

Ion Beam Modification of Al-Doped ZnO Thin Films

O. Fukuoka¹, N. Matsunami¹, T. Shimura¹, M. Tazawa², M. Sataka³

¹Center for Integrated Research in Science and Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Fax:81-52-789-5204, e-mail:n-matsunami@nucl.nagoya-u.ac.jp

²National Institute of Advanced Industrial Science and Technology, Nagoya 463-8560, Japan

³Department of Materials Science, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-1195, Japan

We have investigated ion-beam-induced modifications of Al-doped ZnO thin films with c-axis on SiO₂ glass, prepared by using a RF-sputter-deposition method. The samples were irradiated at room temperature (RT) by 100 keV-Ne⁺ ions up to $\sim 10^{17}$ cm⁻² and followed by annealing at 200-600 °C in vacuum. We find the followings. The conductivity increases by an order of magnitude after irradiation of 1×10^{17} cm⁻² and annealing at 200-400 °C. This modification is primary due to the mobility increase. The optical-absorption-edge spectrum becomes less sharp after irradiation of 1×10^{17} cm⁻² due to ion-induced disorder. The disorder is not annealed below 500 °C, but the spectrum is nearly recovered from the disorder by annealing at 600 °C. The conductivity increase is discussed in terms of the crystalline quality, grain growth and impurities.

Key words: Ion irradiation and annealing, electric and optical properties, conductivity increase, grain growth

1. INTRODUCTION

Al-doped ZnO (AZO) is known as an n-type semiconductor with the band gap of 3.3eV and AZO films have been extensively studied for application to electric devices and thin film solar cells [1-3]. Generally, the films consist of grains with size of several ten nm, and the electric mobility is typically ~ 1 cm²/V · s and smaller by two order of magnitude than that of a single crystal [4]. It is considered that the mobility is mainly determined by the crystalline quality. For the applications, it is desired to improve the crystalline quality of grains and increase the grain size in order to increase the mobility and minimize the grain boundary effects. However, these investigations are scarce. Recently, Matsunami et al have observed the grain-growth and alignment of the grain orientation of ZnO thin films with a-axis on MgO substrates by ion irradiation [5,6]. It is of interest to investigate whether ion irradiation improves the AZO film quality or not.

This paper reports the ion irradiation and post-irradiation annealed effects on the electric properties, crystalline quality, optical properties and grain growth of AZO thin films on SiO₂ glass.

2. EXPERIMENTAL

The experimental method is similar to that described in [5,6]. AZO films were grown on SiO₂ glass ($10 \times 10 \times 0.5$ mm³) by using an off-axis RF-magnetron-sputter-deposition method with RF power of 40 W and AZO target of (Al/Zn=3.2%) in 5 Pa Ar gas. The SiO₂ glass was away by ~ 6 cm from the target.

Ne⁺ ions of 100 keV were used for irradiation at RT. The beam current and size were ~ 1 μA and ~ 1 cm², respectively.

DC conductivity and Hall coefficient were measured by four-probe and the van der Pauw methods,

respectively, to deduce the carrier density and mobility. The crystalline quality and orientation were examined by X-ray diffraction (XRD). Optical absorption spectra were measured by using a conventional spectrometer. Surface morphology and grain size of the films were evaluated by atomic force microscopy (AFM). Annealing was performed in vacuum of $\sim 10^{-3}$ Pa for 1h at each temperature. Rutherford backscattering spectroscopy (RBS) was employed to analyze the composition and film thickness.

3. RESULTS AND DISCUSSION

The films were prepared at the substrate temperature Ts=RT to 800 °C. The deposition time was 30 min. RBS shows that the film thickness is 100 (± 20) nm, the O/Zn composition is nearly stoichiometric and Al/Zn=5 %. The films grown in this study have c-axis orientation (c-axis, perpendicular to the basal plane of the hexagonal structure, is perpendicular to the substrate surface). This orientation is commonly observed and can be explained in terms of the lowest surface-free-energy [7].

The electric properties of the present films are similar to those in [1]. Both the conductivity and carrier density at Ts=RT exhibit the maximal 2-10 S/cm and 5×10^{20} /cm³, respectively. A factor of ~ 5 is observed for the conductivity variation on sample and this is partly due to the fact that the conductivity and mobility depend strongly on the film thickness. The carrier density is much larger than the value of $\sim 2 \times 10^{19}$ /cm³ estimated from the solubility limit of 0.05 % for Al in the AZO single crystal [4], assuming that all Al's are in the Zn substitutional sites and generate a carrier (an electron) for each Al. The conductivity reaches the minimum at Ts=400 °C and increase at Ts=800 °C. The carrier density and mobility reach their minimum values at Ts=400 °C and increase for higher Ts. The mobility at Ts=RT is ~ 0.1 cm²/V · s

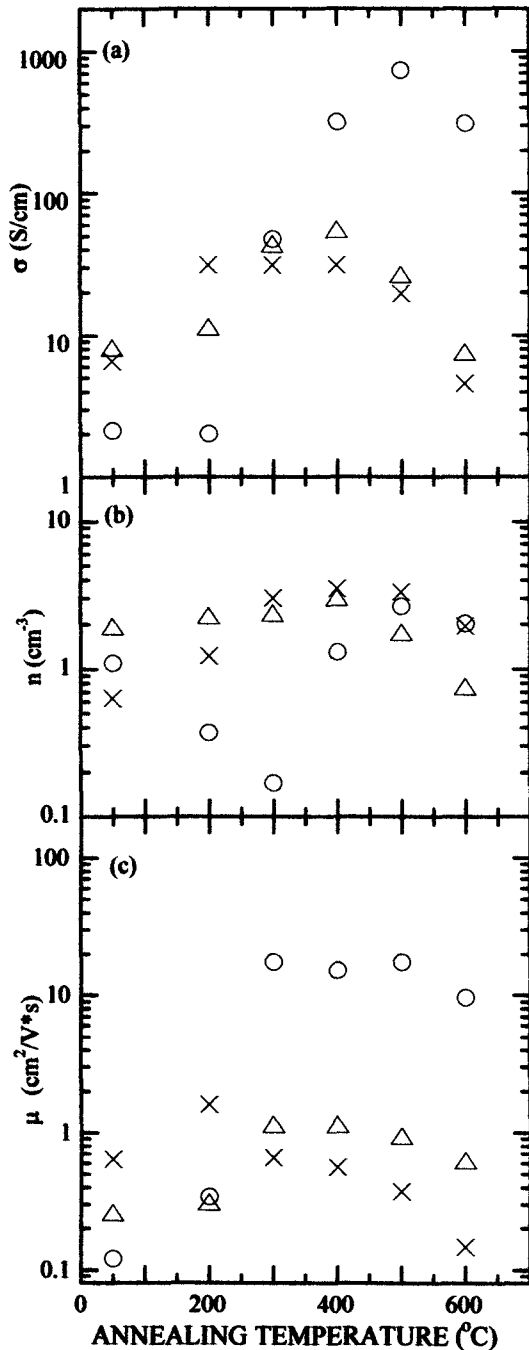


Fig. 1 (a) Conductivity: σ , (b) carrier density: n and (c) mobility: μ vs annealing temperature. Open circles, triangles, crosses indicate unirradiated, irradiated ($5 \times 10^{16} \text{ cm}^{-2}$) and irradiated ($1 \times 10^{17} \text{ cm}^{-2}$) films, respectively.

and this is much smaller than that of a single crystal, $100 \text{ cm}^2/\text{V} \cdot \text{s}$ [4], as already mentioned.

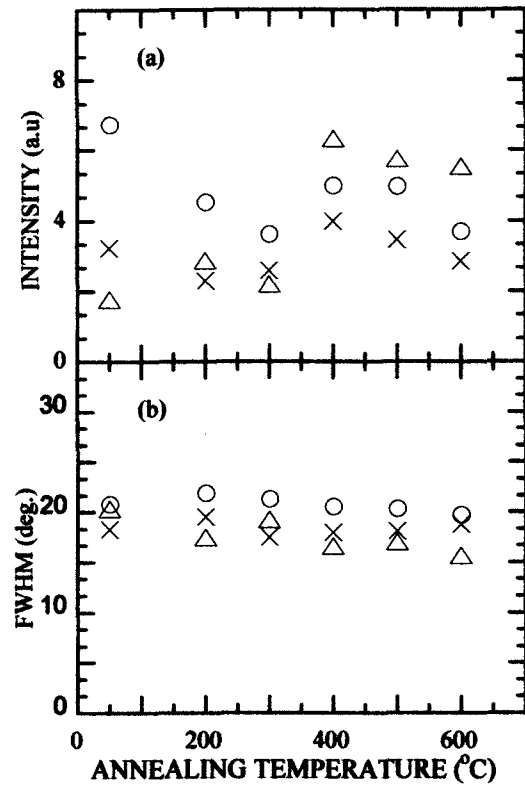


Fig. 2 (a) XRD intensity and (b) FWHM of the rocking curve of AZO vs annealing temperature. The symbols are the same as in Fig. 1.

The FWHM (full width at the half maximum) of the XRD rocking curve of (002) diffraction peak (diffraction angle $\sim 17^\circ$) shows the maximum of $\sim 20^\circ$ at $T_s = \text{RT}$, reaches the minimum of $\sim 4^\circ$ at $T_s = 400\text{--}600^\circ\text{C}$ and then increases to $\sim 7^\circ$ at $T_s = 800^\circ\text{C}$. The XRD intensity exhibit maximum at $T_s = 400^\circ\text{C}$. These indicate the film at $T_s = \text{RT}$ is the poorest in view of the XRD. With increasing T_s up to 500°C , FWHM decreases, i.e., the crystalline quality is improved, while the mobility decreases. Thus the crystalline quality is not a major factor for the mobility change in this case.

For irradiation, the films of RT deposition were chosen, because the conductivity is the maximum. Fig. 1 shows the conductivity, carrier density and carrier mobility of unirradiated and irradiated films vs the annealing temperature T_a . After 100 keV-Ne^+ irradiation, the conductivity increases by a factor of 4 as shown in Fig. 1(a). It is noticed that the conductivity increase depends on the starting film as mentioned above. The intensity and FWHM of the XRD vs annealing temperature are shown in Fig. 2. The FWHM slightly decreases from the unirradiated value of ~ 20 to $\sim 18^\circ$ and the XRD intensity decreases following the Ne^+ irradiation. Figs. 3 and 4 show

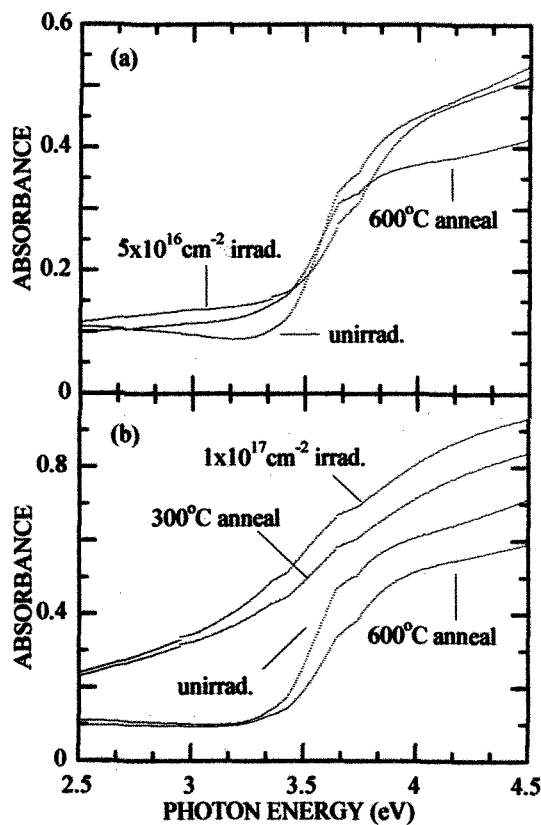


Fig. 3 (a) Optical-absorbance spectra of unirradiated, irradiated ($5 \times 10^{16} \text{ cm}^{-2}$) and post-irradiation annealed (600°C) AZO films. (b) Similar to (a) except for irradiation of $1 \times 10^{17} \text{ cm}^{-2}$ and followed by annealing at 300 and 600°C .

optical absorption spectra and AFM images of the unirradiated, irradiated and post-irradiation annealed samples, respectively. The absorption spectrum of a SiO_2 glass without AZO film after irradiation of $1 \times 10^{17} \text{ cm}^{-2}$ is nearly the same as the unirradiated one and thus the change in the absorbance is due to that in AZO films by ions. Optical absorption spectra of the band edge become less sharp by ion irradiation of 10^{17} cm^{-2} , as shown in Fig. 3(b). Grain growth is not observed but the grain size is reduced for high dose, as seen in Fig. 4(e). RBS shows that the composition is nearly unchanged under ion irradiation.

Next, we have performed annealing of irradiated and unirradiated AZO films. As shown in Fig. 1, the conductivity of the irradiated samples increases by an order of magnitude after annealing at 200 - 300°C , but decreases at higher annealing temperature T_a . Surprisingly, the conductivity of the unirradiated samples increases by two order of magnitude at $T_a = 500^\circ \text{C}$. The conductivity modifications are primary due to the mobility changes.

The XRD intensity and FWHM of both the unirradiated and irradiated films show no appreciable change after annealing (see Fig. 2). These indicate no improvement of the crystalline quality by annealing. Hence the conductivity increase shown in Fig. 1 is due to factors other than the crystalline quality, contrary to the general expectation.

The degree of the absorption-edge-sharpness represents the crystalline quality of grains, because the absorption-edge spectrum of the RT deposition films (the crystalline quality is the poorest) is less sharp. The absorption spectrum around the band gap is slightly modified by irradiation of $5 \times 10^{16} \text{ cm}^{-2}$ and also by post-irradiation annealing. A drastic modification is

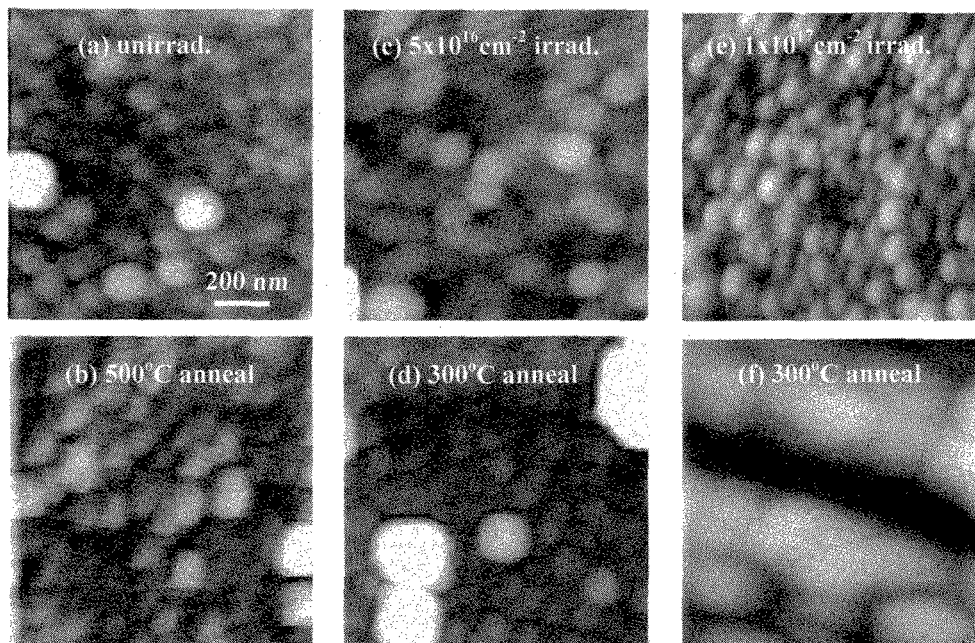


Fig. 4 AFM images of AZO films with c-axis orientation: (a) before irradiation, (b) after annealing of unirradiated film at 500°C , (c) after irradiation of $5 \times 10^{16} \text{ cm}^{-2}$, (d) after irradiation of $5 \times 10^{16} \text{ cm}^{-2}$ irradiation followed by annealing at 300°C , (e) after irradiation of $1 \times 10^{17} \text{ cm}^{-2}$ and (f) after irradiation of $1 \times 10^{17} \text{ cm}^{-2}$ followed by annealing at 300°C .

seen for irradiation of $1 \times 10^{17}/\text{cm}^2$ and this is caused by ion-induced disorder, but is not reflected in the XRD. The absorption spectrum after irradiation of $1 \times 10^{17}/\text{cm}^2$ is not recovered by annealing below 500°C and the recovery occurs by annealing at 600°C . Again, the conductivity increase at $200\text{--}400^\circ\text{C}$ does not correspond to the recovery of the ion-induced disorder.

The grain size of AZO film on SiO_2 deposited at RT is $50\text{--}100\text{ nm}$. No grain growth at $T_a=500^\circ\text{C}$ is observed for the unirradiated samples (Fig. 4(b)). The samples after irradiation of $5 \times 10^{16}/\text{cm}^2$ and post-irradiation annealing show no grain-growth. In contrast, the grain size is reduced by a factor of 2 after irradiation of $1 \times 10^{17}/\text{cm}^2$ and increases to $\sim 200\text{ nm}$ at $T_a=300^\circ\text{C}$ (Fig. 4(c) and (d)). It is speculated that migration of defects generated by ion irradiation leads to the grain-growth. The grain-growth of AZO films is observed by annealing at 300°C in H_2 [8]. The details of mechanism and similarity of the grain-growth are to be investigated.

Mean free path (mfp) for the electronic conduction is estimated as order of 0.1 nm for the carrier density $=10^{20}/\text{cm}^3$ and mobility $=1\text{ cm}^2/\text{V} \cdot \text{s}$ [2]. This value is much smaller than the grain size and thus the grain growth is not expected for the improvement of the conductivity but for crystalline quality improvement. As already mentioned, the increase of the conductivity or mobility does not originate from the improvement of the crystalline quality. If the electric conduction at surface is dominant and the surface conductance is independent of the film thickness, the conductivity decreases with increasing the film thickness. This is not the case, because experiments show that the conductivity increases with the film thickness. Origin of the conductivity modification is not known at present, but possibilities are the followings. Since the carrier density is $\sim 10^{20}/\text{cm}^3$, the fraction of Al's at substitutional sites (Zn sites) is $\sim 0.2\%$. The majority of the remaining Al's are at nonsubstitutional sites (interstitial, grain boundary and/or surface). Al's at interstitial sites may act as the scattering center for the electric conduction and the fraction may vary by ion irradiation and annealing. Furthermore, RBS shows no appreciable impurities heavier than aluminum. Thus, another possibility is the low atomic-number impurities. According to preliminary results of nuclear reaction analysis (NRA) with 1.2 MeV d and elastic recoil detection (ERD), $\sim 10^{16}/\text{cm}^2$ of carbons and considerable amount of hydrogen's ($\sim 10^{17}/\text{cm}^2$) are detected. These impurities might play important roles.

4. CONCLUSION

Effects of 100 keV-Ne^+ ion irradiation and post-irradiation annealing on Al-doped ZnO on SiO_2 glass have been investigated. We demonstrate the conductivity increase by an order of magnitude and grain-growth by a factor of 5. No simple relationship is observed between these modifications and the crystalline quality in view of XRD and optical absorption of the band edge.

Acknowledgements

The authors thank Dr. S. Miyagawa (National Institute of Advanced Industrial Science and Technology) for helpful discussion and experiments of ERD, and Mr. T. Masuda for technical assistance of RBS and NRA, using a KN Van de Graaff acceleration at Nagoya University.

References

- [1] T. Minami, T. Miyata, T. Yamamoto, *J. Vac. Sci. Technol. A* 17,1822(1999).
- [2] Z. L. Pei, C. Sun, M. H. Tan, J. Q. Xiao, D. H. Guan, R. F. Huang, L. S. Wen, *J. Appl. Phys.* 90,3432(2001).
- [3] D. Song, P. Widenborg, W. Chin, A. G. Aberle, *Solar Energy Materials & Solar Cells* 73,1(2002).
- [4] N. Ohashi, T. Sekiguchi, I. Sakaguchi, N. Ebisawa, T. Ohgaki, T. Takenaka H. Haneda, *Key Engineering Materials* 173,228-229(2000).
- [5] N. Matsunami, M. Itoh, Y. Takai, M. Tazawa, M. Sataka, *Nucl. Instrum. Meth. B* 206(2003)282.
- [6] N. Matsunami, O. Fukuoka, M. Tazawa, M. Sataka, *Int. Conf. Surface Modification of Materials by Ions (San Antonio, USA, Sept. 2003)*.
- [7] N. Fujimura, T. Nishihara, S. Goto, J. Xu, T. Ito, *J. Crystal Growth* 130,269(1993).
- [8] S. Gosh, A. Sarkar, S. Chaudhuri, A. K. Pal, *Thin Solid Films* 64,205(1991).

(Received October 9, 2003; Accepted January 20, 2004)