Structural, Electrical and Optical Characterization of Sputtered ZnOx Thin Film.

T.Nishihara*, N.Fujimura and T.Ito

*Student: University of Osaka Prefecture
Metallurgical Engineering, College of Engineering
University of Osaka Prefecture
Mozu-Umemachi, Sakai, Osaka 591 Japan

1. Introduction

As Zinc oxide films have many available characteristics, a large number of crystallographic studies have been reported on the films deposited by sputtering. However, most of those are about the influence of deposition conditions for (002) (c-axis) oriented films(1)-(2). The growing process of ZnOx films has not been necessarily manifested.

In this paper, the influence of deposition parameters on the (002) and (110) preferred orientation were evaluated about ZnOx films deposited by a rf magnetron sputtering. Moreover, the growing process of ZnOx films, the electrical and optical properties were investigated.

2. Experimental Procedure

ZnOx films were deposited by a rf magnetron sputtering method. A pressed disk of ZnO(99.0% ,Inc.Kishidakagaku) was used as the target. Corning 7059 was used as the substrates. The sputtering conditions were rf power of 100W and gas pressure of 6m Torr. The gas composition ($Ar:O_2$) was changed extensively(3)-(4). The structural change of prepared ZnOx films was evaluated by using X-ray Diffraction (XRD)(Shimazu XD-3A type), X-ray Photoelectron Spectroscopy (XPS)(Perkin-elmer PHI 5100). The electrical resistivity and the optical transmittance spectra in visible radiation were measured by using a conventional four probe system(Kyowariken K-705RD) and spectra photometer(Shimazu UU-265FS), respectively.

3. Results and Discussion

ZnOx films deposited on Corning 7059 without heating substrates were evaluated by X-ray diffraction. Figure 1 shows gas composition dependence on preferred orientation of films. The (002) or (110) oriented films were obtained by controlling gas compositions. Figure 2 shows the layered structure of ZnO, called wurtzite type. Only Zn or O atom exists in the each (002) plane, while, both Zn and O atoms exist in (110) plane alternately.

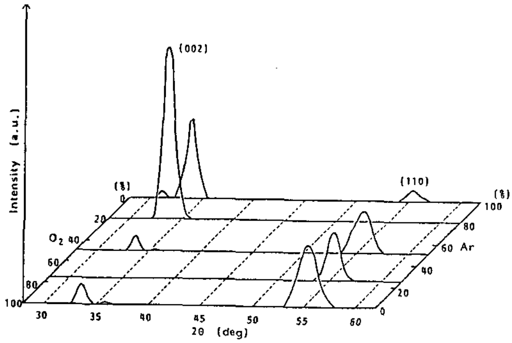

Fig.1 Gas composition dependence on the preferred orientation.

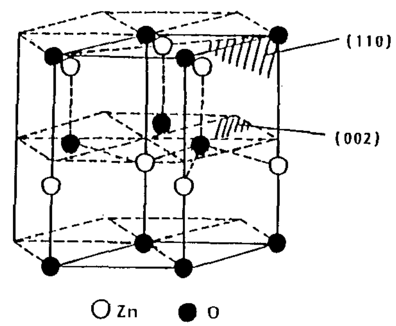

Fig.2 Crystal structure of ZnO.

The substrate temperature dependence on the orientation was studied under the sputtering condition which promoted the excellent (110) oriented films (Fig.3). The (110) oriented films can be formed under the low substrate temperature and the suitable O_2 partial pressure. As the substrate temperature(Ts) was raised, the (110) peak disappeared and the (002) peak became strong.

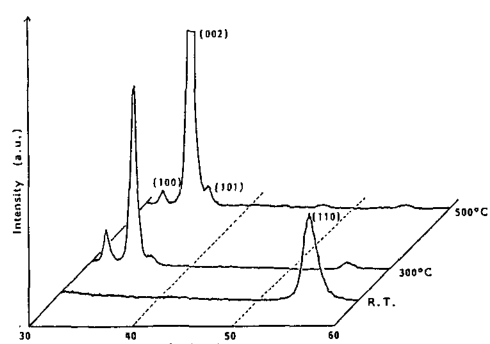

Fig.3 Effect of the substrate temperature on the preferred orientation.

But, when the excellent (110) oriented films deposited without heating substrates were post-annealed, the (110) preferred orientation was kept and became stronger with increasing annealing temperature. We suggest that as metallic binding can not exist at high temperature because of high vapor pressure of Zn, the structure necessarily become layered one, that is, (002) orientation at high Ts.

At the same time, the obvious peak shift was observed in X-ray diffraction angle, 2Θ. Those of (002) and (110) peaks of ZnOx films prepared without heating substrates were much lower than those of the bulk. These peak shifts to lower angles indicate the expanding of c-axis and a-axis. But these expansion decreased and the composition approached that of stoichiometric ZnO with increasing annealing temperature.

By the way, ZnOx films were darkened by X-ray irradiation(5). The optical transmittance at visible radiation decreased after X-ray irradiation, but the change in band gap was not observed. This darkened film returned by annealing, which is called photochromism. This may be caused by the F center. The degree of darkness by X-ray irradiation was not influenced by the difference in the orientation.

So, we evaluated as-deposited, X-ray irradiated and post-annealed (in vacuum) ZnOx films by XPS to investigate the composition and the change of valence electron state. Figure 4 shows spectra of Zn(auger electron, LMM) from ZnOx films with (110) orientation. The shoulder which is seen on the skirt of main peak at lower energy is considered to be Zn^{+}. But this shoulder did not change and remarkable peak shift was not observed by X-ray irradiation and annealing. Therefore, we suggest that this is because the volume of oxygen defects introduced by X-ray irradiation is not so much. While, the increase in the adsorbed oxygen is observed in the spectra of O 1s. The adsorbed surface oxygen would be pushed out from the inside of the film by X-ray irradiation. Comparing to

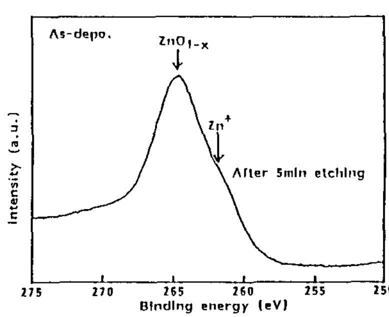

Fig.4 XPS spectrum of Zn (auger electron,LMM)

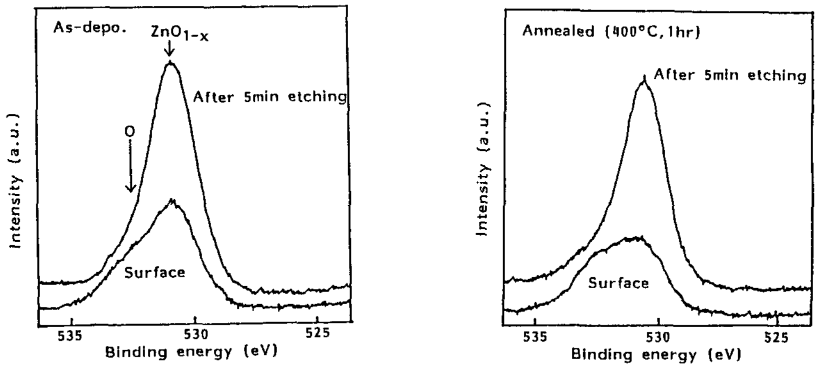

Fig.5 XPS spectra of O 1s.

the film after X-ray irradiation, the increase was more remarkable after annealing in vacuum(Fig.5). We suggest that the above-mentioned decrease of expansion by annealing in vacuum is mainly caused by interstitial oxygen atoms going up from the inside.

It is a preferable result for the application to a transparent conductive film that the resistivity decreased with increasing Zn concentration, but is not preferable one that the transmittance decreased at the same time. By annealing in vacuum, the shifts of fundamental absorption edge was investigated to estimate the band gap. I case of ZnO, it shifted to the longer wavelength, while in case of Al doped ZnO, it shifted to the shorter wavelength. These results are concerned with the change of carrier concentration(6).

References

(1) Characterization of ZnO piezoelectric films prepared by rf planar-magnetron sputtering
T.Yamamoto, T.Siosaki and A.Kawabata: J.Appl.Phys. 51(1980)P3113-3120.
(2) Reactive synthesis of well-oriented zinc-oxide films by means of the facing targets sputtering method
M.Matsuoka, Y.Hoshi and M.Naoe: J.Appl.Phys. 63(1988)P2098-2103
(3) The effect of O on reactively sputtered zinc oxide
C.R.Aita, A.J.Purdes, R.J.Lad and P.D.Funkenbusch: J.Appl.Phys. 51(1980)P5533-5536.
(4) Effects of oxygen partial pressure on the structure of ZnO thin films prepared by reactive RF sputtering
H.Kobayashi, Y.Igasaki and G.Shimaoka: Bull.Res.Inst.Electron. Shizuoka Univ. 19(1984)P47-53.

(5) Photochromism and anomalous crystallite orientation of ZnO films prepared by a sputtering-type electron resonance microwave plasma
M.Matsuoka and K.Ono: Appl.Phys.Lett. 53(1988)P1393-1395.
(6) The interpretation of the properties of Indium Antimonide
T.S.Moss: Proc.Phys.Soc.Lonson Sect. B67(1954)P775-782