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Optical and electrical properties of laser-irradiated In_2O_3–4 mol % SnO_2

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The structural, electrical and optical properties of r.f. sputtered indium–tin oxide films on fused silica substrates and laser-treated films in air were investigated. The transmittance in the visible range was increased and the electrical resistivity was decreased by the laser treatment. The laser treatment was also found to annihilate dislocations and to promote grain growth. The improvement in these optical and electrical properties may be mainly due to the annihilation of defects such as vacancies and interstitials.

1. Introduction

Indium–tin oxide (ITO; In_2O_3–SnO_2) film has been used for transparent electrodes such as the windows of solar cells and the displays for liquid crystals [1, 2]. Sputtering is the most popular method for forming ITO thin films, because of the ease of chemical composition control [3]. Usually an as-deposited film contains many defects, viz. dislocations, vacancies, interstitials and Ar, which may affect the optical properties as well as the electrical properties, causing impurity levels in the proper bandgap. An improvement in optical properties can be achieved by annealing to annihilate such defects [4]. A laser is used for annealing a film, the film being heated in a small local area, rather than as a whole system including the substrate. The laser treatment of as-deposited film may be an attractive method for the recording of signals, if the local area optical transmission can be changed by laser irradiation. However, there is still little information on the physical properties of film after laser treatment.

The focus of the work reported here was on the change in the structural, electrical and optical properties of r.f. sputtered ITO films on fused silica substrates by laser irradiation.

2. Experimental

ITO thin films were formed by the r.f. magnetron sputtering method using an In_2O_3– 9 mol % SnO_2 target. Fused silica substrates were cleaned and then mounted in the sputtering equipment. The substrate temperature was 300 K. After etching of the substrate, deposition was performed under the following sputtering conditions: base pressure 1.3×10^{-4} Pa, Ar gas flow standard 7 $cm^3 min^{-1}$, vacuum during sputtering 0.93 Pa and target-to-substrate spacing 50 mm. The thickness of the film was about 800 nm and the deposition rate was about 1 $nm s^{-1}$. The composition of the films on fused silica were measured by energy-dispersive X-ray spectroscopy (EDS) employing an H-540 scanning electron microscope. A CO_2 laser ($\lambda = 10.6$ μm) was applied to a spot 2 mm in diameter perpendicular to the film which was on fused silica. The beam intensity profile of the spot was approximately Gaussian. A continuous-wave laser was applied to a film–substrate system which was moving at a constant velocity. Laser irradiation of the whole film surface was carried out by sliding the substrate up 1 mm after each pass of irradiation. This irradiation was performed at a power of 13–33 W, because of the evaporation from the deposited film caused by irradiation power above 33 W. The structure of as-sputtered and laser-treated films was observed by X-ray diffractometry and transmission electron microscopy. The spectral transmittance for the visible wavelength range was measured by optical spectroscopy. The resistivity, Hall mobility and carrier concentration were measured by the van der Pauw method and the conventional four-point method.

3. Results

Fig. 1 shows the X-ray diffraction pattern for as-deposited and laser-treated samples. The laser was applied to a spot 2 mm in diameter perpendicular to the film moving at a velocity of 1 $mm s^{-1}$. All reflection peaks were indexed by those from the cubic In_2O_3 phase without any other phases. As-deposited ITO film was indicated to have almost the same intensity ratio of X-ray reflection peaks as that of the In_2O_3 profiles observed in American Society for Testing and Materials (ASTM) data for the powder diffraction, although the film had a larger intensity of 4 0 0 reflection than that of the powder diffraction [4]. This means that the film grew on fused silica with an almost uniform distribution of growth orientation but with a slightly preferred orientation of 1 0 0. After laser irradiation, the profile of X-ray reflection peaks was found to be changed as seen in Fig. 1, which shows

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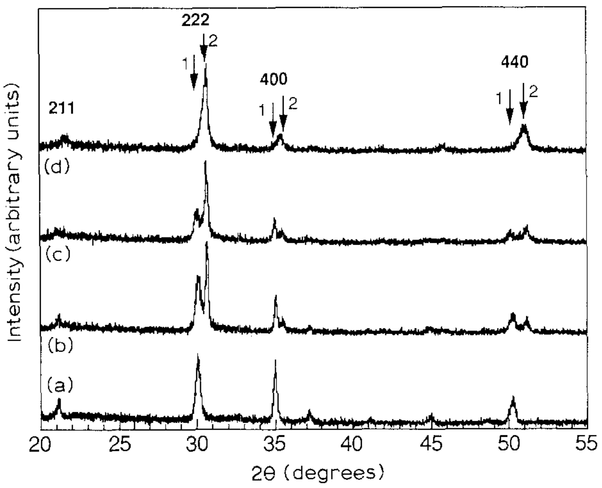

Figure 1 X-ray diffraction profiles (CuK_{α} radiation) obtained from (a) as-deposited and laser-irradiated In_2O_3–4 mol % SnO_2: (b) 14 W, (c) 23 W and (d) 33 W.

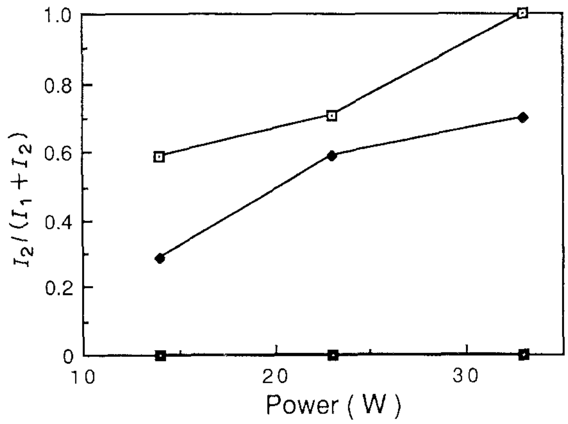

Figure 2 Laser power dependence of the X-ray intensity ratio: scanning velocity (□) 1, (◆) 10 and (■). 100 mm s^{-1}.

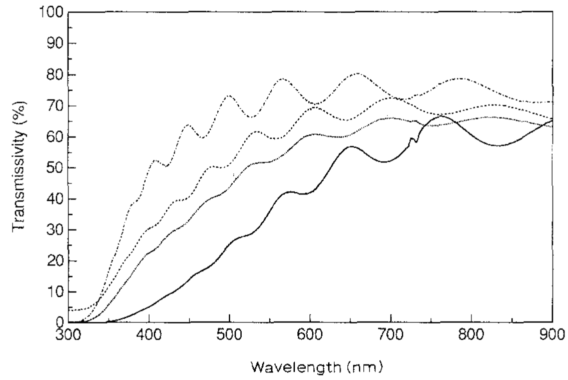

Figure 3 Wavelength dependence of the transmittance of light for (——) as-deposited and laser-irradiated ITO: (· · · · ·) 14 W, (– – –) 23 W and (–·–) 33 W.

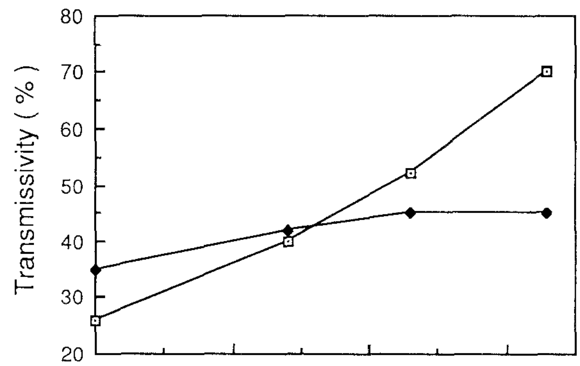

Figure 4 Transmittance at the wavelength of 500 nm versus laser power: scanning velocity (□) 1 and (◆) 100 mm s^{-1}.

four different kinds of laser power at a constant scanning velocity of 1 mm s^{-1}. The new peaks (labelled 2) appear at slightly higher angles for all as-deposited reflections (labelled 1) and their intensities increased with increasing laser power. This strongly suggests that the newly appeared reflections result from the same crystal structure as ITO with a slightly smaller lattice parameter than that of as-deposited ITO. The accurate lattice parameter was estimated by the extrapolation method to be 1.029 nm for the as-deposited film and 1.011 nm for the new reflections that appeared after the laser irradiation [5]. EDS analysis of the film surface revealed that the Sn content of the film was not changed before or after laser irradiation and was about 4 mol % SnO_2. Since the ionic radius of Sn^{4+} is smaller than that of In^{3+}, the increase in Sn content in the solid solution decreases the lattice parameter [6]. The decrease in the lattice parameter after laser irradiation is not the result of the loss of Sn due to the decomposition and evaporation of Sn caused by laser irradiation. The lattice parameter of 1.011 nm after laser irradiation is close to that of bulk In_2O_3 given on the ASTM card, and the expansion of the lattice parameter of as-deposited films seems to be caused by the introduction of defects such as vacancies, interstitials, dislocations and Ar during sputtering [4]. The expansion of the lattice parameter of as-deposited film was about 1.8%. The intensity of second peaks, which appeared after the laser irradiation, increased with increasing laser power (Fig. 2). The structure of films treated with a laser power of 33 W and a scanning velocity of 1 mm s^{-1} was completely changed to the proper ITO lattice parameter of 1.011 nm. An increase in the scanning velocity led to a decrease in the intensity of second peaks; in particular, there were no second peaks in the case of a scanning velocity of 100 mm s^{-1}.

Fig. 3 shows the transmissivity versus wavelength relationship within the visible range. An as-deposited film on fused silica had low transmissivity and was about 25% at a wavelength of 500 nm. An increase in laser power led to an increase in transmissivity. The absorption edge of laser-treated samples was about 350 nm, which is equal to that of the ITO films deposited by other methods, even though the absorption edge of an as-deposited film moved to a slightly longer wavelength than that of a laser-treated film [2]. Fig. 4 shows the laser power dependence of the transmittance at a wavelength of 500 nm for two scanning velocities. The transmissivity of the film treated with a power of 33 W and a scanning velocity of 1 mm s^{-1} was about three times that of the as-deposited film. This indicates that the laser can improve the transmissivity without any change in the chemical composition of a film. An increase in the scanning velocity reduced the decrease in the gradient of the transmissivity versus laser power relationship. It should be pointed out that the area of transmissivity change can be controlled to control the size of the spot and the power of the laser irradiation.

Fig. 5 shows the electrical resistivity versus power of laser irradiation, in which the resistivity of the as-deposited film was about $3 \times 10^{-3}\,\Omega$ cm. The resistivity decreased with increasing laser power and was of the order of $10^{-4}\,\Omega$ cm, which is the same order as the resistivity of the film obtained by the r.f. sputtering method employing a heated substrate [7]. The resistivity was also affected by the scanning velocity of the substrate; it decreased with decreasing scanning velocity for a constant power of laser irradiation. This means that laser irradiation caused a decrease in the resistivity and an increase in the transmittance at the same time. Fig. 6 shows the laser power dependence of the Hall mobility and carrier concentration in the case of a scanning velocity of 1 mm s^{-1}. The values for as-deposited film are also shown in this figure. The carriers in ITO film are electrons introduced by the addition of SnO_2. The carrier concentration of laser-treated films gradually decreased with increasing laser power from the value for as-deposited film. On the other hand, the Hall mobility increased with increasing laser power. These results are quite reasonable because of the annihilation of defects, which are the source of carriers as well as the scattering centres of

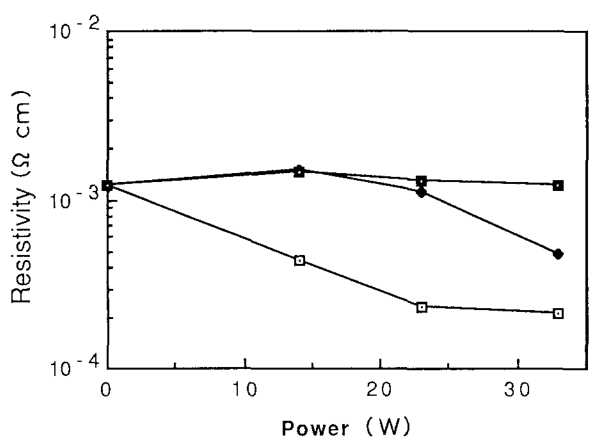

Figure 5 Electrical resistivity versus laser power for ITO: scanning velocity (□) 1, (◆) 10 and (■) 100 mm s^{-1}.

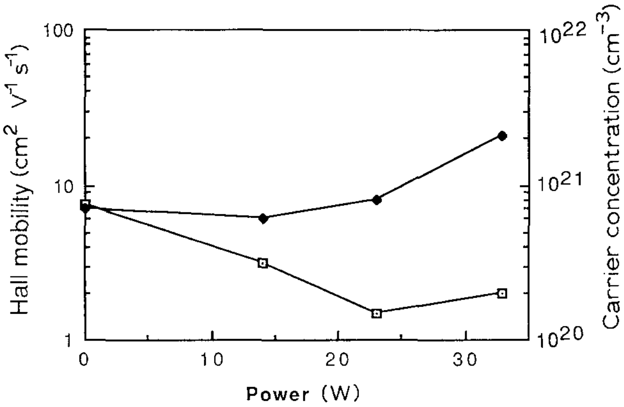

Figure 6 The Hall mobility (◆) and carrier concentration (□) versus laser power for ITO.

carriers, due to laser treatment. Thus, laser annealing caused an increase in the mobility of carriers and a slight decrease in the carrier concentration.

The microstructure of ITO films was inspected on samples parallel to films by transmission electron microscopy. Figs 7 and 8 are electron micrographs of as-deposited and laser-treated ITO films, respectively, under conditions of power 33 W and scanning velocity 1 mm s^{-1}. No pores or precipitates in a grain or grain boundaries were found although an as-deposited film includes irregularly shaped grains and many dislocations (see the dark-field image in Fig. 7). The electron diffraction pattern taken from the parallel section of an as-deposited film revealed that all reflections, which should appear in ITO, can be found under these experimental conditions. This is consistent with the result of X-ray diffraction, that the grains did not have any preferred orientations. Dislocations in a grain were annihilated and grain growth took place due to the laser treatment as shown in Fig. 8. Thus, it can be seen that laser treatment changed a highly faulted structure to a defect-free structure. It should be noted that the pores and precipitates cannot be seen in a grain or at grain boundaries after the laser treatment.

4. Discussion

The present experiment showed that transmittance can be improved by laser irradiation. The transmittance of light through thin films is determined by several factors such as the surface roughness, pores, precipitates, grain boundaries, vacancies and interstitials. From the results of electron microscopic observation, pores and precipitates were not present before or after laser irradiation in the present experiment. The increase in grain size by laser irradiation

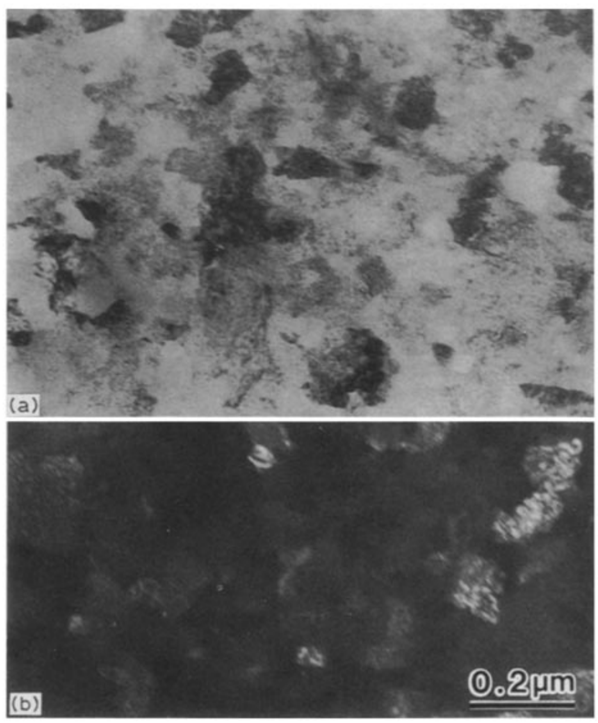

Figure 7 Electron micrograph of as-deposited ITO film: (a) bright-field image and (b) dark-field image of the same area as (a).

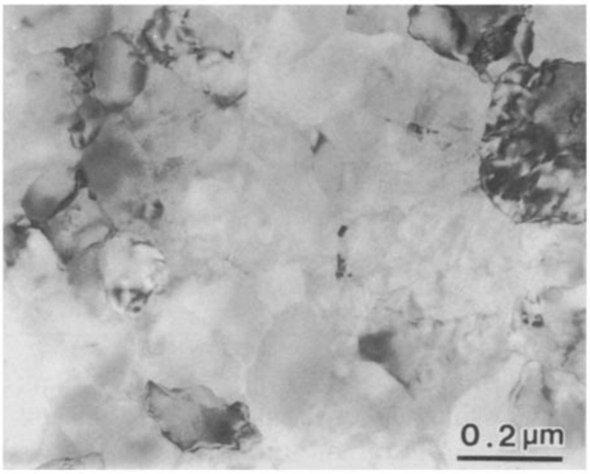

Figure 8 Electron micrograph of laser-annealed ITO film.

was less than twice the grain size of an as-deposited film. Thus, the important factor determining the improvement in transmittance seems to be related to atomic-level defects such as vacancies and interstitials. Annealing in air causes the annihilation of vacancies and interstitials to diffuse out of or into the ordinary lattice sites and to be swept away by dislocations. At the same time, annealing supplies oxygen atoms to the lattice sites and decreases the extra oxygen vacancies introduced during the deposition by sputtering. This is the reason why the optical transmittance and the electrical resistivity are improved through the increase in the carrier mobility.

The temperature distribution on the surface of materials subjected to laser scanning was calculated in a two-layer structure by Burgener and Reedy [8]. It depends on the thermal conductivities, scanning velocities and thickness ratios of both phases. The calculation indicated that the temperature distribution of film was rather uniform within because of the larger thermal conductivity of In_2O_3 than that of SiO_2 [9]. If substrate with a better thermal conductance than that of the film is used, the temperature distribution is localized in a small area. These results show the possibility of using laser annealing to make very small dots that have a transmittance different from that of the matrix.

5. Conclusion

The structural, electrical and optical properties of r.f. sputtered ITO films on fused silica substrates were investigated before and after laser treatment in air. The transmittance in the visible range and Hall mobility were increased by laser treatment. On the other hand, the electrical resistivity and the carrier concentration decreased with increasing laser power. The annihilation of dislocations and the promotion of grain growth were achieved by laser treatment. The improvement in these properties may be due mainly to the annihilation of defects such as vacancies and interstitials.

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