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Achieving high performance Ga₂O₃ diodes by adjusting chemical composition of tin oxide Schottky electrode

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Abstract

High performance Ga_2O_3 Schottky barrier diodes (SBDs) are achieved by adjusting chemical composition of SnO_x Schottky electrode. The SnO_x is produced by radio frequency sputtering under various oxygen partial pressures (P_{O}). A synergic study on Raman, X-ray photoelectron, and optical transmission spectroscopy of the SnO_x films illustrates that: the films with $P_{\text{O}} = 0 \sim 3.1\%$ consist mainly SnO and Sn with high conductivity; the films with $P_{\text{O}} = 4.6 \sim 5.4\%$ are composed of both p-type SnO and n-type SnO_2 with high resistance; the films with $P_{\text{O}} = 10.0 \sim 13.1\%$ are mainly dominated by n-type SnO_2 with low resistivity. In addition, as P_{O} increased from 0 to 3.1%, the SBDs performances are significantly improved due to that the SnO-dominated films reduce effectively the oxygen-deficiency at the Ga_2O_3 interfaces and the related interface state density. With $P_{\text{O}} = 5.4\%$, the high resistive SnO_x results in degraded diode performance because that the SnO_2 component with oxygen vacancy defects may aggravate the oxygen-deficiency at the Schottky interface. With the optimized P_{O} of 3.1%, the SBD shows high performance with a large barrier height of 1.12 eV, a near unity ideality factor of 1.22, and a high rectification ratio of $> 10^{10}$.

Keywords: Ga_2O_3 , Schottky barrier diodes (SBDs), tin oxide (SnO_x), oxygen partial pressures

1. Introduction

Oxide semiconductor-based Schottky junctions form the basis of a series of devices such as rectifiers, photodetectors, and metal-semiconductor field effect transistors [1-3], which are basic building blocks for logic gates, radio frequency identification tags, resistive random-access memories, etc [4-7]. Gallium oxide (Ga_2O_3) has attracted extensive research interest in development of Schottky barrier diodes (SBDs), due to its extremely wide bandgap of 4.5 ~ 4.9 eV and high breakdown electric field strength of about 8 MV/cm [8-10]. Various geometries, such as field-plated vertical SBDs [11], filed-plated lateral SBDs [12], MOS-type SBDs [13], and p-n heterojunction diodes [14-15], have been demonstrated for improving the performance of Ga_2O_3 SBDs. Most of these Ga_2O_3 SBDs use high work function (Φ_M) metals, such as Ni, Pt, Pd, and Au, as Schottky anodes. Müller et al. fabricated high performance $\text{PtO}_x/\text{Ga}_2\text{O}_3$ Schottky contact with an extremely large barrier height (Φ_B) of 1.94 eV, a near unity ideality factor (n) of 1.09, and a moderate on/off ratio ($I_{\text{on/off}}$) of 4.5×10^9 at ± 2 V [16]. Besides the high work function of PtO_x , the large barrier height is due to that oxygen included sputtering atmosphere reduces effectively the oxygen-deficient-related interface state density at the Schottky interface [16]. It was also reported that introduce of metal oxides at the Schottky contact interface improves effectively Φ_B and n for wide-band-gap semiconductors such as ZnO or InGaZnO [17-20].

In contrast to the expensive metal such as Pt, Pd, and Au, with high work functions, Sn is rather inexpensive and convenient to deposit with low melting point and high saturated vapor pressure. Element Sn has multiple valences including Sn^{0+} , Sn^{2+} , and Sn^{4+} . Because that Sn is metallic, SnO is normally p-type conductive, and SnO_2 is typically n-type conductive, tin based

oxide, SnO_x , can be tuned in electrical properties in large extent by adjusting its composition [21-22]. The microstructure and optical properties are also adjusted by the composition. In this work, we have realized high performance $\text{SnO}_x/\text{Ga}_2\text{O}_3$ SBDs via carefully adjusting the SnO_x chemical composition. The microstructure, optical, and electrical properties of SnO_x thin films with various composition, the microstructure of Ga_2O_3 flake, and the electrical properties of the corresponding $\text{SnO}_x/\text{Ga}_2\text{O}_3$ SBDs have been studied. Our results indicate that SnO_x can be an excellent Schottky electrode in contact with Ga_2O_3 .

2. Experimental

2.1. SnO_x films and $\beta\text{-Ga}_2\text{O}_3$ bulk single crystal growth and characterization

Various 50-nm SnO_x films were deposited on SiO_2/Si and corning glass (7059) by radio frequency (RF) sputtering with a Sn metallic target (99.9%, 3 inch in diameter). Prior to deposition, the substrates were sequentially cleaned in an ultrasonic bath of acetone, ethanol, and de-ionized (DI) water and dried by N_2 . The SnO_x films were deposited at a constant power of 50 W and various oxygen partial pressures, P_{O} ($P_{\text{O}} = \text{O}_2/(\text{Ar} + \text{O}_2)$, vol%), from 0 to 13.1%. In addition, Si-doped $\beta\text{-Ga}_2\text{O}_3$ bulk single crystal was grown by the edge-defined film-fed growth technique and the (100)-oriented $\beta\text{-Ga}_2\text{O}_3$ flake ($\sim 220 \mu\text{m}$ in thickness and $5 \text{ mm} \times 10 \text{ mm}$ in size) was obtained by mechanical exfoliation. The microstructures were elucidated by a confocal microscope Raman spectrometer (Renishaw in Via-Reflex) using a 532 nm laser wavelength. The chemical compositions were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The binding energies were calibrated by setting the C 1s at 284.6 eV. The transmission spectra were obtained using a double-beam UV-visible

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spectrophotometer (TU-1901). The morphology and roughness were analyzed by atomic force microscope (AFM, Dimension FastScanTM).

2.2. SnO_x/β-Ga₂O₃ SBDs fabrication and characterization

Prior to metal deposition, the surface of the back side was etched with inductively coupled plasma (ICP) technique using a mixture gas of BCl₃ (15 sccm) and Ar (5 sccm) for 2 min under the ICP/RF power of 150 W/15 W. And then full-area back ohmic contact was created using Ti/Au (60 nm/20 nm) deposited by e-beam evaporation and followed by annealing in N₂ gas at 350 °C for 2 min to achieve better ohmic contact. Finally, Schottky anode SnO_x (50 nm) films were fabricated by RF sputtering at a constant power of 50 W and various P_O of 0, 1.5, 3.1, and 5.4%, and then capped with an e-beam evaporated Ti (60 nm) layer for better contact with the probe tip during electrical performance measurements. The active areas of these diodes are $3.14 \times 10^{-4} \text{ cm}^2$. The cross-sectional structure of Ti/SnO_x/Ga₂O₃ was analyzed using a scanning electron microscope (SEM, FEI Nova 450). Current density-voltage (J - V) characteristics were measured using a semiconductor analyzer (Agilent 2902B) at room temperature.

3. Results and discussions

3.1. Composition analysis of the SnO_x film

3.1.1. Raman measurements

In order to investigate the composition-dependent microstructures of the SnO_x films deposited at $P_O = 0 \sim 13.1\%$, Raman spectra were measured with a laser centered at 532 nm in power of 0.5, 2.5, 5.0, and 25 mW, as shown in Figures 1(a)-(g). At $P_O \leq 3.1\%$, the two peaks located at 110 and 210 cm⁻¹, as shown in Figures 1(a)-(c), correspond well to the low frequency

E_g^{low} and Al_g of crystalline SnO, respectively [22-23]. It is notice that with increased laser power, the two peaks became sharper, and this attributes to the more sufficient SnO crystallization induced by stronger local heating effect of the laser with higher power [23]. It is revealed by CCD images (Figure 1(h)) that under laser with the power of 25 mW, the SnO_x films with $P_O = 0 \sim 3.1\%$ even can form a crystalline island at the position of laser spot. For SnO_x films with $P_O = 4.6 \sim 5.4\%$, no clear Raman peaks and crystalline island was observed even under the laser with a power of 25 mW, as shown in Figures 1(d), (e), and (h), suggesting the amorphous phase films. This was suggested to be attributed to that the increased SnO₂ components inhibit the crystallization of SnO. For SnO_x films with $P_O = 10.0 \sim 13.1\%$, a peak centered at 305 cm^{-1} was perceived corresponding well to the infrared-active mode of SnO₂ [24], as shown in Figures 1(f) and (g). Although no crystalline island appeared under the laser radiation, this Raman-active mode illustrated unambiguously the existence of SnO₂. These Raman results indicate that SnO is included in the SnO_x films with $P_O = 0 \sim 3.1\%$, SnO₂ is included in the SnO_x films with $P_O = 10.0 \sim 13.1\%$, and both SnO and SnO₂ may be included in the SnO_x films with $P_O = 4.6 \sim 5.4\%$.

Figure 1. (a-g) Raman spectra of the SnO_x films sputtered with various P_{O_2} of 0 ~ 13.1%, and the SnO films are measured with laser powers of 0.5, 2.5, 5.0, and 25 mW. (h) CCD images of the SnO_x films after Raman measurements, in which A, B, C, and D are the regions nearby the laser points with powers of 0.5, 2.5, 5.0, and 25 mW, respectively.

3.1.2. XPS measurements

In order to further confirm the chemical composition of these SnO_x films, XPS measurements were performed. To get rid of the contribution of the topmost native oxide layer (SnO_2) in these SnO_x films, argon plasma with ion energy of 3 KeV were used to sputter away this topmost oxidation layer. Figure 2(a) shows Sn 3d core-level spectra with deconvoluted

Sn^{0+} (484.4 and 492.8 eV), Sn^{2+} (485.9 and 494.3 eV), and Sn^{4+} (486.6 and 495.0 eV) components for the SnO_x films [25]. For SnO_x films with $P_{\text{O}} = 0 \sim 3.1\%$, predominated Sn^{2+} and Sn^{0+} were confirmed to be included. As P_{O} increased from 0 to 3.1%, the SnO component became more dominate due to more sufficient oxidation of Sn to SnO. The film with $P_{\text{O}} = 0\%$ even has SnO component, and this is suggested to be caused by the topmost oxide coverage in the Sn target. As P_{O} further increased from 4.6 to 13.1%, it is observed that the Sn^{0+} component disappeared, the Sn^{2+} component gradually decreased, and the Sn^{4+} component gradually increased and became dominated in the SnO_x films with $P_{\text{O}} = 10.0 \sim 13.1\%$. The contents of the oxidization states (Sn^{0+} , Sn^{2+} , Sn^{4+}) in the SnO_x films were calculated based on the XPS results and illustrated in Figure 2(b). As P_{O} was increased to 4.6%, the Sn^{0+} content decreased from 41.8 to 0%. The Sn^{2+} content increased firstly with increasing P_{O} to a maximum value of 77.9% at $P_{\text{O}} = 3.1\%$, and then decreased with further increase of P_{O} . With the increase of P_{O} , the Sn^{4+} remained a very low content $\sim 3\%$ at $P_{\text{O}} \leq 3.1\%$, and then increased to 83.8% at $P_{\text{O}} = 13.1\%$. The XPS results are in good agreement with the Raman spectroscopy, and they confirm that the SnO_x films with $P_{\text{O}} = 0 \sim 3.1\%$ are dominated by Sn and SnO, the films with $P_{\text{O}} = 4.6 \sim 5.4\%$ are dominated by SnO and SnO_2 , and films with $P_{\text{O}} = 10.0 \sim 13.1\%$ are predominated by SnO_2 .

Figure 2. (a) XPS spectra of Sn 3d core levels in SnO_x films under various P_O of 0 ~ 13.1%. (b) Content evolutions of Sn⁰⁺, Sn²⁺, and Sn⁴⁺ in the films as a function of P_O .

3.2. Optical properties of the SnO_x films

Figure 3(a) shows the transmission spectra of the films in UV-visible region. As expected, the film with P_O of 0 ~ 3.1% have rather low transmittance ($T\%$) in the whole region due to the intensive light absorption of the metallic Sn component [22]. At $P_O \geq 4.6\%$, the transmittance edge shifted gradually to the shorter wavelengths as P_O increased, indicating an enlarged band gap, and this was because of the increased SnO₂ amount in the films. The intrinsic absorption edges, λ_0 , of SnO and SnO₂ are 564 and 345 nm, respectively, given by $\lambda_0 = 1240/E_g$, where the band gap E_g is 2.2 and 3.6 eV for SnO and SnO₂, respectively [25]. To evaluate the amount of SnO and SnO₂ component in the films with P_O of 0 ~ 13.1%, the dependences of $T\%$ at 564 and 345 nm on P_O were plotted, as shown in Figure 3(b). Both the $T\% \sim P_O$ curves can be divided into three regions by the transmittance slop: (1) $P_O = 0 \sim 3.1\%$, in this region the films showed a low transmittance due to a large amount of metallic Sn were involved. With P_O increased from 0 to 3.1%, the $T\%$ at 564 nm increased from 5.7% and 14.6% while the $T\%$ at 345 nm showed a steady value of ~7%, indicating increasing amount of SnO but only trace

SnO₂ included in the films. (2) $P_O = 3.1 \sim 10.0\%$, both $T\%$ at 564 and 345 nm increased significantly with the P_O increased, confirming increased amount of SnO₂. (3) $P_O = 10.0 \sim 13.1\%$, in this region the films showed a saturated transmittance due to the dominated SnO₂ composition.

Figure 3. (a) UV-visible transmission spectra of the SnO_x films with different P_O of 0 ~ 13.1% as a function of the wavelength. (b) The transmittances at 345 and 564 nm versus the P_O .

3.3. Electrical characteristics of SnO_x films

To investigate the conductivity of the SnO_x films, channel structures with two Ti/Au electrodes were fabricated, as shown in the inset of Figure 4(a). The channel length and width are 60 and 2000 μm , respectively. It is observed that the films with $P_O = 0 \sim 3.1\%$ have high conductivity with high current density of $\sim 10^2$ - 10^{-1} A/cm² at ± 1 V, and the conductivity reduces with P_O increases, due to decrease amount of Sn in these films. The films with $P_O = 4.6 \sim 5.4\%$ exhibited high resistivity with low current density of $\sim 10^{-6}$ - 10^{-9} A/cm² at ± 1 V, which is due to the positive and negative charge compensation effect because of the coexistence of p-type SnO and n-type SnO₂ phases [22]. For $P_O = 10.0 \sim 13.1\%$, the SnO₂ dominated films show high conductivity again with high current density of 2.5×10^{-1} A/cm² at ± 1 V, indicating the two

films have high electron concentrations which are usually suggested caused by high oxygen vacancy (V_O) defect density.

In addition to the conductivity of the films, we studied the root mean square (RMS) surface roughness of the SnO_x films by AFM, as shown in Figure 4(b). Surface roughness is important for the quality of Schottky contact. At $P_O = 0\%$, the SnO_x film has a large RMS surface roughness of 13.7 nm with distinct metallic particles and/or clusters. In contrast, at $P_O = 1.5 \sim 13.1\%$, the surface of the film is atomically flat with a roughness of ~ 1 nm. The results indicate that the introduce of oxygen during the sputtering deposition of the SnO_x films reduces effectively the roughness of the films, which facilitates the formation of a uniform Schottky contact.

Figure 4. (a) J - V curves of the SnO_x films with two Ti/Au contacts at different P_O of 0 ~ 13.1%. (b) RMS surface roughness of the SnO_x films as a function of P_O . Inset of (a) shows the schematic of the Au/Ti/ SnO_x /Ti/Au structure. Inset of (b) shows the AFM images of the SnO_x films with P_O of 0 and 13.1%.

3.4. Microstructure properties of Ga_2O_3 flake

The exfoliated Ga_2O_3 flake has been characterized by Raman spectroscopy and XPS, as shown in Figure 5. Figure 5(a) shows a typical micro-Raman spectrum of the Si-doped Ga_2O_3 bulk single crystal. The Raman spectra showed 10 clear Raman reactive peaks of Ga_2O_3 at 116,

147, 172, 201, 348, 417, 477, 632, 659, 768 cm^{-1} . These Raman peaks with rather small FWHMs indicate high crystallinity. The strongest low frequency peak located at 201 cm^{-1} is correlated to the characteristic vibration and translation mode of Ga-O chains [26]. The phonon peaks between 300 and 500 cm^{-1} are related to the mid-frequency deformation of Ga₂O₆ octahedral [27], and the peaks between 600 and 800 cm^{-1} are attributed to the high-frequency and result of stretching and bending of GaO₄ tetrahedral [27]. The XPS spectrum shown in Figure 5(b) illustrated clearly that Si is successfully doped in the Ga₂O₃ by determinations of the core levels of Si, Ga, and O.

Figure 5. Raman spectrum (a), XPS wide scan spectrum (b) of exfoliated Ga₂O₃ flake.

3.5. Electrical performance of SnO_x/Ga₂O₃ Schottky diodes

It is reported that tin vacancies (V_{Sn}) are the main defects with the lowest formation energy among vacancy and interstitial defects in p-type SnO [28], and V_{O} are the main defects for n-type SnO₂ [29]. It is reasonable that V_{Sn} may attenuate and V_{O} may aggravate the oxygen-deficiency at the Ga₂O₃ Schottky surface, and thus SnO-dominated electrode with high conductivity, e.g. the film with $P_{\text{O}} = 3.1\%$, was suggested an ideal Schottky electrode for Ga₂O₃. To confirm this, we fabricated Ga₂O₃ SBDs with SnO_x Schottky electrode deposited under P_{O} of 0, 1.5, 3.1, and 5.4%, and investigated their electrical properties, as shown in Figure 6. The

cross-sectional structure and typical SEM image of the $\text{SnO}_x/\text{Ga}_2\text{O}_3$ SBD are shown in Figure 6(a). The Ga_2O_3 (100) wafer was mechanical exfoliated to serve the fresh and clean surface. The typical SEM image indicates the SBDs have rather smooth Schottky interface. Figure 6(b) shows J - V characteristics of $\text{SnO}_x/\text{Ga}_2\text{O}_3$ SBDs in which the SnO_x films were deposited at various P_{O} . The J - V curves of the fabricated Schottky diodes were analyzed using a thermionic emission (TE) model given by [30],

$$J = A^*T^2 \exp\left(\frac{-q\Phi_{B,JV}}{kT}\right) \left[\exp\left(\frac{qV - IR_s}{nkT}\right) - 1 \right] \quad (1)$$

where q is the element charge, R_s is the series resistance, k is the Boltzmann constant, n is the ideality factor and is an evaluation of the conformity of the diode to pure TE, A^* is the effective Richardson constant which is $41.1 \text{ Acm}^{-2}\text{K}^{-2}$ for Ga_2O_3 [9, 31], and $\Phi_{B,JV}$ is the effective barrier height measured by J - V characteristics. The values of n and $\Phi_{B,JV}$ were extracted by fitting the subthreshold region of the semi-logarithmic J - V curves using Equation (1). With P_{O} increased from 0 to 3.1%, the extracted $\Phi_{B,JV}$ increased from 0.86 to 1.12 eV and n decreased from 1.59 to 1.22, and this results in the significantly decreased off-current density. This is mainly due to that the V_{Sn} defects in the SnO with oxygen dangling bonds can compensate for the V_{O} defects in the Ga_2O_3 at the Schottky interface and reduce the related interface state density. For an ideal SBD, $n = 1$. Our data show that the n of the diodes is above 1, and the possible origins can be the existences of interface states, barrier height inhomogeneity, etc. [32-33], caused by the doping of Ga_2O_3 , structure inhomogeneity, etc. Here, the plasma bombardment induced interfacial defects during sputtering of the SnO_x Schottky anode can be neglected although without any post-annealing [34], because that the optimized Schottky diode based on Cr-doped Ga_2O_3 single crystal and as-sputtered SnO_x achieves near unity n of 1.02 [35]. The ON-

resistance (R_{ON}) extracted from the slope of the linear region in Figure 6(c) is shown in table 1. At $P_O \leq 3.1\%$, the R_{ON} of 28-36 $m\Omega cm^2$ mainly derived from the insulating interfacial Ga_2O_3 layer [35]. As we expected, at $P_O = 5.4\%$, the high resistive SnO_x electrode composed by a large amount of SnO_2 (with SnO/SnO_2 mole ratio of $\sim 1:1.05$ as shown in Figure 2(b)) increases the interface state density. The corresponding SBD shows a significantly degraded electrical characteristics [29], with an enlarged n , an increased R_{ON} , and a decreased $I_{on/off}$. Such tendency of interface state density is also indicated by capacitance-voltage measurements (not shown here). These results confirm that the conductive SnO component in the SnO_x films contributes to the formation of a high quality Schottky contact, and the SnO_2 component degrades the Schottky contact quality. By adjusting P_O during the deposition of SnO_x films to conductive SnO -dominated Schottky electrode, with optimized P_O of 3.1%, excellent Ga_2O_3 Schottky contact can achieved with a large $\Phi_{B, JV}$ of 1.12 eV, a low n of 1.22, and a high $I_{on/off}$ of $>10^{10}$, as shown in table I.

Figure 6. (a) Schematic structure of the diode and SEM image of the cross-sectional structure of $Ti/SnO_x/Ga_2O_3$. J - V curves in semi-logarithmic (b) and linear (c) scale of the SnO_x/Ga_2O_3 diodes.

Table I. Schottky barrier height ($\Phi_{B, JV}$), ideality factor (n), ON-resistance (R_{ON}), rectification ratio ($I_{on/off}$) at -1 ~ 2 V for the SnO_x/Ga_2O_3 SBDs

P_O	0%	1.5%	3.1%	5.4%
$\Phi_{B, JV}$ (eV)	0.86	0.99	1.12	1.12
n	1.59	1.24	1.22	1.30
R_{ON} (m Ω cm ²)	28	33	36	456
$I_{on/off}$ (at -1~2 V)	1.94×10^5	2.78×10^7	$> 10^{10}$	8.63×10^7

4. Conclusion

Ga₂O₃ Schottky diodes were fabricated with SnO_x Schottky electrode prepared by radio frequency magnetron sputtering at various P_O . With $P_O = 0 \sim 3.1\%$, the SnO_x electrode is dominated by metallic Sn and SnO with high conductivity, the p-type SnO with V_{Sn} defects reduces effectively the oxygen-deficiency-related interface state density at SnO_x/Ga₂O₃ interface, and high quality Schottky contact can be achieved. With $P_O = 4.6 \sim 5.4\%$, the SnO_x electrode is dominated by p-type SnO and n-type SnO₂ with high resistivity because of the compensation of the positive charge in the SnO and negative charge in the SnO₂. With $P_O \geq 10\%$, the films are dominated by n-type SnO₂ with low resistance. The n-type SnO₂ with V_O defects may aggravate the oxygen-deficiency at the Ga₂O₃ Schottky surface and thus result in diode performance degradation. By carefully adjusting the SnO_x electrode chemical composition to be conductive SnO-dominated, a high performance Ga₂O₃ Schottky diode was achieved at an optimized P_O of 3.1%, with a large barrier height of 1.12 eV, a near unity ideality factor of 1.22, and a high rectification ratio of $> 10^{10}$. The results indicate that conductive SnO electrode can be an excellent Schottky electrode with n-type semiconductors such as Ga₂O₃.

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