Deposition of Fe doped nanocrystalline SnO\textsubscript{2} thin films by the photochemical deposition method

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Fe-doped SnO\textsubscript{2} thin films were deposited by the photochemical method. The SnO\textsubscript{2}-deposition solution is an aqueous solution containing 10 mmol/L of SnSO\textsubscript{4}. A small amount of the solutions was repeatedly dropped on the glass substrate and irradiated by the UV light. For the Fe doping, FeSO\textsubscript{4} was mixed in the SnO\textsubscript{2} deposition solution, or another solution for the Fe doping was prepared separately and alternately dropped and irradiated. The Auger electron spectroscopy measurement revealed that Fe was contained in the deposited thin films. The dependence of electrical properties of the films on annealing temperature was studied. The Fe-doped SnO\textsubscript{2} thin films showed enhanced electrical conductivity after 300 and 400°C annealing in a nitrogen atmosphere.

Keywords: SnO\textsubscript{2}, photochemical deposition (PCD), doping, resistivity.

1. INTRODUCTION

Tin dioxide SnO\textsubscript{2} is a wide band gap (3.6–3.8 eV) semiconductor and shows n-type conductivity without intentional doping. It is a technologically important material due to its various applications such as gas sensors, chemical sensors, and transparent conducting thin films. For most of those application, doping of impurities is needed to modify its conductivity, optical absorption and gas sensitivity. In most cases, electrical conductivity has been controlled by doping antimony or fluorine.\textsuperscript{1-5} Recently, Fe-doped SnO\textsubscript{2} has attracted a lot of interest because Fe doping can modify conductivity, gas sensitivity, and band gap. In the past, Fe-doped SnO\textsubscript{2} thin films have been obtained by sol-gel\textsuperscript{6,7} and spray pyrolysis.\textsuperscript{8,9} So far, there is no report on Fe-doped SnO\textsubscript{2} thin films by the photochemical deposition (PCD) technique. In our previous works, we deposited undoped and Pd-doped nanocrystalline SnO\textsubscript{2} thin films by the photochemical technique and applied them to hydrogen sensors.\textsuperscript{10-12} In PCD, an aqueous solution containing Sn\textsuperscript{2+} ions is irritated by UV light, and SnO\textsubscript{2} is formed owing to photochemical reactions in the solution. The deposition process is easy and simple, and the apparatus is of very low cost. In the deposition, SnO\textsubscript{2} particles are formed in the solution and deposited on a substrate. Therefore, the films constitute of small particles, and the resulting high surface-to-bulk ratio is expected to enhance the number of sites for the gas reaction and thus enhance the sensitivity. We also deposited SnO\textsubscript{2} doped with Sb and Cu by the PCD technique.\textsuperscript{13} We obtained lower resistivity for the Cu-doped film than for the undoped and Sb-doped films. In this work, Iron Fe is selected as the impurity to incorporate into SnO\textsubscript{2}. Electrical and optical properties of Fe-doped SnO\textsubscript{2} are investigated and compared with the previous reports.

2. EXPERIMENTAL DETAIL

Doped and undoped SnO\textsubscript{2} thin films were fabricated by the drop-photochemical deposition (drop-PCD) method.\textsuperscript{10,11} The SnO\textsubscript{2}-deposition solution is an aqueous solution containing 10 mmol/L of SnSO\textsubscript{4} with the pH adjusted to 2.0 with HNO\textsubscript{3}. For deposition of undoped SnO\textsubscript{2} films, a small amount of the SnSO\textsubscript{4} solution was dropped on the glass substrate and irradiated by the UV light, as shown in Fig. 1. The light source was an ultrahigh-pressure mercury arc lamp of 500 W, and the substrate area of about 1 cm\textsuperscript{2} was irritated through a spherical lens. One irradiation time was 5 min, and the substrate was washed with water and dried before the new solution was dropped on it. We obtained a SnO\textsubscript{2} film with a thickness of about 0.15 µm by repeating the above process 10 times.

The Fe doping was attempted by two kinds of methods. In the first one, 2 mmol/L FeSO\textsubscript{4} was mixed in the above-mentioned SnO\textsubscript{2}-deposition solution containing 10 mmol/L of SnSO\textsubscript{4} and the films were deposited by the same drop-irradiation cycles. In the second one, a solution for the SnO\textsubscript{2} deposition and another solution for the doping were prepared separately. A small amount of each of these solutions was alternately dropped on the glass substrate, and irradiated by the UV light. In this process, a thin SnO\textsubscript{2} film is
deposited in the first drop-irradiation cycle, and then in the next cycle, impurity atoms will replace some of the Sn atoms in the deposited films. The doping solution containing 20 or 200 mmol/L \( \text{FeSO}_4 \) with 20 mmol/L \( \text{Na}_2\text{SO}_3 \). It was reported that the formation of metal oxide is promoted by using the \( \text{SO}_3^{2-} \) ions as a reducing agent.\(^{14}\) Thus, if the \( \text{SO}_3^{2-} \) ions act as a reducing agent in the PCD process, incorporation of Fe atoms into the film could also be promoted. We repeated the drop-irradiation cycles 20 times (10 times for the \( \text{SnO}_2 \) deposition and 10 times for the doping, alternately) and obtained doped \( \text{SnO}_2 \) thin films with a thickness of around 0.15 \( \mu \)m. We confirmed that no film was deposited when only the doping solution was dropped and irradiated. The \( \text{SnO}_2 \) thin films were annealed in nitrogen ambient at 200°C, 300°C and 400°C.

The Auger electron spectroscopy (AES) analysis and scanning electron microscopy (SEM) observation were carried out using the model JEOL JAMP-9500F at probe voltage 10 kV. An argon-ion sputtering with acceleration voltage 2 kV and current 2.6 \( \mu \)A was used to sputter the film surface. The optical transmission measurement was performed using the JASCO U-570 spectrometer with the glass substrate as the reference. In addition, indium electrodes (electrode size 1x1 mm\(^2\)) were thermally evaporated and the current-voltage characteristics were measured for the as-deposited as well as the annealed films. The conduction type was judged by the hot-probe method.

3. RESULTS AND DISCUSSION

In the AES measurement, the peak of Fe was not observed when the \( \text{FeSO}_4 \)-mixed solution was used. Thus the Fe content is less than the detection limit of AES (a few percents). On the other hand, the Fe signal was observed for the films deposited using the separate doping solution. Figure 2 shows the AES spectra of the as-deposited \( \text{SnO}_2 \) thin films doped with Fe after 10 s Ar-ion sputtering. From those spectra, contents of impurity elements were evaluated using standard Auger efficiencies for elements. The Fe/Sn atomic ratios were about 0.07 and 0.11 with the doping solution containing 20 or 200 mmol/L \( \text{FeSO}_4 \) respectively. It should be noted that although Na ions are contained in the deposition solution, no Na signal was detected in the AES spectra. This will be because Na has a high ionization tendency and thus remains in the solution as an ion.

Figure 3 shows the optical transmission of the undoped \( \text{SnO}_2 \) film and the Fe-doped film deposited by the separate solution containing 20 mmol/L. The result shows that both the Fe-doped and undoped \( \text{SnO}_2 \) thin films have fairly high transmission in the visible region of the spectrum. The optical transmissions result is the almost same for the Fe-doped \( \text{SnO}_2 \) films deposited using the \( \text{FeSO}_4 \)-mixed solution and the separate doping solution containing 200 mmol/L \( \text{FeSO}_4 \).

The optical band gap energy was calculated from the classical relation for direct-band optical adsorption.

\[
\alpha = k(\hbar \nu - E_g)^{1/2}/\nu \tag{1}
\]

where \( \alpha \) is the absorption coefficient, \( k \) a constant, \( E_g \) the band gap and \( \hbar \nu \) the photon energy. Figure 4 shows the variation of \( (\hbar \nu)^2 \) versus \( \hbar \nu \), which is linear in the higher energy domain, indicating a direct optical transition. The band gap energy \( E_g \) was obtained by extrapolating the linear portion of the graph to the energy axis at \( \alpha = 0 \). The obtained band gap values are around 3.8-3.9 eV for both the undoped and Fe-doped \( \text{SnO}_2 \) thin films.

Figure 5 shows the plots of resistivity for the undoped and Fe-doped samples annealed at different temperatures.

![Fig. 2 AES spectra of the Fe-doped \( \text{SnO}_2 \) films deposited using the separate doping solution containing (a) 20 mmol/L \( \text{FeSO}_4 \), and (b) 200 mmol/L \( \text{FeSO}_4 \). The inset shows the expanded AES spectra near the position of Fe.](image1)

![Fig. 3 Optical transmission of the undoped and Fe-doped as-deposited films. The Fe doped film was deposited using the separate doping solution containing 20 mmol/L \( \text{FeSO}_4 \).](image2)

![Fig. 4 Plot of \((\hbar \nu)^2\) against \( \nu \) of the undoped and Fe-doped \( \text{SnO}_2 \) as-deposited films. The Fe doped film was deposited using the separate doping solution containing 20 mmol/L \( \text{FeSO}_4 \).](image3)
(the data for the as-deposited film were plotted at 27 °C). The resistivity higher than 10^{-6} \Omega cm cannot be measured by our measurement system. Therefore, the electrical resistivity could be higher than 10^6 \Omega cm for the as-deposited films and the films annealed at 200 and 300 °C of undoped SnO_2. The resistivity was decreased by the 400 °C annealing. The conduction type judged by the hot probe method was n-type for all the samples annealed at 400 °C. As is well known, oxygen deficiency is the main reason for the conductivity of undoped SnO_2. Therefore, for the undoped film, the nitrogen annealing is thought to increase oxygen vacancies, which act as donors in SnO_2, resulting in decrease in resistivity. For the film deposited using the FeSO_4-mixed solution, the resistivity was found to become significantly lower than that of the undoped film after annealing at 300 and 400 °C, as shown in Fig. 5. A similar resistivity result was obtained for the film deposited by the separate doping solution containing 20 mmol/L FeSO_4. However, the resistivity of the film deposited by the separate doping solution containing 200 mmol/L FeSO_4 is higher than that of the undoped film.

The morphology of the undoped and Fe-doped SnO_2 thin films is shown in Figs. 6 (a)-(d). The SEM results reveal that all the SnO_2 films have almost the same surface morphology. Consequently, change in the morphology (grain size) is not the main reason why electrical resistivity was reduced by the Fe-doping.

Characterization results of Fe-doped SnO_2 films have been reported by a few groups. In ref.9, it was reported that electrical resistivity increases with Fe doping. They considered that Fe acts as an acceptor in SnO_2. Consequently, the compensation of electrons with holes leads to reduction of the overall carrier concentration. The Fe doping also has influence on optical band gap of the SnO_2 film. By increasing the doping level, the band gap gradually decreases, which was considered to be related to carrier density reduction (diminish of the Moss-Burstein shift). The similar results have also been reported in ref.7.

In our research, the conduction type of the Fe-doped SnO_2 thin films is n-type. Therefore, the possible explanation for the resistivity reduction is that some portion of the doped Fe atoms are at interstitial sites and act as a donor. In our previous research, we indicated that Cu in SnO_2 films can occupy an interstitial site and act as a donor. Similarly, the Fe ions at interstitial sites will act as a donor and increase electron concentration.

The increase in the resistivity of the film deposited by separate doping solution containing 200 mmol/L FeSO_4 could be due to the structural disorder caused by Fe impurity. Another possibility is that when the Fe concentration is high, some portion of Fe atoms occupy a substitutional site and act as an acceptor, leading to compensation of donors. In our results, the band gap was not significantly changed by the Fe doping, as shown in Fig. 4. This would be because of the low doping level compared with the previous works.7,9

4. CONCLUSIONS

Fe-doped SnO_2 thin films have been deposited on glass substrates using the PCD technique. SnO_2-deposition solution is an aqueous solution containing 10 mmol/L SnSO_4. For the Fe doping, FeSO_4 is mixed in the SnO_2 deposition solution, or another solution for the Fe doping is prepared separately and alternatively dropped and irradiated. The optical transmission of the film is fairly high in the visible region, and the band gap obtained is 3.8-3.9 eV. The resistivity of the 300 and 400 °C annealed films is significantly reduced by the Fe-doping using the 2 mmol/L FeSO_4-mixed solution or the separate solution containing 20 mmol/L FeSO_4. However, the resistivity of Fe-doped SnO_2 films deposited with the separate solution containing 200 mmol/L FeSO_4 is higher than that of undoped films.

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REFERENCES


![Fig. 5 Resistivity of the various SnO_2 films annealed at different temperatures.](image)

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