Diagnostic Study of ICP Assisted Sputter-Deposition of Al-doped ZnO Thin Films

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Abstract: Inductively coupled plasma assisted magnetron sputtering has been applied for the deposition of transparent conducting aluminum-doped zinc oxide (AZO), and good quality AZO thin films with high transmittance of more than 90% and low resistivity of around $10^{-3} \Omega \text{cm}$ have been deposited so far. Plasma diagnostic systems for the investigation of this process and the preliminary experimental results are reported.

Keywords: Sputtering, zinc oxide, ICP, transparent conductive films, plasma diagnostics

1. Introduction

Transparent conducting oxide films have been widely used as transparent conducting electrodes of various optoelectronic devices such as solar cells, flat panel displays, etc. Tin-doped Indium oxide (ITO) film has been mainly used so far due to high transmittance in the visible region, high chemical stability and low resistivity. For the last ten years, however, aluminum-doped zinc oxide (AZO) has been a focus of attention as a transparent conducting material that takes the place of ITO. The inherent electric conductivity of AZO is lower than that of ITO, but the former has advantages over ITO in environment resistance and resource cost.

To replace ITO with AZO, a reproducible and highly-reliable fabrication process of good quality AZO thin films has to be developed. We have been investigating AZO film deposition process by using inductively coupled plasma (ICP) assisted sputtering. [1-6] In the process of ICP-assisted sputter-deposition, we can expect that the sputtered particles are efficiently ionized, and the enhanced ion fluxes are efficiently transported to substrate; thus, the ion fluxes with moderate ion energy onto the substrates would contribute to the decrease in surface roughness and promote the crystallinity of thin films without substrate heating. In fact, we have succeeded in depositing high quality AZO thin films with resistivity of around $10^{-3} \Omega \text{cm}$ by using this technique so far.[7,8]

To understand the fundamental plasma surface interactions in this process, plasma diagnostics are very important. Thus, we have recently constructed several diagnostic systems such as absorption spectroscopic system for measuring number densities of neutral species, thermal probe system for measuring heat flux onto the substrate, optical reflectance interferometer system for the in-situ monitoring of depositing films, and high speed camera system for monitoring arcing which sometimes occurs at high target input power condition without ICP. This paper reports the outlines of these diagnostics.

2. ICP-Assisted Sputtering of AZO Target

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: Al2O3 (2wt%) of 60 mm diameter and 6mm thick was used as target, and glass substrates were set on a 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.

3. Absorption Spectroscopy of Sputtered Atoms

For the measurement of sputtered aluminum (Al) and zinc (Zn) atoms from the AZO target, absorption measurement has been done by using a hollow cathode lamp (HCDL). The experimental setup is shown in Fig.1. Optical emission from a HCDL (Hamamatsu Photonics, L233-30NQ(Zn) or L233-13NB(Al)) was chopped by an optical chopper (NF, 5584A), and guided to the monochromator (JASCO, CT25) through the ICP-assisted sputtering chamber by lens, prism and optical fiber optics. The time modulated output signal from the photomultiplier tube (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 in light source and plasma reactor and assumed optical path length (0.3m). In the experiment, absorption measurements were done for Zn with 307.6 nm (4s^2 1S_0-4s5p
and for Al with 396.15 nm (3s^2 3p^2 3P_3/2 - 3s^2 3s 2S_1/2), respectively. It is noted that the ground state of Al atom is composed of two sublevels, and the measured Al level (3P_3/2) is 112cm^{-1} high from the lowest level (3P_{1/2}). Thus, the Al atom density measured here is considered to be about 50-70% of the total ground state Al density.

Fig. 2 shows the DC sputtering power dependence of Al and Zn atom densities for the condition of ICP-RF assist power of 0W at the working pressure of 30 mTorr. Both Zn and Al densities increase with increasing sputtering power, but there is a difference in the sputtering power dependence. It is also noted that the Zn density is 10^{11}-10^{13}cm^{-3}, while the Al density is 10^8-10^9cm^{-3}. This difference is not consistent with the difference in element ratio in the AZO target (100:4). The reasons are not yet clear, but it may be due to the difference in the free energy for oxide formation. The free energy for oxide formation of Aluminum oxide is 1580\times 10^{-6} Jkg^{-1}mol^{-1}, which is much larger than that of zinc oxide (318.4\times 10^{-6} Jkg^{-1}mol^{-1}). This suggest that the sputtering rate of Zn atom is much larger than that of Al atom from AZO target.

Figure 3 shows the ICP-RF assist power dependence of sputtered Zn atom density. With increasing ICP-RF power, Zn density abruptly increased for ICP-RF power less than 100W, then saturated and gradually decreased for ICP-RF power more than 100W. The initial steep increase of Zn density is possibly due to the increase in sputtering area on the AZO target surface. For the case of conventional planar magnetron sputtering without ICP assist, sputtering occurs predominantly in the erosion area. For the case of ICP assist, on the other hand, high density ICP spreads out over the doughnut-shaped planar magnetron plasma. Thus, eroded area is expanded to the all target surface, while the target current is increased and the target voltage is decreased. In addition to this effect, dissociation of sputtered zinc oxide can be enhanced. We speculate the cause of gradual decrease in Zn density for higher ICP-RF power is possibly due to the further ionization of dissociated Zn atoms. We have also investigated the ICP-RF power dependence of Al atom density, but the behavior was different from that of Zn atoms. Detailed results will be reported in near future.

4. Heat Flux Measurement by Thermal Probe
To investigate the effect of ICP assist on the AZO deposition process, determination of heat flux onto the substrate is important. Two different thermal probe systems have been constructed to observe the heat flux onto the substrate. The one is a heat flux probe in which the heat flux is directly obtained from the temperature difference between two different locations on a stainless rod of by using two thermocouples.[10] The stainless steel rod is covered with heat insulation materials. The other is a...
small heat capacity probe in which power flux is obtained by measuring the temporal change of probe temperature.[11,12]

Preliminary bench mark test was done with type 1 thermal probe (6mm in diameter, 300mm long stainless rod). The end of the probe was water cooled and the other end surface of the probe was set about 10cm from ICP antenna. An example of the experimental result obtained during on and off period of 100W ICP at 5mTorr with prototype thermal probe is shown in Fig.4. From a temperature difference at the thermally stationary condition, overall heat flux was estimated to be 0.1Wcm^{-2}. This value is consistent with previously reported values,[12] but we need to upgrade the probe in order to reduce the thermal time constant by two or three order of magnitude. This improvement is under way.

5. Optical Reflectance Interferometry

In-situ monitoring of deposition rate of thin films is beneficial for simultaneous monitoring of plasma and thin films growth processes. It will be useful to establish an inexpensive and handy in-situ monitoring method. For the purpose, we have focused attention on the optical reflectance interference [13] using a small power laser. For the benchmark test, we have investigated the reflectance interference signal during CVD process of hydrocarbon thin films in Ar/CH_{4} ICP and its removal process in Ar/O_{2} ICP.

To monitor the reflectance interference, He-Ne laser or diode laser beam was incident onto a polished surface of Si (001) substrate. Both the incidence and reflection angles were about 5 degrees; thus, the geometry is approximated to vertical incidence. Reflected beam was focused by a lens on the sensing area of a photodiode detector. Temporal change of the photodiode output due to the reflectance interference was monitored by a digital tester and the temporal waveform was displayed and recorded on a PC. The experimental setup is shown in Fig.5.

As a result, a clear interference was observed in the reflected beam intensity as shown in Fig.6. From the temporal evolution of the interference fringes, the change in the refractive index or the change in the deposition during deposition can be deduced. By once calibrating the real film thickness and refractive index in ex-situ ways, temporal changes in deposition rate and in refractive index can be followed in-situ. In the case of hydrocarbon thin films, we found that the change in refractive index was small compared with that of deposition rate during deposition and removal processes. The refractive index of the hydrocarbon films was 1.67-1.73 during the process, while the deposition rate was estimated to change by 30% depending on substrate temperature. This method can be applied for the AZO deposition process.
6. Arc Monitoring

Arcing (abnormal electrical discharge) to occur during deposition is a severe problem in sputtering. When the arcing occurs, target surface may melt and fly apart. It may change the thin film characteristics.[14,15] Especially, the arcing is easy to occur on AZO target than ITO target for the case of DC sputter-deposition without ICP assist. The arc sometimes occurs when the sputtering power density was too high, or the target voltage was too high, or the target surface was not smooth or not clean. Basic understanding of arc mechanism is important to suppress the arc. Thus, we have observed arc cathode spot in DC planar magnetron sputtering with a poisoning AZO target. By using a high speed camera and an arc counter, it was confirmed that the cathode spot moves in the opposite direction of \( j \times B \) (retrograde direction) as shown in Fig.7. Here, electrons are ejected and turns in the direction of \( E \times B \). As a result of investigation of the discharge power dependence of arc velocity as a parameter of working pressure, we found that the arc velocity was larger for higher pressure.

For the arc suppression, several ideas have been already proposed and applied practically, for example, such as bipolar pulsing, use of arc-suppression control of power supply with arc pre-sensing and rapid power cut. Improvement of target quality is also very important. In addition to these methods, however, we found that the ICP assist sputtering is very effective for suppressing arcing, since uniform sputtering of a target with low impedance sputtering discharge is realized there.

![Fig.7 Retrograde motion of arc cathode spot observed in a dc planar magnetron discharge with AZO target (5mTorr, 60W). The center magnetic pole is S, and the outside circle magnetic pole is N. Erosion area is a range of radius 8-23mm. The image was viewed from substrate side. In the case of ICP assisted sputtering, such the arcing did not occur.](image)

7. Conclusion

Several plasma diagnostic systems for the investigation of ICP assisted sputter-deposition process have been constructed. As a result of preliminary benchmark experiments, the effect of ICP assist on the sputter-deposition of AZO thin films has been gradually made clear. Further detailed measurements will provide many valuable insights on this process.

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