

Fabrication of ITO Bragg Gratings : An Application of Excimer Laser Crystallization of Amorphous ITO Thin Films

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Polycrystalline indium-tin-oxide (ITO) thin films were prepared at a room temperature by KrF excimer laser irradiation (pulse energy $40\text{mJ}/\text{cm}^2/\text{pulse}$) to amorphous (a)-ITO films. Electrical conductivity of laser crystallized specimen was increased from 1.4×10^3 to 1.8×10^3 S/cm. A periodic structure of a-ITO and crystalline (c)-ITO was made by irradiation of excimer laser through a SiO₂ glass phase mask. The Bragg gratings made of c-ITO was formed by wet-etching of the laser irradiated specimens.

Key Words: indium-tin-oxide, amorphous, crystallization, excimer lasers,

1. INTRODUCTION

Tin doped Indium Oxide (ITO) have high conductivity, high transparency and excellent etching properties. They are the most widely used transparent conducting oxides.^{1,2)} ITO thin films deposited on plastic substrates have a great merit comparing with those deposited on glass substrates such as flexibility, light weight and small volume. However heating substrates to a temperature $>200^\circ\text{C}$ during deposition or postdeposition annealing is required to obtain crystalline (c)-ITO thin films. Most plastic substrates cannot endure such a high temperature. Because the technique of ITO thin films deposited on at a low temperature have much attracted. Some authors have already reported fabrication and electrical properties of ITO thin films deposited on plastics substrates.^{3,4)}

We proposed the KrF excimer laser crystallization of a-ITO for quickly obtaining c-ITO thin films deposited

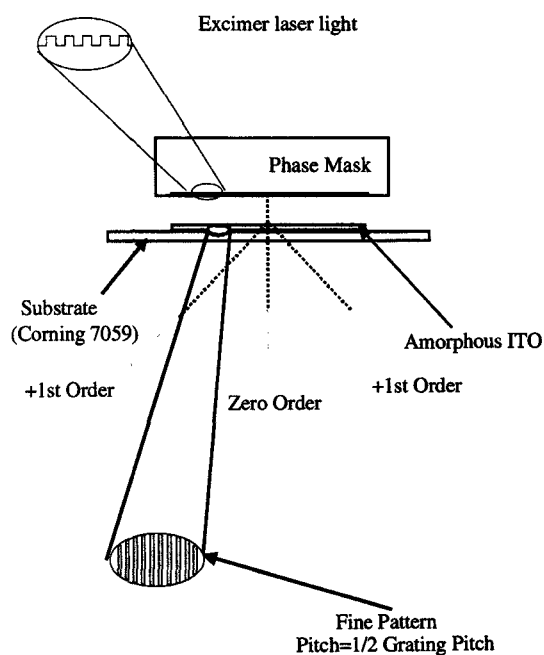


Fig 1. Schematic of KrF excimer laser irradiation to the amorphous ITO through the phase mask.

on plastic substrates. The KrF excimer laser was applicable to the fabrication of c-ITO thin films deposited on plastic substrates by crystallization of a-ITO. Because the absorption coefficient of a-ITO is $2.25 \times 10^5 / \text{cm}$ at the wavelength of KrF laser light (248nm).⁵ The penetration depth of the laser light into the a-ITO is 40-50nm. The thickness of as deposited a-ITO thin films is 200nm. Therefore KrF light does not reach substrates and the laser irradiation damages of substrates is restrained. It is possible to write desired patterns of c-ITO by selective laser crystallization and chemical etching technique

In this paper we report that prepared c-ITO thin films by KrF excimer laser irradiation to a-ITO thin films at room temperature and that a Bragg gratings fabrication of c-ITO was made by combining irradiation of KrF excimer laser through a phase mask with chemical etching.

2.EXPERIMENT

ITO thin films were deposited on glass substrates (Corning 7059) by dc-magnetron sputtering using sintered $\text{In}_2\text{O}_3(90\text{wt}\%):\text{SnO}_2(10\text{wt}\%)$ target. The glass substrate was cooled by flowing water during deposition. The thickness of each specimens were about 190nm.

Fig 1. Schematic of KrF excimer laser irradiation to the amorphous ITO through the phase mask.

The amorphous nature of the resulting thin film was confirmed by glancing angle X-ray diffraction (incident angle; 0.5° , source; Cu-K α radiation, power; 50kV-200mA.). The crystallization of a-ITO thin films by irradiation of KrF excimer laser (Lamda Physik, Compex 102, pulse duration; 20ns, wavelength; 248nm) in air and at room temperature. The Hall mobility, carrier concentration of a-ITO and c-ITO films were estimated from Hall-voltage measurements. The chemical etching rates of a-ITO and c-ITO films were estimated by measuring the remaining film thickness with a surface profilometer (DEKTAK III) after the specimens were immersed in a standard etchant ($\text{HCl}:\text{H}_2\text{O}:\text{HNO}_3=1:1:0.08$ in vol).⁶ A phase mask (10mm \times 5mm \times 5mm)with a grating period of 1070nm and a groove depth of 220nm for the KrF laser (OPS

Technology) was employed for the formation of fine periodic pattern. Laser irradiation was performed using the phase mask, which was carefully positioned in front of a-ITO thin films, to encode the fine pattern, as shown in Figure 1.^{7,8} The periodic pattern of ITO thin films were immersed in etchant for removing a-ITO by etching rates between a-ITO and c-ITO. The remained c-ITO worked as the Bragg gratings. The surface morphology of the thin films was observed with an atomic force microscope (AFM, SEIKO SPA300).

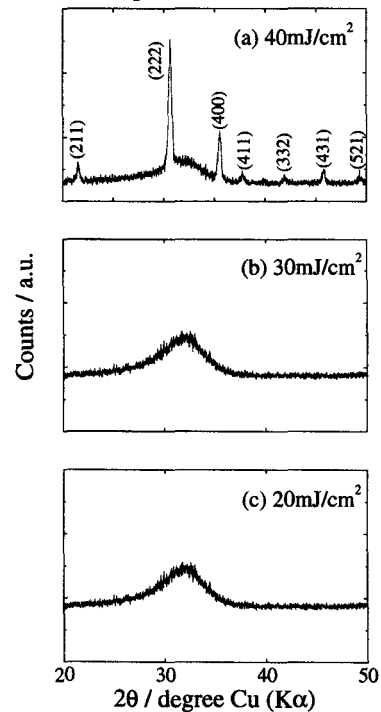


Fig 2. XRD patterns of the specimens before and after laser irradiation. (a)40mJ/cm²/pulse \times 1200pulse (b) 30mJ/cm²/pulse \times 1200pulse (c)20mJ/cm²/pulse \times 1200pulses. All the sharp diffraction peaks are indexed from In_2O_3 phase.

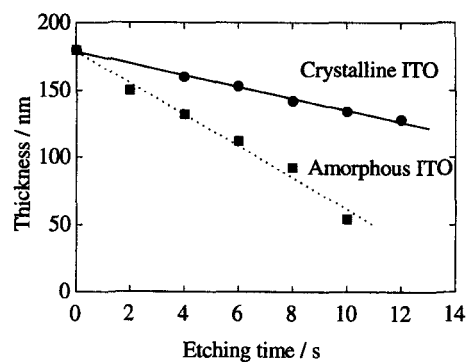


Fig 3. Changes in the thickness of amorphous (before irradiation) and Crystalline ITO (after irradiation). Etchant: ($\text{HCl}:\text{H}_2\text{O}:\text{HNO}_3=1:1:0.08$ in vol). The etching rates of a-ITO and c-ITO was 12.5 nm/s and 5.1 nm/s respectively.

3.RESULTS AND DISCUSSION

The Crystallization of a-ITO films by isothermal heating was not observed at temperatures below 190°C, by irradiation of KrF excimer laser was observed at room temperature. When the total pulse irradiation was fixed at 1200, crystallization was observed for power densities =40 mJ/cm². Figure 2 shows the X-ray diffraction (XRD) patterns of the ITO thin films before and after irradiation. The pulse repetition rate was changed from 1 to 20 Hz but it was no significant difference by XRD measurement.

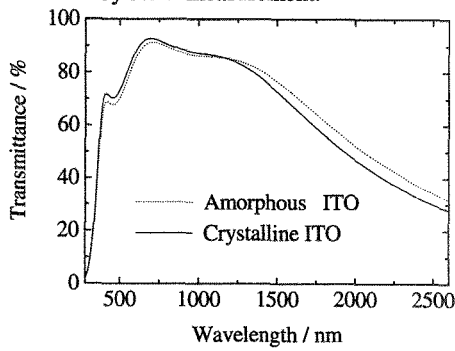


Fig 4. Optical Transmittance spectra of ITO thin films before and after irradiation laser pulses.

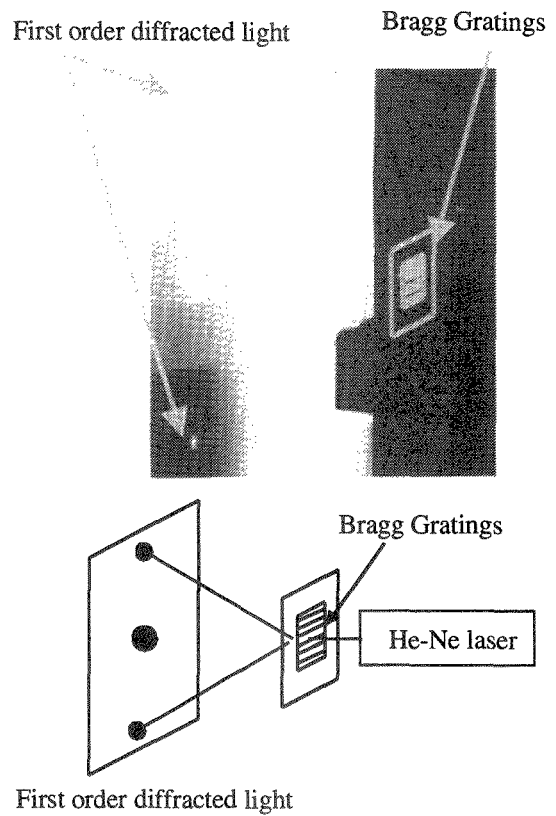


Fig 6. Demonstration of out-of-plane diffraction by ITO Bragg gratings.

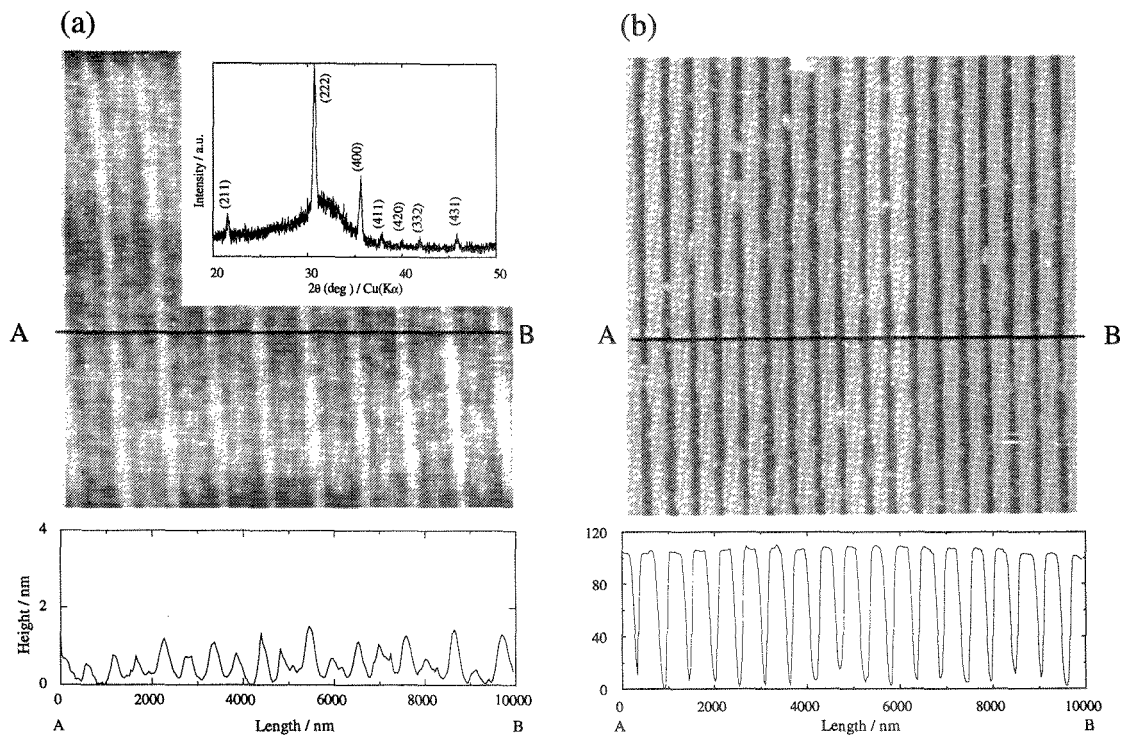


Fig 5. (a)AFM image of the ITO thin film after KrF excimer laser irradiation through phase mask. The inset shows the XRD pattern of the specimens. All diffraction peaks are indexed from In₂O₃ Phase. irradiation condition, 40mJ/cm²/pulse × 1200pulses. (b)AFM image of ITO thin films after etching.

Therefore it was determined that the decisive factor of excimer laser crystallization was power densities. XRD measurement after wet etching revealed that laser crystallization was occurred up to the depth of 170nm from the surface of specimen under present laser irradiated condition.

Electrical conductivities of ITO thin films were changed 1.4×10^3 to 1.8×10^3 S/cm after crystallization. The Hall mobility and carrier concentration in the specimens were changed upon crystallization from $17 \text{cm}^2/\text{V/s}$, and $5.4 \times 10^{20}/\text{cm}^3$ to $12 \text{cm}^2/\text{V/s}$ and $9.3 \times 10^{20}/\text{cm}^3$ respectively. The decrease in Hall mobility is tentatively ascribed to scattering in the grain boundaries of polycrystalline. ITO Crystallization of ITO generated conduction electron because Sn^{4+} ions occupying the site of In^3 ions. This is the primary cause of the increase in the carrier concentration.

Figure 3 shows the change in the film thickness of amorphous and laser crystallized ITO thin films as a function of the immersion time in a standard acid solution for wet etching. The etching rates calculated from the slope of the straight line were 12.5 nm/s and 5.1 nm/s for a-ITO and c-ITO. The etching rate ratio of a-ITO to c-ITO is about 2.4.

Figure 4 shows optical transmission spectra of a-ITO and c-ITO. The transmittance of c-ITO thin film decreased in the near infrared region and absorption edge was shifted to ultraviolet. It was consistent with the increase in the carrier concentration.

Figure 5(a) shows the AFM image of the thin film surface irradiated with KrF laser pulses through the phase mask. A periodic thickness modulation is reflecting the grating period of the phase mask. XRD measurements revealed that the periodic structure is composed of a-ITO and c-ITO. Figure 5(b) shows the AFM images of the thin film surface of periodic structure after immersed in etchant. a-ITO was selectively dissolved in the etchant because of the large etching rate ratio of a-ITO to c-ITO. Therefore the periodic structure was mainly composed of c-ITO. It can be seen that a periodic structure of the after etching film was terraces and valleys both 500nm in width and 100nm in depth.

It may be concluded from comparison with the grating period of the phase mask (the period of the encoded pattern, P_m , and the grating period, d , are related by $P_m = d / 2n$ where n denotes the diffraction order) that this periodic structure is encoded by the first order diffraction light (period = $1070 / 2 \times 1$ nm) from the phase mask.

Figure 6 shows that the micropatterned c-ITO thin films worked as Bragg gratings. The ratio of incident He-Ne laser to first order diffraction light was observed. The diffraction efficiency defined as the 1st order intensity to the incident light was 24% (12×12).

4. CONCLUSION

The crystalline ITO thin films deposited on glass substrates was successfully fabricated by crystallization of amorphous ITO with KrF excimer laser irradiation at room temperature. The primary factor of KrF excimer laser crystallization was the power density. The fabrication of the ITO Bragg Gratings was succeeded by utilizing the large wet etching rate ratio between c-ITO and a-ITO. Laser crystallization of a-ITO thin films deposited on plastic substrates is in now progress.

References

- 1 I. Hamberg and C. G. Granqvist, *J. Appl. Phys.*, **60**, R123, (1986)
- 2 K. L. Chopra, S. Major and D. K. Pandya, *Thin Solid Films.*, **102**, 1, (1983)
- 3 A. K. Kulkarni, K. H. Schulz, T. S. Lim and M. Khan, *Thin Solid Films.*, **308/309**, 1, (1997)
- 4 J. Ma, D. Zhang, S. Li, J. Zhao and H. Ma, *Jpn. J. Appl. Phys.*, **37**, 5614, (1998)
- 5 J. R. Bellingham, W. A. Phillips and C. J. Adkins. *J. Phys.: condens. Matter.*, **2**, 6207, (1990)
- 6 H. Harada and T. Haranoh, *Report. Res. Lab. Asahi. glass. Co., Ltd.*, **40**, 25, (1990)
- 7 K. O. Hill, B. Malo, F. Bilodeau, D. C. Johnson, and J. Albert, *Appl. Phys. Lett.*, **62**, 1035, (1993)
- 8 J. Nishii, H. Yamanaka, H. Hosono and H. Kawazoe, *Optics. Letters.*, **21**, 1360, (1996)

(Received December 11, 1998; accepted February 28, 1999)