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Evaluation of zinc self-diffusion at the interface between homoepitaxial ZnO thin films and (0001) ZnO substrates

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ABSTRACT

Isotopic ZnO thin films were deposited on the *c*-plane of ZnO single crystals by pulsed laser deposition. The isotopic abundance of Zn in the films was determined with a secondary ion mass spectrometry before and after the films was diffusion annealed. The diffusion profiles across the film/substrate interface behaved smooth features. The zinc diffusion coefficient (D_{Zn}) was obtained by analyzing the slope of the profile in the annealed sample. The temperature dependence of D_{Zn} was determined to be $D_{Zn}(cm^2/s)=8.0\times10^4\exp(-417[kJ/mol])/RT$, where R and T are gas constant and temperature. The zinc ion diffusion coefficients were of the same order as that in a ZnO single crystal. A comparison of the experimental and theoretical values indicated that the zinc ions diffused in the thin film and the single crystal through a vacancy mechanism.

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1. Introduction

Zinc oxide (ZnO) is a functional metal oxide that is useful in many optical and electronic applications due to its unique properties [1]. It can potentially be used in thin film technology such as in semiconducting [2] and photoconducting [3] applications, and in piezoelectric [4,5] and optical waveguide materials [6,7]. The point defect structure of ZnO and the point defect concentration are generally important factors in these applications and materials. It is well known that electrical conductivity and photoconductivity are affected by the carrier density, which is governed by the donor concentration and oxygen and zinc defect concentrations. Various methods have been used to characterize the point defect structure to better understand the characteristics of point defects [8,9].

We have focused on the diffusion characteristics of zinc in ZnO thin films, which are closely related to the structure and/or concentration of point defects. In the diffusion of various types of cations, it is important to understand the details of zinc [10–12] and donor [13,14] diffusion in ZnO in order to fabricate ZnO based thin film devices. Previously, Kim [11] and Moore and Williams [10] revealed the zinc diffusivity in ZnO single crystal. Kim indicated that the anisotropy of zinc diffusivity depended on the crystal orientation. On the contrary, Moore and Williams found that the zinc diffusivity was independent of the crystal orientation. Tomlins et al. [12] carefully performed zinc diffusion experiments and reported that the zinc self-diffusion in ZnO single crystal was controlled by the zinc vacancy. Another approach to obtain the zinc defect is to evaluate the diffusion characteristics of Co, which has the same valence as Zn ions [15]. However, the diffusion characteristics of Zn and Co are expected to differ because the interaction between a diffusion species and point defects depends on the species. The ion implantation technique for studying the diffusion of Ga and In was recently applied to produce diffusion samples [13,14]. The Ga and In diffusion exhibited the behavior of the concentration-dependent diffusion, and was controlled by the vacancy-mediated mechanism.

However, these published diffusion studies on zinc and donors in ZnO were limited to the single-crystal form. Therefore, in order to fabricate ZnO thin film based devices, it is expected that studies on the point defect at the thin film/substrate interface and in the thin film will be increasingly important. Matsumoto et al. experimentally investigated the zinc diffusion in ^{64}ZnO/^{68}ZnO/^{64}ZnO heterostructure thin films [16] and found that zinc ions diffuse via the lattice. They further reported that the diffusion coefficient in a multi-layered ^{64}ZnO/^{68}ZnO thin film grown on an Al_2O_3 substrate depends on the position of the ions in the film [17]; the self-diffusion coefficients were found to increase as the Zn ions move nearer to the film/substrate interface.

We focused in our study on the diffusion phenomenon of zinc across the film/substrate interface. Isotope ZnO thin films were

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homoepitaxially grown on single-crystal ZnO. The zinc diffusion profiles were evaluated by secondary ion mass spectrometry (SIMS). We show two approaches for determining the zinc diffusion coefficients. Finally, we discuss the zinc diffusion mechanism in the lattice of the thin film and the single-crystal ZnO.

2. Experimental procedure

Zn-isotopic ZnO thin films were grown by pulsed laser deposition (PLD) [18]. The precursor materials were commercially available isotopic enriched ZnO powders (Trace Science International). Polycrystalline ZnO targets with concentrated ^{64}ZnO (isotopic purity of 98%) or ^{68}ZnO (isotopic purity of 98%) that were to be used in the PLD were sintered in air at 1473 K. The sintered densities were above 90%. The substrates were cleaned in an ultrasonic bath of acetone and then in an ultrasonic bath of ethanol, and then placed in a growth chamber. Ceramic targets of ^{64}ZnO and ^{68}ZnO were placed in the chamber separately. The base pressure of the growth chamber was about 3×10^{-7} Pa. The fourth harmonic of a neodymium-doped yttrium-gallium-garnet pulsed laser (Nd:YAG, $\lambda=266$ nm) with a pulse width of 5 ns and a repetition rate of 5 Hz was focused onto the target in the chamber through a silica glass window. The films were deposited at a substrate temperature of 873 K in O_2 at 2×10^{-3} Pa. The samples were diffusion annealed in air in the temperature range from 873–1093 K for 600–14,400 s.

The isotopic abundance of zinc was analyzed by SIMS using a double focusing mass spectrometer (CAMECA, IMS-4f) with O_2^+ as the primary ion species at an accelerating voltage of 12.5 kV and a beam current of ~5 nA. A normal induced electron gun was used to prevent the sample surface from charging up. The secondary ion intensities of $^{64}\mathrm{Zn}^+$, $^{66}\mathrm{Zn}^+$, and $^{68}\mathrm{Zn}^+$ ($I(^{64}\mathrm{Zn})$, $I(^{66}\mathrm{Zn})$, and $I(^{68}\mathrm{Zn})$) were measured, and the ^{64}Zn fraction at depth x (C_x) was calculated as

$$C\left[{}^{64}\mathrm{Zn}\right]=I\left[{}^{64}\mathrm{Zn}\right]/\left(I\left[{}^{64}\mathrm{Zn}\right]+I\left[{}^{66}\mathrm{Zn}\right]+I\left[{}^{68}\mathrm{Zn}\right]\right) \qquad (1)$$

The final depth of the crater sputtered by the primary ion beam was measured using a profilometer (Dektak 3030), and the depth for each data point was determined from the measured crater depth and the sputter time by assuming a constant sputtering rate. Data from a preliminary experiment confirmed that this assumption was valid, as it resulted in an error margin of only ~1% under the present experimental conditions.

The phases and crystal orientations of the ZnO thin films were determined by X-ray diffraction (XRD, Philips, X'Pert PRO MRD). Since the crystals in the films were strongly oriented parallel to the c-axis of the wurtzite lattice, only (00n) family peaks were observed in the θ–2θ scan profile. The electrical properties of the grown films were evaluated by measuring their Hall coefficients at room temperature.

3. Results and discussion

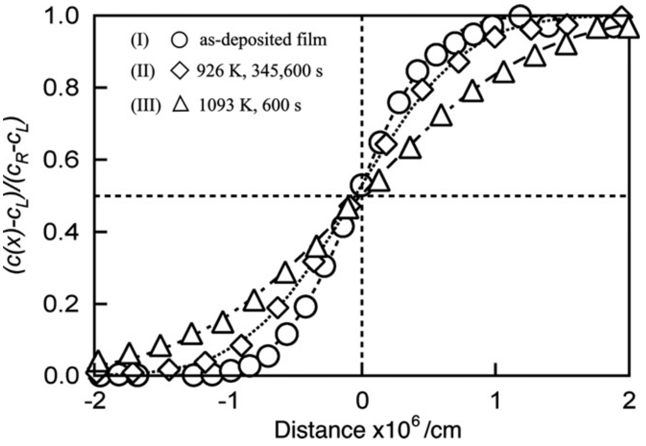

Fig. 1. Zinc diffusion profiles across film/substrate interface. Annealing temperatures are indicated in the figure.

Fig. 1 shows the depth profiles of Zn in the homoepitaxial thin films grown on (0001) single crystal. Profile (i) shows the depth profile in the as-deposited thin film. The Zn distribution across the thin film-substrate interface indicates that the data contain the broadening due to the analysis. Profiles (ii, iii) show the depth profiles of Zn after the diffusion annealing, and reveal that the Zn diffuses between thin films and substrate through the interface. It is noted that the zinc diffusion across the film/substrate interface showed smooth profiles and that the features of these profiles suggest a smooth interface for Zn diffusion between the thin film and the substrate. We analyzed the profiles in order to calculate the Zn diffusion coefficient from the Zn diffusion profile by using two approaches described below. Fig. 2 plots the depth profile in the sample annealed at 993 K for 14,400 s and the fitted values calculated from the equation below. The first approach is based on the assumption that the diffusion coefficients in the thin film and substrate were the same. The diffusion profile was analyzed with the following simple error function [19]

$$\frac{C(x)-C_{Substrate}}{C_{Thin\ Film}-C_{substrate}}=\frac{1}{2}\times erfc\left(\frac{x-x_0}{2\sqrt{Dt}}\right), \qquad (2)$$

where $C(x)$ is the intended isotopic concentration at depth x for diffusion duration t, and $C_{Thin\ Film}$ and $C_{Substrate}$ are the initial isotopic concentrations in the thin film and substrate. The variable x_0 is the distance between the thin film surface and the film-substrate interface. As shown in Fig. 2(a), the calculated values are in excellent agreement with the observed ones, and the calculated diffusion coefficient is 1.0×10^{-17} cm^2/s. The apparent diffusion coefficient in Eq. (2) was corrected with analytical broadening to obtain the real diffusion coefficient; the equation reported previously [17,20] was used to obtain the diffusion coefficient.

The other approach for the diffusion analysis is based on the assumption that a thin film and a single-crystal substrate would be expected to have different diffusion coefficients. Here, diffusion coefficients are obtained for the different regions

For $x\geq x_0$,

$$\frac{C(x)-C_{thin\ film}}{C_{substrate}-C_{thin\ film}}=\frac{1}{1+\sqrt{D_{Thin\ Film}/D_{Substrate}}}\times\left(1+\sqrt{D_{Thin\ Film}/D_{Substrate}}\right)\times erf\left(\frac{x-x_0}{2\sqrt{D_{Substrate}t}}\right), \qquad (3)$$

and for $x<x_0$,

$$\frac{C(x)-C_{thin\ film}}{C_{substrate}-C_{thin\ film}}=\frac{1}{1+\sqrt{D_{Thin\ Film}/D_{Substrate}}}\times\left(1+\sqrt{D_{Thin\ Film}/D_{Substrate}}\right)\times erfc\left(\frac{x-x_0}{2\sqrt{D_{Thin\ Film}t}}\right). \qquad (4)$$

In Fig. 2(b), the fitting to Eq. (3) is also shown by the curve marked with 'x' symbols. The calculated values are almost the same as those obtained from Eq. (4), and the corrected diffusion coefficients, $D_{Thin\ Film}=1.1\times10^{-17}$ cm^2/s and $D_{Substrate}=9.6\times10^{-18}$ cm^2/s, have the same amount of experimental error. The defect concentration responsible for zinc diffusion is equilibrium between thin film and the single-crystal.

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