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High Mobility Titanium-Doped In_2O_3 Thin Films Prepared by Sputtering/Post-Annealing Technique

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High-electron-mobility Ti-doped In_2O_3 (ITiO) thin films were prepared on soda-lime glass substrates by rf magnetron sputtering followed by a post-annealing process. Both carrier concentration and electron mobility were considerably improved by annealing in a vacuum at 530 °C. A highest electron mobility of 105 $cm^2 V^{-1} s^{-1}$ with a resistivity of 1.95×10^{-4} Ω cm was obtained for an annealed ITiO thin film. The ITiO thin film exhibited an optical transmission of approximately 80% at wavelengths ranging from 400 to 1800 nm. Post-annealing in a vacuum is one of the effective methods for improving the electrical properties of ITiO thin films without sacrificing optical transmission.

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Transparent conducting oxide (TCO) thin films are key materials for optoelectronic devices such as thin film solar cells, light-emitted diodes, and flat-panel displays.[1)] For such devices, TCO thin films are required to have high electron mobility to increase optical transmission without sacrificing electrical conductivity.[2)]

Among these TCO's, tin-doped indium oxide (ITO) is widely utilized at present because of its good optical and electrical properties. However, the carrier concentration is relatively high, resulting in low optical transmission in near infrared regions due to free carrier absorption. This is attributable to the relatively low electron mobility of around 30 $cm^2 V^{-1} s^{-1}$. It has been reported over the past three years that titanium (Ti)-doped In_2O_3 (ITiO) thin films exhibited very high mobilities >80 $cm^2 V^{-1} s^{-1}$, carrier concentrations of $(2-4) \times 10^{20}$ cm^{-3}, and optical transmissions higher than 80%.[2)] The high-mobility ITiO thin films have been deposited by various techniques including hollow cathode sputtering,[3)] DC magnetron sputtering,[4)] and combinatorial deposition.[2)] More recently, Gupta *et al.* have shown extremely high-mobility (up to 199 $cm^2 V^{-1} s^{-1}$) ITiO thin films with low resistivity (9.8×10^{-5} Ω cm), and high optical transmission (~80%) by pulse laser deposition.[5)]

In the present work we have focused to achieve high-mobility ITiO thin films by rf magnetron sputtering which could be applied to large-area devices such as thin film solar cells and flat panel displays. In order to achieve further improvement in the electrical properties without sacrificing optical transmission a post-annealing of ITiO thin films was carried out.

250-nm-thick ITiO thin films were deposited on soda lime glass substrates by rf magnetron sputtering using a 4-in.-diameter ceramic target with 1 wt% TiO_2 doped In_2O_3. The Ar working pressure was maintained at 1.0, 1.2, 1.5, and 3.0 mTorr. Prior to each deposition run, the sputtering chamber was evacuated to below 1.1×10^{-7} Torr. As-deposited films were annealed in a vacuum ($<8 \times 10^{-6}$ Torr) at a substrate temperature of 530 °C for 45 min. The resistivity (ρ), carrier concentration (n), and electron mobility (μ) of ITiO thin films were determined at room temperature using Hall measurement. Optical measurement was performed using a spectrophotometer at wavelengths ranging from 300 to 1800 nm.

Figure 1 shows the carrier concentration n (circles), electron mobility μ (triangles), and resistivity ρ (squares) of as-deposited ITiO thin films as functions of substrate temperature (T_{sub}).

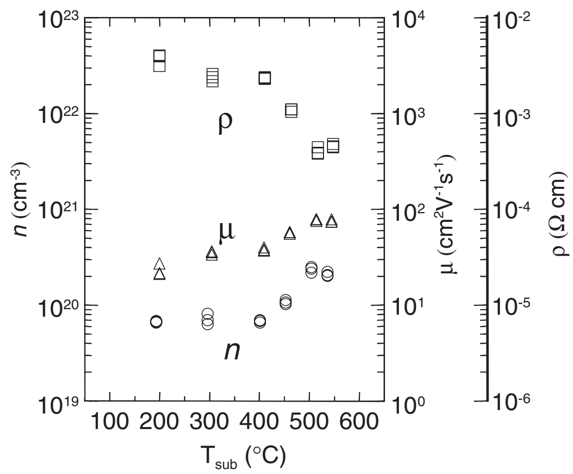

Fig. 1. Carrier concentration n (circles), electron mobility μ (triangles), and resistivity ρ (squares) of as-deposited ITiO thin films as a function of substrate temperature (T_{sub}).

The ITiO thin films deposited at substrate temperatures higher than 500 °C had electron mobilities higher than 70 $cm^2 V^{-1} s^{-1}$ and resistivities lower than 5×10^{-4} Ω cm. A maximum electron mobility of 75 $cm^2 V^{-1} s^{-1}$ and a minimum resistivity of 3.3×10^{-4} Ω cm were obtained at a substrate temperature of 500 °C.

The carrier concentration of ITiO thin film deposited at low substrate temperatures was significantly low as compared to that of ITO. The cause for the low carrier concentration is presumably because of the interstitial oxygen in ITiO matrix as mentioned later.

In our previous work,[6)] we have revealed that a post-annealing is very effective to improve the electrical and optical properties of molybdenum (Mo)-doped In_2O_3 (IMO) thin films. We thus have applied the post-annealing process to improve the electrical and optical properties of ITiO thin films.

Figure 2 shows the electrical properties of ITiO thin films deposited at 500 °C before and after post-annealing in a vacuum at 530 °C for 45 min as a function of Ar working pressure. As Ar working pressure increased from 1.0 to 1.2 mTorr, the electron mobility of ITiO thin films increased

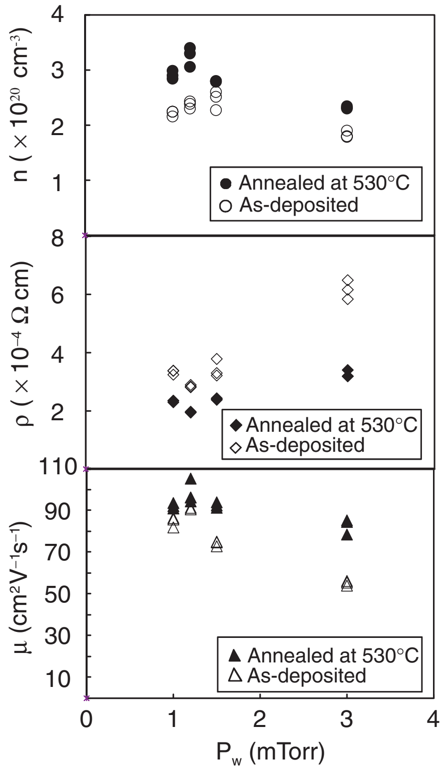

Fig. 2. Electrical properties of ITiO thin films deposited at 500 °C before and after post-annealing as a function of Ar working pressure.

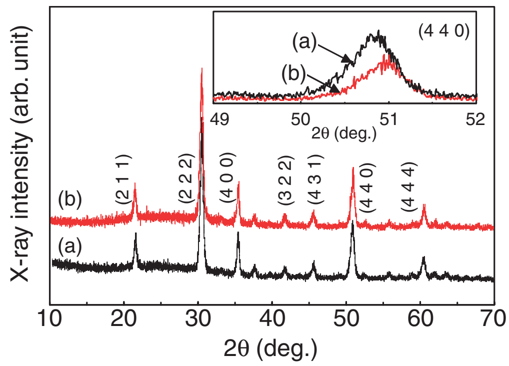

Fig. 3. X-ray diffraction patterns of (a) before and (b) after post-annealing ITiO films.

from 75 to 96 $cm^2 V^{-1} s^{-1}$. Both carrier concentration n and electron mobility μ increased and hence the resistivity decreased significantly after post-annealing. The annealed film showed a minimum resistivity of 1.9×10^{-4} Ω cm, an electron mobility of 105 $cm^2 V^{-1} s^{-1}$ and a carrier concentration of 3.1×10^{20} cm^{-3}.

In this experiment, soda lime glass (SLG) was utilized as a substrate material since ITiO on SLG is commonly used for solar cells such as $Cu(In,Ga)Se_2$ devices. Secondary ion mass spectroscopy (SIMS) analysis revealed that the small amount of sodium diffused into ITiO thin films. However, the influence of sodium on the electrical properties of ITiO thin films was not clear at present.

Recently National Renewable Energy Laboratory group[7] have proposed a compensation mechanism for IMO thin films as follows; $(2Mo_{In}{}^{3+} - 3O_i{}^{2-}) \leftrightarrow 2Mo_{In}{}^{+} + 2e + (3/2)O_2(g)$. In this model, the substitutional Mo dopants ($Mo_{In}{}^{+}$) are compensated by interstitial oxygen ions ($O_i{}^{2-}$) at quasi-anion sites, which results in the formation of electrically neutral $(2Mo_{In}{}^{3+} - 3O_i{}^{2-})$ complexes. As the oxygen pressure is lowered, the interstitial oxygen is removed and the valence state of Mo changes from $Mo_{In}{}^{3+}$ to $Mo_{In}{}^{+}$. Therefore these complexes are decomposed and consequently the carrier concentration increased with decreasing the partial oxygen pressure. We have previously demonstrated that the electron mobility of IMO thin films increased after post-annealing in a vacuum, and it could be explaned by this model.[6]

On the other hand, a similar model could be proposed for the post-annealing effect of ITiO thin films as follows; $(2Ti_{In}{}^{+} - O_i{}^{2-}) \leftrightarrow 2Ti_{In}{}^{+} + 2e + O_2(g)$. In this model, the substitutional Ti dopants ($Ti_{In}{}^{+}$) are compensated by interstitial oxygen ions ($O_i{}^{2-}$), which results in the formation of electrically neutral $(2Ti_{In}{}^{+} - O_i{}^{2-})$ complexes. If the interstitial oxygen is removed by the post annealing in a vacuum, the complexes are decomposed and carrier concentration increased. The improvement in the electron mobility by post-annealing could also be explained in terms of removal of interstitial oxygen which acts as a scattering center. Hence, the removal of the interstitial oxygen by post-annealing could lead to an increase in both electron mobility and carrier concentration.

Figure 3 shows X-ray diffraction patterns of (a) as-deposited and (b) annealed ITiO thin films. All diffraction lines were assigned to In_2O_3 (JCPDS No. 06-0416). The inset shows a magnified view of the (440) lines. The position of the diffraction peaks shifted to the higher diffraction angle after post-annealing, which indicates a decrease in the lattice constant. The lattice constant of as-deposited film was determined to be 10.143 nm, whereas it decreased after post-annealing to 10.118 nm which is the same value of pure In_2O_3 (JCPDS No. 06-0416). This result indicates a decrease in the lattice strain of the ITiO thin films. Jerman and Mergel[8] have shown that the incorporation of interstitial oxygen in ITO induced lattice strains and the removal of interstitial oxygen lead to the relaxation of the lattice strains. This implies that the decrease in the lattice strain of the ITiO thin films after post-annealing may reflect the desorption of interstitial oxygen. This model is consistent with the observed improvement in carrier concentration and electron mobility after post-annealing.

Figure 4 shows the optical transmission curves for 250-nm-thick ITiO thin films before and after post-annealing. The data on an ITO thin film with the same thickness and SLG is also shown for comparison. The transmission curves were not normalized for the glass substrate. The electrical properties of these films are shown in Table I. The optical transmission of ITiO thin films on glass substrates showed approximately 80% at wavelengths ranging from 400 to 1800 nm. It is noted that the optical transmission was higher than that of ITO thin film at long wavelength regions because of relatively low carrier concentration as compared to that of ITO. The electrical properties of ITiO thin films reported in the literature are summarized in Table II. As can be seen in this table, the electron mobility of ITiO thin film prepared in this work is the highest among ITiO thin films deposited by sputtering process.

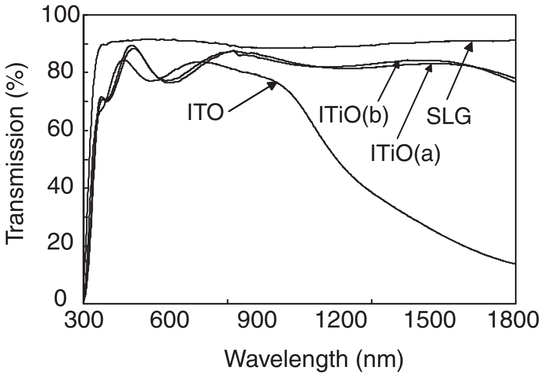

Fig. 4. The optical transmission curves of 250-nm-thick ITiO thin films (a) before and (b) after post-annealing. The data on 250-nm-thick ITO thin film and SLG are also shown for comparison.

Table I. The electrical properties of (a) before and (b) after post-annealing ITiO films. The data on an ITO thin film is also shown for comparison.

	ρ ($\times 10^{-4}\,\Omega\,$cm)	n ($\times 10^{20}\,$cm^{-3})	μ [cm^2/(V s)]	d (nm)
ITiO (a)	2.8	2.3	96	250
ITiO (b)	1.9	3.1	105	250
ITO	1.9	8.8	36	250

In summary, we have investigated the post-annealing effect on the electrical and optical properties of ITiO thin films deposited by rf magnetron sputtering. Both carrier concentration and electron mobility were markedly improved by post-annealing process. A minimum resistivity of $1.9 \times 10^{-4}\,\Omega\,$cm with a high electron mobility of 105 cm^2 V^{-1} s^{-1} was obtained for an annealed ITiO film at 530 °C for 45 min in a vacuum. The annealed ITiO thin films on a glass substrate exhibited an optical transmission of approximately 80% at wavelengths ranging from 400 to 1800 nm. It is concluded that post-annealing is one of the effective methods for achieving high-electron-mobility ITiO thin films.

Table II. Electrical properties of ITiO thin films deposited by various techniques.

Deposition technique	T_{sub} (°C)	ρ ($\times 10^{-4}\,\Omega\,$cm)	n ($\times 10^{20}\,$cm^{-3})	μ [cm^2/(V s)]	Ref.
Hollow cathode sputtering	300	1.8	4.3	80.6	3
DC sputtering	300	3	2	89.5	4
Conbinatorial deposition	550	2.6	2.89	83.3	2
Pulsed laser deposition	500	0.98	0.8	199	5
rf sputtering	530	1.95	3.06	105	This work

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