ITO Thin Film Ablation Using KrF Excimer Laser and its Characteristics

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This study aimed to develop ITO (Indium Tin Oxide) thin films ablation with a pulsed type KrF excimer laser required for the electrode patterning application in flat panel display into small geometry on a large substrate area. The threshold fluence for ablating ITO on glass substrate is about 0.1 J/㎠. And its value is much smaller than that using 3rd harmonic Nd:YAG laser. Through the optical microscope measurement the surface color of the ablated ITO is changed into dark brown due to increase of surface roughness and transformation of chemical composition by the laser light. The laser-irradiated regions were all found to be electrically isolating from the original surroundings. The XPS analysis showed that the relative surface concentration of Sn and In was essentially unchanged (In:Sn=5:1) after irradiating the KrF excimer laser. Using Al foil mask made by 2nd harmonic Nd:YAG laser, the various ITO patterning is carried out.

Keywords : ITO, KrF excimer laser, Flat panel display, Threshold fluence, Surface patterning

1. INTRODUCTION

ITO thin films have high luminous transmittance, high infrared reflectance, good electrical conductivity, and therefore, have been widely and intensively studied for many years[1-3].

ITO thin films are wide-bandgap, and degenerate n-type semiconductor. The conduction band is partly filled and its Fermi level, E_F, is very close to the conduction band. It is essentially formed by substitutional doping of In_2O_3 with Sn, which replaces the In^{3+} atoms from the cubic bixbyte structure of indium oxide. An Sn forms an interstitial bond with oxygen and exists either as SnO or SnO^{2-}. Accordingly it has a valency of +2 or +4 respectively. Fig. 1 is a schematic diagram of ITO ionic structure[4].

In_2O_3 is an ionic-bond semiconducting oxide. During its formation, point defects are formed relatively easily compared with covalently bonded materials. These defects consists mainly of oxygen vacancies and possibly the interstitial indium atoms or even reduced metallic indium particles, giving rise to free electrons.

Due to their unique optical and transparent properties, ITO (indium tin oxide) films have given rise to numerous micro and opto-electronic applications such as thin film gas and image sensors, liquid crystal display elements, thin film solar cells and OELD (organic electro-luminescence device)[5-7].

Many of these applications need a patterning of the ITO film, which is generally carried out by lithography and wet etching in acidic solutions or reactive ion etching. However, these etching techniques have a few defects such as under- and over-etching, consumption of hazardous solvents and corrosive gases related to environmental matters. And if the use of the mask and related chemicals can be eliminated in some of these steps, advantages such as improved cleanliness, fewer process steps, reduction of cycle time could be realized. Table 1 shows the etching characteristics of ITO by conventional methods.

Alternatively, the study on the efficiency of laser patterning of ITO using different harmonics of a diode-

pumped Q-switched Nd:YLF (neodymium-doped yttrium lithium fluoride) laser has been reported to make clean-cut lines. Also, by a fourth harmonic of the Nd:YLF laser (λ=262 nm) in the ultraviolet region it has been reported that the ripple structure of the etched groove in the result of incomplete removal of ITO can be overcome[8]. In this study, we intend to investigate and evaluate characteristics of the ITO ablation using KrF excimer laser, which is used most extensively and commercially.

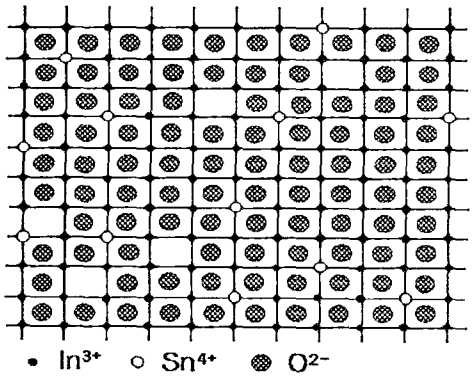

Fig. 1. A schematic diagram of ITO ionic structure.

Table 1. The conventional ITO etching methods and its defects.

	wet etching	plasma etching
etchant	$HF:H_2O_2:H_2O$ =1:1:10	$SiCl_4/CF_4$, CH_4
etch rate	125 Å/sec	435 Å/sec
defects	under-over etching, hazardous solvents	corrosive gases

2. EXPERIMENTAL

The experiments were conducted using pulsed type KrF excimer laser (λ =248 nm), with a pulse duration of 23 ns (full width at half maximum) and a pulse repetition rate of f=30 Hz. Its maximum pulse energy is 300mJ. It could be varied continuously by changing the applied voltage. The laser beam was focused using a lens with focal length of 230 mm made of BK7. The ITO films used in this study are commercial available samples with thickness of 150 or 200 nm sputter deposited on a lime glass substrate. The glass used for substrate is all but opaque, so that it was not possible to ablate the ITO film by irradiation through the substrate. Fig. 2 shows a schematic diagram of experimental system to pattern ITO, which is mounted onto a vibration isolation optical table.

Investigations by XPS (X-ray Photo-Electron Spectroscopy) gave information on the relative chemical composition of In, Sn, O and C before and after laser irradiation. An observation by optical microscope is used for monitoring and finding the threshold fluence for ablating the transparent conductive thin films. AFM (Atomic Force Microscopy) measurements show surface roughness image. And Experiments to form some specific appearances are conducted after making aluminum mask using second harmonic Nd:YAG laser.

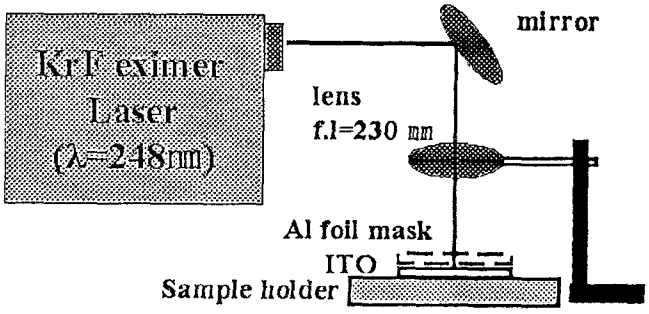

Fig. 2. A schematic diagram of experimental system.

3. RESULTS AND DISCUSSIONS

Experiments to find the ablation threshold laser fluence were conducted with directly irradiating the laser light on the sample surface using KrF excimer laser (λ =248 nm). The optical bandgap of ITO and the photon energy of the excimer laser are approximately 3.75 eV and 5 eV ($E_g = \lambda$ [μm]/1.24) respectively. In the IR, for example, the ITO films absorb about 20% of the incident laser light and the glass substrate is completely transparent. In the UV, on the other hand, the ITO film absorbs about 80% of the incident laser light [8] and in addition, the glass substrate is completely opaque. Fig 3 shows an optical micrographs of stationary ablated surface on ITO in the vicinity of the ablation threshold laser fluence, which is around 0.1 J/cm^2.

The unique characteristics of ITO film, high conductivity and high transmittance in the range of visible region, are influenced by a number of effects, which include surface roughness and optical inhomogeneity. We found that ITO decomposed or damaged, became opaque and its surface came to be very rough. In addition, the color of the laser-irradiated surface was changed to dark brown due to increase of surface roughness and transformation of chemical composition by the laser light. Furthermore, the conductivity of the laser-irradiated surface, albeit

slightly, was zero. And the transmittance of ITO film goes down drastically to zero in the laser-irradiated surface and it becomes opaque.

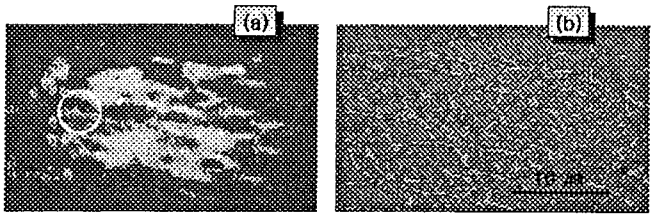

Fig. 3. (a) Optical microscope graphs of laser-irradiated ITO surface in the vicinity of the threshold laser fluence, and (b) enlarged view of circle part of (a). F=0.11 J/㎠.

Before this experiment, we expected that the threshold value of ITO would be smaller than 0.6 J/㎠. And it is that of ITO in case of using 3rd harmonic Nd:YAG laser (λ=354 ㎚)[9]. It is explained that the ablation characteristics of ITO thin films shows dependence on the laser wavelength used, in other words, the magnitude of photon energy. In the UV regions, the ITO film absorbs about 80% of the incident laser light. So the films are easily influenced even by the laser fluence of very small amount. In general, when UV energy, in this case from a UV laser, is observed by the surface of a solid, the electromagnetic energy of the laser light is converted to mechanical, thermal, chemical, and electronic energy. And the resulting ejected ablative debris, in the form of a plume including atoms, molecules, ions, photons, electrons, and agglomerations or fragments of the laser-irradiated material.

We note first that adventitious organic carbon contamination present on all the ITO surfaces, irrespective of laser treatment. The reference ITO surface (original unexposed sample) showed a strong O(1s) peak at 530.6±0.1 eV(inorganic oxides) and a second O(1s) peak at 531±0.1 eV, and C(1s) peak at 278.3, 281, 284,8 and 286 eV and so on. The C(1s) peaks indicate organic contamination. Furthermore, the presence of strong carbon and oxygen signals in the ablated surfaces implies that the ablation is also caused by a thermal reaction due to temperature rise on the laser-irradiated local area. Fig. 4 and Fig. 5 show C(1s) XPS graph of the laser-irradiated ITO surface and reference one and surface morphology by AFM images, respectively. It is reported that thermal effect dominates the irradiation process at an extremely low or high fluence in case of polymer ablation[10]. Similar to this report, it is thought that the ablation of ITO is mainly caused by a thermal effect. But in the vicinity of threshold laser fluence, surface transformation such as broken ionic bonding structure and formation of larger fragments can be generated by the high photon energy.

Table 2 shows the change of atomic percentages for each component as the XPS result in the KrF excimer laser-irradiated ITO surface. This analysis indicate that relative surface concentration of Sn and In was essentially unchanged (In:Sn 5:1) by the laser irradiation. And the $In3d_{5/2}$ peak shown at 444.9 eV of original unexposed ITO surface was shifted to 444.1 eV at the laser-irradiated surface. And it means that the majority of $In3d_{5/2}$ peak consisting of In^{3+} bonding state from In_2O_3 was changed into the In^0 bonding state from In-In bonds even though multiple components maybe existed at both bonding states. Also in case of Sn, SnO_2 peak at 486.7 eV of reference ITO sample was shifted to 486 eV at the laser-irradiated surface. So we can induce through those XPS analysis that lots of In-O and Sn-O bonding were broken after laser irradiation.

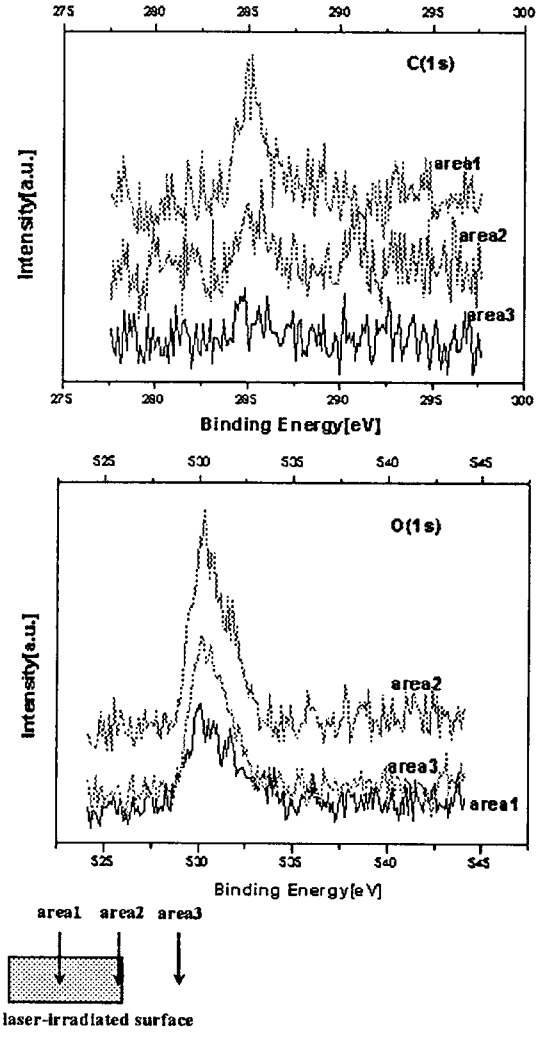

Fig. 4. C(1s) and O(1s) XPS analysis of reference ITO sample (area3), the center of laser irradiated surface (area1) and the edge of the surface (area2). F=0.42 J/㎠.

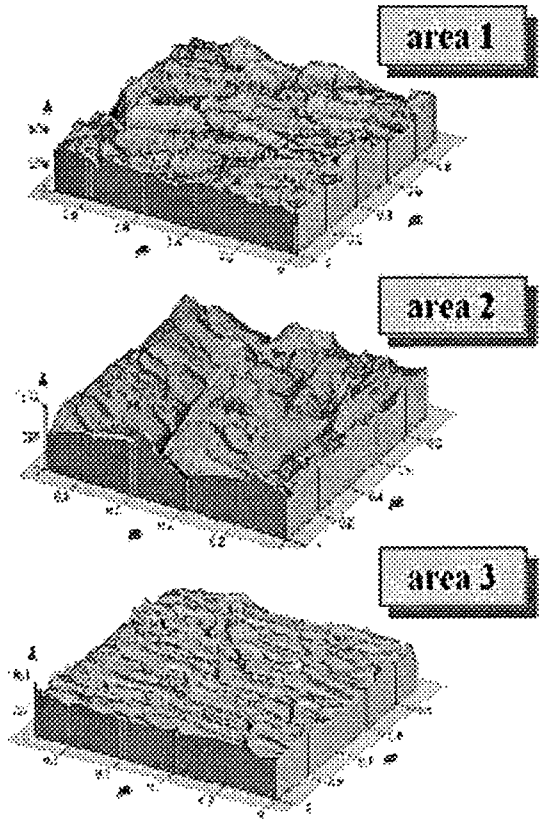

Fig. 5. The surface morphology of reference ITO sample, the center of laser irradiated surface and the edge of the surface. F=0.42 J/㎠.

Table 2. Atomic percentages of each component as the XPS result in the KrF excimer laser-irradiated ITO surface. F=0.42 J/㎠.

atomic(%)	area1	area2	area3
O(1s)	53.9	41.3	38.6
$In3d_{5/2}$	30.8	30.4	30.6
C(1s)	8.5	21.7	23.9
$Sn3d_{5/2}$	6.8	6.6	6.9

Fig. 6 is an optical microscope view of laser-irradiated ITO surface. This image shows the surface color change after laser irradiation. Even though the laser fluence is near about the threshold one, strong absorption of the laser light by ITO surface and underlying glass substrate makes it possible for the laser-irradiated surface to be melted and re-solidified. This melting and fast re-solidification of an ITO film, induced by pulsed laser heating, form residual fragments or agglomerations on the surface, which increase surface roughness and change the surface color.

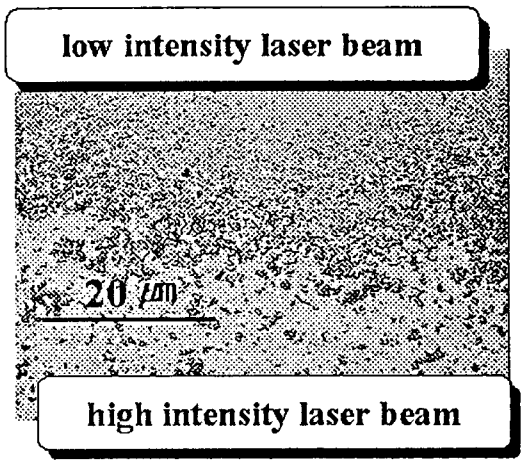

Fig. 6. An optical microscope view of laser-irradiated ITO surface. This image shows the surface color change after laser irradiation. F=0.15 J/㎠.

Fig. 7 shows SEM images of laser-irradiated surface at different laser beam incident position. At the relatively low laser fluence (3), the laser-irradiated ITO surface was hardly ablated compared to the other one. In this figure, the relatively weak ionic bonding consisting of the material, especially point defects generated during formation of In_2O_3, seems to be broken because of high photon energy of KrF excimer laser. These ultraviolet photons (=5 eV) interact slightly with the materials. But the incident energy is not sufficient for complete ablation of ITO. At the center of laser-irradiated surface (1), the ITO was nearly ablated. The photon absorption causes electronic (vibrational and rotational) excitation within the molecule of the material being exposed to the laser beam. Sufficient incident output energy will overcome the bonding energy of the molecule, rupturing the molecule into atomic, molecular, and larger fragments or agglomerations. In this experiment, the laser beam was fixed at the above of the ablative material. If the laser beam with high repetition rate (generally above 10 Hz)is scanned over the material, these different ablated shapes at the same output energy will not be shown. In our former experiment using 2nd (λ=266 ㎚) and 4th harmonic Nd:YAG laser (λ=266 ㎚), these shapes were not appeared. And the patterned lines were almost clean even though by-product exists in the vicinity of the ablated surface region.

Fig. 8 shows SEM and optical microscope image of patterned ITO. We first produced gear-shaped aluminum foil mask using 2nd harmonic continuous wave Nd:YAG laser with high power intensity. As seen in this figure, the ITO is well patterned by KrF excimer laser. In this

case, ITO and Al foil mask is attached tightly.

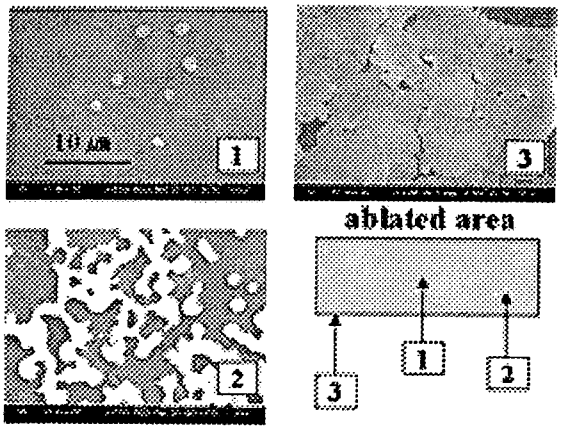

Fig. 7. SEM views of laser-irradiated surface at different incident position. F=0.42 J/㎠.

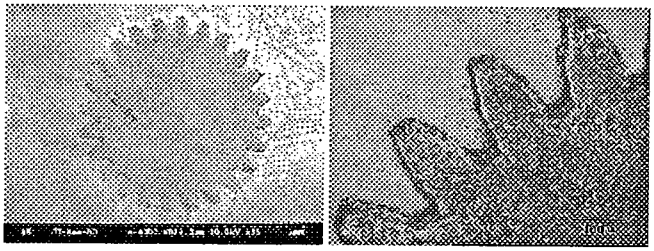

Fig. 8. SEM and optical microscope views of ITO patterned by excimer laser using gear-shaped Al foil mask. F=0.25 J/㎠

4. CONCLUSIONS

We tried to find the ablation threshold laser fluence to etch an ITO thin film of transparent conductive oxides and its value is about 0.1 J/㎠. ITO decomposed or damaged by laser irradiation became opaque, and its surface became very rough and the ITO film lost its natural characteristics after laser irradiation even though its magnitude was near the threshold laser fluence. In addition, the color of the laser-irradiated surface was changed to dark brown in the result of measurement by optical microscope. The XPS results show the presence of relatively strong carbon and oxygen signals in the ablated surfaces. It means that the ITO ablation is also caused by a thermal reaction due to temperature rise on the local irradiated area. It is thought that the ablation of ITO is mainly caused by a thermal effect due to temperature rise. But the ablation of ITO in the vicinity of threshold laser fluence is mostly influenced, forming large fragments, by high photon energy of the laser beam. Some patterning experiments were conducted using aluminum foil mask for device manufacturing application. The ITO is well patterned by KrF excimer laser.

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REFERENCES

[1] K.H. Maeng, "The fabrication of ITO/p-InP solar cells", *Journal of KIEEME*, Vol. 7, No. 3, p. 243, 1994.

[2] H.J. Ha, "The study on formation of ITO by DC reactive magnetron sputtering", *Journal of KIEEME*, Vol. 8, No. 6, p. 699, 1995.

[3] H. Kim, "Electrical and optical properties of indium tin oxide thin films grown by pulsed laser deposition", *Appl. Phys*, A69[Suppl.], S447, 1999.

[4] J.S. Kim, " X-ray photoelectron spectroscopy of surface-treated indium-tin oxide thin films", *Chem. Phys. Lett.*, Vol. 315, p. 307, 1999.

[5] Furong Zhu, "Optimized indium tin oxide contact for organic light emitting diode application", *Thin Solid Fims*, Vol. 363, p. 314, 2000.

[6] C.M. Hockensmith, "Thermal studies of new precursors to indium-tin oxides for use as sensor materials in the detection of Nox", *Thermochimica Acta*, Vol. 340-341, p. 315, 1999.

[7] C. Nunes de Carvalho, "Effect of substrate temperature on the surface structure, composition and morphology of indium-tin oxide films", *Surface and Coatings Technology*, Vol. 124, p. 70, 2000.

[8] O. Yavas, "Effect of substrate absorption on the efficiency of laser patterning of indium tin oxide thin films", *Journal of Applied Physics*, Vol. 85, No. 8, p. 4207, 1999.

[9] B. Thestrup, "Transparent conducting AZO and ITO films produced by pulsed laser ablation at 355 ㎚", *Appl. Phys.* A69, S807, 1999.

[10] C. Lee, " Etching of the PDP barrier rib material using laser beam", *The journal of the KIEEME*, Vol. 13, No. 6, p. 526, 2000.