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Solution-Processed TiO₂-Based Schottky Diodes with a Large Barrier Height

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Abstract—Thin-film Schottky diodes are one of the key elements in large-area flexible electronics. In such devices, a highly uniform semiconductor film is vital for the device performance. Here we propose a novel solution-based anodization method to form a conformal oxide semiconductor layer for Schottky diodes. The thickness of the anodized TiO₂ layer varied from 12 to 22.5 nm. The optimized Pt/TiO₂/Ti Schottky diode demonstrated a large barrier height of 1.19 eV, an on/off ratio as high as 3.5×10^6 at ± 2 V, and an ideality factor of 1.5. The average breakdown electric field was 5.5 MV/cm, which is higher than typical values of conventional solution processed TiO₂. The diode with a 15-nm-thick TiO₂ layer also showed good rectification properties up to 0.7 MHz.

Index Terms—Schottky diode, TiO₂, anodization, high frequency.

I. INTRODUCTION

TITANIUM oxide (TiO₂) is a popular material due to its high permittivity, superior chemical stability and high optical transmittance in the visible-IR spectral range [1]. Such properties make TiO₂ widely used in applications such as gas and humidity sensors [2], solar cells [3] and photoelectrochromic cells [4]. Schottky contacts can be formed between titanium oxide and a high work function metal [5]. The barrier heights of TiO₂-based Schottky diodes can be tuned sensitively by the introduction of hydrogen, making these diodes applicable as hydrogen sensors [6]. TiO₂-based Schottky diodes are also used to produce steady-state current flow in the steady-state catalytic reactions [7]. Under irradiation of 350-nm UV light, a high responsivity of 3.1 A/W was obtained by TiO₂ Schottky diode-based UV detectors [8]. However, most of the reported TiO₂ Schottky diodes exhibited large reverse leakage currents and small rectification ratios, which limit the use of TiO₂ in thin-film electronics [9]–[11].

There are several methods to produce TiO₂ films including

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chemical vapor deposition (CVD) [12], pulsed laser deposition (PLD) [13], atomic layer deposition (ALD) [14], electron-beam evaporation [15] and thermally oxidizing titanium [16]. Compared to these methods, anodization is one of the most promising techniques, because it is simple, fast, suitable for large-area electronics and does not need vacuum technologies [17]. Most studies of TiO₂-based Schottky diodes fabricated by anodization so far focused on porous or nanotube structures to obtain highly active surface and high surface to volume ratio [18]–[20]. This paper reports on anodized conformal TiO₂ layer with high uniformity and TiO₂-based Schottky diodes with high performance. Capacitance-voltage and current-voltage measurements were performed to study the electrical characteristics of the TiO₂ Schottky diodes. The high-frequency characteristics of the TiO₂ Schottky diodes were measured in a single-stage rectifier circuit. Due to the simple preparation process and excellent electrical properties, the low-voltage anodized TiO₂ Schottky diodes offer a wide range of potential applications in the electronics and optoelectronics.

II. EXPERIMENTS

The Pt/TiO₂/Ti Schottky diodes shown in Fig. 1(a) were fabricated on Corning 7059. Titanium film with a thickness of 100 nm was deposited onto the glass substrates using RF magnetron sputtering. An Ar pressure of 1.2 Pa and a RF power of 30 W were utilized to deposit Ti. Then the titanium film was anodized in a 10^{-3} mol/L citric acid solution using a gold wire as the cathode at room temperature. A Keithley 2400 Source Measure Unit supplied a constant current of 0.2 mA/cm². TiO₂ films were anodized at 8 V, 10 V, 12 V and 15 V, respectively. Finally, a circular Pt pad of a radius of 180 μ m and a thickness of 50 nm was deposited by RF magnetron sputtering to form the Schottky anode. Atomic force microscope (AFM) images were obtained by using Bruker Dimension FastScan. The thickness of the titanium oxide was measured using a Woollam M-2000 Ellipsometer. Current-voltage (*J-V*) and breakdown characteristics were examined by using an Agilent E5270B semiconductor analyzer. Capacitance-voltage (*C-V*) characteristics were measured by using an Agilent E4980A LCR meter. High frequency measurements were performed by using a HP 8116A pulse/function generator and an Agilent 34411A digit multimeter. The elemental constituents of TiO₂ films were examined by X-ray photoelectron spectroscopy (XPS) with ThermoFisher Scientific ESCALAB 250.

III. RESULTS AND DISCUSSIONS

The key structure of the proposed diode is the Schottky contact between Pt and TiO₂, so a smooth surface of anodized titanium oxide is a critical prerequisite. A porous structure can be formed with a high anodizing voltage [21] which is avoided here. Fig. 1(b) shows an AFM image of 15 V anodized titanium oxide. The surface is smooth and uniform with an RMS roughness of 0.38 nm, showing no porous structure. 15 V is the highest anodizing voltage used in this work, and all the titanium oxide films anodized at lower voltages did not show a porous or nanotube structure either. The smooth surface results from the low concentration and weak acidity of citric acid, the low voltages and short times of anodization [22]. The thicknesses of titanium oxide anodized at different voltages can be estimated by the ratio 1.5 nm/V [23]. Measured by an ellipsometry, the actual thicknesses of titanium oxide anodized at 10 V and 15 V were 15.6 nm and 24.7 nm, showing a good agreement with the estimation.

Fig. 1. (a) Schematic cross-sectional view of the TiO₂ Schottky diodes. (b) AFM micrograph of TiO₂ anodized at 15 V. (c) Current density as a function of bias voltage (J - V) of the TiO₂ Schottky diodes fabricated with different anodization voltages.

The solution-processed method is suitable for large area fabrication. The size of every sample is 2 cm × 1 cm, and there are 36 diodes on each sample. The performance of all diodes on a sample are very similar. For instance, the standard deviation of the barrier height is ~ 1.3 %, and the standard deviation of the ideality factor is ~ 4.5 %. Fig. 1(c) shows the current density as a function of voltage curves of the Schottky diodes anodized at different voltages. The diode anodized at 8 V has the highest forward current and the highest reverse current. The large leakage current can be attributed to the small thickness of the titanium oxide and inhomogeneity in the Schottky barrier height [24]. At anodization voltage > 10 V, i.e. thicknesses larger than 15 nm, the reverse current is reduced to < 10⁻⁷ A/cm², which agrees with the previously reported result when anodized TiO₂ was used as the gate dielectric in thin film

transistors [23]. The performance of the diode significantly deteriorates when the anodizing voltage reaches 15 V. The forward current decreases because the series resistance (R_s) significantly increases as shown in Tab. I.

TABLE I
PARAMETERS OF THE PROPOSED SCHOTTKY DIODES ANODIZED AT DIFFERENT VOLTAGES

Anodization voltage (V)	n	Φ_B (eV)	Φ_{Bi} (eV)	$I_{on/off}$	R_s (k Ω)	O:Ti Atomic ratio
8	1.5	1.14	0.87	2.4×10^5	0.7	2.8
10	1.5	1.19	1.00	3.5×10^6	2.1	2.4
12	1.5	1.23	1.15	5.3×10^5	5.2	2.6
15	2.9	1.18	2.45	1.9×10^4	116.5	2.5

The ideality factor n , effective barrier height Φ_B , rectification ratio $I_{on/off}$ and series resistance R_s can be extracted from the current density versus voltage curves [25] and are shown in Tab. I. Excluding the diode anodized at 15 V for its bad performance, the barrier height Φ_B and series resistance R_s of the diodes increase linearly with increasing anodizing voltage. The diode anodized at 10 V has the highest rectification ratio $I_{on/off}$ of 3.5×10^6 , which benefits from the lowest reverse current. The lowest reverse current may be attributed to the smallest inhomogeneity in the Schottky barrier height between Pt and TiO₂ [24]. The elemental constituents of TiO₂ films were obtained by XPS measurement. The O:Ti atomic ratios of all TiO₂ films are greater than 2, which may be related to hydroxyl groups appeared in the TiO₂ films during anodization. The diode anodized at 10 V has the lowest O:Ti atomic ratio and the highest $I_{on/off}$.

TABLE II
COMPARISONS OF BARRIER HEIGHT BETWEEN OUR WORK AND OTHER DIODES IN PUBLICATIONS

References	Electrode	Semiconductor	Barrier height (eV)
[26]	Pt	IGZO	0.79
[27]	TiW	InP	0.83
[8]	Ag	TiO ₂	0.85
[13]	CS-AFM	TiO ₂	0.50
[28]	Pt	TiO ₂	1.05
[16]	Si	TiO ₂	0.73
This work	Pt	TiO ₂	1.14-1.23

Fig. 2. Capacitance versus voltage characteristics of the Schottky diodes anodized at different voltages. The inset is the curve of the diode anodized at 15V, shown separately due to its bigger range.

It should be noted that the barrier heights of our TiO₂

Schottky diodes fabricated by anodization, from 1.14 eV to 1.23 eV, are much larger than those diodes reported previously which are shown in Tab. II.

Capacitance measurement using 1 kHz frequency was also carried out to confirm the trend of the barrier heights. The capacitance versus voltage (C-V) characteristics of the Schottky diodes anodized at different voltages are shown in Fig. 2. The built-in potential (V_{bi}) of the Schottky diodes anodized at different voltage can be obtained from Fig. 2 and are shown in Tab. I. Except the diode anodized at 15V, the built-in potentials V_{bi} is smaller than the barrier height Φ_B and linearly increases from 0.87 eV to 1.15 eV with the increasing anodizing voltage. The trend of the built-in potential V_{bi} agrees with that of barrier height Φ_B .

Fig. 3. (a) Breakdown measurements of the Schottky diodes with different anodization voltage. (b) Frequency response of a Schottky diode anodized at 10 V. The inset shows the measurement circuit.

The breakdown voltage is one of the key performance parameters for Schottky diodes [12]. Fig. 3(a) shows the measured breakdown characteristics. The breakdown voltage becomes larger as the anodizing voltage increases. The devices anodized at 8, 10, 12, 15 V, break down at 6.5, 8.1, 10.6 and 12.5 V, respectively. The breakdown electric field strengths in all devices are similar with an averaged value of 5.5 MV/cm.

The frequency response of the diode is characterized by applying a sinusoidal signal and measuring the output DC voltage as shown in the inset of Fig. 3(b). Fig. 3(b) shows the measured frequency response of the diode anodized at 10 V. The input root mean square voltage (V_{RMS}) is 2.8 V, the output load is a 10 M Ω resistance (R_L) in parallel with a 100 nF capacitance (C_L). The measured cut-off frequency is 700 kHz, and the diode still produces a DC output voltage of 1 V at 1 MHz.

IV. CONCLUSION

In summary, high-performance Schottky diodes with TiO₂ anodized at different voltages were fabricated on glass substrate. The diode anodized at 10 V exhibited a high rectification ratio of 3.5×10^6 and a large barrier height of 1.19 eV. The TiO₂ semiconductor film and Schottky diodes, as well as other similar materials and devices, produced by such simple solution process may have useful implications in development of thin-film electronics.

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