introducing 3% O\(_2\) during the deposition of IGZO serves to reduce the number of dangling bonds at the Pt-IGZO interface and may unintentionally oxidize the Pt surface, thus improving the rectification properties of the diode.

An alternative solution is to intentionally create an oxygen-rich phase at the Pt-IGZO interface. It is found that device C showed the highest barrier height, the highest on/off ratio, and the lowest ideality factor among the three devices. In the C-V measurements, it also showed a higher built-in voltage than the value of device B, which suggests that depositing Pt in Ar/O\(_2\) mixture gas helps to reduce oxygen deficiencies and thus contributes to a better Schottky junction.

The current-voltage-temperature characteristics of device C are shown in Figs. 2(a) and 2(b). The linear dependency of \(\ln(J_0/T^2)\) on \(T^{-1}\) indicates that the thermionic emission dominates the current transport in the diode. The barrier height decreases with increasing temperature, which may be due to the inhomogeneities at the Schottky interface.\(^{16}\) Assuming these inhomogeneities in barrier height are Gaussian distributed,\(^{16}\) the mean barrier height is found to be 1.46 eV with a standard deviation of 0.16 eV. The potential fluctuation at the Schottky junction may be caused by the amorphous structure of IGZO, the grain boundaries, and the different crystalline orientations of the Pt layer. An additional thermal annealing step could serve to minimize these fluctuations.

The rectification properties of device C at different frequencies are shown in Fig. 3. The inset shows the setup of

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Fig. 1. (Color online) (a) J-V characteristics of Pt-IGZO Schottky diodes with different fabrication conditions. The inset shows the structure of the diodes. (b) C\(^{-2}\)-V characteristics of devices B and C. The fittings were shown by the dashed lines.
the single-stage rectifier circuit. The signal was generated by HP8116A signal generator through a 50 Ω resistor. The output voltage was measured by Agilent 34401A digital multimeter. As shown in Fig. 3, when the peak amplitude of the input signal was 1.0 V, the output voltage was found to be around 0.56 V. Thus, the –3 dB point was found to be around 6 MHz when the output voltage dropped to 0.39 V. At 13.56 MHz, the diode was still able to generate an output voltage of around 0.14 V with the input voltage of 1 V. As the capacitance of the fully depleted diode is around 0.16 nF and the input resistance is 50 Ω, the cut-off frequency is estimated to be 20 MHz by using \( f = \frac{1}{2\pi RC} \). This value is higher than the experimental results, which might be due to the extra series resistance in the diode. By adopting a similar design as mentioned in Ref. 9, it is possible to further improve the operating frequency.

In the setup shown in Fig. 4(a), an amplitude modulation (AM) signal with a carrier frequency, \( f_c = 1.5 \text{ MHz} \), and an information frequency, \( f_i = 1 \text{ kHz} \), is used as the input signal. The diode in the setup was fabricated under the same conditions as device C. The radius of the active area was increased to 0.5 mm to reduce the total resistance of the diode. The low pass filter is composed of a 12 kΩ resistor and a 1 nF capacitor. The rectified voltage is amplified 20 times and measured by an oscilloscope. Figure 4(b) shows the waveforms of the input and the output signals. The amplitude of the AM signal was set to be 250, 300, and 350 mV, respectively. The peak voltage of the corresponding rectified signals are found to be 0.565, 0.653, and 0.931 V, respectively. Figure 4(c) shows a potential application, namely, an AM radio receiver, using the IGZO Schottky diode. A 5 m-long metal wire was used as the antenna to receive the radio signal (Gold at 1.458 MHz in Manchester). The input AM signal was rectified by the IGZO Schottky diode. The rectified AM signal was converted to the audio signal with a cut-off frequency of 13 kHz through the low-pass filter and amplified 20 times by an SR560 low noise voltage amplifier. Then, the amplified audio signal was connected to a speaker. The demonstration of the fully functional radio receiver is shown in supplementary video.17

IV. SUMMARY AND CONCLUSIONS

In this work, we proposed an alternative fabrication process to improve the rectification properties of Pt-IGZO Schottky diodes. The J-V and C-V characteristics showed superior performance to the values obtained from the devices
fabricated with the conventional processes. The role of oxygen in the formation of the Schottky barrier has been elucidated and could be further understood by the use of quantitative analytical methods such as secondary ion mass spectroscopy. The cut-off frequency of the diode was found to be around 6 MHz, which could be further improved by adopting the high-frequency coplanar waveguide design. We also demonstrated an AM radio receiver by using the Pt-IGZO Schottky diode as the demodulator. These results shed light on potential applications of IGZO Schottky diodes.

ACKNOWLEDGMENTS

The authors are grateful to the support of the National Natural Science Foundation of China (Grant Nos. 11374185 and 11304180), the Natural Science Foundation of Shandong Province (ZR2013EMQ011), and an Independent Innovation Fund of Shandong University (2013TB008).

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17See supplementary material at http://dx.doi.org/10.1116/1.4945102 for the demonstration of a fully functional AM radio receiver using the IGZO Schottky diode as the demodulator.
Chapter 8

Analysis of Carrier Transport and Band Tail States in $p$-type Tin Monoxide Thin-film Transistors by Temperature Dependent Characteristics

J. Zhang, X. Kong, J. Yang, Y. Li, J. Wilson, J. Liu, Q. Xin, Q. Wang, and A. Song.

*Appl. Phys. Lett.* Accepted

My contributions:

I have participated in the fabrication, performed the measurements excluding the XRD analysis, analysed the data excluding the Rietveld analysis, and prepared all the graphs.
Analysis of Carrier Transport and Band Tail States in $p$-type Tin Monoxide Thin-film Transistors by Temperature Dependent Characteristics

Jiawei Zhang,1* Xi Kong,2* Jia Yang,2 Yunpeng Li,2 Joshua Wilson,1 Jie Liu,2 Qian Xin,3,a) Qingpu Wang,3 and Aimin Song3,b)

1 School of Electrical and Electronic Engineering, University of Manchester, Manchester M13 9PL, UK
2 State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, P.R. China
3 School of Physics, Shandong University, Jinan, 250100, P. R. China

*These authors contributed equally to this work
Corresponding authors: a) xinq@sdu.edu.cn b) A.Song@manchester.ac.uk

Tin monoxide (SnO) has drawn much attention in recent years due to its high hole mobility, transparency and potential for mass production. However, due to its metastable nature, the deposited film often contains multi-phases such as metallic tin and tin dioxide, which may degrade its electrical properties. Here we presented the temperature dependent characteristics of $p$-type SnO thin-film transistors. The hole transport mechanism is dominated by band conduction at high temperatures and variable-range hopping at low temperatures. The maximum activation energy was found to be 302 meV, which denotes a bandgap of around 0.6 eV. The density of states was found to be 1.12 × 10$^{21}$ cm$^{-3}$ eV$^{-1}$ at $V_G = -80$ V, and 6.75 × 10$^{20}$ cm$^{-3}$ eV$^{-1}$ at $V_G = 0$ V, respectively.

I. INTRODUCTION

Metal oxide semiconductors such as indium-gallium-zinc-oxide (IGZO) have already started to be used in industry, in particular to replace amorphous silicon for high-end display drivers.1-3 However, most metal oxide semiconductors are $n$-type.1-3 In order to develop complementary circuits by using metal oxides, it is necessary to find $p$-type oxide semiconductors.2 However, it is difficult to obtain a $p$-type oxide with a high hole mobility since O 2p orbitals are likely to form the localized valence band maximum (VBM) which causes percolation and hopping conduction.2,4 In recent years, tin monoxide (SnO) was found to be a promising $p$-type oxide as its VBM was composed of hybridized orbitals of Sn 5s and O 2p.2,4-9 This valance band structure gives SnO the potential to obtain a hole mobility higher than 10 cm$^2$ V$^{-1}$ s$^{-1}$.8 However, unlike another tin oxidation state, tin dioxide (SnO$_2$), SnO is a metastable phase and sensitive to temperature.1 Thus, physical vapour deposition requiring high temperature processes becomes challenging for SnO. The most common method of SnO deposition is reactive radio-frequency (RF) sputtering using a metallic Sn target followed by a low-temperature thermal annealing process.6,9,11 The $p$-type SnO can only be obtained in a narrow window of growth conditions.8 It is found that the obtained film often shows multi-phases including metallic tin (Sn) and SnO$_2$, rather than pure SnO.2 Many studies have shown that the on/off ratios of SnO TFTs are around 10$^3$ at room temperature (RT),2,4,8,9 which is much lower than the values obtained from
IGZO TFTs.\textsuperscript{12} Such high off current may be attributed to defects in the bandgap and the carrier transport mechanism in the VBM.\textsuperscript{4} However, for such a disordered system, the carrier transport mechanism remains debatable.\textsuperscript{13} Percolation conduction, where the carrier paths circumvent the high potential barriers above the mobility edge, has been regarded as a plausible carrier transport mechanism in disordered systems.\textsuperscript{14} For amorphous IGZO, it is found that the log of conductivity ($\sigma$) follows a $T^{-1/4}$ law at low temperatures, suggesting a carrier transport regime dominated by percolation conduction as.\textsuperscript{15} However, another explanation for the $T^{-1/4}$ behaviour is Mott’s variable-range hopping (VRH), which suggests that a carrier hops between localized sites.\textsuperscript{16} VRH has been widely observed in non-crystalline materials, highly doped crystalline semiconductors and polycrystalline semiconductors.\textsuperscript{13,16,17} Trap-limited conduction model has also been raised to describe the carrier transport in amorphous semiconductors when the tail state energy is higher than the thermal energy at low temperature where log ($\sigma$) is proportional to $T^{-1}$.\textsuperscript{18} At higher temperatures, where the carriers have the energies higher than the mobility edge, band conduction dominates the carrier transport and log ($\sigma$) follows a $T^{-1}$ law.\textsuperscript{15}

The temperature dependent mobility and carrier concentration of SnO films obtained by Hall effect measurements have been discussed in several studies, which found that both mobility and carrier concentration exhibited thermally activated behaviours.\textsuperscript{2,6} The temperature dependent hole concentration can be explained by the existence of a shallow acceptor level but the reason for the thermally activated mobility remains unclear. However, compared with the Hall effect measurements, the characteristics of the thin-film transistors at different temperatures are able to reveal more properties within the bandgap.\textsuperscript{13} The Fermi level ($E_F$) at the interface can be modified by changing the gate voltage ($V_G$). However, so far, the characteristics of SnO TFTs have only been studied from 298 K to 348 K, where the band conduction dominates.\textsuperscript{19} By analyzing the temperature dependent characteristics of the TFT in off state at lower temperatures, the reasons for the high off current can be elucidated.

In this letter, we present the temperature dependent characteristics of the SnO TFT. The carrier transport mechanisms at different temperatures are discussed. The activation energy, $E_a$, at different gate voltages is obtained. We also demonstrate and evaluate the density of states, $N(E)$, in the bandgap of the SnO film.

II. EXPERIMENTS

Bottom gate top contact TFTs were fabricated on thermally-oxidized SiO$_2$/p$^+$-Si substrates. The thickness of the SiO$_2$ layer was 300 nm. Patterns were defined by shadow masks. A 27 nm-thick SnO film was deposited by reactive RF sputtering by using a Sn target with a substrate temperature of 100 °C. The argon/oxygen ratio was 23:3 during the deposition. The deposition power was fixed at 150 W and the pressure was 4.3 mTorr. Before forming the source and drain, the SnO film was annealed in air at 225 °C for 1 h. The source and drain were formed by 50 nm-thick Pd contacts which were deposited by using an electron-beam evaporator. The channel width, W, is 2000 µm and the channel length, L, is 60 µm. Current-voltage characteristics were measured using Agilent B2902A source/measure unit at room temperature (RT) in dark. The low temperature measurements were performed with a 4 K helium cryostat from 5 K to 300 K in vacuum. The sample for the X-ray diffraction (XRD) analysis was prepared on a Si-SiO$_2$ wafer under the same deposition conditions. The XRD image of the 1 µm-thick SnO film was obtained using a D8 Advance X-ray diffractometer.

III. RESULTS AND DISCUSSIONS
The transfer characteristics of the SnO TFT measured in vacuum from 300 K to 5 K are shown in Fig. 1(a). The drain voltage, $V_D$, was set to -1 V. The output characteristics of the SnO TFT at RT are shown in Fig. 1(b), which suggests that the TFT is in the linear regime when $V_D = -1$ V. In the transfer curve, the drain current, $I_D$, drops with the temperature. At RT, the off current is around $10^{-7}$ A which is quite high compared with the gate leakage current (around $10^{-10}$ A). At temperatures around 150 K, the off current drops to $10^{-10}$ A and becomes dominated by the leakage current. By using $I_D = \mu C_{ox} \frac{W}{L} \left( V_G - V_{th} \right) V_D - \frac{1}{2} V_D^2$ where $C_{ox}$ is the dielectric capacitance per unit area and $V_{th}$ is the threshold voltage, the mobility, $\mu$, is found to be 0.73 cm$^2$ V$^{-1}$ s$^{-1}$ at RT and it decreases with temperature as shown in Fig. 1(c). The threshold voltage decreases when decreasing the temperature. The subthreshold swing ($SS$) decreases beyond 150 K and reaches a minimum around 100 K. When the temperature is lower than 100 K, $SS$ starts to increase with decreasing temperature. The lowest $SS$ is found to be 8.6 V dec$^{-1}$ at 130 K which corresponds to a total interface trap density of $1.02 \times 10^{13}$ cm$^{-2}$ eV$^{-1}$. In Figs. 2(a) and 2(b), the output characteristics of the SnO TFT at 200 K are shown from 0 V to 50 V and 80 V to 100 V.

Figure 3(a) shows the drain current at different temperatures from 300 K to 10 K with various gate voltages. At high temperatures, $\ln (I_D)$ is found to be proportional to $T^{-1}$. According to the band conduction model, the results follow the Arrhenius equation,$^{20,21}$

$$I_D = I_{DG} \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

![FIG. 1. (a) Transfer characteristics of the SnO TFT at temperatures from 300 K to 5 K. The insert shows the cross-section of the TFT. (b) Output characteristics of the SnO TFT at RT. (c) Mobility, subthreshold swing and threshold voltage of the SnO TFT at different temperatures.

![FIG. 2. Output characteristics of the SnO TFT at 200 K with gate voltages (a) from 0 V to 50 V, and (b) from 80 V to 100 V.](image-url)
where \( k_B \) is the Boltzmann constant, \( E_a \) is the activation energy and \( I_{D0} \) is a prefactor of \( I_D \). For \( n \)-type conduction, \( E_a \) equals \( (E_C - E_F) \), and for \( p \)-type conduction, \( E_a \) equals \( (E_F - E_V) \).\(^{22}\) Thus, the activation energy can be obtained. Fig. 3(b) shows the relationship between \( E_a \) and \( V_G \). In the linear region, the minimum \( E_a \) is around 12.5 meV. With the increasing gate voltage, the activation energy \( E_a \) also increases until reaching a maximum at around 0.3 eV. However, above 40 V, \( E_a \) starts to decrease, suggesting that the Fermi level becomes closer to the conduction band. As shown in Fig. 1(a), the drain current increases with the gate voltage beyond around 40 V at low temperatures, indicating \( n \)-type field-effect behaviour. This agrees well with the output characteristics at 200 K shown in Figs. 2(a) and 2(b). Similar observations of ambipolar behaviour have also been observed in Refs. 11 and 23. Hence, the SnO film starts to accumulate electrons to form an \( n \)-type channel, indicating that the bandgap of SnO is around 0.6 eV, which agrees well with the theoretical indirect bandgap of SnO.\(^{2,6,23}\) The gradual increase of \( E_a \) may be attributed to the trap states in the SnO film.\(^{24}\) When the temperature is lower than 80 K, as shown in Fig. 3(a), the \( \ln (I_D) \) vs. \( T^{-1} \) curves become nonlinear, which suggests that the Arrhenius equation cannot be used to describe the drain current. This indicates that at low temperatures, band conduction is no longer the dominant transport mechanism in the SnO film.

However, Fig. 4(a) shows that \( \ln (I_D) \) becomes linearly dependent on \( T^{1/4} \) at temperatures lower than 80 K. According to the percolation theory, the mobility is more likely to increase with the carrier concentration as the paths of the electrons with higher energies are shorter.\(^{12}\) Since the hole mobility of SnO films has no clear dependencies on the hole carrier concentrations,\(^{8}\) carrier transport is more likely to occur through variable-range hopping rather than percolation conduction. Thus, according to Mott’s equation, the relation between \( I_D \) and \( T \) is given by

\[
I_D = I_{D0}\exp \left\{ -2/\left[ \frac{\alpha^3}{k_B N(E)}T\right]*\right\}^{1/4} \tag{2}
\]
where \( N(E) \) is the density of states at the Fermi level and \( \alpha \) is the reciprocal of the Bohr radius, \( a \). For SnO, 
\[
\alpha = \frac{a_0 \varepsilon_r m_0}{m^*}
\]
where \( a_0 \) is the Bohr radius of a hydrogen atom, 0.53 Å, \( \varepsilon_r \) is the permittivity of SnO which is 15, \( m_0 \) is the free electron mass and \( m^* \) is the effective mass of holes in the valance band in SnO which is around 2.05\( m_0 \). Thus, the Bohr radius of SnO is calculated to be 3.87 Å. Mott’s VRH model indicates that the access current in the Arrhenius plot is caused by carriers tunnelling between localized states close to the Fermi level.

According to Eqn. 2, the density of states of SnO can be expressed as a function of \( I_D \). In Fig. 4(b), a plot of \( N(E) \) as a function of \( V_G \) was obtained. The density of states at the Fermi level is found to be 1.12\( \times 10^{21} \) cm\(^{-3} \) eV\(^{-1} \) at \( V_G = -80 \) V, and 6.75\( \times 10^{20} \) cm\(^{-3} \) eV\(^{-1} \) at \( V_G = 0 \) V, respectively. According to the VRH model, a carrier hops between the adjacent localized states. The most probable hopping distance and the average hopping energy are given by

\[
R_{\text{hop}} = \left( \frac{3}{2 \pi a N(E) \hbar^2 T} \right)^{1/4}
\]

and

\[
W_{\text{hop}} = \frac{3}{4 \pi N(E) R_{\text{hop}}^3}
\]

Using the value of \( N(E) \) determined previously, \( R_{\text{hop}} \) and \( W_{\text{hop}} \) were calculated and shown in Fig. 5(a). As expected, when decreasing the temperature, the most probable hopping distance increases and the average hopping energy decreases. As shown in Fig. 3(b), the density of states at \( V_G = -80 \) V is higher than the value at \( V_G = 0 \) V. As a result, at \( V_G = -80 \) V, the hopping distance becomes shorter and the average hopping energy is lower.

**FIG. 4.** (a) Drain current as a function of \( T^{1/4} \) with gate voltages from 0 V to -80 V. The linear fittings are shown as dashed lines. (b) Density of states obtained from Mott’s equation as a function of gate bias.
In crystalline SnO, the defects are mainly composed of tin vacancies ($V_{Sn}$), oxygen vacancies ($V_{O}$), interstitial tin atoms ($Sn_i$) and interstitial oxygen atoms ($O_i$).\textsuperscript{25} According to first principle calculations, the $p$-type conductivity of SnO is caused by $V_{Sn}$.\textsuperscript{25} $V_{Sn}$ contributes to acceptor-like shallow defect states which may correspond to the density of states shown in Fig. 4(b). The inhomogeneities at the VBM may also contribute to the large density of states. The oxygen vacancies may distort the potentials of neighbouring atoms and cause shallow defect states near the VBM and CBM. However, at RT, the concentration of $V_{O}$ is orders of magnitude smaller than the concentration of $V_{Sn}$, which means it is unlikely that $V_{O}$ will affect the $p$-type conductivity.\textsuperscript{25} The interstitial oxygen atoms are likely to become $O^2-$ and ionize $Sn^{2+}$ to $Sn^{4+}$ to maintain charge neutrality, which may improve electron transport in the CBM. Tin interstitial atoms create huge defect states between the planes of the SnO crystal, where hole transport predominantly occurs.\textsuperscript{25} Thus, both tin and oxygen interstitials may contribute to the observed large $N(E)$.

In Fig. 5(b), the XRD image of a 1 µm-thick SnO film shows that there are excess Sn atoms (mass fraction of 12.75 % according to the Rietveld analysis) remaining after annealing the sample at 225 °C for 1 h. As the $p$-type conductivity implies the existence of tin vacancies,\textsuperscript{25} it suggests that there are excess O atoms in the SnO film. The redundant Sn and O atoms may originate from incomplete reactions during the deposition and thermal annealing of the SnO film. It is plausible that the interstitial Sn and O atoms could cause large defect states in the bandgap and thus result in a high off current at RT. As those defects are mainly composed of the Sn 5p-orbitals and O 2p-orbitals,\textsuperscript{25} at low temperatures, hopping between localized states becomes more difficult, resulting in a lower off current.

**IV. CONCLUSIONS**

For SnO TFTs, two types of hole transport mechanisms have been observed at different temperatures. Analysis of band conduction revealed that the maximum activation energy was around 0.3 eV and the bandgap was around 0.6 eV, which agrees well with the theoretical value. Carrier transport at low temperatures (<80 K) was dominated by VRH. In the $\ln(I_D)-T^{-1}$ regime, the role of the tail states could be further evaluated by the trap-limited conduction theory.\textsuperscript{19} A large trap density of states was also observed in the VRH regime, which may be attributed to the interstitial Sn and O atoms present in the film.
V. ACKNOWLEDGMENTS

We are grateful to the support by North-West Nanoscience Doctoral Training Centre, EPSRC grant EP/G03737X/1. This work was financed by the National Natural Science Foundation of China (Grant Nos. 11374185 and 11304180), the Natural Science Foundation of Shandong Province (ZR2013EMQ011), and an Independent Innovation Fund of Shandong University (2013TB008).

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Chapter 9

Ring Oscillator Based on Complementary $p$-SnO and $n$-IGZO Thin-Film Transistors

Oxide semiconductors are regarded as promising materials for large-area and/or flexible electronics. In this chapter, a ring oscillator based on $n$-type indium-gallium-zinc-oxide (IGZO) and $p$-type tin monoxide (SnO) is presented for the first time. The IGZO thin-film transistor (TFT) shows a linear mobility of 11.9 cm$^2$/V·s and a threshold voltage of 12.2 V. The SnO TFT exhibits a mobility of 0.39 cm$^2$/V·s and a matched threshold voltage of 26.3 V. At a supply voltage of 40 V, the complementary inverter shows a gain of 6.5 with both TFTs having the same channel aspect ratio. At a supply voltage of 40 V, the 3-stage metal oxide ring oscillator is able to operate at 2.63 kHz and the peak to peak oscillation amplitude reaches 36.1 V.

9.1. Introduction

Oxide semiconductors have received much attention for a wide range of emerging applications such as flexible screens and wearable electronics [1], [2]. Compared with conventional thin-film semiconductors such as amorphous silicon, they have a number of advantages including high electron mobilities, low fabrication temperatures, scalable deposition methods, highly uniform surfaces, and mechanical flexibility [3]. The desirability of metal oxide semiconductors is furthered by their large band gap which allows for high optical transmittance in the visible spectrum, a prerequisite for transparent electronics [2].

So far, vast progress has been made in $n$-type metal oxide semiconductors such as ZnO and InGaZnO (IGZO). For instance, IGZO has started to be commercialized to replace amorphous silicon for backplane drivers of flat-panel displays. In contrast, there are relatively few studies on $p$-type oxide semiconductors. P-channel thin-film transistors (TFTs) are necessary in order to fabricate CMOS logic gates for practical applications in order to achieve high noise immunity, low static power consumption, high yield, and high reliability [2]. Currently, SnO has been regarded as the most promising $p$-type oxide semiconductor due to its high stability in air and carrier mobility in comparison to copper.
oxide Cu$_2$O [4]. SnO exhibits excellent $p$-type conductivity due to the effective overlap of Sn 5s orbitals at the valance band maximum [4]. So far, CMOS inverters using $n$-type semiconductors (such as SnO$_2$, ZnO) and $p$-type SnO TFTs have been fabricated [5]-[8]. CMOS-like inverters based on bipolar SnO TFTs have also been demonstrated [9-11]. From the application point of view, it may be highly desirable to complement SnO with IGZO for CMOS logic gates because IGZO is currently the most promising $n$-type oxide semiconductor and the industry has started using it to replace amorphous silicon in flat-panel displays. In this work, we fabricated $n$-type IGZO and $p$-type SnO TFTs in an optimized condition. Complementary inverters based on IGZO and SnO TFTs were demonstrated with matched threshold voltages. By cascading the inverters with large noise margins, a 3-stage IGZO and SnO ring oscillator was fabricated to operate at 2.63 kHz with a high output amplitude.

9.2. Experiments

The TFTs were fabricated on highly $p$-type doped Si substrate with 100 nm thick thermally oxidized SiO$_2$. By using a 3 inch metallic Sn target, a 27 nm-thick SnO film was deposited by using RF sputtering at 150 W in the Ar/O$_2$ mixture gas. The pressure was 4.6 mTorr and the flow rates of Ar and O$_2$ were 21 sccm and 3 sccm, respectively. Then the film was thermally annealed in air at 225 °C for 1 h. 50 nm thick Pt source/drain contacts were deposited by RF sputtering at 80 W in Ar.

For the $n$-type TFTs a 24 nm-thick IGZO active layer was deposited by using RF sputtering at 80 W with a pressure of 4.2 mTorr. The atomic ratio for the target was In:Ga:Zn=1:1:1. Titanium source/drain contacts were deposited by E-beam evaporator for 50 nm.

The channel width and the channel length of the TFTs were 2 mm and 60 µm, respectively. All patterns were defined by shadow masks as shown in Fig. 9-1(a). The electrical characteristics were measured by using Agilent E5260B at room temperature in dark. The output of the ring oscillator was measured by using Agilent 54622A oscilloscope.

9.3. Results and Discussion

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Figures 9-1(b) and 9-1(c), show the transfer characteristics of the IGZO TFT and the SnO TFT at different drain voltages, respectively. Table 9-1 summarizes the obtained parameters. For the IGZO TFT, it is found that in the linear regime, the threshold voltage ($V_{TH}$) is 12.2 V and the linear mobility is 11.9 cm$^2$/V·s. The subthreshold swing (SS) was 1.84 V/dec which is slightly high due to the thick SiO$_2$ dielectric layer. The extracted interface trap density, $N_{it}$, was 6.41×10$^{12}$ cm$^{-2}$ eV$^{-1}$, which is comparable with the values found in other studies [12]. For the SnO TFT, the linear mobility was found to be 0.39 cm$^2$/Vs. The threshold voltage was 26.3 V which is higher than the valued of the IGZO TFT, making it possible to form a high-performance complementary inverter by using SnO and IGZO TFTs. The extracted interface trap density was 1.45×10$^{15}$ cm$^{-2}$ eV$^{-1}$, which might be due to the polycrystalline structure and the multi-phases in the SnO active layer [2], [13]. The low on/off ratio is not uncommon in SnO TFTs because of the very small indirect bandgap and sub-gap traps [4].

Figure 9-2(a) shows the surface morphology of an annealed SnO film which was fabricated under the same conditions as the SnO in the TFT. The root-mean-square roughness is 0.83 nm. The grain size is estimated to be around 50 nm, which might contribute to a better hole conduction as the grain boundaries would restrain the electron transport [5]. The XRD

<table>
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<th>Table 9-1. Electrical Characteristics Properties of TFTs</th>
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<td>$\mu$ (cm$^2$/V$^{-1}$·s$^{-1}$)</td>
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<tr>
<td>$V_{TH}$ (V)</td>
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<td>SS (V/dec)</td>
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<td>$N_{it}$ (cm$^{-2}$ eV$^{-1}$)</td>
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pattern of the 1 µm-thick SnO film is shown in Fig. 9-2(b). The film still contains a small amount of metallic Sn, which may lower the on/off ratio and contribute to a higher trap density [13].

The operation of the IGZO and SnO complementary inverter at different supply voltages, \( V_{DD} \), is shown in Fig. 9-3(a). The gain at \( V_{DD} = 40 \) V was found to reach as high as 6.5 as shown in Fig. 9-3(b). The threshold voltage is found to be 17 V where \( V_{in} = V_{out} \). It is close to the ideal value, \( V_{DD}/2 \). The input-low voltage (\( V_{IL} \)) and the input-high voltage (\( V_{IH} \)) are defined as the point where \( d(V_{out})/d(V_{in}) = -1 \). It is found that \( V_{IL} = 10.4 \) V and \( V_{IH} = 20.7 \) V. The transition region can be determined by \( V_{IH} - V_{IL} \) which equals 10.3 V. The noise margin high was 19.3 V by using \( V_{DD} - V_{IH} \), and the noise margin low was 10.4 V which equaled \( V_{IL} \). The large values suggest that the complementary inverter could withstand a high noise level. The inverter performance can be further improved by using high-\( \kappa \) dielectrics [9].

As the maximum gain of the inverter was obtained at a positive input voltage, a ring oscillator can be built by directly stacking 3 inverters together as shown in Fig. 9-4(a). The

\[ \text{Fig. 9-3. (a) Output voltage and (b) gain of the complementary inverter as a function of input voltage at different } V_{DD}. \]
extra inverter was used as a buffer to allow measurement of the output without disturbing the oscillation. The output voltage as a function of time is shown in Fig. 9-4(b) at different supply voltages. The output amplitudes and frequencies are summarized in Table 9-2. It is found that the peak to peak amplitude and the frequency of the output signal at 40 V were 36.1 V and 2.63 kHz, respectively. Thus, the delay time for each stage was estimated to be 63 µs by using $f = 1/(6t_d)$ where $t_d$ represents the delay time.

The oscillation frequency of the complementary ring oscillator depends on the transit frequency of the TFT [14], which is proportional to $\mu/[L_{ch}(L_{ch} + L_{ot})]$ where $L_{ch}$ is the channel length and $L_{ot}$ represents the length of the total overlapping area between source/drain and the gate. In this work, $L_{ot}$ + $L_{ch}$ equals 1.3 mm. By reducing $L_{ch}$ to 2 µm and $L_{ot}$ to 5 µm, it is possible to improve the oscillation frequency to 13.56 MHz, which could be used as the clock generator in metal-oxide-semiconductor-based flexible radio-frequency identification tags. Despite that being the subject of future work, the demonstration of the complementary SnO/IGZO ring oscillator shows the potential of the fully-oxide-based complementary electronics.

9.4. Conclusions

In this chapter, complementary inverters composed of the $n$-IGZO TFT and the $p$-SnO TFT were fabricated on Si substrates. The SnO TFT was annealed in air at 225 °C for 1 h to
obtain p-type performance. By cascading the inverters, a 3-stage ring oscillator was demonstrated. The output frequency was 2.63 kHz with a supply voltage of 40 V. Our study suggests that other CMOS logic gates and more complex CMOS circuits can be made using SnO and IGZO TFTs with large noise margins in potential larger-area transparent electronics fully based on metal-oxide-semiconductors.

References


Chapter 10  Conclusions and Future Work

10.1. Conclusions
This thesis focuses on the development of oxide-semiconductor-based electronic devices. High-performance Pt-IGZO Schottky diodes have been fabricated at RT on glass and flexible substrates. Two methods for improving the cut-off frequency of the IGZO Schottky diode have been demonstrated, allowing the optimised device to surpass the benchmark frequency of 2.45 GHz. The low-frequency noise properties of IGZO Schottky diodes have also been investigated, bringing the use of IGZO Schottky diodes in practical applications closer to realisation. For oxide-based electronics to achieve their full potential complementary circuits are required, with this in mind, the fabrication processes of p-type SnO TFTs have been expounded. The carrier transport mechanisms of SnO TFTs have been analysed at low temperatures. An inverter and a ring oscillator based on n-type IGZO TFTs and p-type SnO TFTs have also been demonstrated. Detailed conclusions can be drawn as shown in the following sections.

10.1.1. High-frequency IGZO Schottky Diodes
By introducing 3\% oxygen during the deposition of IGZO or Pt, high-performance Pt-IGZO Schottky diodes were obtained. According to the small-signal equivalent circuit, the cut-off frequency was determined by the depletion-layer capacitance and the effective series resistance. Thus, two methods were proposed to improve the operation frequency of the Pt-IGZO Schottky diodes, namely increasing the thickness of the IGZO layer and decreasing the active area of the diode.

In the first method, the thickness of the IGZO layer should not exceed the depletion width at zero bias, as the extra bulk resistance of the IGZO layer will contribute to the effective series resistance and thus lower the cut-off frequency. In order to optimise the high-frequency performance, three different thicknesses of the IGZO layers, 50 nm, 80 nm, and 100 nm, were evaluated. In the single-stage rectifier circuit, the 80 nm-thick IGZO Schottky diode exhibited the best overall performance in terms of cut-off frequency and output voltage.

By shrinking the active area of the Schottky diode, the depletion-layer capacitance can be
reduced. High-frequency measurements at zero bias showed that on glass substrates, a cut-off frequency higher than 20 GHz was attainable by the device with an active area of 200 µm². The diode on the flexible substrate showed a highest cut-off frequency of 6.3 GHz, which is higher than the benchmark frequency of 2.45 GHz.

10.1.2. High-performance IGZO Schottky Diodes

The oxygen dependent electrical performance of the Pt-IGZO Schottky diodes have been evaluated by introducing various oxygen treatments at different stages in the fabrication processes. Oxygen deficiencies cause additional defect states at the interface, resulting in Fermi level pinning. Thus, by introducing 3 % O₂ during the deposition of IGZO, the diode showed an improved performance compared with the device fabricated in pure Ar. By treating the Pt surface with oxygen plasma, the barrier height of the diode can be further improved. However, the series resistance was found to be much higher, which may be caused by oxidation of the Pt film. Without introducing any extra fabrication processes, high-performance IGZO Schottky diodes can also be obtained by depositing the Pt film with 3 % O₂. This method produced the best overall DC characteristics including barrier height, ideality factor, and series resistance. In addition, the diode was used as the demodulator in a fully functional AM radio receiver.

10.1.3. Low-frequency Noise Properties of IGZO Schottky Diodes

The low-frequency noise properties of the as-deposited and thermally annealed Pt-IGZO Schottky diode were analysed. For the as-deposited diode, the low-frequency noise was governed by two different mechanisms. At low biases, $S_I$ was proportional to the current, $I$, indicating that the noise was generated in the space-charge regime. When the bias was higher than the built-in voltage, $S_I$ became proportional to $I^2$. This suggested that the noise from the series resistance dominated the current noise spectra. After annealing the device at 100 °C in air for 1 h, the electrical characteristics of the diode degraded, which was due to an increase in interface traps. According to the low-frequency noise properties, the interface trap density was found to be $3.6 \times 10^{15}$ cm⁻² eV⁻¹.

10.1.4. Carrier Transport Mechanism in SnO TFTs

In the low temperature measurements, the hole mobility of the SnO TFT dropped with decreasing the temperature. Two distinct carrier transport mechanisms were found in the SnO TFTs. At temperatures above 80 K, the drain current was proportional to $T^{1.5}$. This
suggested that band conduction was the dominant mechanism. The activation energy reached a maximum of 302 meV when $V_G$ was around 40 V, indicating that the bandgap of SnO was around 0.6 eV. At temperatures below 80 K, the drain current became proportional to $T^{-1/4}$, due to variable-range hopping dominating the carrier transport. The band-tail states and the deep defect states of the SnO were obtained from Mott’s equation, which provided a deeper insight into the formation of $p$-type conduction.

10.1.5. Complementary Circuits Based on $n$-IGZO and $p$-SnO TFTs

Complementary circuits based on $n$-type IGZO TFTs and $p$-type SnO TFTs are vital for the realisation oxide-based flexible electronics. The IGZO/SnO-based complementary inverter obtained a gain of 6.5 at a supply voltage of 40 V. By cascading three inverters, a three-stage ring oscillator was demonstrated. The oscillation frequency was 2.63 kHz with a supply voltage of 40 V.

10.2. Limitations and Future work

Although the IGZO Schottky diodes showed a record cut-off frequency on both flexible and glass substrates, the rectification ratios are still quite low compared with the value of the thermally annealed devices. However, thermal annealing is not suitable for flexible electronics due to the plastic substrate. According to Chapter 7, the electrical properties can be further improved by optimising the Ar/O$_2$ ratio during the deposition of the Pt layer. In future, the oxidation degree at the interface could be quantitatively analysed by using secondary ion mass spectroscopy or X-ray photoelectron spectroscopy [1].

As mentioned in Chapter 8, the multi-phases in the SnO film may cause degradation in performance, including lower mobilities, smaller on/off ratios and higher trap densities. Furthermore, in order to form $p$-type SnO films annealing processes beyond 200 °C are required, which is not compatible with most plastic substrates. Thus, the deposition conditions still need further optimisation to realise flexible complementary electronics.

Another issue with the $p$-type SnO is the material for the ohmic contact. In order to realise transparent electronics, it is necessary to find a proper contact material with a high transparency and a high work function. Possible candidates are graphene-based conductive layers [2], transparent conducting oxides [3] such as ITO, GaInO, and ZnInO, organic materials like PEDOT:PSS [4], and silver nanowires [5]. However, further studies are required.
The successful demonstration of the complementary ring oscillator based on IGZO and SnO TFTs shows the possibility of realizing large-area oxide-semiconductor-based electronics. Employing solid-state electrolytes [6] or self-assembled monolayers [7] as gate dielectrics may contribute to a higher gate capacitance and a better flexibility. These factors may lead to further improvements in the performance of flexible oxide-based complementary circuits. For practical applications, the manufacturing cost also determines the market success of the fully oxide-based electronics. Thus, adopting roll-to-roll techniques or solution based printing processes may promote further development in the large-area electronics using oxide semiconductors [8].

References


