Available online at www.sciencedirect.com
SCIENCE DIRECT
Surface & Coatings Technology 196 (2005) 50–55
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Electronic structure modification of ZnO and Al-doped ZnO films by ions

Noriaki Matsunami[a,*], Osamu Fukuoka[a], Masato Tazawa[b], Masao Sataka[c]

[a]Center for Integrated Research in Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[b]National Institute of Advanced Industrial Science and Technology, Nagoya 463-8560, Japan
[c]Department of Materials Science, Japan Atomic Energy Research Institute, Tokaimura, Ibaraki 319-1195, Japan

Available online 30 September 2004

Abstract

We present ion beam modifications of the electrical and optical properties of zinc oxide (ZnO) and Al-doped ZnO (AZO) films such as increase of the electrical conductivity, the modification of the optical absorption edge. Ions used here are 100 keV Ne and Ar, and it is shown that the elastic collisions (i.e., collisions between ions and target atoms, and between target atoms without electronic excitation and ionization) play a major role. Also presented are ion-induced growth of grains and redistribution of grain orientation as well as ion-induced degradation of the crystalline quality, knowing that grains with several tens of nanometers in size constitute the films. Their effects on the electrical and optical properties are described.

Keywords: ZnO and Al-doped ZnO films; Ion irradiation; Electric and optical properties; Grain growth

1. Introduction

Zinc oxide (ZnO) and metal-doped ZnO, known as an n-type semiconductor (band gap=3.3 eV) [1] have attracted much attention because of their electric [2,3], optical [4,5], piezoelectric [6] and gas sensing properties [7]. ZnO and metal-doped ZnO films have been grown on a variety of substrates, i.e., SiO_2 glass, quartz, sapphire, Si, MgO, $ScAlMgO_4$, metals such as Au, Zn and stainless steel, and so on by using various methods, sputtering [2,3,7,8], pulse-laser deposition (PLD) [4,6], chemical vapor deposition (CVD) [5], chemical solution deposition [9], etc. Compositions as well as crystalline quality are of crucial importance in determining the properties of ZnO films. Grain size control is another important subject, because the grain boundary effects would be less important with increasing the grain size. Ion beams may offer a way to modify the film properties, which is different from the conventional thermal annealing.

This paper describes ion beam modification of the dc resistivity and carrier mobility, optical absorption, crystalline quality, grain growth of ZnO and Al-doped ZnO (AZO) films. Ions of 100 keV Ne and Ar were employed for modification of the film properties. Unique aspects of ion beam modification of the films are described. It is also examined whether the elastic collisions play a major role or not.

2. Experimental

ZnO and Al (5%)-doped ZnO films were grown on MgO(100) and SiO_2 glass substrates with a size of ~5×10×0.5 mm^3, respectively, by using an off-axis rf-magnetron sputter deposition method with rf power of 40 W [10–12], and a disk target of 99.99% purity of ZnO in 5 Pa of $Ar+O_2$ gas mixture ($Ar:O_2$=1:1) or that of AZO in 5 Pa Ar gas.

Ne^+ and Ar^+ ions of 100 keV were used for irradiation at RT and at normal incidence. Beam current and size were 1~4 μA and ~1 cm^2, respectively. The channeling effect and temperature rise due to ion irradiation (estimated to be below 50 °C [13]) are insignificant.

Ion beam modifications of ZnO films were investigated by the following methods. The resistivity and carrier concentration were measured by two-terminal or four-

* Corresponding author. Tel.: +81 52 789 5204; fax: +81 52 789 5204.
E-mail address: n-matsunami@nucl.nagoya-u.ac.jp (N. Matsunami).

0257-8972/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.surfcoat.2004.08.093

terminal methods and the Hall effect measurements. Optical absorption spectra were measured by using a conventional spectrometer. The crystalline quality was examined by X-ray diffraction (XRD). Surface morphology and grain size of the films were evaluated by atomic force microscopy (AFM). Thickness and composition were analyzed by Rutherford backscattering spectrometry (RBS) of 1.8 MeV He ions. Using the stopping powers [14], the film thickness used in this study was obtained as 50–100 nm and the composition remained nearly stoichiometric under ion irradiation to a dose of 10^{17}/cm^2. This point will be discussed further in Sections 3.4 and 3.5. Here, the density of ZnO and AZO is taken as 5.67 g/cm^3 (oxygen density=4.2×10^{22}/cm^3).

3. Results and discussion

3.1. ZnO on MgO(100)

The crystal orientation of ZnO films grown on MgO is *a*-axis of hexagonal structure (hexagonal basal plane is normal to the MgO substrate surface) for the MgO substrate temperature higher than 400 °C, in contrast to *c*-axis oriented films (hexagonal basal plane is parallel to the MgO surface) which are grown at lower temperature [11,12,15].

The parameters such as the projected range R_P and nuclear energy deposition relevant to this study are calculated using TRIM1997 (Table 1) [14]. R_P of 100 keV Ne and Ar is 123 and 61 nm, respectively. The film thickness for 100 keV Ne and Ar ions is chosen ~100 and ~50 nm, respectively, so that as many as ions pass through the film (ion–substrate interaction is not a subject in this study) and RBS analysis is not too difficult. The majority of Ne ions passed through the films and was at rest in MgO substrate, while some fraction of Ar was retained in the film. Nevertheless, Ar in the film is reasonably assumed to have insignificant effects on the film properties, because of no chemical reaction between Ar and ZnO. With this reason and the reason that RBS analysis is much easier for thicker film, Ne ion irradiation is more suitable than Ar ion irradiation. Moreover, some properties of films often show deviations from expected linear dependence on the film thickness.

Table 1
Calculated values (TRIM1997) of projected range R_P (nm), the nuclear energy deposition S_d (eV/nm), ionization by recoils S_{eR} (eV/nm), total electronic energy deposition S_{et} (eV/nm) and dpa averaged over the film thickness of 100 and 50 nm for 100 keV Ne and Ar, respectively

Ion	R_P (nm)	Average (eV/nm)				Surface (eV/nm)		
		S_d	S_{eR}	S_{et}	dpa	S_d	S_{eR}	S_{et}
Ne	123	246	119	386	2.4	212	58	331
Ar	61	696	314	617	7.3	726	140	475

The values near surface are also given.

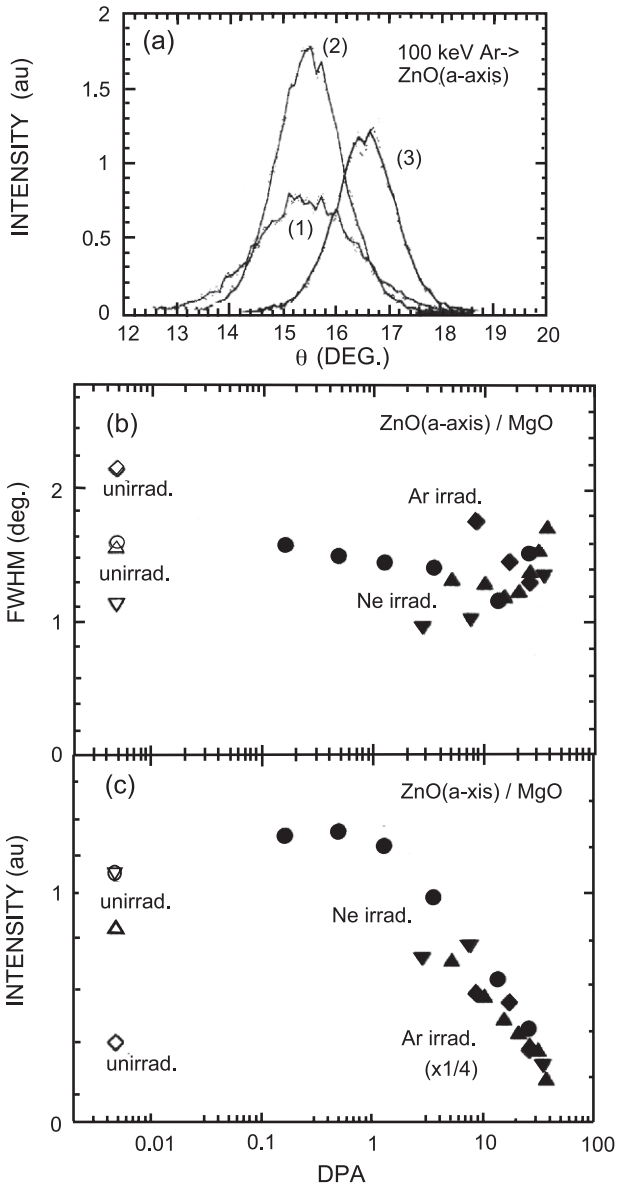

Fig. 1. (a) XRD rocking curve of (100) peak (*a*-axis ZnO film/MgO): (1) unirradiated, irradiated with 100 keV Ar to doses of (2) 2.4×10^{16}/cm^2 and (3) 3.7×10^{16}/cm^2. (b) FWHM in degrees of (100) peak (*a*-axis film) vs. dpa (Ar irradiation (♦) and Ne irradiation (●,▲,▼)). Four data points indicated by unirrad. (open symbols) are those of unirradiated films. (c) XRD intensity vs. dpa. XRD intensity for Ar irradiation was multiplied by 4. Estimated errors of the FWHM and intensity are 5 and 20%, respectively.

Misfit between ZnO film and MgO, foreign atom diffusion from the substrate into film and etc may be reasons, but it has not been clarified yet. RBS spectra show no diffusion of Mg into ZnO film and thus Mg atoms in the film are well below the RBS accuracy, even if it occurred. Since the misfit is quite large (more than 20%) [10] and a small amount of Mg atoms diffused into ZnO slightly changes the band gap [16], it is reasonably assumed that these factors, which may depend on the film thickness, do not significantly affect the ion beam modification, though properties such as XRD