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Authors	F. Siah,J. Yang,Z. K. Tang,G. K. L. Wong,M. Kawasaki,A. Ohtomo,H. Koinuma,Y. Segawa
Citation	Journal of Applied Physics, Vol. 88, No. 5,
発行日/Pub. date	2000, 9
公式ホームページ /Journal home page	http://jap.aip.org/
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In-plane anisotropic strain of ZnO closely packed microcrystallites grown on tilted (0001) sapphire

F. Siah, Z. Yang,^{a)} Z. K. Tang, and G. K. L. Wong

Department of Physics and the Advanced Materials Research Institute, Hong Kong University of Science and Technology, Clearwater Bay, Kowloon, Hong Kong

M. Kawasaki, A. Ohtomo, and H. Koinuma

Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuda, Midori-ku, Yokohama 227, Japan

Y. Segawa

Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN), 19-1399 Nagamachi Koeji, Aoba-ku, Sendai 980, Japan

(Received 4 November 1999; accepted for publication 31 May 2000)

We have found that ZnO films consisting of epitaxially ordered arrays of closely packed hexagonal microcrystallites grown on vicinal (1000) sapphire exhibit biaxial in-plane optical anisotropy. The optical anisotropy resonance occurs near the band gap energy of ZnO. The line shape of the resonance is consistent with that induced by an in-plane anisotropic strain. The direction of the anisotropy coincides with the projection of the miscut direction of the (0001) sapphire substrates onto the sample surface plane. The magnitude of the anisotropy is generally larger for films with high crystalline quality, and on substrates with larger miscut angles. A possible origin of the strain anisotropy due to the miscut angle and the difference in thermal expansion rate of sapphire along its *c* and *a* axes is proposed. © 2000 American Institute of Physics. [S0021-8979(00)06217-4]

INTRODUCTION

In recent years, wide-gap semiconductor compounds have attracted much attention because of the intense commercial interest in developing practical short-wavelength semiconductor diode lasers (SDLs) for the huge market needs. Worldwide research efforts on the development of short-wavelength SDLs were initially focused on ZnSe-based heterostructures, but recently the interest in InGaN materials has grown considerably. These developments have culminated in the demonstration of room-temperature operating green-blue as well as blue SDL structures. ZnO is another wide-gap semiconductor, but it has received relatively little attention despite its large exciton binding energy of 60 meV, which could allow efficient excitonic lasing mechanisms to operate at room temperature (RT). Ultraviolet (UV) stimulated emission and lasing have been extensively studied in bulk ZnO crystals at cryogenic temperatures,^{1–3} but observation of lasing at RT was mentioned only briefly in the works of Klingshirn³ and others.^{4–6} Recently, we reported on RT UV lasing from ZnO thin films grown on sapphire (0001) substrates.⁷ As a result of the large lattice mismatch, these films consist of an epitaxially ordered array of closely packed hexagonal microcrystallites. The facets of all hexagons within a few tens to a hundred micrometers are parallel to those of the others, forming natural Fabry-Pérot lasing cavities. Under moderate excitation, the optical gain responsible for the RT UV stimulated emission is of an excitonic nature. For a 55-nm-thick film, an excitonic gain of

320 cm⁻¹ is measured at a fluence of 3.0 μJ/cm², an order of magnitude larger than the gain reported for bulk ZnO crystals measured at much higher fluence.⁸

We report here our study of biaxial optical anisotropy within the surface plane of these ZnO films. The optical anisotropy resonance occurs near the band gap energy of ZnO. The line shape of the resonance is consistent with that induced by an in-plane anisotropic strain. The direction of the anisotropy coincides with the miscut direction of the (0001) sapphire substrates. The magnitude of the anisotropy is generally larger for films with high crystalline quality, and on substrates with larger miscut angles.

EXPERIMENTS

ZnO microcrystallites were grown on sapphire substrates by the laser molecular beam epitaxy technique,⁹ at a deposi-

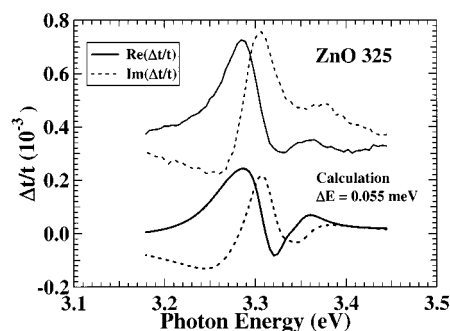


FIG. 1. Typical transmission difference spectra (upper solid and dashed curves) of ZnO films. The lower pair of curves is the calculated transmission difference spectra assuming the strain induced band gap shift of 0.055 meV.

^{a)}Electronic mail: phyang@ust.hk

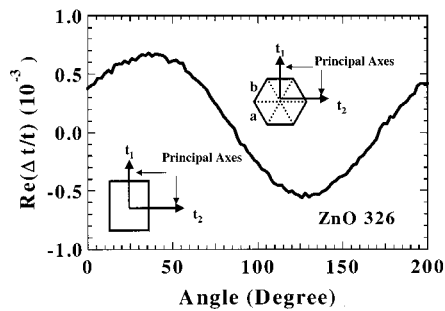


FIG. 2. The azimuthal angular dependence of the transmission anisotropy amplitude of a ZnO film.

tion temperature of 500 °C and an oxygen pressure of 1×10^{-6} Torr. A pure ceramic ZnO target (99.999%) was ablated in an ultrahigh vacuum chamber using a KrF excimer laser. X-ray diffraction measurement revealed that the ZnO microcrystallites have high crystallinity with *c*-axis orientation. The thin film consists of close-packed hexagons as revealed by atomic force microscopy, and by transmission electron microscope. Detailed room temperature lasing and structural characterizations have been reported earlier.^{6,7}

The in-plane optical anisotropy measurements were carried out by transmittance difference spectroscopy (TDS) in the visible to UV spectral range. TDS is a variation of reflectance difference spectroscopy (RDS),¹⁰ in which the difference in transmittance for the incident light polarized light along two perpendicular directions is measured. The setup of the TDS is the same as RDS except that the sample normally placed for RDS measurements is replaced by an (100) Si wafer which has negligible in-plane optical anisotropy, and the ZnO sample under investigation is placed in the optical path after the light is reflected by the Si wafer. The sample can be rotated in the plane parallel to the substrate surface. A HeNe laser is used to fix the off-plane orientation of the sample to ensure that the TRD is always in normal incidence to the sample surface.

RESULTS AND DISCUSSIONS

The upper two curves in Fig. 1 are typical TDS spectra of these ZnO films. A resonance structure near the band gap energy of ZnO is clearly observed. Figure 2 shows the de-

pendence of the resonance amplitude on the azimuthal angle of the sample relative to the horizontal direction. The angular dependence has a period of 180°. This means that the anisotropy possesses C_{2v} bi-axial symmetry rather than hexagonal symmetry (see the inset of Fig. 2), because in the hexagonal symmetry, although at some azimuthal angles the optical response along the two perpendicular directions probed by TDS should be different, such anisotropy should have an azimuthal period of 60° as shown in our earlier work.⁷ The reason that we did not observe the hexagonal symmetry in TDS is because our TDS measures the average response of an area about 1 mm in diameter, within which there are many microcrystallites with different in-plane orientations.

We now discuss the origin of the observed optical anisotropy. Table I shows the azimuthal angle of the miscut direction of the substrate projected onto the sample surface, as measured by Laue x-ray diffraction, together with the azimuthal angle at which the measured anisotropy amplitude is maximum. The straight edge of the half round disk shaped samples is chosen as the reference line. It is seen from Table I that the major axis of the biaxial optical anisotropy coincides with the miscut direction, except for sample ZnO-317 which is of poor crystalline quality as revealed by x-ray diffraction. The optical anisotropy is therefore closely related to the miscut. There are two possible causes for this. First, because of the miscut, the *c* axis of the ZnO films is not completely perpendicular to the sample surface, if the growth follows the substrate *c* axis. In TDS, one of the polarization directions would sense a small portion of the dielectric function of ZnO along the *c* axis ($\epsilon_{||}$), and the other would only sense that in the hexagonal plane (ϵ_{\perp}). Second, due to the miscut and the large lattice mismatch between ZnO and sapphire, although the films are already stress relaxed because the films are beyond the critical thickness, there could be some small residual anisotropic strain in the films. Such anisotropic strain would cause optical anisotropy, as will be shown below.

The optical anisotropy of the ZnO films under investigation was calculated in order to identify the origin of the anisotropy. The formulism for the dielectric function of bulk ZnO perpendicular to the *c* axis is given below:¹¹

TABLE I. Summary of the thickness and the experimental results of the ZnO samples investigated in this study. The miscut projection angles and the maximum anisotropy angles are measured using the straight edge of the half-round shaped samples against the horizontal direction. The values of ΔE are the ones used in the calculation to fit the amplitude of the experimental spectra.

Sample number	Thickness (nm)	Projection of miscut angle ($\pm 5^\circ$)	Maximum anisotropy direction ($\pm 4^\circ$)	Intensity of Bragg peak (counts)	Miscut angle ($\pm 0.5^\circ$)	$\Delta E (\times 10^{-5} \text{ eV})$
328	24.4	33°	35°	34.8	1.4°	2.3
330	29.8	37°	42°	30.4	0.6°	1
329	37.3	23°	22°	88.4	0.9°	2.5
327	38.1	69.5°	65°	31.5	0.8°	2.5
325	45.5	6.5°	8°	131.2	1.5°	5.5
317	54.8	108.5°	88°	34.4	1.0°	2
318	58.2	78°	70°	134.5	1.3°	5

$$\varepsilon_{\perp}(E) = \frac{A}{2E^2} \left\{ \sum_{n=1}^{\infty} [g_{b,n}(E + i\Gamma_n) - g_{b,n}(i\Gamma_n)] + g_u(E + i\Gamma_0) - g_u(i\Gamma_0) \right\}, \quad (1)$$

where

$$g_{b,n}(\xi) = \frac{4R}{n^3} \left[\frac{1}{(E_0 - \xi) - \frac{R}{n^2}} + \frac{1}{(E_0 + \xi) - \frac{R}{n^2}} \right], \quad (2)$$

$$g_u(\xi) = -\ln \left(\frac{E_0^2 - \xi^2}{R^2} \right) - \frac{1}{2} \sum_{n=1}^{\infty} g_{b,n}(\xi) - \pi \left[\cot \left(\frac{\pi \sqrt{R}}{\sqrt{E_0 - \xi}} \right) + \cot \left(\frac{\pi \sqrt{R}}{\sqrt{E_0 + \xi}} \right) \right]. \quad (3)$$

The five parameters are the amplitude A , the direct-band-gap energy E_0 , the excitonic binding energy R , the broadening of the direct band gap Γ_0 , and the broadening of the excitonic peak Γ_0^{ex} . The broadening of the n th exciton peak is determined using the empirical relation

$$\Gamma_n = \Gamma_0 - \frac{\Gamma_0 - \Gamma_0^{\text{ex}}}{n^2}. \quad (4)$$

The parameters for the dielectric function perpendicular to the c axis are $E_0 = 3.372$ eV, $R = 0.056$ eV, $\Gamma_0 = 0.02$ eV, $\Gamma_0^{\text{ex}} = 0.04$ eV, $A = 8$, and $\varepsilon_{\infty} = 2.6$. The broadening parameters used in this work are larger than that in Ref. 11 in order to better reproduce the experimental dielectric function. The effective refractive index for light polarized parallel to the miscut direction is given by¹²

$$n_p = \left\{ (n_{\perp})^2 - \sin^2 \theta_0 \left[\left(\frac{n_{\perp}}{n_{\parallel}} \right)^2 - 1 \right] \right\}^{1/2}, \quad (5)$$

where $n_{\parallel} = \sqrt{\varepsilon_{\parallel}}$, and ε_{\parallel} is given by Eqs. (1)–(4) with the value of E_0 replaced by the band gap along the c axis, which is 33 meV higher than the one in the hexagonal plane. The refractive index for light polarization perpendicular to the miscut direction is simply $n_{\perp} = \sqrt{\varepsilon_{\perp}}$. The dielectric function of sapphire was taken from Ref. 13. The transmission for light polarized along the two directions was then calculated for the air–ZnO–sapphire structure. The calculated results for misorientation induced anisotropy at a miscut angle of $\theta_0 = 5^\circ$ show that although the calculated TDS spectra reproduce the observed line shapes well, the amplitude is 1000 times smaller than that of the experimental one. Therefore, the misorientation of the c axis of the films cannot account for the observed anisotropy.

Residual anisotropic strain will cause the band gap to be different by a small amount ΔE along the two strain anisotropy axes. The dielectric functions along this two axes are then $\varepsilon(E_0, E)$, and $\varepsilon(E_0 + \Delta E, E)$ given by Eqs. (1)–(4). The bottom curves in Fig. 1 are the calculated TDS spectra with $\Delta E = 0.055$ meV. The nominal thickness of the ZnO film was used in the calculation. The value of E_0 was also varied slightly and the best fit was found to be 3.35 eV. It is

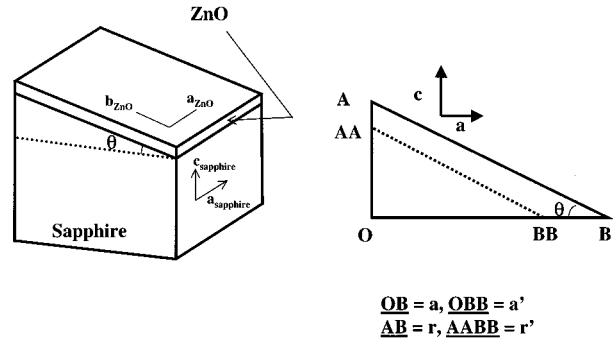


FIG. 3. Schematic diagram of the strain anisotropy due to miscut orientation of sapphire substrates.

seen that the calculated TDS spectra reproduce the observed ones well. The calculated spectra for other samples with different thickness also match with the experimental ones well.

The values of ΔE , which reflects the average strain anisotropy throughout the entire ZnO layer, for all the samples together with their x-ray diffraction Bragg peak amplitudes and the values of the miscut angles of the corresponding substrates and are all summarized in Table I. It is seen that, in general, a larger miscut angle together with good crystal-line order (higher Bragg amplitude) result in larger strain anisotropy. For example, the two samples with the highest ΔE ($=0.05$ meV) also have the largest miscut angle of 1.3° and 1.5° and the highest Bragg amplitudes. On the other hand, although the miscut angle of sample ZnO-328 is large (1.4°), but because it has weak Bragg amplitude, the strain anisotropy is still small. Using the deformation potential values given in Ref. 14, the maximum amount of strain difference in the two directions is estimated to be of the order of 5×10^{-6} . The value of $E_0 = 3.35$ eV obtained from our fitting really is higher than that reported in Ref. 14. It is not clear whether this indicates the existence of a substantial amount of strain in the films to significantly shift E_0 by more than 50 meV.

In-plane anisotropic strain has also been observed in GaN grown on misoriented (1000) sapphire substrates.¹⁵ This indicates that such strain may be common for thin epitaxial films grown on misoriented sapphire. In the following we discuss the origin of such in-plane anisotropic strain.

Due to the difference of thermal expansion of film and substrate strain is induced in the film when the sample is cooled from growth temperature to room temperature, even though the film thickness has already exceeded the critical value for strain relaxation. Because of the miscut angle and the difference in thermal expansion of the a axis and c axis of sapphire, an in-plane anisotropic strain is induced. This is schematically shown in Fig. 3. During cooling, the length perpendicular to the miscut tilt direction changes from a to a_1 , while the length parallel to the tilt direction projection in the plane changes from r to r_1 . The in-plane strain anisotropy is given by

$$\Delta e = \frac{r - r_1}{r} - \frac{a - a_1}{a} = (\alpha_c - \alpha_a) \Delta T \sin^2 \theta, \quad (6)$$

where α_c and α_a are the thermal expansion coefficients of sapphire along the c and a axes, respectively, ΔT is the difference between the growth temperature and room temperature (20 °C), and θ is the miscut angle. Using the data in Ref. 16 and with $\theta=1^\circ$, the strain anisotropy is $=1.4 \times 10^{-7}$, which is about 40 times smaller than the observed maximum value. Due to the large uncertainty of the miscut angle ($\sim 0.5^\circ$) and possible large strain nonuniformity due to grain boundary, the actual strain anisotropy could be much larger than the estimation given here. Atomic steps could also create local strain anisotropy. Further study is being conducted to clarify the origin of the strain anisotropy.

SUMMARY

In summary, biaxial anisotropic strain has been found in ZnO films consisting of an epitaxially ordered array of hexagonal microcrystallites by transmission difference spectroscopy. The strain anisotropy is of the order of 10^{-6} , and is along the direction of the miscut angle of the sapphire substrate. The anisotropic strain is larger for larger miscut angles and films with high crystalline quality. A possible origin of the strain anisotropy due to the miscut angle and the difference in thermal expansion rate of sapphire along its c and a axes is proposed.

ACKNOWLEDGMENTS

The authors are in debt to the reviewer's contribution in suggesting the anisotropic strain model. This work was sup-

ported by the Research Grant Council grant HKUST 6113/98P, and was carried out in the Joice Kowk Photonics Laboratory and the William Mong's Semiconductor Cluster Laboratory at the Hong Kong University of Science and Technology.

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