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# ZnO Films Deposited on Glass by Means of DC Sputtering

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## Abstract

ZnO films were deposited on glass substrates by means of a direct current (DC) sputtering technique. The physical properties of the films were investigated on the basis of X-ray diffraction measurements. It was found that as-deposited films show c-axis oriented crystal normal to the surface with the extension of c axis by 1.27% that is estimated from the shift of the peak in the X-ray diffraction pattern. Post-deposition annealing in air at higher than 400˚C eliminates the shift and sharpens the diffraction peak structure at the same time. The electrical resistivity continues to decrease from 500 Ω·cm down to 0.6 Ω·cm by annealing as high as 600˚C.

## Keywords

ZnO Film, DC Sputtering, Annealing, X-Ray Analysis

## 1. Introduction

ZnO has a long history of its research but the study in the scope of electronic device application has been made in comparatively recent years. Epitaxial growth of ZnO on sapphire was reported no earlier than 1970s [1]. It is partly because the control of the stoichiometry between Zn and O is difficult. It has been commonly accepted that oxygen vacancy and zinc interstitial defects are natively introduced [2], [3].

Many kinds of compound semiconductors such as GaAs, InP and GaN are nowadays playing an important role in the semiconductor field. In this circumstance, ZnO attracts more and more attention because of a direct wide band gap of 3.3 eV [4]. On the other hand, ZnO is expected to be a transparent conductor replaced by indium tin oxide [5]. ZnO is also an attractive material to solar cell [6], liquid crystal display [7] and spintronics [8]. Thin film transistors are now developed with ZnO [8].

As for the deposition methods, various deposition techniques have been challenged such as radio frequency (rf) sputtering [9], [10], molecular beam epitaxy [11], [12], pulsed laser deposition [13], [14] and chemical vapor deposition [15], [16]. We are engaged in ZnO deposition using direct current (DC) sputtering with ZnO target. The DC sputtering is well known as an excellent method for metal deposition, but not so much for compound materials. The advantage of the DC sputtering is the simplicity of the apparatus; it does not require any radio frequency system. The technique has not been widely applied with exception of the DC sputtering of zinc target under oxygen atmosphere [17], [18]. The ZnO target has been very recently investigated in DC sputtering deposition experiments [19]-[22].

It was reported [23] that ZnO was deposited on Si substrate by a DC sputtering method. The interesting results were obtained that excess oxygen was included in the deposited film to stoichiometric ZnO on the basis of X-ray diffractometry and energy dispersive X-ray spectroscopy. The excess vanishes through post-deposition annealing above 400˚C. In this article, we focus on the ZnO deposition on glass substrates.

## 2. Experimental Details

In this experiment, a ZnO ceramic target round disk (4 N) with 70 mm in diameter was used. A substrate of borosilicate glass plate (S1225 by Matsunami Glass Ind., LTD.) was installed at a distance of 30 mm from the target.

The deposition was performed for an hour under the ambient pressure of 7.5 Pa and input power of 24 W. The substrate was not intentionally heated during the deposition. After the deposition was completed, annealing was performed by an electric furnace at 200˚C, 400˚C and 600˚C for half an hour in the air. The annealing temperature was not raised above 600˚C in order not to soften the glass substrate.

The obtained samples were examined by means of an X-ray diffraction (XRD) measurement. The XRD pattern was taken with a spectrometer (Ultima IV, Rigaku) equipped with a Cu target and a Ni filter. An X-ray tube was loaded with 40 kV and 40 mA in the experiment. The resistivity of the deposited films was analyzed by means of the van der Pauw method.

## 3. Results and Discussion

The XRD patterns taken from both as-deposited and annealed (600˚C) samples were shown in **Figure 1**. Both samples have shown single peak structure around 34.48 degree that is assigned to the diffraction from (002) plane of ZnO. Four other main peaks at 31.8, 36.5, 47.5 and 57.1, corresponding to (100), (101), (102) and (110) planes of ZnO, were not observed. This suggests the preferred orientation during the growth in such a way that c-axis is normal to the surface of the substrate. The background increase toward the lower $2\theta$ stems from the signal from the glass substrate.

The as-deposited sample shows that the observed peak is located at 34.03 degree with the FWHM of 0.91 degree. The reported (002) diffraction data for the bulk ZnO is 34.48 degree. The observed low-side shift suggests the lattice expansion along c-axis by

1.27%.

On the other hand, the sample annealed at 600˚C shows that the peak was observed at 34.48 degree that agrees well with the bulk ZnO data. The FWHM was reduced to 0.798 degree by the annealing. The similar results were reported when the substrate was Si wafer. The expansion along c-axis is due to the inclusion of excess oxygen elements into the deposited film as was reported [23]. The comparison with the results in the literature is interesting because the experimental condition was the same. The shift of the peak in this experiment was 0.45 degree that is smaller than 0.62 degree reported before. The FWHM in this experiment was 0.91 degree that is larger than 0.88 degree reported before. These two features lead us to conclude that, as for the glass substrate, the inhomogeneous strain is smaller but that the homogeneous strain is larger. Whether the substrate is crystalline or non-crystalline affects the structural state of the deposited film.

The annealing effect is considered next. **Figure 2** shows the peak position of (002) line of the XRD spectrum as a function of annealing temperature. It tells us that

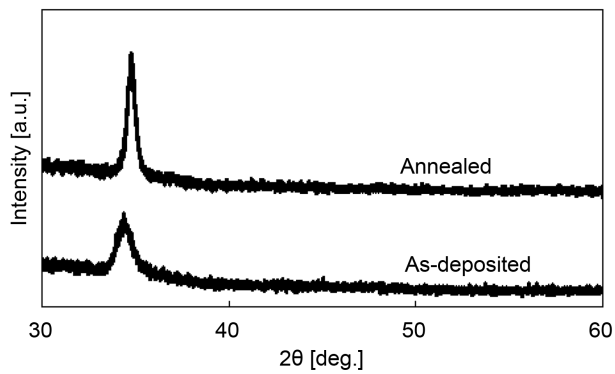


**Figure 1.** X-ray diffraction spectra from the samples that were as-deposited (lower) and annealed at 600˚C (upper). Only one reflection peak assigned to (002) diffraction was observed in the both spectra.

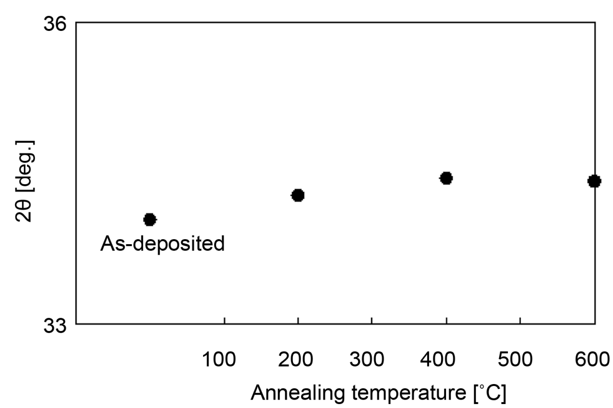


**Figure 2.** The dependence of the (002) peak position on the annealing temperature. The peak shift from 34.47 degree was completely vanished over 400˚C.

annealing at greater than 400˚C completely released the strain. The tendency is also observed in the sample deposited on the Si substrate [23]. **Figure 3** shows, on the other hand, how the FWHM of the peak depends on the annealing temperature. The FWHM seems to reach the lowest limit at 0.5 degree as is also in the same manner as the Si substrate [23]. We cannot confirm further decrease of the FWHM with the higher temperature as shown in the literature because the annealing at the higher temperature cannot be loaded on the glass substrate. Although there is some influence of the kind of substrates on the deposited film, the annealing effects show in the same way in these two kinds of substrates. It means the post-deposition annealing is effective to restore the crystalline of ZnO films.

Abduev *et al*. reported ZnO films on glass with a DC magnetron sputtering method [21]. They reported the similar XRD diffraction patterns of only one peak corresponding to (002) diffraction. The $2\theta$ was at 43.154 degree for the sample without heating the substrate during the deposition. This value is similar to ours. On the other hand, when the substrate was kept at 250˚C during the deposition, the $2\theta$ was at 34.45 degree that is similar to our annealed sample. However, the surface morphology is, as they reported, quite rough if the substrate temperature was 250˚C during the deposition. Kim *et al*. reported the surface was smoothened by post-deposition annealing by preferential evaporation. In this point of view, the post-deposition annealing seems to be superior to heating substrates during the deposition. In our experiment, annealing was performed no higher than 600˚C, where Kim *et al*. at 800˚C. Actually the deposition at room temperature provided a smooth surface morphology as was reported by Kim *et al*.

Ozaki *et al*. reported that annealing below 700˚C induced the c-axis orientation in ZnO films deposited by rf-sputtering [24]. Our results show the c-axis orientation without annealing. It shows that the DC sputtering is desirable to obtain a film of oriented crystal. Their result on photoluminescence at 2.5 eV was noticeably improved even with the post-deposition annealing at 600˚C. It is hopeful for our sample to be applied to light emission.

Next interesting discussion is the comparison with the results reported by Hiramatsu

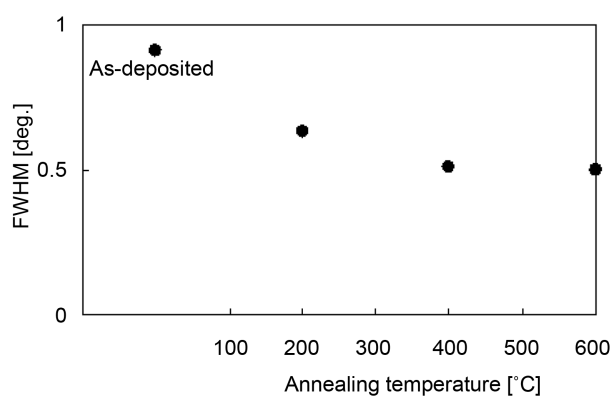


**Figure 3.** The FWHM of the (002) peak as a function of the annealing temperature. At 400˚C, the FWHM is lowered enough.

*et al*. They reported the annealing induced crystallization only with the sample only when the film deposited under the chamber pressure of 0.5 Pa [25]. The film deposited under 7.0 Pa showed no influence by the annealing up to 350˚C. We assumed the possibility, in the former report [23], that the improvement of crystalline quality and stoichiometry of ZnO is induced by the diffusion of oxygen into silicon substrate. This assumption is hardly applied to in this article because the substrate is made of borosilicate glass.

The dependence of resistivity on annealing temperature is shown in **Figure 4**. As-deposited sample showed around 500 Ω·cm. The post-deposition annealing has a large effect on decreasing the resistivity. At 600˚C, the resistivity comes down to 0.6 Ω·cm. The interesting point is that while the peak position and the FWHM of XRD spectrum is not so different between 400˚C and 600˚C, the resistivity is nevertheless different by no less than two digits. We assume that the crystallite size is the one reason for the reduction of the resistivity. The annealing higher than 600˚C is attractive but we need some ideas to avoid the deformation of glass substrate during annealing. It is possible conceivably that the softening of the substrate helps the enhancement of the crystalline quality. Along with the discussion above, it cannot be completely excluded that the larger FWHM in XRD pattern from the both samples non-annealed and annealed at 200˚C is due to the smallness of the crystallites in the film.

Quemener *et al*. reported electronic properties of Al-doped ZnO deposited on p-type Si wafer by DC magnetron sputtering [22]. They observed the rectifying feature in I-V characteristics. They annealed their samples at from 100˚C to 350˚C. Their data shows that the annealing suppresses the current density at both sides of bias voltage. They also describes that the annealing above 250˚C gradually degrades the hetero structure. The reduction of resistivity is incompatible with that of hetero interface between ZnO and Si layers.

Finally, the DC sputtering has not been left for the research. We believe that it is valuable to investigate compound materials such as ZnO deposited by means of the DC sputtering. Further study is expected to reveal the film properties of ZnO in this way.

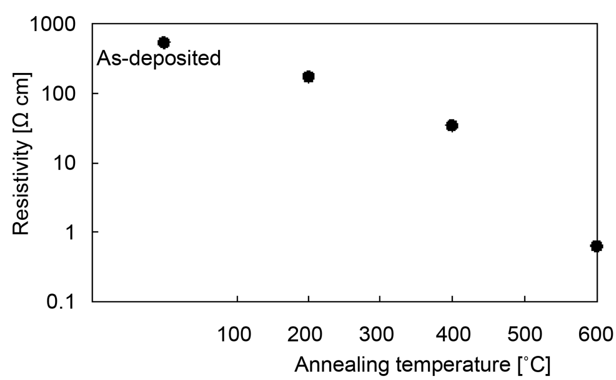


**Figure 4.** The resistivity of the deposited film as a function of the annealing temperature. It is noticeably decreases with the annealing temperature even over 400˚C.

## 4. Conclusion

ZnO film was deposited on glass substrates by means of a DC sputtering technique. X-ray diffraction measurements show that the film consists of (001) oriented crystallites even at room temperature during the deposition in the similar way as a Si wafer is used as a substrate. Post-deposition annealing was performed up to 600˚C. The dependence of the peak shift of (002) diffraction and the FWHM of it revealed that the improvement in crystalline quality is saturated over 400˚C. However, the resistivity decreases monotonically with the annealing temperature even above 400˚C.

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