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Characterization of biaxial stress and its effect on optical properties of ZnO thin films

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Biaxial stress of ZnO film deposited on quartz was measured by side-inclination x-ray diffraction technique, indicating that the film is subjected to a tensile stress. One part of the stress is induced by thermal mismatch between the ZnO and the quartz and increases with annealing temperature, while another part results from lattice mismatch and is about 1.03 GPa. The optical band gap of the ZnO film shows a blueshift with increasing biaxial tensile stress, opposed to the change of the band gap with biaxial tensile stress for GaN. The mechanism of the stress-dependent band gap is suggested in the present work. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2757149]

Zinc oxide (ZnO) has attracted much attention in recent years because of its many potential application, especially in short wavelength optoelectronic devices, such as ultraviolet (UV) light-emitting diodes and laser diodes.[1] Many heteroepitaxy techniques, such as magnetron sputtering, metal organic vapor phase epitaxy, and molecular beam epitaxy, etc., are used to fabricate ZnO films. However, residual stress always exists inevitably in the ZnO films due to lattice mismatch between the substrate and the film as well as thermal mismatch induced by difference in the thermal expansion coefficients of the substrate and the film. It affects crystalline quality as well as optical and electrical properties of ZnO film. Hence, it is significant to characterize the biaxial stress of ZnO film and to study the influence of the biaxial stress on the crystal quality and the properties for obtaining ZnO films with high crystal quality and good properties.

There are several measurement methods for biaxial stress of film, for example, x-ray diffraction (XRD),[2] Raman spectroscopy,[3] the technique of curvature measurement,[4] etc. XRD is often used to measure biaxial stress of film because strain can be calculated directly by Bragg's equation. In addition, it is also a nondestructive measurement method. In some reported literatures,[5,6] biaxial strain of ZnO film is calculated by measurement of diffraction peak position shift compared to bulk ZnO. But the correction of the strain measurement by this method is strongly dependent on the precision of the measured lattice constants as well as value of lattice constants of bulk ZnO you selected. Since there are errors in XRD measurement and various lattice constants for bulk ZnO in reported literatures, the correction of the stress measurement is strongly affected by precision of the XRD measurement as well as selected value of lattice constants of the bulk. Even tensile stress (or compressive stress) in films can be considered wrongly as compressive stress (or tensile stress). However, with the side-inclination x-ray diffraction method, biaxial stress measurement is not dependent on absolute position of the diffraction peak but relative shift of the peak position at various inclination angles, making the biaxial stress measurement precise and reliable.

In the present work, the biaxial stress of ZnO film was measured by the side-inclination XRD technique. The origin of the biaxial stress and effect of the stress on band gap of the ZnO film were investigated by combining the measurement results with first-principles calculation.

ZnO films were deposited on quartz substrate at 240 °C for 2 h by sputtering ZnO target (99.99% pure) with Ar gas using reactive radio-frequency magnetron sputtering technique. The growth pressure is 1.0 Pa and the sputtering power is 100 W. The ZnO film was annealed for 30 min in oxygen ambient in a temperature ranging from 400 to 800 °C. The structure and stress measurements were performed by using XRD with Cu K_α radiation of 0.154 05 nm. The surface morphology was observed by using field-emission scanning electronic microscope (FESEM). The absorption spectra of the ZnO films were recorded by UV-vis near infrared spectrophotometer.

Since polycrystalline ZnO film can be considered as an isotropic thin film according to elastic properties of ZnO, its biaxial stress can be measured by the side-inclination XRD method, which is described in detail elsewhere[7] and is calculated by using following equation:

$$\sigma_{xx} = -\frac{E}{2(1+\nu)}\frac{\pi}{180}\cot\theta_0\frac{\partial(2\theta)}{\partial\sin^2\psi}, \quad (1)$$

where σ_{xx}, E, ν, θ_0, ψ, and 2θ are the biaxial stress, Young's modulus, Poisson ratio, diffraction angle of bulk material, inclination angle, and diffraction angle at inclination angle ψ, respectively.

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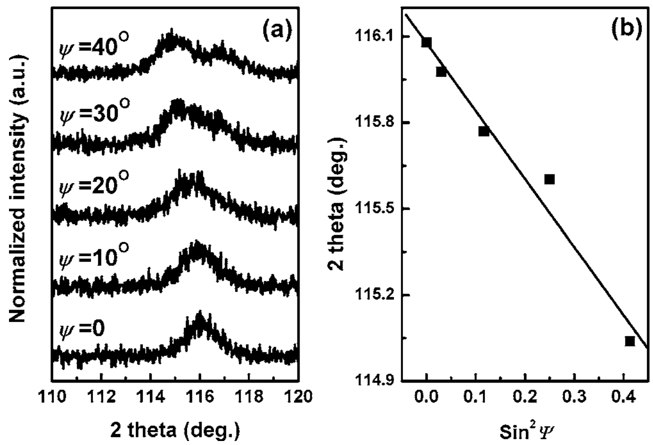

FIG. 1. (a) XRD patterns of (213) diffraction peak for the as-grown ZnO film measured at different inclination angles ψ and (b) a plot of diffraction angles of the (213) peak as a function of $\sin^2\psi$.

Since high diffraction angle has good resolution and (213) diffraction peak of the ZnO film located at diffraction angle of $2\theta \approx 116°$ has stronger intensity, the (213) peak was used to measure biaxial stress in the present work. Figure 1(a) shows XRD patterns of the (213) peak of the as-grown ZnO film (denoted as S1) measured at inclination angles (ψ) between 0° and 40°, indicating that the diffraction angles (2θ) decrease with increasing inclination angle ψ. An additional weak shoulder appears at higher diffraction angle side of the peak while ψ=40°, it is attributed to peak shape asymmetry, which is induced by difference in paths that the incidence and diffraction rays go in the thin film as inclination angle is not zero. But the shoulder does not affect the measurement result of biaxial stress. Figure 1(b) shows a plot of the diffraction angle 2θ of the sample S1 as a function of $\sin^2\psi$, presenting a good linear relationship between the 2θ and $\sin^2\psi$. By fitting the data of Fig. 1(b) with a linear function, a slope is obtained, as shown in Fig. 1(b). Obviously, the slope is less than zero. By using the slope and Eq. (1), the biaxial stress (σ_{xx}) of the as-grown ZnO film was calculated, as listed in Table I. The σ_{xx} is larger than zero, indicating that the as-grown ZnO film is subjected to a biaxial tensile stress. By using the method mentioned above, the biaxial stresses of the ZnO annealed at various temperatures were calculated, and listed in Table I. Table I shows that as-grown and annealed ZnO films are subjected to a biaxial tensile stress, which increases gradually from 1.45 to 2.01 GPa with increasing annealing temperature from 240 to 800 °C. In addition, it is found from Table I that diffraction angles of (002) peak of all samples, as shown in Table I, is larger than 34.42° of the bulk ZnO, implying that the ZnO films are subjected to a compressive stress in *c*-axis

TABLE I. Diffraction angles of (002) peak, measured biaxial stress, as well as calculated thermal and lattice mismatch stresses of as-grown and annealed ZnO films.

Samples	T_{anneal} (°C)	σ_{xx} (GPa)	σ_{th} (GPa)	σ_{latt} (GPa)	2θ (deg)
S1	240	1.45	0.30	1.15	34.64
S2	400	1.60	0.51	1.09	34.80
S3	600	1.71	0.78	0.93	34.82
S4	800	2.01	1.05	0.96	34.81

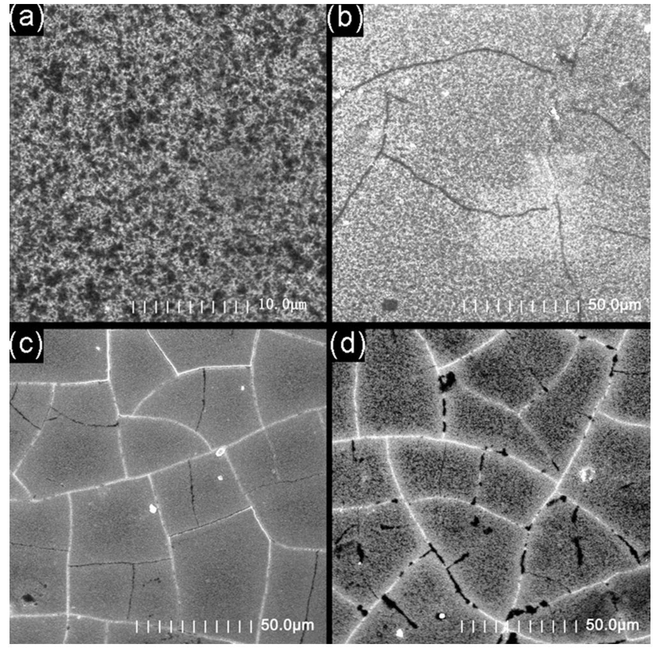

FIG. 2. FESEM photomicrograph of (a) the as-grown ZnO film and the film annealed at (b) 400, (c) 600, and (d) 800 °C, respectively.

direction. That confirms the existence of biaxial tensile stress in the all ZnO films. Figure 2 shows surface morphologies of all samples. There is no any crack at surface of the as-grown ZnO. The cracks begin to appear at the surface of the ZnO film annealed at 400 °C, and the density of the cracks increases with increasing annealing temperature. These results demonstrate further that there is biaxial tensile stress in the ZnO films and that the tensile stress increases as annealing temperature rises.

It is well known that the biaxial stress of thin film originates from intrinsic and extrinsic stresses. The intrinsic stress is associated with defects and impurities. The extrinsic stress is mainly related to lattice mismatch, and thermal mismatch and can be expressed as

$$\sigma_{xx} = \sigma_{th} + \sigma_{latt}, \tag{2}$$

where σ_{th} and σ_{latt} are the stresses induced by thermal mismatch and lattice mismatch, respectively. It is difficult to calculate the stress introduced by lattice mismatch between ZnO film and quartz substrate because quartz is amorphous material. However, the stress resulted from thermal mismatch can be calculated by following formula:

$$\sigma_{th} = \int_{T_{growth/anneal}}^{RT} (\alpha^f - \alpha^b)\frac{E}{1-\nu}dT, \tag{3}$$

where α^f are thermal expansion coefficients of the film deposited on substrate and α^b are thermal expansion coefficients of the corresponding bulk material. If the stress is not relaxed, α^f can be replaced by the thermal expansion coefficients of the substrate α^s. The thermal expansion coefficients can be considered as a constant within the narrow range of temperature. Using Eq. (3), the σ_{th} of the as-grown and annealed ZnO was estimated, as listed in Table I, indicating that the stress induced by thermal mismatch is a tensile stress and increases with increasing annealing temperature. By using Eq. (2) and the estimated σ_{th}, the σ_{latt} is calculated to be about 1.03 GPa for all samples, as listed in Table I, which

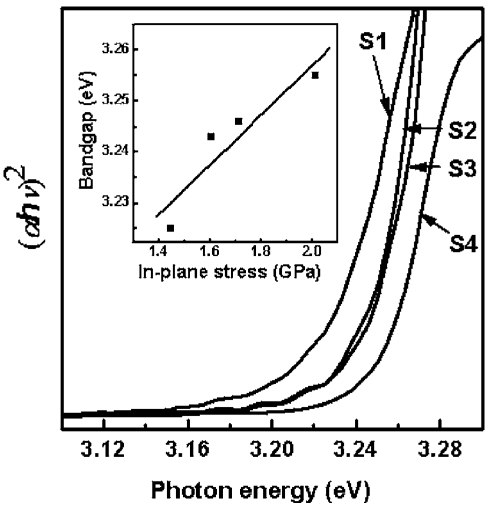

FIG. 3. Absorption spectra of (S1) as-grown ZnO film and the film annealed at (S2) 400, (S3) 600, and (S4) 800 °C, respectively. The inset shows the band gap of the ZnO films as a function of the biaxial stress.

indicated that the stress resulted from lattice mismatch is also a tensile stress and almost is not related to annealing temperature. Therefore, the increase of the biaxial tensile stress with increasing annealing temperature is due to the increase of thermal mismatch stress.

Figure 3 shows the absorption spectrum of the as-grown and annealed samples. With the increase of annealing temperature, the absorption edge of ZnO films shows blueshift, indicating that the band gap of the ZnO film increases with increasing temperature. The inset shows the band gap determined by absorption spectrum as a function of the biaxial stress. The experimental data are fitted linearly by the following equation:

$$E_g = 3.160 + 0.048\sigma_{xx}, \tag{4}$$

where 3.160 eV is optical band gap of stress-free ZnO films, less than that of bulk ZnO, which can be due to that the barrier at the grain boundary in polycrystalline ZnO films makes the effective band gap decrease.[8]

It is well known that the band gap decreases with increasing lattice constant induced by tensile stress. For example, the band gap of GaN, which has similar crystal structure to ZnO, decreases with the increase of in-plane tensile stress, that is, the band gap decreases as the lattice constant of a axis rises.[9–11] However, Eq. (4) indicates that the band gap of the ZnO film increases with increasing in-plane tensile stress, implying that the band gap increases with increasing lattice constant of a axis induced by the tensile stress; it seems to be in disagreement with the relation between band gap and lattice constant mentioned above.

In order to understand effect of the strain on the band gap, the electronic structures of the wurtzite ZnO and GaN under different tensile stresses in the plane perpendicular to c-axis direction were calculated by using the first principles based on local density approximation (LDA). For simulating the biaxial stress in preferentially orientated ZnO films, the diagonal elements of the stress tensor were set as follows: $\sigma_{zz}=0$ and $\sigma_{xx}=\sigma_{yy}$. The calculated results indicate that the band gap increases with increasing biaxial tensile stress for ZnO, but decreases for GaN, in agreement with experimental results observed in the present work and reported previously.[9–12] It is also found from the calculation that the lattice constant increases in the a-axis direction (tensile strain) and decreases in the c-axis direction (compressive strain) for both ZnO and GaN. Above calculation results imply that there is a competition between in-plane tensile strain and out-of-plane compressive strain to the variety of band gaps. The in-plane tensile strain makes the band gap decrease and the out-of-plane compressive strain makes the band gap increase.

It is known that biaxial relaxation coefficient is defined as $R^B=-\varepsilon_{zz}/\varepsilon_{xx}$, where ε_{xx} and ε_{zz} are the strain perpendicular and parallel to c-axis direction, respectively. By calculating, we obtain that the R^B are 1.035 for ZnO and 0.419 for GaN, respectively. The $R^B=1.035$ means that the out-of-plane compressive strain is bigger than the in-plane tensile strain for ZnO, implying that effect of the compressive strain on the band gap is dominant. So, the change of the band gap for ZnO comes mainly from contribution of compressive strain in c-axis direction. However, the small R^B value of GaN means that the in-plane tensile strain is larger than the out-of-plane compressive strain, implying that the change of the band gap is determined by in-plane tensile strain.

In summary, the biaxial stress of ZnO films grown on quartz substrate was measured by side-inclination x-ray diffraction technique. The biaxial stress originates from thermal mismatch and lattice mismatch stresses, the former increases with increasing annealing temperature, and the latter is almost independent of annealing temperature and is about 1.03 GPa. The band gap of ZnO films shows blueshift with increasing annealing temperature, that is attributed to that the compressive strain of out of plane is larger than tensile strain of in plane and increases with annealing temperature.

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