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Reflective second harmonic generation from ZnO thin films: A study on the Zn–O bonding

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The structures of the Zn–O bonding in ZnO (0002) thin films prepared by metal organic chemical vapor deposition have been studied by reflective second harmonic generation (RSHG). The polar Zn–O bond on the top layer is not canceled out and presents 3 mm symmetrical structures on the well-grown ZnO (0002) surface. The average polar strength of the Zn–O bond is correlated with the quality of the ZnO (0002) thin film. The mirror symmetry is caused by the nonvanished polar of twin boundary due to the mismatch between the ZnO film and sapphire substrate and analyzed using *s*-polarized RSHG with *s*-polarized fundamental light irradiation. These results demonstrate that the Zn–O heteropolar bonds on the smooth ZnO surface contribute to the SHG intensity. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2723671]

Zinc oxide (ZnO) is a II-VI semiconductor commonly with a hexagonal wurtzite crystal structure and possesses a room temperature (RT) direct wide band gap of 3.37 eV, a large exciton binding energy of 59 meV (>GaN of 28 meV) and other unique properties.[1] It offers great potential for the fabrication of optoelectronic devices, such as light emitting diodes (LEDs), lasers, solar cell, and transparent transistors,[2] and a wide range of applications.[3] Recently, research interests have arisen on ZnO as a new nonlinear optical (NLO) material for potential application in integrated optics, in addition to expensive NLO single crystals like $LiNbO_3$, $KTiOPO_4$, and $LiTaO_3$ and other ZnSe and GaAs based semiconductor heterostructures.[4,5] The second harmonic generation (SHG) effects were studied for ZnO thin films deposited on sapphire by pulsed laser ablation,[4] on fused silica by sputtering,[5] on float glass by spray pyrolysis,[6] and on Si by magnetron sputtering.[7] SHG studies were also performed for bulk ZnO crystals in comparison with ZnO films.[5]

In previous publications,[4–6] SHG intensity variations with the beam incident angle were studied. Thin ZnO films showed high SHG intensity and provided an even more efficient harmonic generation than bulk crystals which was interpreted to be due to the influence of intergrain boundaries.[4–6] Recently, we measured *P*-polarized reflective second harmonic generation (RSHG) intensity from thicker ZnO films ($\sim$1.6 μm) grown on Si by rf sputtering and drew the conclusions that the total RSHG intensity is contributed from the sum of the ZnO surface and ZnO bulk, and that the contribution of the ZnO surface dominates the final results if the surface ratio is larger.[7] However, further detailed investigation about the fine structure of the ZnO surface is needed. In this letter, we perform a penetrating RSHG study of ZnO films with different material qualities, their surface and ZnO–O bonding structures, and related phenomena, which were not studied yet in the literature.

Let us discuss some related theoretical concepts first. ZnO is a hexagonal wurtzite crystal structure and its structure belongs to a 6*mm* symmetry, as shown in Fig. 1(a). The

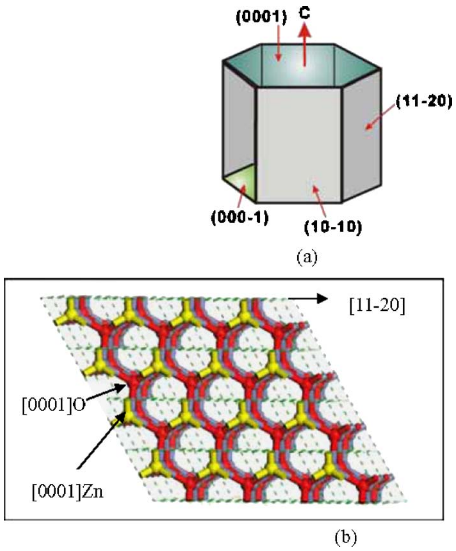

FIG. 1. (Color online) (a) Hexagonal wurtzite crystal structure of ZnO (0002); (b) symmetrical structure of Zn–O bonding on the surface of ZnO (0002).

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bonds of Zn–Zn and O–O do not contribute to the SHG intensity since the covalent bonds are nonpolar. The nonlinearity of the tetragonal bonding geometry between the layers of Zn and O can be deduced from the fit by using the bond additivity model.[8] ZnO bonds cannot generate SHG, except that ZnO bonds must be ordered in polar structure. Perfect ZnO (0002) has the polar surface with alternate hexagonal Zn and O layers. Looking into the (001) surface of a wurtzite ZnO crystal, the threefold symmetry bonding of the first layer and another threefold symmetry with 180° rotation from the second layer are exhibited, as shown in Fig. 1(b). Thus, the perfect surface of ZnO breaks the bulk symmetry and reduces to a 3*mm* symmetry, and therefore, the surface configuration is an influencing factor for RSHG measurement of ZnO thin films.

In order to clarify the variation of the structure, in this study, we employed the *S*-polarized RSHG light generated from *S*-polarized fundamental light incident on the samples (SS-RSHG), recorded with the variation of the azimuthal angle, which can achieve a high discrimination to the surface structure of the well-grown ZnO film. However, our results will illustrate that the Zn–O heteropolar bonds on the smooth ZnO surface contribute to the SHG intensity and are different from the previous works on ZnO films which focuse on the amplitude of the RSHG intensity.

Experimental ZnO thin films (undoped) were grown on *c*-plane sapphire by metal organic chemical vapor deposition (MOCVD) in a modified vertical injection commercial MOCVD reactor.[9,10] Two samples were involved for this study, with film thicknesses of about 830 and 550 nm for samples A and B, respectively. They were characterized by x-ray diffraction (XRD) and photoluminescence (PL). XRD 2θ-ω scans showed the wurtzite ZnO (0002) peak at 2θ of $\sim 35\,°$ and the (0004) peak at 2θ of $\sim 73°$, without other orientation peaks. The full width at half maximum (FWHM) for the (0002) peak (2θ) is 0.200° for sample A and 0.214° for sample B. Both samples possess a PL peak near 3.29 eV (RT) from the direct band edge recombination of wurtzite ZnO, with a PL FWHM of 97 meV for sample A and 150 meV for sample B. These XRD and PL allow for a quality analysis and comparison of these two samples; i.e., the material quality of sample A is superior than that of sample B.

The RSHG experimental setup was described in Ref. 7. The laser source of the SHG experimental system herein is a pulsed *Q*-switched heodymium-doped yttrium aluminum garnet laser with a wavelength of 1.064 μm and a pulse duration time of 6 ns. The laser power was held under 40 $\mathrm{MW/cm^2}$ to prevent surface damage.

The ZnO thin films are considered to have the same crystal structure as bulk ZnO, which has a hexagonal close packed structure, with the 6*mm* point group symmetry.[11] In the Kleinman approximation, the second-order susceptibility tensors of ZnO bulk have only two independent nonzero components: $\chi^{(2)}_{xzx}=\chi^{(2)}_{yzy}=\chi^{(2)}_{xxz}=\chi^{(2)}_{yyz}=\chi^{(2)}_{zxx}=\chi^{(2)}_{zyy}$ and $\chi^{(2)}_{zzz}$. Since the values of $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ measured by Neumann for ZnO thin films agree well with these bulk values,[12] our RSHG results from ZnO thin films are interpreted based on this assumption. For ZnO (0002), the relationship between the RSHG polarization and the azimuthal angle is

$$P^{(2),\mathrm{ZnO(0002)bulk}}_{s\to s}(2\omega)=0, \qquad (1)$$

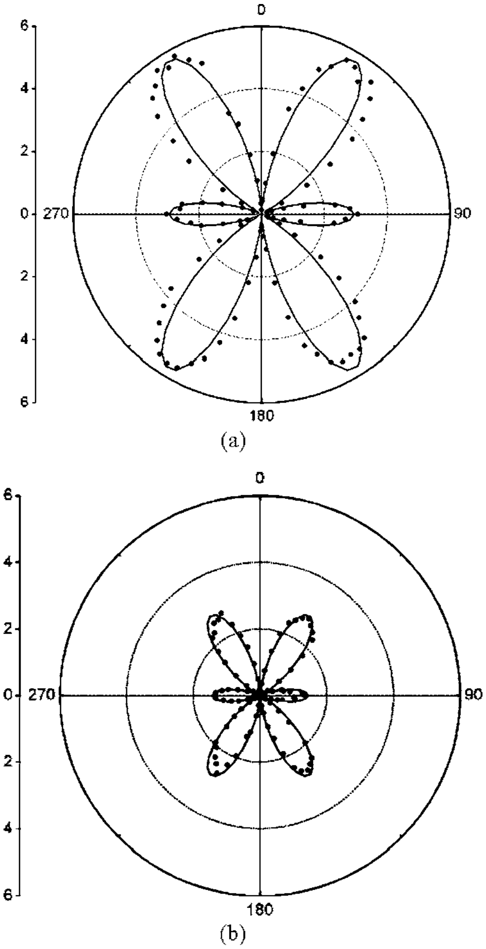

FIG. 2. RSHG patterns from two ZnO films of (a) sample A and (b) sample B. Theoretical fits of the SS-RSHG experimental patterns are drawn in solid line.

$$P^{(2),\mathrm{ZnO(0002)bulk}}_{s\to p}(2\omega)=\chi^{(2)}_{zxx}E_0^2\hat{z}, \qquad (2)$$

where the subscript of the RSHG polarized light refers to the polarization of the fundamental and second harmonic generation light, perpendicular to the incident plane (*s* polarized) or parallel to the incident plane (*p* polarized). The azimuthal angle ϕ is the angle between the x axis parallel to the $[2\bar{1}\bar{1}0]$ direction of ZnO and the plane of incidence. Equations (1) and (2) indicate that the *p*-polarized RSHG light is independent of the azimuthal angle, and the *s*-polarized RSHG light is zero if the direction of ZnO (0002) is the z axis of the ZnO thin film.

The *s*-polarized SHG intensity $I_{s\to s}(2\omega)$ for an *s*-polarized fundamental field $E_s(\omega)$ is most sensitive to the symmetry of the surface structure since this polarization combination contains only anisotropic nonlinear susceptibility tensor elements.[13] The SHG rotational anisotropy result of $I_{s,s}(2\omega)$ is named as SS-SHG for the convenience of the following discussion. In order to discover the surface configuration of the ZnO thin films, the SS-RSHG measurement is used here since the SS-RSHG intensity is zero for the bulk of ZnO(0002), as described in Eq. (2).

SS-RSHG patterns from these two samples are shown in Figs. 2(a) and 2(b). They reveal the 3*mm*-like symmetrical structure on the surface of ZnO(0002) and reflect the additional contribution with mirrorlike symmetry. The final SS-RSHG intensity from ZnO(0002) is expressed as

$$I_{SS} = |ae^{i\psi}\sin(\phi) + b\sin(3\phi)|^2, \tag{3}$$

where ϕ is the azimuthal angle between the incident plane and x axis on the surface [direction of $[11\bar{2}0]$ for the ZnO (0002) hexagonal wurtzite structure], a is the strength of nonlinearity due to the formation of twin boundaries,[14] b is the polar strength of Zn–O bonding with $3mm$ symmetry, and ψ is the relative phase difference of the SHG field from the $3mm$ symmetric structure of Zn–O bonding and twin boundary.

The theoretical fits of SS-RSHG experimental patterns for two ZnO thin films with different thicknesses are exhibited in Figs. 2(a) and 2(b). It shows an excellent agreement of our experimental results with the theory. The fitting parameters from Eq. (3) are for sample A, $a=0.54$, $b=2.15$, and $\psi=30°$, and for sample B, $a=0.56$, $b=1.47$, and $\psi=50°$. The SS-RSHG patterns are not zero, as described in Eq. (1), which are contributed from the bulk ZnO (0002). The Zn–O bonding on the surface exhibits a $3mm$ symmetry in the optical scope. This result only appears on the smooth surface of high-quality ZnO (0002).

ZnO thin films epitaxied on sapphire (0001) substrates are with a large lattice mismatch of ~18%, but remain multicrystalline in nature, with incoherent grain boundaries.[15] The formation of twin boundaries is the regular growing together of crystals of the same sort, sharing some of the same crystal lattice with a mirror symmetry operation. It can arise during crystal growth or through mechanical stress.[16] Yan *et al.*[14] predicted that a nonvanishing polarity existed in the twin boundary, which exhibits a mirror relation across the boundary plane. Its corresponding second-order nonlinear optical susceptibility tensor components have an even-number y subscript with x along the $[11\bar{2}0]$ direction, which leads to a tensor form with six independent components.[17] These effects are described in Eq. (3), which depicts well the measured SS-RSHG intensity.

SS-RSHG reflects the surface structure of ZnO (0002), which is influenced by the growth conditions rather than the thickness of ZnO. The value of b in sample A is larger than that in sample B. The nonlinear source generated from the polar surface with alternate hexagonal Zn and O layers is stronger from the surface of the better crystallized ZnO (0002) film. This result is confirmed by eliminating the bulk contribution of ZnO (0002) and the domination of the grain boundary on the ZnO surface since the isotropic contribution is forbidden to the SS-SHG intensity. It also predicts a better crystalline quality for sample A than sample B, which is consistent with results from XRD and PL measurements. A detailed investigation of the correlation of the SHG and ZnO film quality will be reported in a future publication.

The values of a are close for both samples. The twin boundaries were only observed from the tunneling electron microscopy images,[18] but the result herein reveals the trend of the twin boundary in the optical scale. This phenomenon is interesting for the growth mechanism of the thin film. The relative SHG phase difference ψ between two samples is 20° which may be caused by the difference between the effective dipole of the Zn–O bond on the surface and that of the mirrored structures formed by twin boundary.

In conclusion, RSHG technology has been employed to investigate the Zn–O bonding in ZnO (0002) thin films grown on sapphire by MOCVD. A technique using SS-RSHG is developed, which is different from previous work in the literature where the focus is more on the effective nonlinearity of ZnO films by varying the incident angle. The observation of the SS-SRHG pattern and its sensitivity to the surface structure reveal the polar strength and the symmetrical structure of the top layers of ZnO (0002). It is believed that polycrystalline ZnO films would not have this phenomenon, which only appears in the smooth surface of ZnO (0002). In the optical view, the SS-RSHG intensity is accumulated for an irradiated optical area and averaged over the nonlinear optical effect. If the polar direction of Zn–O bonding is weak in ordering, the average polar strength will be canceled out and the SS-RSHG field will be zero. However, the effect of the twin boundary is independent of the ZnO surface quality, and the mirror symmetry of these planar defects still exists in ZnO films. SS-RSHG reflects the surface structure of ZnO (0002), which is influenced by the film crystalline quality, which is also confirmed from the experimental results of x-ray diffraction and photoluminescence. These results may deepen our understanding of physics on ZnO materials and SHG effects.

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