Absorption Measurement of Sputtered Atom Density during ICP-Assisted Sputter-Deposition of Al-doped ZnO Thin Films

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Abstract: Deposition of transparent conducting aluminum-doped zinc oxide (AZO) films using inductively coupled plasma (ICP) assisted sputtering has been investigated. The metal atom densities were measured by absorption spectroscopy using two different absorption systems: one consists of a hollow cathode lamp (HCL), monochromator and photomultiplier tube (HCL-M-PMT) and the other consists of a light emitting diode (LED), spectrometer, and CCD detector (LED-S-CCD). Measured density ratio of Al to Zn atom density during ICP assisted sputtering with AZO target using HCL-M-PMT was estimated to be two orders of magnitude smaller than the elemental ratio in both the AZO target and deposited films. The evaluated absolute Al density was confirmed to be highly reliable, since both Al densities measured with HCL-M-PMT and LED-S-CCD agreed well in a DC planar magnetron discharge with Al target.

Keywords: Sputtering, zinc oxide, ICP, transparent conductive films, absorption spectroscopy

1. Introduction

Transparent conducting oxide (TCO) films have been widely used as transparent conducting electrodes of various optoelectronic devices such as solar cells, flat panel displays, etc. Some TCO materials such as tin oxide and indium oxide have already been put to practical use in industry. In particular, tin-doped indium oxide (ITO) has been mainly used so far due to its high transmittance in the visible region, high chemical stability and low resistivity. For the last ten years, however, aluminum-doped zinc oxide (AZO) received attention as one of the alternatives to the ITO. Though the AZO has lower inherent electric conductivity than ITO, it has advantages over ITO in environment resistance and resource cost.

To actually replace ITO with AZO, however, a reproducible and highly-reliable fabrication process of good quality AZO thin films has to be developed. Thus, we have been investigating AZO film deposition process by using inductively coupled plasma (ICP) assisted sputtering. [1-6] The advantages of ICP-assisted sputtering are as follows: 1) the target is sputtered with low target voltage and high target current, 2) the usage efficiency of the target is much improved due to the expansion of erosion area, 3) ionization and excitation of the sputtered particles are enhanced in the ICP and the enhanced ion fluxes to the substrate promote the crystallinity of thin films without intentional substrate heating, and 4) lateral homogeneity of the deposited film is much improved. In fact, we have succeeded in depositing high quality AZO thin films with resistivity of around 10³Ωcm by using this technique so far. [7, 8]

To obtain better quality AZO thin films, it is essential to understand the fundamental plasma surface interaction in this process. For the purpose of estimating the particle flux to the substrate, we have measured metal atom densities by absorption spectroscopy using two different absorption systems: one consists of a hollow cathode lamp (HCL), monochromator and photomultiplier tube (HCL-M-PMT) and the other consists of a light emitting diode (LED), spectrometer, and CCD detector (LED-S-CCD). This paper describes the theoretical calculation of experimental absorbance against optical thickness and the experimental determination of metal atom density for both absorption systems.

2. Principles of Absorption Spectroscopy

In this work, densities of Al atoms and Zn atoms were measured by HCL-M-PMT and LED-S-CCD absorption spectroscopy. Principle of this technique is briefly summarized here. Integral of absorption coefficient profile \( k(\nu) \) over the entire frequency range is theoretically given by the following equation

\[
\int k(\nu)d\nu = \frac{\lambda^2 g_u A N}{8\pi g_i} \tag{1}
\]

where \( \lambda \) is the wavelength of absorption line, \( g_u \) and \( g_i \) : statistical weights of upper and lower levels, \( A \): transition probability, and \( N \): number density of absorber. Absorbance \( \alpha \) is experimentally determined by incident power \( I_{in} \) and transmitted power \( I_{out} \) and is given by

\[
\alpha = \frac{I_{in} - I_{out}}{I_{in}} = 1 - \frac{\int f_s(\nu)\exp[-k_0 f_s(\nu)]d\nu}{\int f_s(\nu)d\nu} \tag{2}
\]

where \( f_s(\nu) \) and \( f(\nu) \) are line profiles of light source and absorber, \( k_0 \): absorption coefficient at line center,
i.e., \( k(\nu) = k_0 f_\nu(\nu) \).

When using HCL-M-PMT in low pressure sputtering condition, line profiles are approximated by Gaussian form with Doppler width \( \Delta \nu_D \).

On the other hand, when using LED-S-CCD, absorbance \( \alpha \) is given by

\[
\alpha = 1 - \frac{1}{A} \int_{\nu_0}^{\nu_f} \exp[-k_0 f_\nu(\nu)] d\nu
\]

by setting \( f_\nu(\nu) \) of Eq. (2) is constant, since LED has continuous spectrum. Here, \( \Delta \nu_D \) is the bandwidth of spectrometer.

Fig.1 shows the calculated results of absorbance \( \alpha \) against the target plasma’s optical thickness \( k_0 l \), for HCL-M-PMT and LED-S-CCD (\( \Delta \nu_D = 0.15 \)nm). The absorbance for LED-S-CCD was two orders of magnitude smaller than that for HCL-M-PMT, but the measurable density range was evaluated to be almost the same because the signal-to-noise ratio of LED-S-CCD is two orders of magnitude better than that of HCL-M-PMT.

### 3. Experimental

The experimental setup of HCL-M-PMT is shown in Fig.2. A vacuum chamber attached with a 3 inch DC planar magnetron, argon gas supply system, and pumping system (turbo molecular pump and rotary pump combination) was used in the experiment. A disk target of ZnO: Al\(_2\)O\(_3\) (2wt%) of 60 mm diameter and 6mm thick was used as target, and glass substrates were set on an earthed substrate holder with a gap length of 80 mm. A single turn coil antenna of 100 mm diameter was installed between these electrodes, and used for the production of 13.56MHz inductively coupled plasma. The antenna was covered with insulator and water-cooled. The distance from the target to the RF coil and the distance from the RF coil to the substrate were set both 40mm.

For the measurement of sputtered Al and Zn atoms from the AZO target, absorption measurement has been done by using HCL-M-PMT. [9] Optical emission from a HCL (Hamamatsu Photonics, L233-30NQ (Zn) or L233-13NB (Al)) was chopped by an optical chopper (NF, 5584A), and guided to a monochromator (JASCO, CT25) through the ICP-assisted sputtering chamber by lens, prism and optical fiber optics. The time modulated output signal from the PMT was monitored and averaged for 1024 times on a digital oscilloscope. By comparing the difference in the modulated amplitude of PMT output between plasma ON and OFF phases, absorbance was measured. The sputtered atom density was obtained by comparing the experimental absorbance and the theoretical absorbance that was calculated using assumed gas temperatures (400K) in light source and plasma reactor and assumed optical path length (0.3m). The absorption measurements were done for Zn with 307.6 nm (\( 3s^2 3p^2 4s^2 1S_0 - 4s^2 1s^2 3p^4 1D_2 \)) and for Al with 396.15 nm (\( 3s^2 3p^2 4s^2 1S_0 - 3s^2 4s^2 2S_1 \)), respectively.

ICP RF power dependence of Al and Zn atom densities was investigated. In the experiments, ICP RF power (= input power to the ICP coil) was varied 0-300W, and the target discharge power (= input power to the planar magnetron) and argon gas pressure were kept constant at 40W and 30mTorr, respectively.

The experimental setup of LED-S-CCD is shown in Fig.3. Absorption measurement of Al atoms was done by using LED-S-CCD in a DC planar magnetron discharge with Al target at 2Pa. The absorption measurements were done for Al with 394.0 nm (\( 3s^2 3p^2 \ 3^2P_{3/2} - 3s^2 4s^2 2S_{1/2} \)) and 396.15 nm (\( 3s^2 3p^2 \ 3^2P_{3/2} - 3s^2 4s^2 2S_{1/2} \)).

Optical emission from a LED (THORLABS, LED405E Ultra Bright Violet LED) was guided to a...
spectrometer with CCD (SpeX, SPEX270M) through the sputtering chamber by lens, prism and optical fiber optics. The transmitted continuous spectrum was obtained by multichannel measurement. As shown in Table 1, four combinatorial states of LED and plasma were arranged and the signal obtained for each state was named from $I_1$ to $I_4$. Absorption spectrum can be obtained by $A = (I_1 - I_2) / (I_3 - I_4)$.

Table 1. Four combinatorial states of LED and plasma

<table>
<thead>
<tr>
<th>Signal</th>
<th>$I_1$</th>
<th>$I_2$</th>
<th>$I_3$</th>
<th>$I_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LED</td>
<td>On</td>
<td>On</td>
<td>Off</td>
<td>Off</td>
</tr>
<tr>
<td>Plasma</td>
<td>On</td>
<td>Off</td>
<td>On</td>
<td>Off</td>
</tr>
</tbody>
</table>

4. Results and Discussion

4.1 Absorption spectroscopy using HCL-M-PMT

As we have described in the experimental section, number densities of sputtered atoms (Al and Zn) were measured by absorption spectroscopy using HCL-M-PMT. Fig. 4 shows the experimental result for ICP RF power dependence of metal atom densities in gas phase. Both Zn and Al atom densities increases with increasing ICP RF power, but there is a difference in the ICP RF power dependence between Zn and Al atom densities. Al atom density monotonously increases with increasing ICP RF power, while Zn atom density increases 4 times with increasing ICP RF power from 0 to 100 W, then saturates for ICP RF power more than 100 W.

Fig. 5 shows ICP RF power dependence of elemental ratio of Al in the film and resistivity. The former was obtained from the XPS analysis of Al 2p signal. With increasing ICP RF power, the elemental ratio of Al in the film increases. Accordingly, the resistivity decreases as shown in Fig. 5. The ICP RF power dependence of elemental ratio of Al in the film seems to be in agreement with the dependence of relative density of Al to Zn atoms in gas phase as shown in Fig. 4. However, the absolute density ratio of Al to Zn in the gas phase was estimated to be two orders of magnitude smaller than the elemental ratio in both the AZO target and deposited films. The cause of such a large gas-phase Zn atom density is unclear, but is possibly due to the re-evaporation or the re-sputtering of Zn atoms from inside the chamber, or the overlapping of OH absorption.

4.2 Absorption spectroscopy using LED-S-CCD

Absorption measurement of Al atoms was done by using LED-S-CCD in a DC planar magnetron discharge with Al target. An example of the results is shown in Fig. 6, indicating clear absorption lines at 394.40nm and 396.15nm of Al. The experimental absorbance using LED-S-CCD was two order of magnitude smaller than that using HCL-M-PMT under the same conditions.

Fig. 7 shows discharge power dependence of sputtered Al atom density using HCL-M-PMT and LED-S-CCD during magnetron sputtering. Both Al densities measured with HCL-M-PMT and
LED-S-CCD agreed well. Thus, the evaluated absolute Al density was confirmed to be highly reliable.

5. Conclusion

We have measured metal atom densities by absorption spectroscopy using HCL-M-PMT and LED-S-CCD, and evaluated the reliability of measurements.

Both Zn and Al atom densities increases with increasing ICP RF power, and the ICP RF power dependence of relative density of Al to Zn atoms in gas phase was in qualitative agreement with that of elemental ratio of Al to Zn in the film. However, the absolute density ratio of Al to Zn in the gas phase was estimated to be two orders of magnitude smaller than the elemental ratio in both the AZO target and deposited films.

The evaluated absolute Al density was confirmed to be highly reliable, since both Al densities measured with HCL-M-PMT and LED-S-CCD agreed well in a DC planar magnetron discharge with Al target.

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