Residual stress and bending strength of ZnO films deposited on polyimide sheet by RF sputtering system

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(Received 16 September 2015; accepted 8 March 2016; published 24 March 2016)

Zinc oxide (ZnO) films were deposited on a soft polyimide sheet substrate by radio frequency sputtering with a ZnO powder target, and the films' crystal orientations and residual stress were investigated using x-ray diffraction as a function of substrate temperature. C-axis oriented ZnO films were achieved using this ZnO powder target method. The ZnO films exhibited high compressive residual stresses between −0.7 and −1.4 GPa. Finally, the authors examined the strength of the obtained film by applying tensile bending loads. No cracks were observed on the surfaces of the ZnO films after a bending test using cylinders with diameters >25 mm. After a bending test using a cylinder with a diameter of 19 mm, large cracks were formed on the films. Therefore, the authors concluded that the tensile bending strength of the obtained films was greater than ∼420 MPa. © *2016 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4944610]

I. INTRODUCTION

Zinc oxide (ZnO) films are desirable for use as liquid crystal panel displays and solar cells because of their high electrical conductivity and optical transparency.[1,2] Compared to indium tin oxide films, ZnO films are more attractive because they can be synthesized at low deposition temperatures (∼200 °C) and the constituent material is easier to obtain at low cost. For the use of ZnO films as transparency electrodes, low resistivity is required, and the films must have c-axis crystal orientation.

Flexible displays are attracting attention as a next-generation technology. In particular, flexible organic electroluminescent displays have been actively researched and developed.[3–5] If a ZnO film can be developed that is resistant to deformation, it may then be possible to develop a flexible liquid crystal display.

In the present investigation, ZnO films were deposited on a soft polyimide sheet using a radio frequency (RF) magnetron sputtering system with a powder ZnO target. The resulting films' c-axis crystal orientations and residual stresses were analyzed using x-ray diffraction. In addition, the bending strengths of the obtained films were examined.

II. EXPERIMENTAL METHODS

A. Film preparation

ZnO films were prepared using a RF planar magnetron sputtering system. The material selected for the target was ZnO powder (Wako Pure Chemical Industries, Ltd.). The grain size of the ZnO powder was about 5 μm, and the purity was 99.9%. The target holder was a stainless-steel dish measuring 100 mm in outside diameter, 5 mm in thickness, 80 mm in inside diameter, and 1 mm in depth. ZnO powder was poured into the dish. The ZnO films were deposited on a polyimide sheet substrate (Kapton H-type: Dupont-Toray Co., Ltd.) measuring $30 \times 20 \times 0.25\,\mathrm{mm}^3$. The Young's modulus and the Poisson's ratio of the polyimide sheet substrate were 3.4 GPa and 0.3, respectively.[6] The coefficient of thermal expansion of the substrate was 2.7×10^{-5}/°C.[6] The substrate was heated using a ceramic heater in the substrate holder. The substrate temperature was measured using a thermocouple placed on the substrate surface.

The ZnO films were deposited by RF sputtering at a constant input power of 120 W, a deposition time of 3 h, a constant argon atmosphere gas pressure of 0.6 Pa, and various substrate temperatures (T_S) between 100 and 300 °C.

B. X-ray stress analysis of c-axis oriented structure

ZnO has a hexagonal wurtzite structure with lattice parameters of $a = 0.3250$ nm and $c = 0.5204$ nm.[7] As will be shown in the results described below, the c-axes of ZnO crystals in the deposited films lie normal to the substrate surface. Therefore, the conventional $\sin^2\psi$ method[8] for stress evaluation is not applicable to the present case. The stress analysis method used for this investigation is briefly explained, as follows.

When the stress in the film is equibiaxial, the relationship between lattice strain $\varepsilon^L_{(hk\times l)}$ and stress σ is given by

$$\varepsilon^L_{(hk\times l)} = \{(s^*_{11} + s^*_{12} - 2s^*_{31})\sin^2\psi_{hk\times l} + 2s^*_{31}\}\sigma, \quad (1)$$

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TABLE I. Diffraction planes and related parameters.

hk × l	2θ (deg.)	ψ (deg.)	$\mathrm{Sin}^2\psi$
00 × 2	34.43	0	0
10 × 1	36.26	61.6	0.774
10 × 3	62.88	31.6	0.275

where s_{ij}^* are elastic compliances of a single ZnO crystal and ψ is the angle between the normal axis of the diffracting plane and the normal axis of the surface, which in the present case corresponds to the c axis. Equation (1) indicates that the lattice strain for each diffraction plane should vary linearly with $\sin^2\psi$. Stress can be estimated from the slope of linear least-squares fit of the data and from the elastic compliance of zinc oxide. The values of s_{11}^*, s_{12}^*, and s_{31}^* are 7.8×10^{-3}, -3.4×10^{-3}, and $-2.2 \times 10^{-3}\mathrm{GPa}^{-1}$, respectively.[7]

In this stress analysis method, we must use various diffraction planes that appear within a wide range of ψ angles. Table I shows the diffraction planes used in the present study, as well as the corresponding Bragg angles, ψ angles, and values of $\sin^2\psi$. CuKα characteristic x-rays were utilized for measurement of lattice strain.

ZnO powder was used as a standard material to prevent errors caused by misalignment of the stress measurement system. At the ψ angle, which is crystallographically determined for each diffraction, the positions of the diffraction lines for the powder and those for the film were measured. Strain was calculated using the following equation:

$$\varepsilon_{33}^L = \varepsilon_{(hk\times l,\,\psi)} = \frac{d_{f(hk\times l,\psi)} - d_{p(hk\times l,\psi)}}{d_{p(hk\times l,\psi)}}, \tag{2}$$

where d_f and d_p are the measured interplanar distances of the film and the powder, respectively.

C. Tensile bending test

Seven steel cylinders of different diameters were prepared for the tensile bending strength test. The diameters of the steel cylinders ranged between 12 and 50 mm, as shown in Table II. The bending test was conducted starting with the cylinder with the greatest diameter of the cylinder and then in order by diminishing diameter, using the same sample each time. The short end of a sample coated with zinc oxide film on a polyimide substrate was fixed to a steel cylinder with a polyimide sheet. It was then wound slowly along the cylinder, as shown in Fig. 1. The zinc oxide film was oriented facing the polyimide sheet for the test. Therefore, tensile bending stress was generated in the zinc oxide film. The tensile bending stress σ_A was calculated by the following equation:

TABLE II. Diameter of steel cylinder used for bending test, and calculated values of bending stress applied to film.

Diameter of cylinder for bending test D (mm)	Calculated bending stress (GPa)
50	0.57
36	0.79
28	1.02
25	1.14
19	1.49
16	1.77
12	2.36

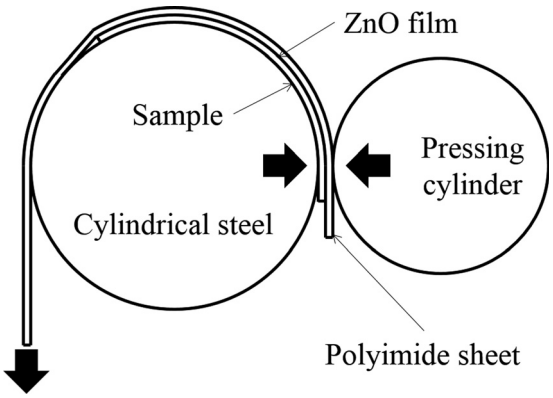

FIG. 1. Tensile bending test.

$$\sigma_A = \frac{1}{s_{11}^* + s_{12}^*} \times \frac{t_f + t_s}{2R + t_s}, \tag{3}$$

where t_f and t_s are thickness of the film and the substrate, respectively, s_{ij}^* represents elastic compliances of a single crystal for the film, and R is the radius of the cylinder. The calculated values of t_f and t_s were 0.7 and 125 μm, respectively. The calculated bending stresses are presented in Table II. After the bending test, we observed the film surface using an optical and scanning electron microscopes.

III. RESULTS AND DISCUSSION

A. Structural evaluation of the ZnO film

Figure 2 shows diffraction patterns taken from the ZnO films deposited at various substrate temperatures ranging from 100 to 300 °C. The peak observed at $2\theta = 27°$ indicates the diffraction from the polyimide substrate. The ZnO film produced a peak at the position of $2\theta = 34.4°$ for all samples.

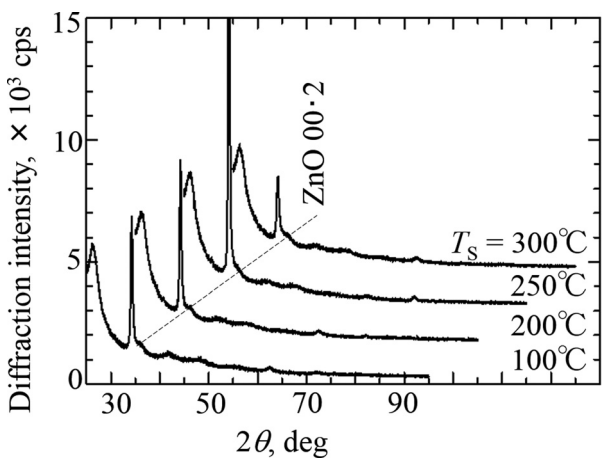

FIG. 2. Diffraction patterns of the ZnO films deposited on polyimide sheet substrate at the conditions of various TS.

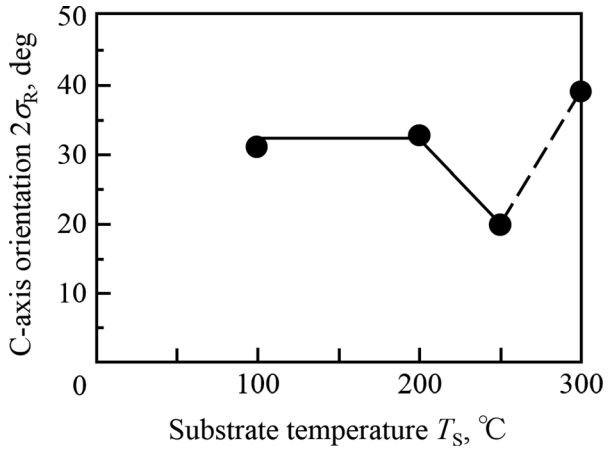

FIG. 3. Effect of substrate temperature on c-axis orientation.

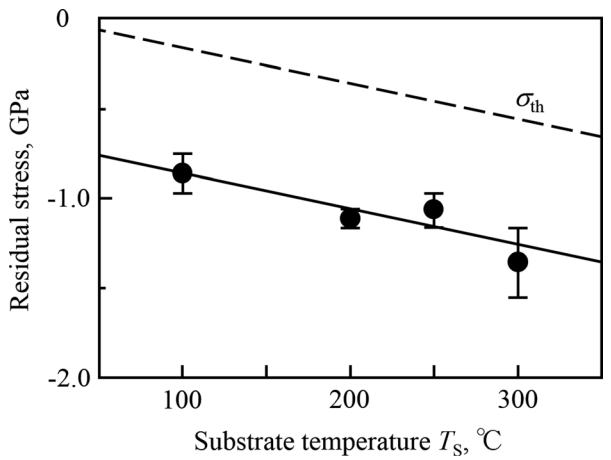

FIG. 4. Effect of substrate temperature on residual stress in ZnO film.

This result indicates that the c-axes of ZnO crystals in deposited films are oriented along the normal axis of the substrate surface. The intensity of 00 × 2 diffraction reached a maximum in the ZnO film deposited at $T_S = 250\,^{\circ}\mathrm{C}$.

B. C-axis orientation

Figure 3 shows the effect of substrate temperature on c-axis orientation. C-axis orientation is equivalent to twice the standard deviation of the rocking curve ($2\sigma_R$). When $2\sigma_R$ is low, c-axis orientation is favorable.[9] The film deposited at $T_S = 250\,^{\circ}\mathrm{C}$ had the most favorable c-axis orientation.

At low substrate temperatures, many atoms deposited on the substrate are restricted from move freely on the substrate surface, resulting in the formation of many crystal nuclei. These nuclei grow without surface diffusion, leading to the formation of many small crystals. As a result, the crystalline quality of the deposited ZnO film degrades. In contrast, at high substrate temperatures, atoms deposited on the substrate have high mobility due to thermal energy imparted by the substrate. As a result, the crystalline quality of the deposited film improves. In the case of $T_S = 300\,^{\circ}\mathrm{C}$, the polyimide substrate is slightly deformed by heat and thermal stress. We attribute this to the fact that the c-axis orientation of the deposited film degrades when the substrate becomes deforms.

C. Residual stress in ZnO film

Figure 4 shows the effect of substrate temperature on residual stress in ZnO films deposited on a polyimide sheet. The residual stresses were compressive for all films. The compressive stress increased linearly with increasing substrate temperature. A dashed line represents the thermal stress σ_{th} that was produced from the difference in thermal contraction between the film and the substrate in the cooling

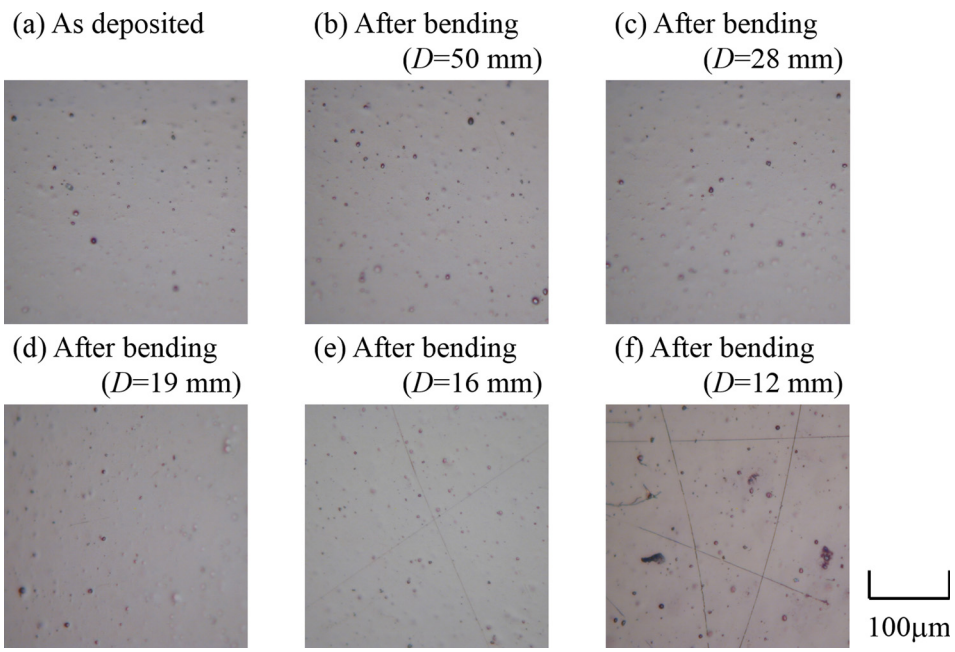

FIG. 5. (Color online) Optical micrographs of the ZnO film surface before and after the bending test.

process. The amount of thermal stress σ_{th} in a film deposited on a substrate is estimated using the following equation:[10]

$$\sigma_{th} = \frac{1}{s_{11}^* + s_{12}^*}(\alpha_f - \alpha_s)\Delta T, \quad (4)$$

where s_{ij}^* are elastic compliances of a single crystal for the film, α_f and α_s are thermal expansion coefficients of the film and the substrate, respectively, and ΔT is the difference between deposition temperature and room temperature.

Residual stress is the sum of the intrinsic stress and thermal stress. In this investigation, the amount of the intrinsic stress in ZnO films was −0.7 GPa. It is thought that this intrinsic stress in the films occurred by ion peening.

D. Tensile bending test of ZnO film

Figure 5 shows the optical micrographs of the ZnO film surface before and after the bending test. The ZnO film deposited on the polyimide substrate at the substrate temperature *T*s of 250 °C was used for this test. There were no cracks on the surface of the as-deposited film. After a bending test using cylinders with diameters of >19 mm, no cracks were observable on the surfaces of the ZnO films. Large cracks were visible after the bending test using a cylinder with a diameter of 16 mm. When a cylinder with 12-mm diameter was tested, the cracks became larger, and some visible peeling of the substrate occurred. This sample had large compressive residual stress (−1.07 GPa). Based on the values given in Table II, the tensile strength of the obtained film was found to be ≥420 MPa.

IV. CONCLUSIONS

ZnO films were deposited on a soft polyimide sheet substrate by RF sputtering with a ZnO powder target. The films' crystal orientations and residual stresses were investigated by x-ray diffraction as functions of substrate temperature. C-axis orientation was achieved for the ZnO films by using the ZnO powder target for sputter deposition, with the most favorable orientation at a substrate temperature of 250 °C. The ZnO films had high levels of compressive residual stress between −0.7 and −1.4 GPa. Finally, we examined the strength of the obtained film by applying tensile bending loads finding that the tensile strength was at least 420 MPa.

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