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Pulsed Laser Deposition of Transparent Conducting Indium Tin Oxide Films in Magnetic Field Perpendicular to Plume

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In_2O_3 doped with 5 wt% SnO_2 (indium-tin oxide(ITO)(5 wt%)) films have been deposited on glass and quartz substrates in a magnetic field generated from three pieces of rare–earth permanent magnets (1.25 T flux density) placed at every 120° angle to surround the plume produced by pulsed laser deposition using an ArF laser ($\lambda = 193$ nm). In all experiments, a repetition rate of 10 Hz, an energy density of 1.5 J/cm^2, and an irradiation time of 20–30 min (12000–18000 shots) were used. The lowest resistivity of 7.2×10^{-5} Ω·cm and an optical transmittance of more than 90% in the visible region of the spectrum were obtained for approximately 30-nm-thick ITO (5 wt%) films deposited at a substrate temperature of 300°C in oxygen with a flow rate of 2 sccm. Very smooth surfaces with an average surface roughness of 0.61 nm were observed by scanning electron microscope (SEM) and atomic force microscope (AFM).

KEYWORDS: low resistivity, surface flatness, indium tin oxide films, pulsed laser deposition, interaction between plume and magnetic flux, liquid crystal transparent electrode, organic electroluminescence transparent anode

Transparent conducting oxide films with unique characteristics of low resistivity (ρ) and high transmittance (T) over the visible wavelength region have found numerous applications in optoelectronic devices including liquid-crystal displays, plasma displays and solar cells. In particular, indium–tin oxide (ITO) films are widely used as transparent electrodes in this field. In order to fabricate low–resistivity ITO films, several methods such as sol–gel process,[1)] rf magnetron sputtering,[2)] molecular–beam epitaxy,[3)] dc magnetron sputtering,[4)] synchrotron radiation ablation,[5)] and pulsed laser deposition (PLD) with KrF (248 nm) excimer laser[6)] have been used. The values of ρ for ITO films obtained by these methods ranged from 3.2×10^{-4} Ω·cm to 1.3×10^{-4} Ω·cm. On the other hand, ITO films have been also widely used as transparent hole–injecting anodes of organic electroluminescent (EL) displays,[7)] and it is considered that an EL device structure has to be fabricated on a flat ITO surface to prevent irregular shortening and leakage induced at the interface between the hole–transport layer (organic) and the hole–injecting layer (ITO).[8)] Therefore, it is important to fabricate ITO films with small average surface roughness (R_a). For that purpose, ITO films have been prepared by such methods as reactive sputtering,[9)] reactive electron gun evaporation[10)] and PLD with KrF excimer laser.[11)] The values of R_a for ITO films obtained by these ways ranged from 6 nm to 1.3 nm. Furthermore, Kim *et al*. reported an R_a of approximately 0.5 nm for the ITO film deposited by PLD with the KrF excimer laser, but the resistivity of the film was 2×10^{-4} Ω·cm.[12)]

We have begun to fabricate ITO films with R_a less than 1 nm and ρ of the order of 10^{-5} Ω·cm by PLD using an ArF (193 nm) excimer laser after our previous report on the surface flatness of transparent conducting ZnO: Ga thin films ($R_a = 0.8$ nm) grown by PLD with an ArF excimer laser.[13)] One way to fabricate ITO films with good conductivity and small surface roughness is to apply an external force such as a magnetic field to the plume generated between the substrate and the target because the magnetic field acts on charged particle or plasma and affects ionization inside the plume, thereby increasing plasma density.[14)] In this work, we have focused on reducing the resistivity as well as flattening of the surfaces of ITO films grown in a magnetic field applied perpendicular to the plume produced by PLD with an ArF excimer laser.

Figure 1 shows a schematic diagram of the pulsed laser deposition system: Fig. 1(a) shows the layout in the chamber and Fig. 1(b) shows the arrangement of magnet. ITO films were deposited on Corning #7059 glass substrates with an area of 38 × 26 mm by irradiating an excimer ArF (193 nm) laser (LAMBDAPHYSIK,COMPex102) that provides 40 mJ pulses of 12 ∼ 16 ns duration at a repetition rate of 10 Hz, on a rotating target under the conditions listed in Table I. The substrate temperature (T_{SUB}), which was measured us-

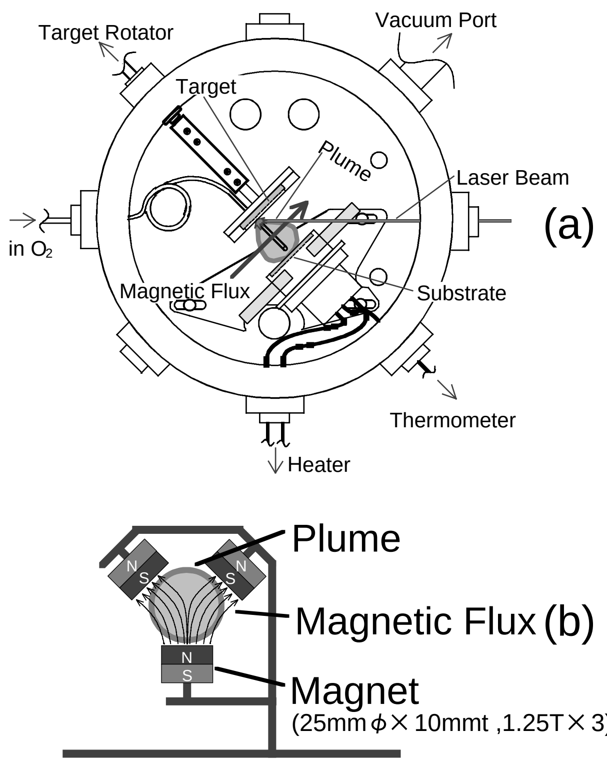

Fig. 1. Pulsed laser deposition system for ITO (5 wt%) films: (a) schematic diagram of the chamber and (b) the arrangement of permanent magnets.

Table I. Preparation conditions for ITO films.

Laser	ArF Excimer ($\lambda = 193$ nm)
Laser energy	40 mJ
Repetition rate	10 Hz
Target-to-substrate distance	40 mm
Target	In_2O_3:SnO_2 (5 wt%)
Magnet	3 pieces (1.25 T/piece)
Substrate	Corning#7059
Substrate temperature	25–300°C
Base pressure	10^{-5} Pa
Gas pressure	$\sim 10^{-3}$ Pa (in O_2)
Ablation time	20 min

ing a thermocouple in contact with the substrate, increased by only 2–4°C after 20–30 min. The laser beam was reduced to a spot with a diameter of approximately 1.8 mm using a spherical quartz lens and focused onto the ITO target to give an energy density of 1.5 J/cm^2. During the laser irradiation, the target was rotated at a speed of one revolution per minute using a pulsed motor controlled by a personal computer, in order to avoid the formation of deep craters that modify material ejection. The composition of the target, which was 5 mm thick and 50 mm in diameter, was In_2O_3 doped with 5 wt% SnO_2 (ITO(5 wt%)) (99.999% purity, Furuuchi Co., Ltd.). As shown in Fig. 1(b), three pieces of rare–earth permanent magnets consisting of NdFeB, each of which was 10 mm thick and 22 mm in diameter and had 1.25 T flux density, were placed at every 120° angle to apply magnetic field perpendicular to the plume. The deposition cell was initially evacuated to $\sim 10^{-5}$ Pa and film deposition was performed at a working pressure of $\sim 10^{-3}$ Pa with an oxygen flow rate of 2 sccm. The sample was allowed to cool naturally to room temperature. Film thickness was measured using a stylus instrument (KLA TENCOR, P-10). The transmittance through the films, with Corning #7059 glass as reference, was measured in the wavelength range of 300–1000 nm using a spectrophotometer (Hitachi, U-3500). Measurement of optical and electrical characteristics as well as observation of surface morphologies and cross sections of the films was carried out according to the method described elsewhere.[13)]

Figure 2 shows the dependence of resistivity (ρ), carrier concentration (n) and Hall mobility (μ) on substrate temperature for ITO (5 wt%) films prepared under the conditions listed in Table I. The deposition rate was reduced to one–half $\sim$ one–third with the application of magnetic field, and then the film thickness was reduced from 60–90 nm without magnetic field to $\sim$30 nm with magnetic field. The lowest resistivity of 7.2×10^{-5} Ω·cm was obtained at $T_{SUB} = 300$°C under the magnetic field, and was attributed to the high carrier concentration of 2.5×10^{21} cm^{-3} (see arrows in the figure). In order to investigate the cause of this effect, drawing of magnetic flux lines was accomplished using iron powder.

Figure 3 shows loci of magnetic flux generated in the space surrounded by the magnets, in which the plume exists. It was found that there was a large magnetic flux at the portion corresponding to the center of the plume. From these results, it is thought to the first approximation that when electrons in the central portion of plume are accelerated by a spiral movement, the ionization of species such as atoms and molecules is effectively promoted and then the plasma density increases.[14)]

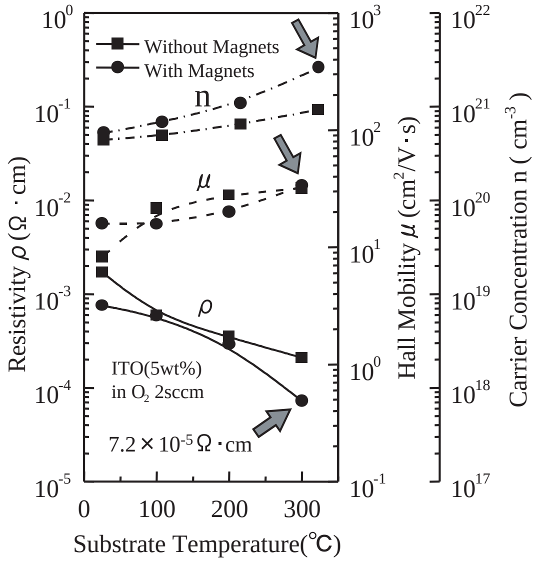

Fig. 2. Substrate temperature dependences of electrical properties of ITO (5 wt%) films deposited on glass substrates.

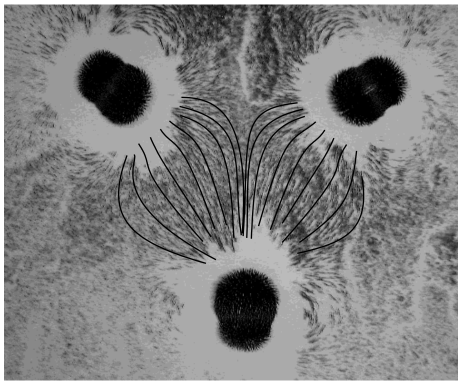

Fig. 3. Loci of magnetic flux generated in the space surrounded by three pieces of permanent magnets.

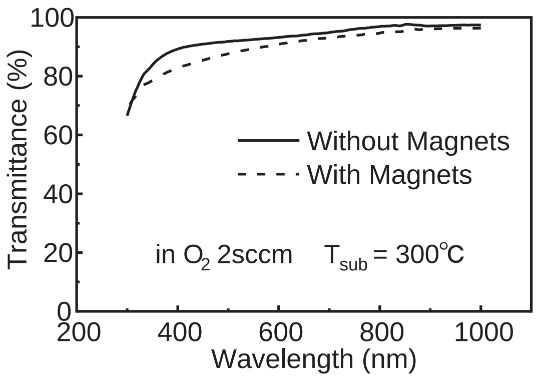

Fig. 4. Optical transmittance spectra of ITO (5 wt%) films deposited on quartz substrates.

Figure 4 shows the transmittance (T) spectra in the wavelength range of 300–1000 nm for ITO(5 wt%) films deposited on quartz substrate at $T_{SUB} = 300$°C. It was found that an average transmittance of more than 90% over the visible light wavelength step of 400–700 nm was obtained irrespective of the magnetic field and the transmittance decrease due to the

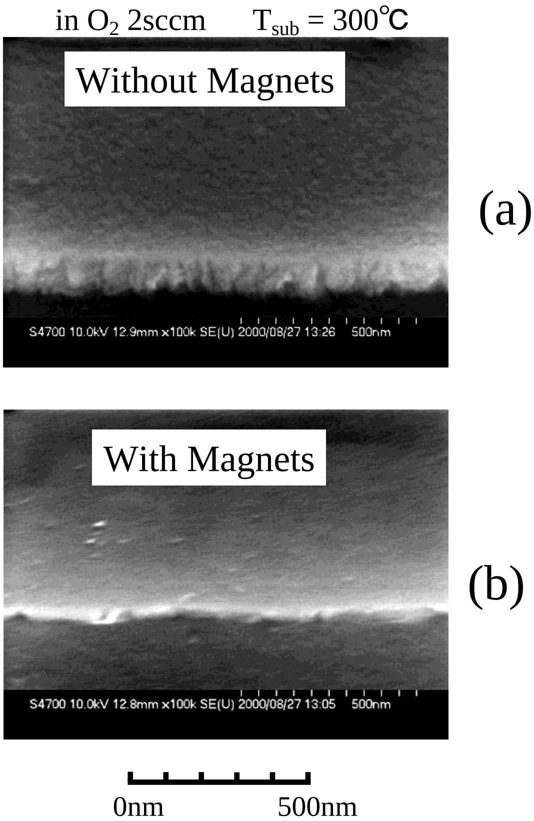

Fig. 5. High–resolution SEM images obtained for ITO (5 wt%) films fabricated (a) without and (b) with magnetic field.

plasma frequency caused by high carrier concentration in the longer wavelength region of more than 1000 nm did not occur because the thin film had a thickness of approximately 30 nm.

Figure 5 shows scanning electron microscope (SEM) micrographs of ITO films prepared at $T_{SUB} = 300°C$ (a) without and (b) with magnetic field. From Fig. 5(a), it was found that columnar structures exist in the cross section of the film whose average surface roughness R_a is 1.5 nm based on atomic force microscope (AFM) observation, while in Fig. 5(b), very smooth surfaces with an R_a of 0.61 nm were obtained. It is supposed that the difference between the two surface structures originates in the change of the deposition rate of the films from 3–4.5 nm without magnetic field to 1.5 nm with magnetic field and the increase of plasma density in the central portion of the plume.

ITO films were deposited on glass substrates in a magnetic field that was applied perpendicular to the plume generated by PLD using an ArF excimer laser. For ITO (5 wt%) films with a thickness of approximately 30 nm grown at $T_{SUB} = 300°C$ in oxygen with a flow rate of 2 sccm, an average transmittance more than 90% over the visible light wavelength range of 400–700 nm, the lowest resistivity of 7.2×10^{-5} Ω·cm and an average surface roughness R_a of 0.61 nm were obtained. From a simple observation using iron powder, it was thought to the first approximation that a large magnetic flux at the portion corresponding to the center of the plume was useful to increase plasma density. The essential mechanism underlying the interaction between plume and magnetic flux is now being studied using some arrangements of rare–earth permanent magnets.

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