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Preferred orientation and interdiffusion in zinc oxide/copper oxide multilayered films

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ZnO/CuO and ZnO/ZnOCuO/CuO multilayered films were deposited on Pyrex substrates at <100° C by ion-beam sputtering. The preferred orientation and interdiffusion of these films were examined for films with varying layer repeat lengths (pair thickness). X-ray diffraction analysis showed a preferred ZnO(0 0 2) orientation parallel to the surface in annealed ZnO layers of ~1 to ~3 nm thickness; no peak was observed for films with a layer repeat length smaller than 1.1 nm. The degree of preferred orientation reduced with increasing layer thickness in ZnO/CuO films and with increasing ZnOCuO thickness in ZnO/ZnOCuO/CuO films. The decay rate of the low-angle X-ray intensity showed that interdiffusivity is largely dependent on the layer repeat length. A smaller layer repeat length gave a larger value of interdiffusivity.

1. Introduction

Optical and electrical properties of the zinc oxide–copper oxide system are being studied for application in useful new devices, for example, a solar cell [1] and a carbon monoxide detector [2]. However, virtually nothing is known about the structural and diffusional properties of the mixture.

Fig. 1 shows the X-ray diffraction (XRD) diagram of the sintered mixture of powders which indicates a poor reactivity between the zinc oxide and the copper oxide. Thus, further investigation of a layer with smaller dimensions of the order of 1 nm or less was undertaken.

In this paper, we describe the preferred orientation and the interdiffusivity in the zinc oxide/copper oxide multilayered films. Preferred (0 0 2) orientation in zinc oxide layers thicker than ~1 nm and a value of interdiffusivity as low as 10^{-19} to $10^{-21}\,\mathrm{cm^2\,sec^{-1}}$ at 300° C are reported.

2. Experimental methods

Multilayered films were deposited on to optically flat Pyrex glasses using an ion-beam sputtering (IBS) apparatus. Details of the IBS apparatus have been published elsewhere [3, 4].

Commercially available zinc oxide (ZnO) and copper oxide (CuO) targets were used; the purity of ZnO and CuO were 99.999% and 99.9%, respectively. An equimolar mixture of ZnO and CuO was also used as a target; it was fabricated by mixing the powders, pressing the mixture into a disc and sintering the compact at 900° C for 10 h. These targets were sputtered alternately to form multilayered films of ZnO/CuO and ZnO/ZnOCuO/CuO as depicted in Fig. 2. The temperature of the substrate did not exceed 100° C during sputtering. Fig. 3 is a schematic illustration of a ZnO/CuO film where d is the pair thickness and l is the total film thickness. This series of film was designed to be $l \sim 200$ nm and $d = 0$ to ~ 9 nm; $d = 0$ means that the film does not have a layered structure and that the film is deposited from the sintered ZnOCuO target. Another series of film, ZnO/ZnOCuO/CuO, consisted of ZnO layers, CuO layers and layers of ZnOCuO. The thickness of the ZnOCuO layer was designated d(ZnOCuO) and it varied from 0 to 1.7 nm.

The film thickness and thus the deposition rate were measured first with a surface measuring instrument (Ferfcom, Tokyo Precision) and then calculated from the low-angle X-ray diffraction (XRD) peaks of the multilayered films composed of ZnO/Pt, CuO/Pt and ZnOCuO/Pt.

The thickness of the as-deposited films is referred to for identifying the films throughout this experiment; although the thickness changed little on annealing. Annealing of these films was carried out in an electric furnace in air. XRD was taken using 30 kV–20 mA nickel-filtered Cu$K\alpha$ radiation (Rigaku, RAD-B). The low-angle X-ray intensity data were collected with a scan speed of $0.1° \min^{-1}$ and a step sampling of 0.002° in 2θ. The integrated intensity was used to obtain a decay rate of a low-angle diffraction peak.

3. Results and discussion

3.1. Deposition rate

A layer repeat length (or pair thickness), d, of a multilayered film is generally determined from the low-angle diffraction peaks of the nth order according to the following Bragg equation

$$d_n = \frac{n\lambda}{2 \sin \theta} \qquad (1)$$

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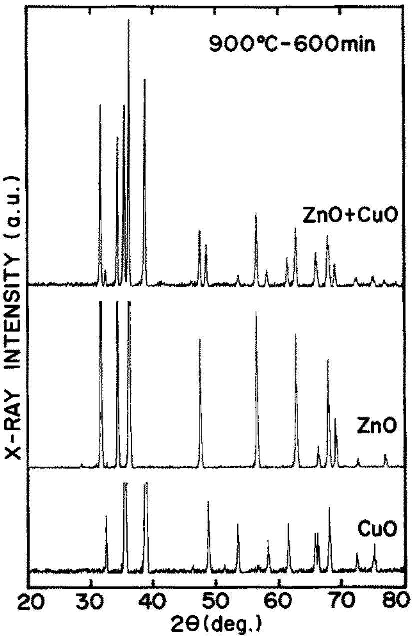

Figure 1 XRD diagrams of ZnO, CuO and (ZnO + CuO) powders sintered at 900° C for 600 min in air.

or

$$d_{n,n+1} = \frac{\lambda}{2}\left(\frac{2n+1}{\sin^2\theta_{n+1} - \sin^2\theta_n}\right)^{1/2} \qquad (2)$$

An example of a diffraction diagram of a ZnO/ZnOCuO/CuO multilayered film is given in Fig. 4. The layer repeat length of this film is 7.5 nm and the corresponding Bragg reflection from $n = 1$ to 5 is clearly observed.

The deposition rate of ZnO, CuO and ZnOCuO was determined using similar XRD charts to that in Fig. 4 in multilayered films of ZnO/Pt, CuO/Pt and ZnO-CuO/Pt. The sputtering time of the platinum was set always to 10 sec and the resulting pair thickness is shown in Fig. 5 as a function of the target sputtering time. The slope of the straight line gives the deposition rate. Thus the deposition rates of ZnO, CuO and ZnO-CuO were found to be 0.046, 0.017 and 0.017 nm sec^{-1}, respectively. The low deposition rate of the sintered ZnOCuO target may be due to the porous texture of the mixture.

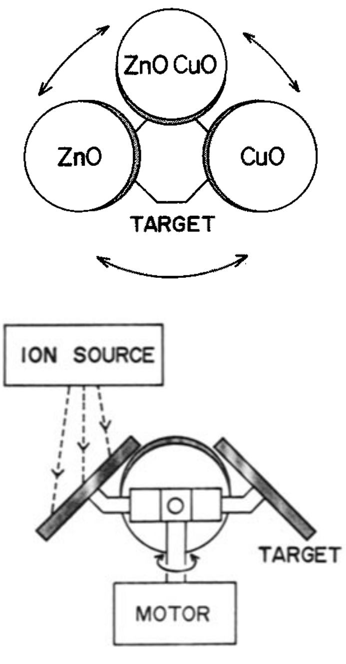

Figure 2 Target configuration for deposited multilayered films of ZnO/ZnOCuO/CuO and ZnO/CuO by ion-beam sputtering. The stepping motor controls the sputtering time and thus the layer thickness.

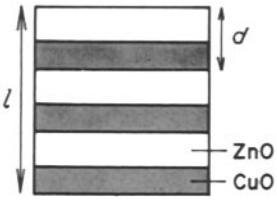

Figure 3 Schematic representation of pair thickness (layer repeat length), *d*, and the total film thickness, *l*, in a multilayered film.

3.2. Preferred orientation

This section deals with the thickness dependence of the preferred orientation of the ZnO(0 0 2) planes parallel to the substrate surface in multilayered ZnO/CuO and ZnO/ZnOCuO/CuO films.

The ZnO/CuO series ($l \sim 200$ nm) were designed so that the ZnO and CuO layers may have equal thickness ($d/2$). However, the composition of the $d = 0$ sample, i.e. the film deposited from the sintered ZnO-CuO target, is left unanalysed.

Nine as-deposited films showed only broad haloes indicating the amorphous or microcrystalline nature of the film. These films were annealed at 500° C and X-rayed. Figs 6 a, b and c show the XRD charts of films annealed for 10, 1000 and 10 000 min, respectively. Fig. 6a shows three outstanding features on the crystallographic orientation in hexagonal würtzite ZnO (JCPDS 5-0664) layer: (1) films with ZnO layer thickness thinner than ~0.6 nm ($d = 1.1$ nm) exhibit

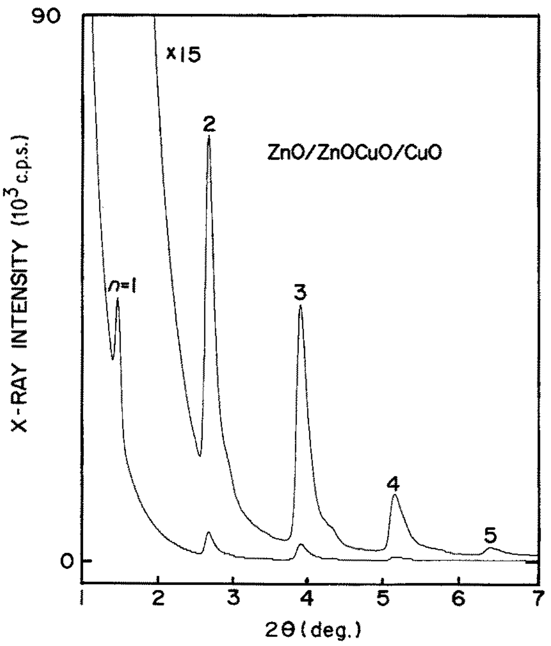

Figure 4 Small-angle XRD diagram from a ZnO/ZnOCuO/CuO multilayered film. The layer repeat length is 7.5 nm.

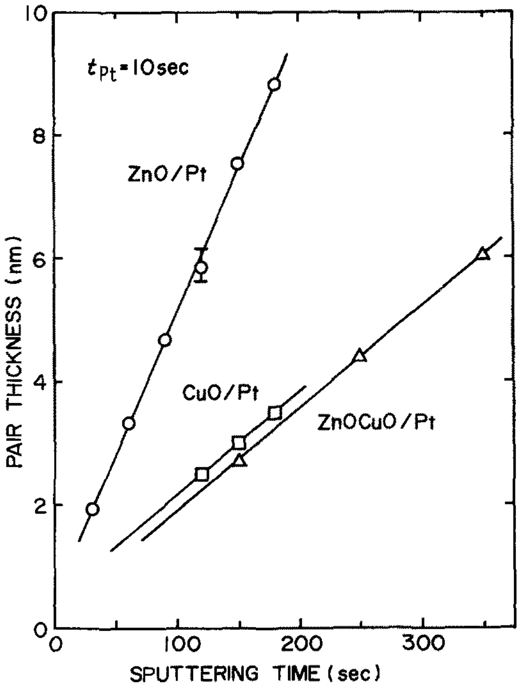

Figure 5 Pair thickness as a function of sputtering time. The sputtering time of platinum is 10 sec.

no sharp XRD peaks indicative of crystallization or grain growth; (2) a sudden occurrence of the preferred (0 0 2) orientation in the ~1.2 nm (d = 2.3 nm) ZnO layer; (3) reducing preferential orientation as the layer thickness increases from ~1.7 to ~4.5 nm (d = 8.9 nm). Annealing the film up to 10 000 min (Fig. 6c) did not change these features except that the X-ray intensity of the d = 4.5 nm film became slightly stronger than that of the d = 3.4 nm film.

The behaviour of the d = 0 to 1.1 nm film is interpreted in two ways. The c-axis of the hexagonal würtzite structure is 0.5205 nm long and this is approximately equal to the ZnO layer thickness, ~0.6 nm, in the d = 1.1 nm film. In other words, ZnO layers thinner than the lattice constant c do not crystallize to the hexagonal würtzite structure but they remain as amorphous or microcrystalline. Another interpretation is that the XRD with a wavelength of 0.154 nm could not detect crystallites as small as ~0.6 nm. Both interpretations seem plausible and we do not know which is really taking place.

The fact that the low-angle Bragg reflection disappeared in all films after annealing at 500° C for 10 min means that the crystallization largely violated the regularity of the layered structure. Further, the occurrence of no peaks at 2θ = 10° to 80° after annealing at 500° C for 10 000 min signifies that the coalescence of the ZnO layers into larger grains and grain growth in the d = 0 film are blocked, because of the negligibly small interdiffusivity of constituent atoms; the interdiffusivity is discussed in the next section.

The films with d = 2.3 to 8.9 nm are characterized by the preferential c-axis orientation normal to the substrate as a function of the ZnO layer thickness, $d/2$, and the annealing time. The strongest (0 0 2) reflection intensity shifted towards a thicker layer side with

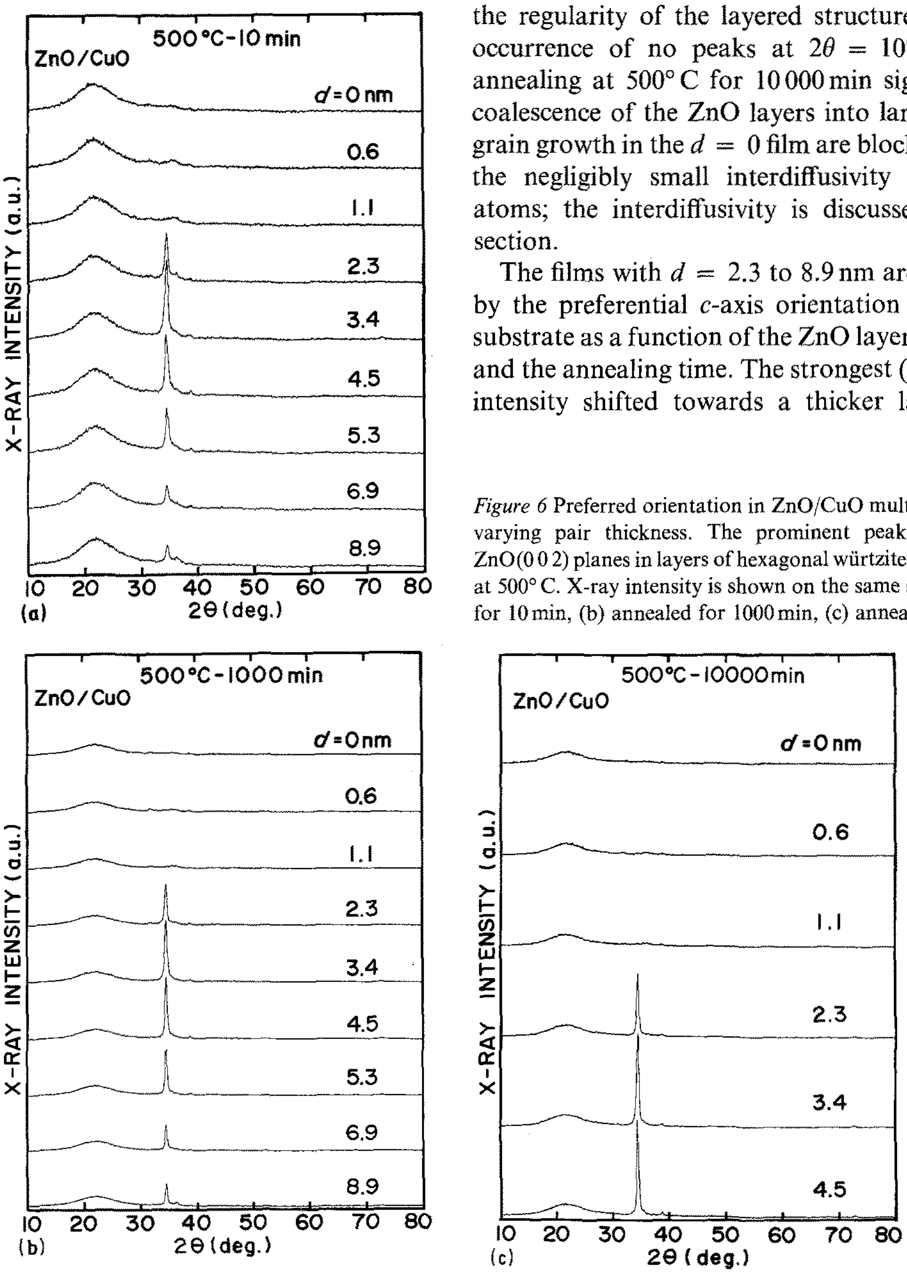

Figure 6 Preferred orientation in ZnO/CuO multilayered films with varying pair thickness. The prominent peak comes from the ZnO(0 0 2) planes in layers of hexagonal würtzite structure annealed at 500° C. X-ray intensity is shown on the same scale. (a) Annealed for 10 min, (b) annealed for 1000 min, (c) annealed for 10 000 min.

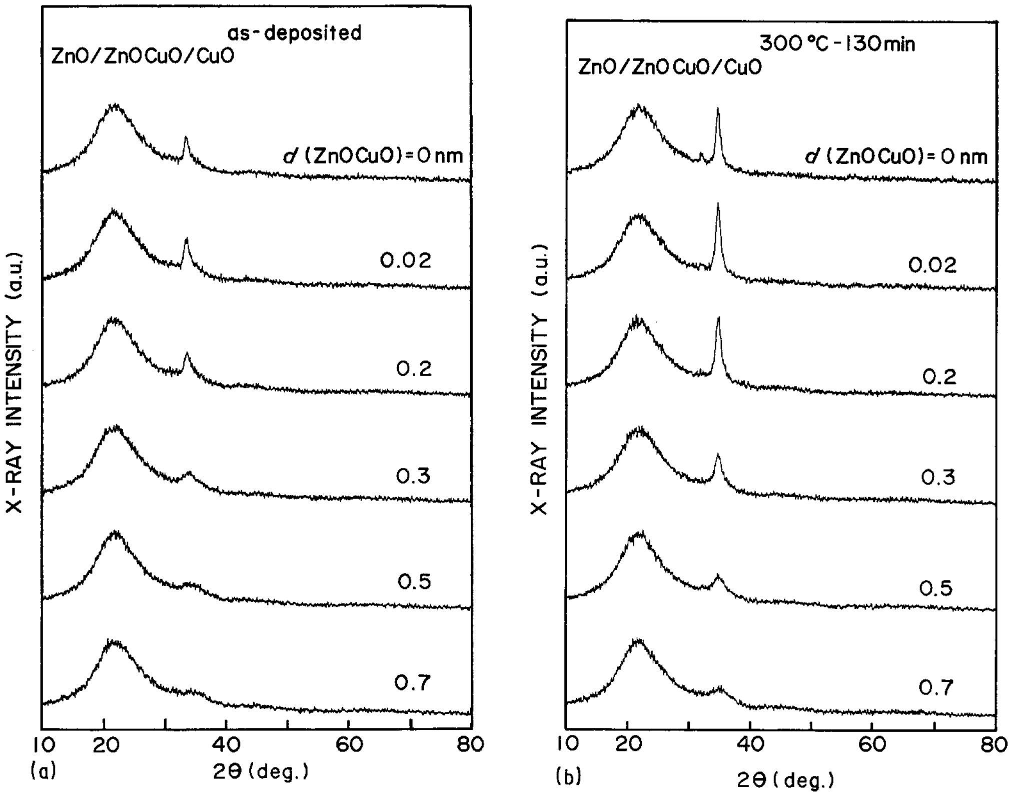

Figure 7 Preferred orientation in ZnO (1.8 nm)/ZnOCuO/CuO (0.7 nm) multilayered films with varying ZnOCuO thickness, d(ZnOCuO). The prominent peak comes from the ZnO(0 0 2) planes in layers of hexagonal würtzite structure. X-ray intensity is shown on the same scale. (a) As-deposited, (b) annealed at 300° C for 130 min.

prolonged annealing; i.e. from $d = 3.4$ nm film annealed for 10 min to $d = 4.5$ nm film annealed for 10 000 min. This suggests that a larger freedom of the c-axis orientation allowed in thicker films was restricted with the grain growth. Thus we see that the ultrathin layers (~ 1 to ~ 3 nm) induced the preferred c-axis orientation normal to the surface. This makes a contrast against the observation in thicker films where a strong c-axis orientation is reported to be independent of thickness [5].

But what is the driving force to make an ultrathin layer preferentially oriented? Supposing one factor to be the ZnO/CuO interfacial stress, preferred orientation in the ZnO/ZnOCuO/CuO series was then examined; insertion of the ZnOCuO layer is expected to relax the stress. Figs. 7a and b show the XRD diagrams of films composed of ZnO (1.8 nm)/ ZnOCuO/CuO (0.7 nm) × 50 pairs; d (ZnOCuO) varied from 0 to 0.7 nm. The ZnO layer thickness, 1.8 nm, corresponds to the optimum thickness causing the strongest c-axis orientation. The small peak at $2\theta \sim 32°$ for d(ZnOCuO) = 0 in Fig. 7b is identified as ZnO(1 0 0). The figures clearly show that the intensity of the ZnO(0 0 2) reflection decreased as the d(ZnOCuO) increased from 0 to 0.7 nm in both as-deposited and annealed films. Thus far the observation is favourable to the supposition that crystallization (or grain growth) and preferred orientation are stress-induced. It is to be noted that the as-deposited film of ZnO (1.7 nm)/CuO (1.7 nm) × 60 pairs was amorphous (or microcrystalline) and that of

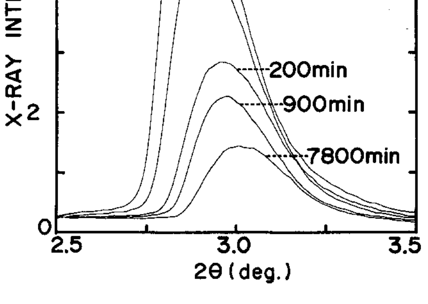

Figure 8 The first order ($n = 1$) diffraction peak from the ZnO (1.7 nm)/CuO (1.7 nm) × 60 pairs as a function of annealing time at 300° C.

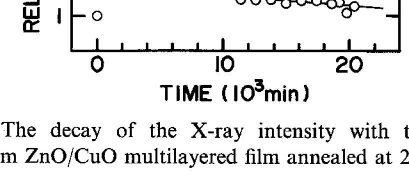

Figure 9 The decay of the X-ray intensity with time in the $d = 2.3$ nm ZnO/CuO multilayered film annealed at 250° C.

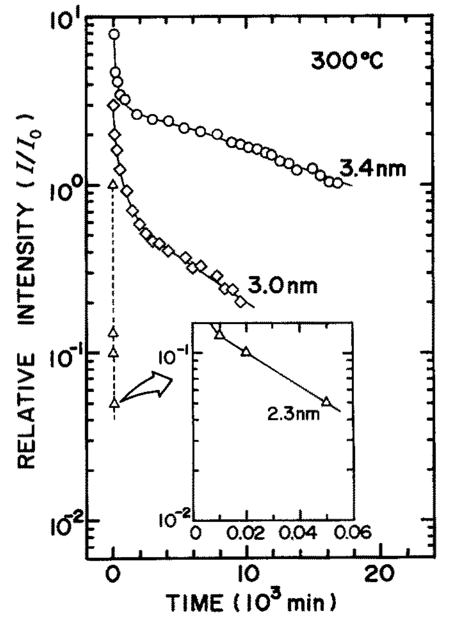

Figure 10 The decay of the X-ray intensity with time in the d = 3.4, 3.0 and 2.3 nm ZnO/CuO multilayered films annealed at 300° C.

ZnO (1.8 nm)/CuO (0.7 nm) × 50 pairs was crystalline.

3.3. Interdiffusion

Properties of the heterojunction in multilayered films are largely dependent on the nature of the interface whose concentration gradient is introduced by the interdiffusion. Thus, the interdiffusivity is one of the most important factors to characterize the physical properties of the multilayered films.

It was Dumond and Youtz [6] who proposed a method of obtaining a very low value of interdiffusivity, $\tilde{D}_d$, from the decay rate of the first order ($n = 1$) satellite X-ray intensity, $I(t)$, in multilayered films

$$\tilde{D}_d = -\frac{\log_e[I(t_0)/I(t)]}{8\pi^2(t - t_0)}\, d^2 \qquad (3)$$

where t is the time. Because the satellite peaks in ZnO/CuO multilayered films disappeared instantly when annealed at 500° C, interdiffusivity at 250 and 300° C was examined here. Fig. 8 shows an example of the $n = 1$ X-ray intensity at various annealing times at 300° C. A general tendency is the shift of the peak position to higher angles and the broadening of the peak with annealing time; the former comes from a shortening of the interplanar distance and the latter mainly from the occurrence of uneven ZnO/CuO interface.

In real polycrystalline films, the decay rate is induced not only by the homogeneous diffusion normal to the ideal layers, as is assumed to derive Equation 3, but also through a heterogeneous diffusion path via dislocations and grain boundaries [7]. However, we adopt Equation 3 as an approximation here, and discuss the interdiffusivity in polycrystalline multilayered films.

Fig. 9 shows the decay rate of the integrated peak intensity at 250° C in ZnO (1.1 nm)/CuO (1.2 nm) × 90 pairs (d = 2.3 nm); the linear portion of the diagram ($t > 10^4$ min) yields $D_d = (1.4 \pm 1.1) \times 10^{-22}\,\text{cm}^2\,\text{sec}^{-1}$. Similarly, as shown in Fig. 10, the change of the X-ray intensity at 300° C in films of ZnO (1.7 nm)/CuO (1.7 nm) × 60 pairs (d = 3.4 nm), ZnO (1.5 nm)/CuO (1.5 nm) × 78 pairs (d = 3.0 nm) and ZnO (1.1 nm)/CuO (1.2 nm) × 90 pairs (d = 2.3 nm) gives $(1.6 \pm 0.1) \times 10^{-21}$, $(2.4 \pm 0.3) \times 10^{-21}$ and $(2.4 \pm 0.3) \times 10^{-19}\,\text{cm}^2\,\text{sec}^{-1}$, respectively.

Thus we see an overwhelmingly important role of the interplanar distance to enhance the interdiffusion; the d = 2.3 nm film has a value of interdiffusivity 100 times higher than that of the d = 3.0 nm film. A large temperature dependence of $\tilde{D}_d$ in the d = 2.3 nm film was also observed; the interdiffusivity increased by nearly three orders of magnitude (10^{-22} to $10^{-19}\,\text{cm}^2\,\text{sec}^{-1}$) on increasing the temperature from 250 to 300° C.

4. Conclusions

Preferred orientation in hexagonal würtzite structure of ZnO layers and the interdiffusion in ZnO/CuO multilayered films were examined.

1. Ultrathin ZnO layers, ~1 to ~3 nm thick, showed the preferred c-axis orientation normal to the surface in multilayered ZnO/CuO films.

2. The degree of preferred orientation was reduced as the layer thickness increased from ~1.7 to ~4.5 nm in ZnO/CuO films at the first stage of annealing. It was also reduced as the ZnOCuO layer thickness increased from 0 to 0.7 nm in ZnO/ZnOCuO/CuO films.

3. Interdiffusivity in ZnO/CuO films was largely dependent on the interplanar distance; the d = 2.3 nm film showed a value ($2.4 \times 10^{-19}\,\text{cm}^2\,\text{sec}^{-1}$) 100 times higher than of the d = 3.0 nm film ($2.4 \times 10^{-21}\,\text{cm}^2\,\text{sec}^{-1}$) at 300° C.

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