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Ion implantation and dynamic recovery of tin-doped indium oxide films

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The effect of O^+ ion implantation on the electronic (carrier density, mobility, resistivity) and microstructural properties of thin film Sn-doped $Sn-doped\ In_2O_3$ (ITO) was studied. Both polycrystalline (c-) and amorphous (a-) ITO thin films, 200 nm thick, were implanted at substrate temperatures ranging from -196 to 300°C with 80 keV O^+ at doses ranging from 0 to $4.0 \times 10^{15}\ cm^{-2}$. X-ray diffraction studies show that polycrystalline ITO remains crystalline even after implantation with 80 keV O^+ at -196 °C to a dose of $4.0 \times 10^{15}\ cm^{-2}$ which suggests that dynamic recovery processes are active in ITO at this low temperature. Although the x-ray diffraction pattern of the polycrystalline ITO remains unchanged with implant dose, the electrical properties were seen to degrade when implanted to a dose of $1.0 \times 10^{15}\ cm^{-2}$ below 200°C. In contrast, amorphous ITO films remains amorphous upon ion implantation and shows almost no degradation in resistivity when implanted below 16°C. The recrystallization temperature of amorphous ITO is about 150°C in the absence of ion implantation.

1. INTRODUCTION

Sn-doped In_2O_3 (ITO) is a highly degenerate wide-gap semiconductor with a technologically important combination of electrical and optical properties, i.e. resistivity as low as $2 \times 10^{-4}\ \Omega\ cm$ and a transmissivity in the visible spectrum of 80-90%.¹ In the partially reduced state, ITO contains $10^{21}\ cm^{-3}$ free carriers which are liberated both from ionized tetravalent substitutional Sn atoms $[Sn^+]$ and from oxygen vacancies $[Vo^+]$. Low resistivity thin film ITO has been extensively used in optoelectronic applications for flat panel displays,^{2,3} solar cells,⁴ smart windows,⁵ and electromagnetic-interference shielding windows.⁶ Current commercial applications demand even lower resistivity of $\approx 1 \times 10^{-4}\ \Omega\ cm$ and higher adhesion when the film is deposited on polymer substrates as are used for color filters.

In order to clarify the key structural factors

which would allow lower resistivity, we have used energetic O^+ and H_2^+ implantations at 25 °C to control crystallinity of the films. This treatment results in increasing resistivity with increasing dose due to generation of neutral scattering centers and decreasing carrier density.⁷ Improved understanding of this degradation is important for ITO film deposition technologies such as sputtering or ion plating which may subject the deposited films to energetic particle bombardment throughout growth. The ion implantation of ITO may also be technologically useful for improved adhesion using "ion beam stitching"⁸ if conditions can be found in which electrical degradation is avoided.

In this work we report on thermal and dynamic processes which take place during ion implantation by studying the effect of implantation dose and temperature on ITO electrical properties and film microstructure.

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Fig. 1: XRD patterns taken from the c-ITO films in the (a) as-deposited state, and after O^+ implantation at -196°C at a dose of (b) 1.0×10^{15} , and (c) $4.0 \times 10^{15} \text{ cm}^{-2}$.

2. EXPERIMENT

Thin-film polycrystalline (c-) ITO ($\text{SnO}_2:5\text{wt}\%$) was deposited to a thickness of 196 nm on SiO_2 -coated soda-lime glass substrates at 350°C using conventional e-beam evaporation. Low resistivity amorphous (a-) ITO films were also deposited to thicknesses of 180 nm at a substrate temperature of 120°C by high density plasma-assisted e-beam evaporation^{6,9-11}. Ion implantation with 80 keV O^+ ions was selected based on TRIM calculations to ensure that most of the implanted ions terminated in the thin ITO film (projected range was calculated to be 100nm). The resistivity (ρ), Hall mobility (μ), and carrier density (n) were determined by the four-point probe method and by Hall-effect measurements.

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of c-ITO films implanted with 80 keV O^+ at -196°C at doses of 0, 1.0×10^{15} , and $4.0 \times 10^{15} \text{ cm}^{-2}$ are shown in Fig 1(a-c). Although TRIM calculations predict that implant doses of 1×10^{15} and $4 \times 10^{15} \text{ cm}^{-2}$ result in the displacement of 60 and 240%,

Fig. 2: XRD patterns taken from the a-ITO films in the (a) as-deposited state, and after O^+ implantation at a dose of $1.0 \times 10^{15} \text{ cm}^{-2}$ at (b) $+16^\circ\text{C}$ and (c) -196°C , and (d) thermally annealed at 150°C for 20 min. in air.

respectively, of the atoms from their lattice positions, all of the implanted c-ITO films have the In_2O_3 bixbyte crystal structure. These results reveal that significant dynamic recovery must occur in c-ITO at -196°C during implantation. The (222) peak at $2\theta=30\sim31^\circ$ showed a slight shift to the smaller 2θ side and a 20~40% decrease in intensity after ion implantation which indicates that the lattice undergoes expansion and the creation of lattice imperfection. The electrical properties of these films are listed in Table.I which shows that the resistivity (ρ) increased after the 10^{15} cm^{-2} implantation due to a decrease both in mobility (μ) and carrier density (n). Previously^{7,11}, this behavior was attributed to an increase in the density of neutral scatter centers (n_N) and carrier trapping at defect sites.

XRD patterns for the a-ITO films are shown in Fig. 2(a-d) for (a) the as-deposited state, and after $1.0 \times 10^{15} \text{ cm}^{-2}$ O^+ implantation at (b) $+16^\circ\text{C}$ and (c) -196°C . All of the implanted and as-deposited spectra show that the ITO remains amorphous after ion implantation. This, in combination with the results described for c-ITO, suggests that while the

Table. 1

Electrical properties of before and after O^+ implanted amorphous and crystalline ITO films.

Film thickness (nm)	Implantation temperature (°C)	Resistivity ($\times 10^{-4} \Omega \text{cm}$)	Carrier density ($\times 10^{20} \text{cm}^{-3}$)	Hall mobility (cm^2/Vsec)	Mean free path of the electron (nm)	Density of the neutral scattering center ($\times 10^{20} \text{cm}^{-3}$)
<u>Crystalline films</u>						
(before implantation)						
196	----	1.91	8.31	39.4	7.51	0.92
(DOSE: $1.0 \times 10^{15} / \text{cm}^2$)						
196	+25	10.04	3.99	15.6	2.33	3.32
196	-196	10.04	4.02	15.4	2.32	3.37
(DOSE: $4.0 \times 10^{15} / \text{cm}^2$)						
196	-196	11.70	3.32	16.1	2.26	3.22
<u>Amorphous films</u>						
(before implantation)						
180	----	4.84	3.47	37.2	5.31	1.10
(DOSE: $1.0 \times 10^{15} / \text{cm}^2$)						
180	+16	4.92	3.27	38.9	5.43	1.03
180	-196	5.70	3.26	33.6	4.70	1.28

dynamic annealing processes of atom re-attachment at the interface between ordered and disordered regions is rapid, the nucleation of crystalline material during implantation in the amorphous film is not kinetically favored at these temperatures (-196~+16 °C). Note that nucleation and rapid crystallization occurs by thermal annealing at +150 °C as shown in Fig.2 (d).

The electrical properties of a-ITO remained in-tact after implantation at temperatures between -196 to +25 °C (Table.1). The electrical properties of 6.0×10^{13} and $2.5 \times 10^{14} \text{ cm}^{-2}$ O^+ implanted c-ITO films are shown in Fig. 3 as a function of implant temperature. The degradation of the electronic properties due to the implantation decreased when the substrate temperatures was above +100~200 °C and were hardly unaffected at +300 °C. The neutral scatter density n_N (Fig.4 (a)) and carrier mean free path (Fig.4 (b)) were estimated based on the ionized and neutral scattering center model and a Fermi gas model.^{7,11-13} Note that

n_N decreased for implants above +150 °C due to thermal annealing and the simultaneous occurrence of dynamic and thermal recovery. Thus, "ion beam stitching"⁸ for adhesion enhancement, which is reported to be effective for Cu or Au films on Teflon substrates may also be useful for a- or c-ITO films if performed at sufficiently high temperature (+100~300°C).

4. CONCLUSIONS

The effect of O^+ implantation on the structural and electrical properties of polycrystalline and amorphous ITO films was studied. A large increase in resistivity was observed for c-ITO films when implanted at -196 to +100 °C. Above an implant temperature of about +150°C the resistivity of c-ITO films remained essentially unchanged. In contrast, a-ITO films showed almost no degradation in resistivity after $1.0 \times 10^{15} \text{ cm}^{-2}$ implantation at -196 to +16 °C. Dynamic recovery processes appear to occur even at -196°C if there is a crystalline

Fig. 3. (a) Resistivity, (b) carrier density, and (c) Hall mobility of the O^+ implanted c-ITO films as a function of implantation temperature.

template available. Nucleation of crystalline ITO from amorphous thin films does not occur during implantation at $+16^\circ\text{C}$ and occurs thermally at about $+150^\circ\text{C}$.

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Fig. 4. Calculated (a) density of neutral scattering center, and (b) carrier mean-free path of the O^+ implanted c-ITO films as a function of implantation temperature.

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