Sol-gel Processed Yttrium-doped SnO₂ Thin Film Transistors

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Abstract: Y-doped SnO₂ thin film transistors were successfully fabricated by means of sol-gel process. The effect of Y concentration on the structural, chemical, and electrical properties of sol-gel-processed SnO₂ films was investigated via GIIXRD, SPM, and XPS; the corresponding electrical transport properties of the film were also evaluated. The dopant, Y, can successfully control the free carrier concentration by suppressing the formation of oxygen vacancy inside SnO₂ semiconductors due to its lower electronegativity and SEP. With an increase of Ywt%, it was observed that the crystallinity and oxygen vacancy concentration decreased, and the operation mode of SnO₂ thin film transistor changed from accumulation (normally on) to enhancement mode (normally off) with a positive Vth shift.

Keywords: Sol-gel; SnO₂; thin film transistor; Yttrium doping

1. Introduction

Metal-oxide semiconductors have received considerable attention as promising active channel materials for transistors for transparent displays and flexible and wearable optical and electronic devices due to their high mobility, high transparency, low cost, robust, CMOS process compatible stability, and good uniformity. Generally, n-type metal-oxide semiconductors, showing high mobility, have been used in these applications [1–4] (i.e., ZnO, In₂O₃, and SnO₂). Among these, SnO₂ has the highest mobility and the transparency due to its high intrinsic mobility and large bandgap [5]. In addition, SnO₂ is inexpensive and shows good chemical and thermal stability at high temperatures [6]. It has been shown to be a candidate for application in gas sensors due to its high surface to volume ratio [7]. The melting point of this material makes crystallization easier than with other semiconductors. This relatively easy crystallization results in improved conductivity and mobility by suppressing grain boundary scattering [8]. In addition, SnO₂ is a paradigmatic indium-free semiconductor. Indium, a costly, rare metal, is found in only a few mining sites worldwide [9]. However, the electronic configuration of Sn (1s²2s²p⁶3s²p⁴d¹⁰5s²p⁶) is similar to that of In (1s²2s²p⁶3s²p⁴d¹⁰4s²p⁴d¹⁰5s²p⁶), and SnO₂ semiconductor films are characterized by promising electrical properties [10–14]. Sol-gel processing represents a promising low-cost fabrication method by which to obtain high-quality SnO₂ films without using a conventional vacuum-based deposition process, requiring a complex and high cost vacuum system [15–20]. Unfortunately, oxygen vacancy inside metal oxide semiconductor leads to problems of stability and of the controllability of Vth.
Therefore, controlling oxygen vacancy is critical to control the device performance. It is well known that the electronegativity and standard electrode potential (SEP) of the dopant can influence its carrier suppressed ability [21,22]. In this work, we choose yttrium as a dopant to suppress the carriers in the SnO$_2$ semiconductor system, due to its lower electronegativity, SEP, and price. Y-doped SnO$_2$ thin film transistors (TFTs) are therefore fabricated for the first-time. We use grazing incidence X-ray diffraction (GIXRD), scanning probe microscopy (SPM), and X-ray photoelectron spectroscopy (XPS) to investigate sol-gel-processed SnO$_2$ films obtained with different Ywt%. To understand the effect of Ywt% on the electrical properties of the SnO$_2$ films, we fabricate bottom gate TFTs on SiO$_2$/Si substrates and evaluate the electrical properties at different Ywt% concentrations.

2. Materials and Methods

A simple inverted coplanar structure was adopted for SnO$_2$ TFT fabrication. Heavily doped p-type Si and dry oxygen, thermally-grown, 100-nm-thick SiO$_2$ layers were used as the bottom gate and insulator. The Au source/drain electrodes were formed by means of an e-beam evaporation and lift-off process. The designed channel width and length were 1000 μm and 100 μm, respectively. A SnCl$_2$ sol-gel precursor (Sigma Aldrich) was prepared for the SnO$_2$ films. A SnCl$_2$ solution (concentration: 0.025M) was prepared by dissolving tin (II) chloride dehydrate (SnCl$_2$·2H$_2$O, 0.25 mmol) in ethanol (10 mL). Then, 0.2, 0.5, and 1.0wt% Y(NO$_3$)$_2$·4H$_2$O was dissolved in the prepared SnCl$_2$ solution. An UV/ozone process was conducted for 60 min to remove organic dust on the substrates. The prepared precursor solution was spin-coated at 3000 rpm for 50 s. After coating, the films were pre-annealed in air at 150 °C for 10 min to evaporate the solvent. To convert into SnO$_2$, the films were annealed in a tube furnace at 500 °C for 2 h in air. The structural characteristics of films were investigated by a grazing incidence X-ray diffraction (GIXRD) (Philips X’pert Pro) with Cu Kα radiation (λ = 1.54 Å), where samples were irradiated at an angle of 0.3°. The surface morphology was examined using a scanning probe microscope (SPM: Park NX20, tapping mode). The chemical compositions of the films were investigated by X-ray photoelectron spectroscopy (XPS) (Quantera SXM), with a monochromatic Al Kα (1488 eV) source and a pass energy of 40 eV. The electrical properties of the TFTs were examined using a Keithley 2636B semiconductor parameter analyzer and a probe station in air.

3. Results and Discussion

Figure 1 shows the effect of Y$^{3+}$ concentrations on the phase evolution of Y-doped SnO$_2$ films annealed at 500°C for 2 h. All the annealed Y-doped SnO$_2$ films are poly-crystalline in nature. The GIXRD patterns revealed that all peaks were well matched with the standard tetragonal SnO$_2$ pattern (JCPDS: 41-1445). The broad diffuse peaks meant that the formed films were in the nanostructured phase. Diffraction peaks at 26.6°, 33.8°, 37.9°, and 51.7° corresponded to the (110), (101), (200), and (211) crystal planes of tetragonal SnO$_2$, respectively. The full width at half-maximum (FWHM) of the obtained GIXRD peak was strongly correlated with the crystallite size of a particular crystal orientation. The FWHM of the SnO$_2$ (110) peak was smaller than those of the other peaks, indicating that SnO$_2$ crystallites grew initially in the (110) plane.
Figure 1. (a) GIXRD patterns and (b) the GIXRD patterns near the (110) lattice plane with different Ywt%.

The average crystalline size of the annealed films was obtained using Scherrer’s formula (Eq. (1)),

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

where D, \( \lambda \), \( \beta \), and \( \theta \) denote the crystalline size, Cu K\( \alpha \) wavelength (1.54 Å), full width at half-maximum of the peak, and position of the peak, respectively. The obtained \( \beta \) values were 1.33, 1.26, 1.28, and 1.3, yielding D values of 6.13, 6.47, 6.37, and 6.27 nm for the (110) phase of formed pure SnO\(_2\) and Y-doped SnO\(_2\) semiconductor films. The microstrain and dislocation density were calculated using the relationship \( \varepsilon = \beta \cos \theta \), and \( \delta = 1/D^2 \), respectively. The calculated values are listed in Table 1. Compared to pure SnO\(_2\) semiconductor films, there was a relative Bragg peak shift towards a smaller angle for Y-doped SnO\(_2\) semiconductor films. This Bragg peak position shift towards lower values in the Y-doped SnO\(_2\) semiconductor films resulted from an increase in lattice parameter values, originating from the internal stress generated by the substitution of host Sn\(^{4+}\) (0.74 Å) ions by dopant Y\(^{3+}\) (1.04 Å) ions. In Y-doped SnO\(_2\) films, the peaks, corresponding to Y\(_2\)O\(_3\), could not obtained. Y\(^{3+}\) ions cannot be segregated to form Y\(_2\)O\(_3\), or the amount is too little to be detected (i.e. <1wt%)

Table 1. Crystalline size, microstrain, and dislocation density of Y-doped SnO\(_2\) semiconductor films with different Ywt%.

| Wt% of Yttrium | Crystalline Size (nm) | Microstrain | Dislocation density (10\(^{-2}\) nm\(^{-2}\)) |
|----------------|----------------------|-------------|------------------------------------------|
| 0.0            | 6.13                 | 0.0225      | 2.24                                     |
| 0.2            | 6.47                 | 0.0185      | 2.01                                     |
| 0.5            | 6.37                 | 0.0174      | 2.08                                     |
| 1.0            | 6.27                 | 0.0171      | 2.14                                     |

The SPM images of the SnO\(_2\) semiconductor films with 0, 0.2, 0.5, and 1.0wt% Y on SiO\(_2\)/Si wafer annealed at 500°C for 2 h are shown in Figure 2. The root mean square (RMS) values of the films obtained from SPM images are 0.97, 1.40, 2.45, and 2.74 nm for SnO\(_2\) semiconductor films with 0, 0.2, 0.5, and 1.0wt% Y, respectively. The RMS values are increased with increased Ywt%. The surface roughness plays a critical factor to effect on device performance and the active channel layer with minimal surface roughness results in the better thin film transistor performance.
The chemical composition of pure SnO₂ and Y-doped SnO₂ semiconductor films was investigated using XPS analysis. The Y-doped films showed XPS spectra, corresponding to Y located at 157.64 and 159.56 eV, and the spectra could be distinguished with two Gaussian Peaks of Y 3d_{5/2} and Y 3d_{3/2}, indicating the formation of Y-O bonding in Figure 3a. The intensity of these spectra increased with increasing Y wt%. Figure 3b shows the XPS spectra of Sn 3d_{5/2} and Sn 3d_{3/2}. Comparing to the binding energy of pure SnO₂ films, the binding energy of the 0.5 wt% and 1.0 wt% Y-doped SnO₂ films were shifted toward higher binding energy values. The binding energy shift towards high values could be associated with a phase transformation from SnO to SnO₂ [23].

Figure 4 shows the O 1s XPS spectra of Y-doped SnO₂ films as a function of Y wt%. The O 1s peak convoluted into two different Gaussian subpeaks, occurring at 529.9 and 531.8 eV. The dominant peak located at 529.9 eV was related to O²⁻ ions binding with neighbor metal ions in the lattice (O₁), and the peak located at 531.8 eV was related to O²⁻ ions in oxygen vacancy regions (Oᵥ). The relative oxygen vacancy quantity was estimated with the area ratio of the convoluted subpeaks. With an increase in the wt% of Y, lower oxygen vacancy density was obtained. The Oᵥ/(O₁+Oᵥ) ratios were 0.46 for pure SnO₂, 0.45 for 0.2 wt% Y-doped SnO₂, 0.40 for 0.5 wt% Y-doped SnO₂, and 0.3 for 1.0 wt% Y-doped SnO₂, respectively. Obviously, the Oᵥ/(O₁+Oᵥ) area ratio gradually decreased with the increase of Y wt%, indicating that the Oᵥ concentration was decreased by Y doping. Y³⁺ ions can act as carrier suppressors in SnO₂ thin film systems, due to their lower electronegativity (1.22) and lower
standard electrode potential (SEP) (~2.38 V). The increased bond strength of dopant-oxygen bond lead to decrease the oxygen vacancy, related to the carrier concentration in the metal oxide semiconductor system. For these reasons, Y is a stronger oxidizer than Sn. During the film formation step, fewer oxygen vacancies were formed in Y-doped SnO₂ films compared to pure SnO₂ films. Huh et al. found that Sn²⁺ binding in SnO₂ leads to the formation of oxygen vacancy defects. Therefore, the reduction in the proportions of the SnO and O₂⁻ peaks with Y content indicated a decrease in electron free carrier density and oxygen vacancy.

Figure 4. Deconvoluted O1s XPS spectra for Y-doped SnO₂ thin films with (a) 0.0, (b) 0.2, (c) 0.5, and (d) 1.0wt% Y annealed at 500°C for 2 h.

Figure 5 shows the variation of the electrical properties of the fabricated Y-doped SnO₂ thin film transistors using different Ywt% at gate voltages of −30 V to 30 V. Figure 5e shows the representative transfer curves (Iₒ–Vₒ) of SnO₂ thin film transistors with different Ywt%. All the fabricated Y-doped SnO₂ thin film transistors showed conventional n-type semiconductor characteristics. The field effect mobility in the saturation regime was calculated from the drain current equation, which is given as follows:

\[ I_D = \frac{\mu C_i W}{2L} (V_G - V_{th})^2 \]  

where \( C_i \) is the capacitance of gate insulator, \( W \) is the channel width, \( L \) is the channel length, and \( V_{th} \) is the threshold voltage. The extracted field effect mobilities in the saturation regime of the pristine, 0.2, 0.5, and 1.0wt% Y-doped SnO₂ thin film transistors were 12, 7.4, 1, and 0.7 cm²/Vs, respectively. When Ywt% increased, the on current and field effect mobility in the saturation regimes were decreased. The crystalline size of the semiconductor active channel layer strongly affects the on-current and field-effect mobility of thin film transistors. Larger crystalline size is helpful to improve device performance via the suppression of boundary scattering. However, based on GIXRD data,
with increased Ywt%, the crystalline size of SnO$_2$ semiconductor films was deceased. Decreased crystalline and strong grain boundary scattering also leads to degraded device performances [24]. It is well known that the main transport mechanism of metal oxide semiconductor systems is percolation conduction mechanism, which is improved by filling the trap state at high carrier concentrations [25]. The degraded field-effect mobility and on-current originated from a significant decrease in the free carrier concentration, originating from the oxygen vacancy in metal oxide semiconductors. In addition, the Y$^{3+}$-Sn$^{4+}$ substitution reaction might generate an extra hole carrier, leading to a decrease in free carrier concentration by compensating for electron carrier concentration [26]. In addition, the threshold voltage exhibited a positive shift, in particular, from 0.5wt% Y. The fabricated devices showed enhancement mode operation. The reduced carrier concentration in the n-type semiconductor based thin film transistors induced higher $V_{th}$. The channel with a lower carrier concentration could be depleted easily and required more gate bias to turn on devices. In this study, these positive shifts in $V_{th}$ originated from the reduced electron density in the SnO$_2$ semiconductor active layer with an Ywt% increase.
Figure 5. Representative electrical characteristics of the fabricated Y-doped SnO$_2$ thin film transistors: (a), (b), (c), and (d) $I_D$-$V_D$ curves with 0.0, 0.2, 0.5, 1.0wt% Y, respectively. (e) $I_D$-$V_G$ curves at high $V_D$ (+30.0 V). (f) Y concentration dependence on the field effect mobility in saturation regime and $V_{th}$.

4. Conclusions

In this study, Y-doped SnO$_2$ thin film transistors were successfully fabricated by means of sol-gel process. The effect of Y concentration on the structural, chemical, and electrical properties of sol-gel processed SnO$_2$ films was investigated using GIXRD, SPM, and XPS. The corresponding electrical transport properties of the film were also evaluated. The dopant, Y, can successfully control the free carrier concentration by suppressing the formation of oxygen vacancy inside SnO$_2$ semiconductors due to its lower electronegativity and SEP. With an increase of Ywt%, it was observed that the crystallinity and oxygen vacancy concentration decreased, and the operation mode of the SnO$_2$ thin film transistor occurred from accumulation (normally on) to enhancement mode (normally off) with a positive $V_{th}$ shift.
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