

Full Length Article

Photocurrent generation in SnO₂ thin film by surface charged chemisorption O ions

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ABSTRACT

We report a photocurrent generation mechanism in the SnO₂ thin film surface layer by the charged chemisorption O ions on the SnO₂ thin film surface induced by O₂-annealing. A critical built-in electric field in the SnO₂ surface layer resulted from the charged O ions on SnO₂ surface prolongs the lifetime and reduces the recombination probability of the photo-excited electron-hole pairs by UV-laser irradiation (266 nm) in the SnO₂ surface layer, which is the key for the photocurrent generation in the SnO₂ thin film surface layer. The critical lifetime of prolonged photo-excited electron-hole pair is calculated to be 8.3 ms.

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1. Introduction

SnO₂-based transparent conducting oxides (TCOs) have been widely applied in many opto-electrics devices, such as, light emitting diodes [1–3], flat panel displays [4], solar cells [5,6], lithium ion batteries [7], and gas sensors [8–10]. Also, owing to the SnO₂ material's wide band-gap (~3.6 eV) property, SnO₂ thin-film has been used to fabricate UV-photodetector [11,12].

It has been reported that the oxidation gas (O₂, NO₂) can chemically adsorb on the SnO₂ thin film, which attracts the free electrons from the SnO₂ thin film and causes the charged surface on the SnO₂ thin film [13–15]. So, it would be interesting to see how does the charged surface by the chemisorption of the oxidation gas (O₂, NO₂) affect the photoelectric effect of the SnO₂ UV-photodetector. In this work, we found that the chemisorption of the oxidation gas (O₂, NO₂) results in a space charge region in the surface of the SnO₂ thin film. The space charge region reduces the recombination possibility of photon-excited electron-hole pairs and, then, it enhances the lifetime of photon-excited electron-hole pairs. The previous reports show that the recombination life time (2.27 ns) [16–18] of photo-carrier of SnO₂ is much lower than the recombination life time (10–100 μs) [19] of Si, which is the most common material for the commercial photodetectors. Hence, the sensitivity of SnO₂ UV-photodetector can be enhanced with the chemisorption of oxidation gas (O₂, NO₂) on the surface of the SnO₂ UV-photodetector.

2. Experimental

The 99.99% SnO₂ target was used to deposit un-doped SnO₂ thin films on the glass substrates by RF sputtering system. Before sputtering, the SnO₂ targets were pre-sputtered for 10 min with the shutter on to clean the target surface. The basal pressure was controlled below 2×10^{-5} torr. In the sputtering process, the background pressure is 2×10^{-3} torr with a mixture ratio of Ar:O₂ gas (3% O₂). The deposition holder rotated with a speed of 60 rpm during the sputtering process to ensure an uniform film quality and thickness. The substrate temperature during sputtering process was controlled at 50 °C. The thickness of SnO₂ thin film is about 50 nm, which is very difficult to be measured by SEM cross-section method. In this study, we used the ellipsometry measurement to determine the thickness of SnO₂ thin film. The ultimate thickness of the SnO₂ thin films is controlled at 50 nm. The power of RF sputtering gun is 100 W with a deposition rate of 0.6 Å/s for the SnO₂ thin film. After the deposition, the as-deposited SnO₂ thin-films were annealed in the N₂ and O₂ ambient for 10 min at 200 °C. The photo-current of SnO₂ thin films were measured by a semiconductor parameter analyzer (Keithley 2400 Power Source System) with a bias voltage of 10 V. The device structure is sketched in the insert of Fig. 1.

3. Results and discussions

Fig. 1 shows the photocurrent of the 50-nm SnO₂ thin films annealed in the N₂ and O₂ ambient. The photocurrent excitation source is the UV-laser irradiation (266 nm, 4.66 eV). As the

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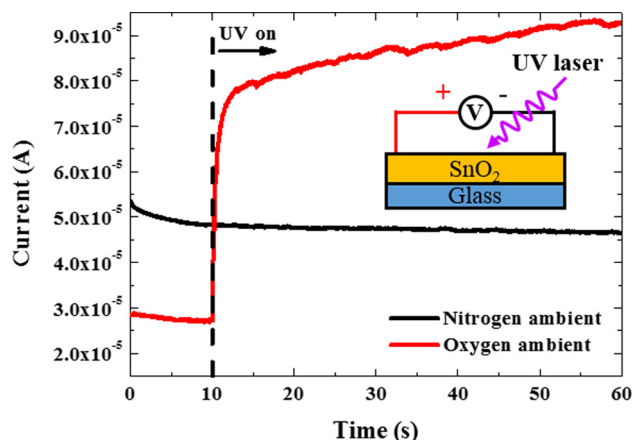


Fig. 1. Photocurrent of 50 nm SnO_2 thin films (annealed in N_2 and O_2 ambient) with UV-laser irradiation.

UV-laser irradiation is turned on (at the 10-s measurement time), the photocurrent of the SnO_2 thin film annealed in the O_2 ambient is measured to be about 9.25×10^{-5} A. However, we found that no photocurrent (no increase in the measured current with UV-laser irradiation) of the SnO_2 thin film annealed in the N_2 ambient can be detected.

Figs. 2 and 3 show the N_{1s} , O_{1s} , and Sn_{3d} core-level peaks for the SnO_2 thin films annealed in the O_2 and N_2 ambient at 200°C , respectively. The blue curve represents the XPS results on the very surface on the SnO_2 thin films. The red curve is the XPS results at the position about 10 nm (with 100 s ion-etching) inside the SnO_2 thin films. We first discuss the XPS results (the N_{1s} , O_{1s} , and Sn_{3d} core-level peaks) on the very surface on the SnO_2 thin films (blue curve). As seen in Figs. 2 and 3, the binding energy of the Sn_{3d} core-level peaks locates at 487.88 eV for the SnO_2 thin films annealed in both O_2 and N_2 annealing ambient. It means that the chemical state of the Sn ions on the surface of the annealed SnO_2 thin films does not change with the annealing ambient. For the position of the O_{1s} core-level peaks of the SnO_2 thin films, it would be affected with the annealing ambient. As seen in Figs. 2 and 3, the O_{1s} core-level peak of the SnO_2 thin films annealed in the O_2 ambient has a higher binding energy (532.48 eV) than that of the SnO_2 thin films annealed in the N_2 ambient (531.58 eV). It has been reported that the O_{1s} core-level peak of the surface O adsorption on the SnO_2 surface locates in the range of 532.40 ± 0.15 eV [20]. Thus, the observed O_{1s} core-level peaks (532.48 eV) of the SnO_2 thin films annealed in the O_2 ambient indicates that O was adsorbed on the SnO_2 surface in the annealing process in the O_2 ambient. We can conclude that O_2 molecules tend to be adsorbed on the SnO_2 thin films surface in the O_2 annealing process.

In the following, we discuss the XPS results (the N_{1s} , O_{1s} , and Sn_{3d} core-level peaks) at the position about 10 nm (with 100 s ion-etching) inside the SnO_2 thin films. Comparing the N_{1s} , O_{1s} , and Sn_{3d} core-level peaks in Figs. 2 and 3, we can find that each peak of the ion-etched SnO_2 thin films (red curves) are located at the same binding energy. It indicates that the annealing ambient (either O_2 or N_2 ambient) does not affect the chemical states of atoms (N, O, and Sn) at the inner annealed SnO_2 thin films. The present XPS results conclude that O_2 molecules would adsorb on the surface of the SnO_2 thin films being annealed in the O_2 ambient, but not in the N_2 ambient. Thus, we believe that the surface O adsorption attributes to the observed photocurrent of the SnO_2 thin films annealed in the O_2 ambient.

A mechanism explaining the photocurrent resulted from the surface O adsorption is proposed below. The surface O adsorption process has been discussed previously [21]. Firstly, the O_2 mole-

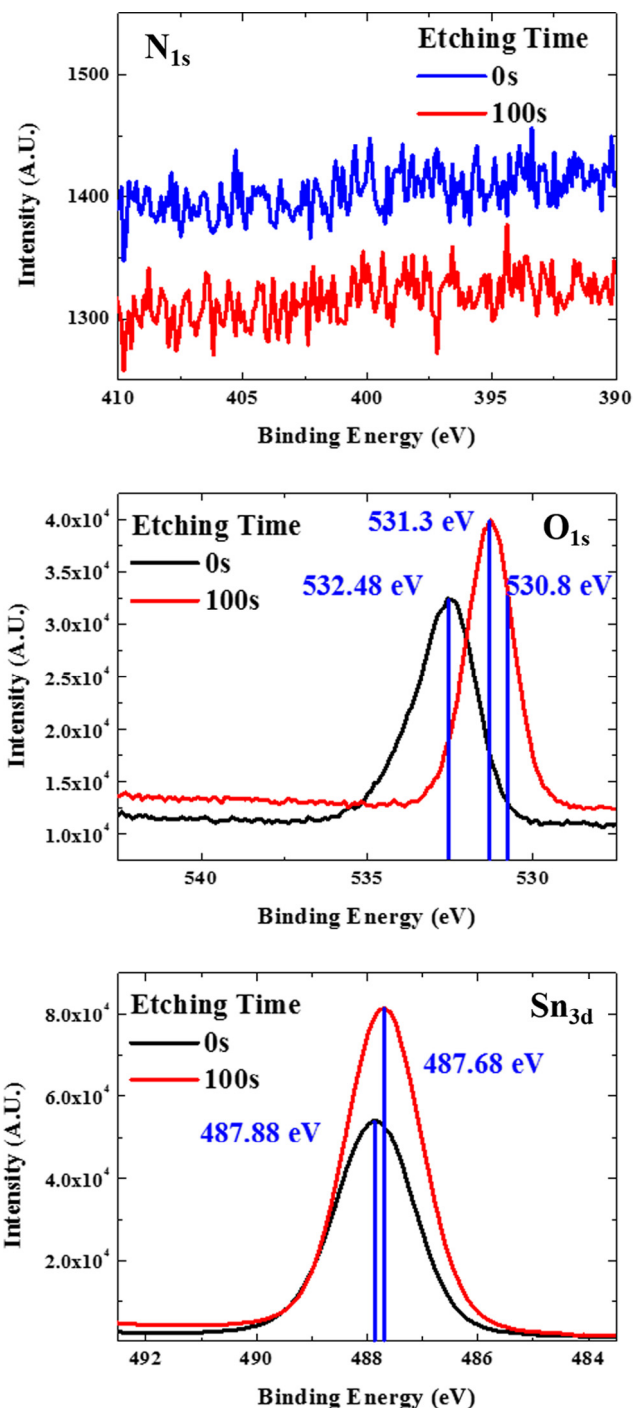


Fig. 2. N_{1s} , O_{1s} , and Sn_{3d} core-level peaks of the 50 nm SnO_2 thin films annealed at 200°C in the O_2 ambient.

cules would be physically adsorbed on the SnO_2 surface. Then, the adsorbed O molecules on the surface would attract free electrons and form ionized O species, i.e., O_{ad}^- and $\text{O}_{\text{ad}}^{2-}$ ions, which is known as the ionic adsorption [21,22]. However, it reported that the $\text{O}_{\text{ad}}^{2-}$ ions is unstable state [23]. Thus, the oxygen absorption mostly would be O_{ad}^- ions. It has been reported that the O_{1s} core-level peak of the surface O adsorption on the SnO_2 surface locates in the range of 532.40 ± 0.15 eV [20]. Furthermore, it knows that the O_{1s} core-level peak of O_{ad}^- ions have higher binding energy than the O_{1s} core-level peak of $\text{O}_{\text{ad}}^{2-}$ ions. Thus, the observed O_{1s} core-

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