Magnetron-Sputtered SnO Thin Films for p-Type and Ambipolar TFT Applications (Postprint)

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Abstract

SnOx films were fabricated by reactive rf magnetron sputtering under various oxygen partial pressures (PO = 1.6%-50%) and then annealed in an air ambient. Four operating window regions of the SnOx films are demonstrated such as metallic Sn dominated films with n-type conduction, polycrystalline SnO dominated films with p-type conduction, SnO-SnO2 composite films with high resistivity, and amorphous SnO2 dominated films with n-type characteristics. TFT devices using the SnO dominated films as channels are investigated. The TFTs with the channels of a hole concentration over 1018 cm−3 show depletion p-type characteristics. The hole concentration can be tunable by changing PO, the channel thickness, and the annealing durations. An ambipolar operating mode is obtained by modulating the hole concentration.

Full Text

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SnOx films were fabricated by reactive rf magnetron sputtering under various oxygen partial pressures (PO = 1.6%-50%) and subsequently annealed in air. Four distinct operating window regions of the SnOx films were demonstrated: metallic Sn-dominated films with n-type conduction, polycrystalline

SnO-dominated films with p-type conduction, SnO-SnO2 composite films with high resistivity, and amorphous SnO2-dominated films with n-type characteristics. TFT devices using the SnO-dominated films as channel layers were investigated. TFTs with channel hole concentrations exceeding 10^18 cm−3 exhibited depletion-mode p-type characteristics. The hole concentration could be tuned by adjusting the oxygen partial pressure, channel thickness, and annealing duration. An ambipolar operating mode was obtained by modulating the hole concentration.

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Introduction

Transparent oxide semiconductors have been proposed as one of the most promising candidates for thin-film transistors (TFTs) and other complex electronic circuits, owing to their low fabrication temperature, good transparency in the visible light region, and high field-effect mobility. However, most high-mobility oxide semiconductors exhibit n-type conduction, with only a limited number of oxides showing p-type conduction and modest hole mobilities. Consequently, the application of oxide semiconductors has been limited to unipolar n-type devices. Bipolar oxide semiconductors, in which both n-type and p-type carriers can be transported freely, are highly desirable for realizing Complementary Metal-Oxide-Semiconductor (CMOS)-like devices and circuits.

Generally, the valence band maxima (VBM) of oxide semiconductors are composed primarily of localized O 2p orbitals, which severely limit hole transport. The use of hybridized orbitals between O 2p and metal cation nd states (such as Ni 3d, Cu 3d, and Ag 4d) has been proposed to enable p-type oxide semiconductors. P-type NiO and Cu2O TFTs with field-effect mobilities of 1.6 × 10^−4 cm^2/Vs and 4.3 cm^2/Vs have been demonstrated, respectively. Similarly, tin monoxide (SnO) has proven to be a good p-type oxide semiconductor due to the incorporation of isotropic extended Sn 5s orbitals into the VBM. P-type SnO TFTs with field-effect mobilities up to 6.75 cm^2/Vs have been reported.

Interestingly, SnO has a small fundamental bandgap (0.5–0.7 eV), which favors ambipolar behavior for electronic devices. Meanwhile, it possesses a large direct optical bandgap (2.5–3.4 eV), leading to high transparency in the visible region. Additionally, SnO has been proposed as a good electron conductor because electron transport near the conduction band minimum follows a free-electron-like model. Therefore, among transparent oxide semiconductors, SnO TFTs have been reported to operate in an ambipolar mode.

SnO thin films can be prepared by several techniques, including electron beam evaporation, pulsed laser deposition, vacuum thermal evaporation, solution processing, and magnetron sputtering. Among these, sputtering offers the advantage of preparing large-area uniform films for large-scale industrial applications.

Nevertheless, previously reported SnO TFTs exhibited either p-type or ambipolar behavior. The mechanism governing the conversion from p-type to ambipolar mode has rarely been reported and remains unclear.

In this article, SnOx films were fabricated by reactive rf magnetron sputtering under various oxygen partial pressures (PO). The structural evolution and electrical properties are discussed in detail to identify the operating window for fabricating SnO-dominated films. The influence of fabrication conditions on the performance of SnO TFTs is also examined.

Experimental

Film Fabrication and Characterization

Approximately 200 nm-thick SnOx films were fabricated by reactive rf magnetron sputtering using a 2-inch Sn target (99.99%) at room temperature. The sputtering power was maintained at 40 W. The Ar flux (fAr) was fixed at 6 sccm, while the O2 flux (fO) was varied from 0.1 to 6 sccm. The oxygen partial pressure (PO = fO/(fAr + fO)) ranged from 1.6% to 50%. Subsequently, the SnOx films were annealed at 200°C in air for 1 hour. The structural and electrical properties of the films were characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer) and Hall-effect (ACCENT, HL5500) measurements, respectively.

TFT Fabrication and Characterization

Top-contact, bottom-gate TFTs were fabricated on commercially available SiO2-Si(n+) substrates (SiO2 105 nm, gate capacitance per unit area C0 33 nF/cm^2). The channel layers, approximately 24 nm thick, were sputtered with PO as the parameter varying between 10.4% and 15.5%. Subsequently, Ni/Au source-drain electrodes were deposited by e-beam evaporation. The SnO channel layer and source-drain electrodes were patterned using shadow masks. The width and length of the TFTs were 1000 m and 100 m, respectively. Before depositing the source-drain electrodes, SnO films were annealed in air at various temperatures (150-300°C) with different annealing durations (tA). Output and transfer characteristics of the TFTs were measured at room temperature in the dark using a semiconductor parameter analyzer (Keithley 4200).

Results and Discussion

Thin Film Properties

Figure 1 [Figure 1: see original paper] shows the XRD patterns of the SnOx films fabricated at various PO values. At PO = 1.6%, both -SnO phase (-PbO structure, P4/nmm, JCPDS card No. 06-0395) and -Sn phase (I41/amd, JCPDS card No. 19-1365) are observed, with the latter dominating. As PO increases, the peak intensity of the -Sn phase decreases and becomes comparable to that of the -SnO phase at PO = 9.1%. At PO = 15.5% and 16.7%, the -Sn phase nearly disappears and only the -SnO phase with attenuated peak intensity is observed. When PO 17.8%, no characteristic peaks are detected, suggesting an amorphous nature. This phase evolution trend is consistent with our previous report. The crystalline structure transition from polycrystalline to amorphous is believed to result from the incorporation of Sn4+ in the SnO matrix, which boosts structural disorder and increases the crystallization temperature.

Figure 2 [Figure 2: see original paper] shows the dependence of Hall mobility and carrier concentration on PO. In conjunction with the crystalline phase evolution, the electrical behavior can be roughly divided into four PO regions. (1) PO 9.1%, where the films exhibit n-type conduction dominated by the metallic Sn phase. The films show very low resistivity (around 1 × 10ˆ−4 (cid:2) · cm) and high electron concentration ($10^{22\text{-}10}$23 cmˆ−3). The resistivity is abnormally high at PO 4.8% because the film is discontinuous (cracks are observable even by naked eye), most likely due to different thermal expansion coefficients between metallic Sn and SnO.

(2) 9.1% < PO < 17.8%, where the films exhibit p-type conduction dominated by the polycrystalline SnO phase. In this region, hole mobility shows an increasing trend (0.26-1.67 cm^2/Vs) while hole concentration decreases from 10ˆ20 cmˆ−3 to 1 × 10ˆ18 cmˆ−3 as PO increases.

(3) 17.8% PO < 25%, where the films exhibit high resistivity (>10ˆ4 (cid:2) · cm) and undergo a transition from polycrystalline to amorphous.

(4) PO 25%, where the films display n-type behavior. In this region, the amorphous SnO2 phase is considered dominant. The conversion from p-type conduction to high resistivity and then to n-type conduction with increasing PO is believed to originate mainly from competition between donor and acceptor generation processes. Specifically, for SnO-dominated films, the majority carriers are holes originating from acceptors. As SnO2 content increases with PO, the acceptors are gradually compensated by donors in SnO2. When the number of acceptors has approximately the same order of magnitude as donors, the SnOx films exhibit maximum resistivity, referred to as the "conductivity dilemma area," observed for films at PO between 17.8% and 25%. N-type behavior appears when the donor effect becomes overwhelming, and vice versa.

TFT Performance

Figure 3 [Figure 3: see original paper] shows the transfer curves of TFT devices with channel layers deposited at PO = 10.4%-15.5%. The TFT at PO = 10.4% displays depletion-mode p-type characteristics. This device cannot be turned off completely even when the gate-source voltage (VGS) increases to 60 V, because the channel layer carrier concentration (10ˆ20 cmˆ−3) is too high to be depleted. As PO increases to 11.8% or 13.0%, the TFTs show weak ambipolar characteristics. At PO = 14.3%, the drain-source current (IDS) sharply decreases to 10ˆ−11 A and the device shows no TFT switching behavior, due to the high resistivity of the SnO-SnO2 composite channel layer. At PO = 15.5%, the TFT displays n-type characteristics due to the SnO2-dominated channel.

The operation mode conversion of the TFTs follows a similar trend to the electrical evolution of the 200 nm-thick SnOx films (Fig. 3), but transitions occur at lower PO values. It is believed that a SnO2 layer a few nanometers thick forms on the surface of SnOx films during air annealing. With the same annealing duration, the thickness of this SnO2 layer remains nearly constant for SnOx films of different thicknesses. Thus, thinner SnOx films have a higher relative SnO2 content, which can compensate holes and consequently yield lower hole concentration. According to Hall results, the hole concentration of the 24 nm-thick film (10^18 cm^−3) decreases by one order of magnitude compared to the 200 nm-thick film (10^19 cm^−3). Additionally, the TFT with a 30 nm-thick channel layer shows a very low on/off current ratio (129) due to the relatively higher conductivity, while the TFT with a 14 nm-thick channel layer demonstrates no TFT switching behavior due to high channel resistivity (as seen in Fig. 4 [Figure 4: see original paper]).

Further investigation of ambipolar TFTs reveals that for the TFT at PO = 11.8%, the on/off current ratio (Ion/Ioff) and linear field-effect mobility (lin) in p-channel operation are 1070 and 1.45 cm^2/Vs, respectively. For the TFT at PO = 13.0%, these values are 1340 and 1.0 cm^2/Vs. The turn-on voltage (Von), defined as the gate voltage at minimum |IDS| in a transfer curve, reflects the symmetry of an ambipolar TFT and is expected to be close to zero for good symmetry. The Von values are 57.8 V and 58.8 V for TFTs at PO = 11.8% and 13.0%, respectively. Summarizing the electrical parameters, the TFT at PO = 11.8% shows relatively acceptable performance and is selected for further discussion.

Figure 5 [Figure 5: see original paper] depicts transfer curves of TFT devices annealed at different temperatures. The TFT annealed at 200°C shows the best performance, particularly a large Ion/Ioff value. At 150°C, IDS remains nearly constant at -2.2 × 10^−7 A across various VGS values, indicating that the channel current cannot be tuned by gate voltage. The most probable reason is that the channel layer has high resistivity and forms a non-ohmic contact with the source-drain electrodes. At 250°C, the device shows weak ambipolar behavior. As annealing temperature increases to 300°C, the TFT shifts to weak n-type mode due to the SnO2-dominated channel.

Figure 6a [Figure 6: see original paper] displays transfer characteristics of TFT devices annealed at 200°C in air for different durations (tA). With increasing tA, the on-current decreases while the off-current first decreases and then rebounds when tA > 2 h, resulting in a maximum Ion/Ioff of 1550 at tA = 2 h (Fig. 6b). Notably, IDS at VGS > 20 V decreases very slowly when tA > 4 h, indicating that the channel layer becomes increasingly difficult to deplete with increasing VGS. Ogo et al. observed a similar phenomenon in SnO TFTs and speculated that the origin may lie in numerous trap states located at deep energies (> 0.2 eV above the valence band) that prevent Fermi level elevation even with large positive VGS. When tA > 2 h, deep-level trap states appear to increase with tA, resulting in larger off currents and threshold voltages. As shown in Fig. 6b, Vth first decreases and then increases with annealing duration, approaching a minimum at tA = 4 h.

Hall-effect measurements were also performed (Fig. 6c). Hole concentration shows a decreasing trend, which correlates with the reduction in on-current and Vth. Hall mobility increases with tA, opposite to the field-effect mobility evolution. As shown in Fig. 6b, field-effect mobilities in the linear and saturation regions (lin and sat) decrease monotonically with tA. Thus, long-time annealing improves film hole mobility but is undesirable for improving device field-effect mobility. The SiO2 dielectric/channel interface deteriorates during long-time annealing, leading to enhanced interface scattering. Consequently, carrier transport in the channel is greatly suppressed and the field-effect hole mobility decreases.

The TFT deposited at PO = 11.8% and annealed at 200°C for 2 h shows relatively optimal performance: Ion/Ioff of 1550, lin of 1.36 cm^2/Vs, sat of 0.67 cm^2/Vs in p-channel operation, Ion/Ioff of 3 in n-channel operation, and Von of 57 V. The output curves are shown in Fig. 6d. In the negative VDS region (left panel), the absolute IDS increases as positive VGS decreases and negative VGS increases, showing typical accumulation p-channel behavior. In the positive VDS region (right panel), IDS at small VDS increases with positive VGS, and a superlinear (diode-like) current signature appears at higher VDS due to hole injection, showing inversion n-channel behavior.

Conclusions

SnOx films were produced by reactive rf magnetron sputtering under various oxygen partial pressures (PO) followed by 200°C air annealing. The structural and electrical evolution of SnOx films occurs in four stages: metallic Sn-dominated films with n-type conduction at PO   9.1%, polycrystalline SnO-dominated films with p-type conduction when 9.1% < PO < 17.8%, SnO-SnO2 composite films with high resistivity when 17.8%   PO < 25%, and amorphous SnO2-dominated films with n-type characteristics at PO   25%.

TFTs with SnO-dominated channels were investigated. The optimal channel thickness and annealing temperature were found to be approximately 24 nm and 200°C, respectively. As PO increases, the TFTs undergo an interesting conversion from p-channel to plausible ambipolar operation mode, primarily determined by hole concentration. As annealing time increases from 0.5 h to 4 h, the threshold voltage shifts to more negative values due to decreasing hole concentration, and field-effect mobility slightly decreases, likely due to enhanced interface scattering at the dielectric/channel interface.

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