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KrF 엑시머 레이저에 의한 ITO 박막의 어블레이션과 표면특성관찰

The ablation of ITO thin films by KrF Eximer laser and its characteristics

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Abstract

This work aimed to develop ITO (Indium Tin Oxide) thin films ablation with a KrF Eximer laser required for the application in flat panel display, especially patterning 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 using third harmonic Nd:YAG laser. Through the optical microscope measurement the surface color of the damaged ITO is changed into dark brown and the irradiated spot is completely isolated from the undamaged surroundings by laser light. The XPS analysis showed that the relative surface concentration of Sn and In were essentially unchanged (In:Sn=5:1) after irradiating Eximer laser. Using aluminum mask made by second harmonic Nd:YAG laser the ITO patterning is carried out.

Key Wards(중요용어) : **ITO, KrF Eximer laser, flat panel display, ablation threshold, surface**

1. Introduction

ITO films have high luminous transmittance, high infrared reflectance, good electrical conductivity, excellent adherence, hardness and chemical inertness and therefore, have been widely and intensively studied for many years.[1-2]

ITO thin films are wide-bandgap, 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 In3+ 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.

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, indium tin oxide (ITO) 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

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solar cells and OELD(organic electro-luminescence device).[3-4]

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 defects such as under- and over-etching, consumption of hazardous solvents and corrosive gases related to environmental matters. Table 1 shows the conventional etching methods of ITO.

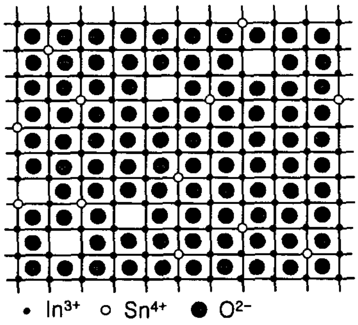

Fig. 1 A schematic diagram of ITO ionic structure. two different types of O^{2-} lattice ions located in the different regions are shown.

Alternatively, the study on the efficiency of laser patterning of ITO using different harmonics of a diode-pumped Q-switched neodymium-doped yttrium lithium fluoride (Nd:YLF) laser has been reported to make clean-cut lines. Also, by a fourth harmonic of the Nd:YLF laser(=262nm) 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.[5]

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	125Å/sec	435Å/sec
defect	under- over etching hazardous solvents	corrosive gases

In this work, we tried to find the ablation threshold fluence of ITO using KrF eximer laser (λ=248nm) with expecting the value to be below 0.6 J/cm², which is a threshold fluence of ITO in case of using 3rd harmonic Nd:YAG laser.

2. Experimental

The experiments were conducted using pulsed type ArF Eximer laser(λ=248nm), with a pulse duration of 23ns (full width at half maximum) and a pulse repetition rate of f=30ns. 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 230mm made of BK7. The ITO films used in this study are commercial available samples with thickness of 150 or 200nm sputter deposited on a lime glass substrate. Fig. 2 shows a schematic diagram of experimental system to pattern ITO.

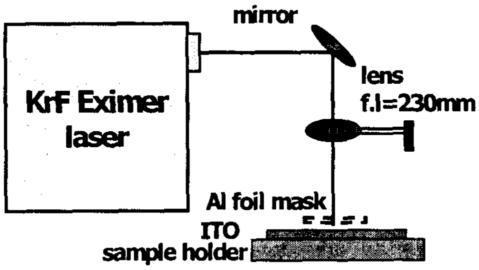

Fig. 2 A schematic diagram of experimental system

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. 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 is conducted after making aluminum mask using second harmonic Nd:YAG laser.

3. Results and Discussion

Experiments to find the ablation threshold laser fluence were conducted with directly irradiating on the sample surface KrF Eximer laser(λ =248㎚). The optical bandgap of ITO and the photon energy of the Eximer laser are approximately 3.75 eV and 5 eV (E_g= λ [㎛]/1.24) respectively. In the IR, for example, the ITO films absorbs 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[5] and in addition, the glass substrate is completely opaque. Fig 3 shows an optical micrograph of stationary etched surface on ITO in the vicinity of the ablation threshold laser fluence, which is around 0.1 J/㎠. The unique characteristics of ITO film, high conductivity and high transmittance in the range of visible region, is severely influenced by a number of minor effects which include surface roughness and optical inhomogeneity. We found that ITO decomposed or damaged, became opaque and its surface come to be very rough. In addition, the color of the laser irradiated surface was changed to dark brown in the result of measurement by optical microscope. Furthermore, the conductivity of the damaged surface, albeit slightly, was zero. And the transmittance of ITO film go down drastically to zero in the laser irradiated surface and it become opaque.

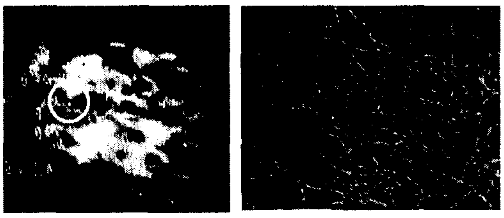

Fig. 3 (a)An optical microscope graphs of laser irradiated ITO surface in the vicinity of the threshold laser fluence and (b) enlarged view of circle part of (a). F=0.11 J/㎠

Before this experiment, we expected that the threshold value of ITO will be smaller than 0.6 J/㎠, which is that of ITO in case of using third harmonic Nd:YAG laser(λ =354㎚).[6] It is explained that the etching characteristics of ITO thin films shows dependence on the laser wavelength used, in other words, the magnitude of photon energy.[5] In the UV regions, the ITO film absorbs about 80% of the incident laser light. So the films is easily influenced by the laser fluence of very small amount.

We note first that adventitious organic carbon contamination is present on all the ITO surfaces , irrespective of laser treatment. The undamaged ITO surface 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 etched surfaces implies that etching is also caused by a thermal reaction due to temperature rise on the irradiated local area. Fig. 4 shows C(1s) XPS graph of laser irradiated ITO surface and virgin one. It is reported that thermal effect dominates the irradiation process at an extremely low or high fluence in case of polymer ablation. Similar to this report, it is thought that the ablation of ITO in the vicinity of threshold laser fluence is mainly caused by a thermal effect.

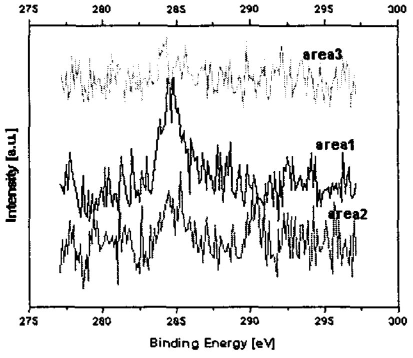

Fig. 4 shows C(1s) XPS analysis of untreated ITO surface(area3), the center of laser irradiated area(area1) and at edge of the laser irradiated area(area2). F=0.42 J/㎠

The XPS analysis showed that relative surface concentration of Sn and In were essentially unchanged (In:Sn≈5:1) by Eximer laser irradiation. And the $In3d_{5/2}$ peak shown at 444.9 eV of untreated ITO surface was shifted to 444.1 eV at the irradiated surface. And it means that the majority of $In3d_{5/2}$ peak consisting of In^{3+} bonding state from In_2O_3 were changed into the In^0 bonding state.

Table 2. Atomic percentages of each component for the XPS in the laser irradiated ITO area, the edge of the area and untreated surface.

atomic(%)	area 1	area 2	area 3
O1s	53.9	41.3	38.6
$In3d_{5/2}$	30.8	30.4	30.6
C1s	8.5	21.7	23.9
$Sn3d_{5/2}$	6.8	6.6	6.9

Fig. 5 shows an optical microscope image of patterned ITO. We first produced gear-shaped aluminum masks using second harmonic continuous wave Nd:YAG laser(λ=532㎚) with high power intensity. As seen in this figure, the ITO is well patterned by KrF Eximer laser.

Fig. 5 An optical microscope top view of ITO patterned by Eximer laser using gear-shaped aluminum mask made by second harmonic Nd:YAG laser. F=0.25 J/㎠

4. conclusion

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 is near the threshold laser fluence. In addition to, 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 strong carbon and oxygen signals in the etched surfaces. It means that the ITO etching is also caused by a thermal reaction due to temperature rise on the local irradiated area. So the ablation of ITO in the vicinity of threshold laser fluence is mainly caused by a thermal effect. Some patterning experiments were conducted using aluminum foil mask for device manufacturing application. The ITO is well patterned by KrF Eximer laser.

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