Reflective second harmonic generation near resonance in the epitaxial Al-doped ZnO thin film

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Abstract: The second harmonic (SH) generation from the highly epitaxial Al-doped ZnO film on sapphire was measured, using the femtosecond Ti:Sapphire laser at the near-resonant SH wavelength, in reflection geometry to avoid the sapphire's contribution in the conventional Maker fringes technique. By investigating SH intensities as a function of the azimuthal angle along the film's normal, we found that the sapphire substrate had a negligible contribution to the reflective SH signal and the film had a pure and well-aligned c-domain. We also developed a new method to calculate the component's ratios of the nonlinear susceptibility tensor by analyzing the polarization diagrams of SH intensities under the incidence with two different angles. The ratios indicate that Kleinman's symmetry is broken due to the absorption at SH wavelength and the dominant component of the nonlinear susceptibility tensor is d_{33}. Calibration using the Z-cut quartz shows a possible overestimate of the nonlinear response by Maker fringes technique.

OCIS codes: (190.4400) Nonlinear optics, materials; (310.6860) Thin films, optical properties; (999.9999) Zinc oxide.

References and links

1. S. H. Jeong, J. W. Lee, S. B. Lee, and J. H. Boo, "Deposition of aluminum-doped zinc oxide films by RF magnetron sputtering and study of their structural, electrical and optical properties," Thin Solid Films **435**, 78-82 (2003).
2. S. J. Henley, M. N. R. Ashfold, and D. Cherns, "The growth of transparent conducting ZnO films by pulsed laser ablation," Surf. Coat. Technol. **177-178**, 271-276 (2004).
3. B. Wacogne, M. P. Roe, T. J. Pattinson, and C. N. Pannell, "Effective piezoelectric activity of zinc oxide films grown by radio-frequency planar magnetron sputtering," Appl. Phys. Lett. **67**, 1674-1676 (1995).
4. M. P. Roe, B. Wacogne, and C. N. Pannell, "High-efficiency all-fiber phase modulator using an annular zinc oxide piezoelectric transducer," IEEE Photon. Technol. Lett. **8**, 1026-1028 (1996).
5. P. Fons, K. Iwata, A. Yamada, K. Matsubara, and S. Niki etc., "Uniaxial locked epitaxy of ZnO on the a face of sapphire," Appl. Phys. Lett. **77**, 1801-03 (2000).
6. C. R. Gorla, N. W. Emanetoglu, S. Liang, W. E. Mayo, and Y. Lu etc., "Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on $(01\bar{1}2)$ sapphire by metalorganic chemical vapor deposition," J. Appl. Phys. **85**, 2595-2602 (1999).
7. A. F. Aktaruzzaman, G. L. Sharma, and L. K. Malhotra, "Electrical, Optical And Annealing Characteristics Of Zno : Al Films Prepared By Spray Pyrolysis," Thin Solid Films **198**, 67-74 (1991).
8. Sang Il Park, Tae Sik Cho, Seok Joo Doh, Jong Lam Lee, and Jung Ho Je, "Structural evolution of ZnO/sapphire(001) heteroepitaxy studied by real time synchrotron X-ray scattering," Appl. Phys. Lett. **77**, 349-351 (2000).
9. M.C. Larciprete, D. Passeri, F. Michelotti, S. Paoloni, C. Sibilia, M. Bertolotti, A. Belardini, F. Sarto, F. Somma, and S. Lo Mastro, "Second order nonlinear optical properties of zinc oxide films deposited by low temperature dual ion beam sputtering," J. Appl. Phys. **97**, 023501-6 (2005).

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10. H. Cao, J.Y. Wu, H.C. Ong, J.Y. Dai, and R.P.H. Chang, "Second harmonic generation in laser ablated zinc oxide thin films," Appl. Phys. Lett. 73, 572-574 (1998).
11. X.W. Sun and H.S. Kwok, "Optical properties of epitaxially grown zinc oxide films on sapphire by pulsed laser deposition ," J. Appl. Phys. **86**, 408-411 (1999).
12. P.L. Washington, H.C. Ong, J.Y. Dai, and R.P.H. Chang, "Determination of the optical constants of zinc oxide thin films by spectroscopic ellipsometry," Appl. Phys. Lett. **72**, 3261-3263 (1998).
13. S.W. Liu, S. Jolly, Min Xiao, Z. Yuan, J. Liu, C.L. Chen, and Wenkai Zhu, "Domain microstructures and ferroelectric phase transition in $Pb_{0.35}Sr_{0.65}TiO_3$ films studied by second harmonic generation in reflection geometry," J. Appl. Phys. **101**, 104118 (2007).
14. R. L. Sutherland, *Handbook of nonlinear optics*, (Marcel Dekker, New York, 1996), Chap. 2.
15. J.E. Sipe, D.J. Moss, and H.M. van Driel, "Phenomenological theory of optical second- and third-harmonic generation from cubic centrosymmetric crystals," Phys. Rev. B **35**, 1129-1141 (1987).
16. B. Lax, J.G. Mavroides and D.F. Edwards, "Non-linear interband and plasma effects in solids," Phys. Rev. Lett. **8**, 166-168 (1962).

1. Introduction

Zinc oxide (ZnO), as a transparent conducting material [1,2], a piezoelectric oxide [3] and a wide band-gap semiconductor, has been widely used as transparent electrodes in flat panels and solar cells, transducers in acoustoelectrical devices [4], and also attracted much interest in the development of various optical devices working in the near ultraviolet region due to the strong commercial desire. ZnO films have been fabricated using many deposition techniques [1,2,5-8]. Typically Al dopants are introduced to achieve n-type ZnO (Al:ZnO). Sapphire (α-Al_2O_3) is widely used as a substrate for the epitaxial growth of ZnO films due to their similar lattice structures. However, as a nonlinear optical material, the second-order nonlinear optical properties of ZnO films have been investigated only in recent years and are still under discussion [9]. Currently, most measurements of second harmonic generation (SHG) were performed on the polycrystalline films on non-polar substrates such as glass or textured ZnO film on sapphire using Maker fringes technique at the fundamental wavelength of 1064 nm by assuming Kleinman's symmetry [9,10]. The boundaries between the grains or crystallites in the films will significantly contribute to the measured SH signal. The SH characterizations on high-quality and highly epitaxial ZnO film as well as at other wavelengths are absent. Also, it is possible that the polar substrate (such as sapphire) will significantly contribute to the measured SH signal because the transmitted SH radiation is analyzed in the Maker fringes technique. In the previous SHG measurements on ZnO film grown on sapphire [9], SH signal from the substrate was not carefully investigated and excluded. Even though the susceptibility of sapphire is much smaller than that of ZnO, the SH signal from the substrate can still be comparable to ZnO film if the film's thickness is much smaller than the coherent length of sapphire (larger than 2 micrometers in transmission geometry at our wavelength). Finally, Kleinman's symmetry only holds when the absorptions at both fundamental and SH wavelengths are negligible. It is well known that ZnO films usually show certain absorption in a wide wavelength range as well as strong absorption near the band edge [11,12]. Deviation from Kleinman's symmetry is expected near the band-edge resonance.

In this paper, we report our SHG measurements at a near-resonant SH wavelength for the epitaxial Al:ZnO thin film in reflection geometry to reduce SH signal from the sapphire substrate (coherent length is about 20 nm in reflection geometry). We fabricated the ZnO film by RF magnetron sputtering with a very low deposition rate to achieve high quality. We present clear evidences showing that the SH signal from sapphire is negligible in our reflection method. We developed a method, which is different from the Maker fringes technique, to calculate the component's ratios of the nonlinear susceptibility tensor by analyzing the polarization diagrams of the reflected SH radiation without assuming Kleinman's symmetry under the incidence of two different angles. The absolute values of the susceptibility were also calibrated by using a Z-cut quartz crystal.

2. Experimental

The sputtering target was a high-density mixture of 99.999% pure ZnO powdered compound doped with 2 wt% Al_2O_3. The films were deposited on (0001) sapphire in the mixture of 50% oxygen and 50% argon at 750°C for four hours. Very low power and pressure were used to achieve a low deposition rate of about 10 Å/min. XRD θ~2θ scan shows that the as-grown film is c-axis aligned. Rocking curve measurement indicates that the FWHM of the (0002) peak is 0.54°. The lattice parameters were measured by high-resolution x-ray diffraction to be a=3.2638(1)Å and c=5.2185(2)Å. Pole-figure measurement (Fig. 1) shows that both ZnO $(10\bar{1}1)$ and Al_2O_3 $(11\bar{2}3)$ poles have a six-fold symmetry with the same ϕ angles indicating the in-plane relationship of ZnO $[10\bar{1}0]$ // α-Al_2O_3 $[11\bar{2}0]$. This corresponds to a 30° in-plane rotation of ZnO unit cell against sapphire unit cell. Cross-sectional TEM image shows that the film has a closely packed structure with a clear lattice plane, a flat surface, a sharp interface, and a thickness of about 285 nm. The clear SAED (selected area electronic diffraction) patterns again indicate the highly epitaxial quality and the excellent crystallinity of our film.

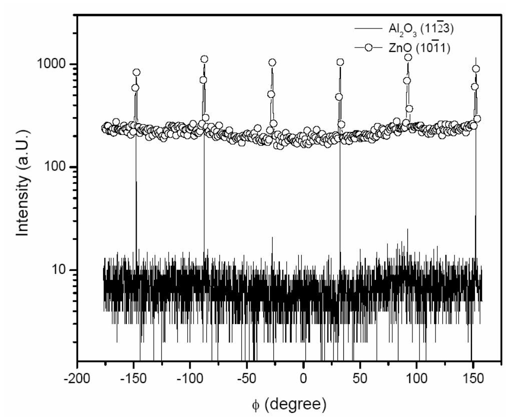

Fig. 1. XRD ϕ scans of Al-doped ZnO film grown on (0001) sapphire

The SH radiation is generated by a mode-locked Ti:Sapphire laser with a repetition rate of 82 MHz at the wavelength of 810 nm, which has a temporal width of about 300 femtoseconds. The laser beam has an average power of nearly 1 W and is focused to a spot size of about 100 micrometers. The SH signal is measured in reflection configuration with two different incidence angles of 45.0° and 20.4°. One long-pass filter and one band-pass interference filter are employed to pass the fundamental laser beam immediately before the sample and filter out SH radiation immediately after the sample, respectively. The SH radiation from the sample is additionally dispersed in a spectrometer and detected by a photo-multiplier tube (PMT). The PMT current is then fed into a lock-in amplifier to improve the sensitivity of the device. About 10% of the fundamental laser beam energy is directed through the reference arm containing a nonlinear BBO crystal. The SH radiation from the BBO crystal passes through the same band-pass interference filter and is detected by another PMT and its current is fed into another lock-in amplifier. The SH radiation from the BBO crystal can be used for providing a reference to remove laser intensity fluctuations. A rotating motor is used to change the azimuthal angle of the sample along its surface normal. Additional polarizer and half-wave plate are mounted on the rotating stepper motors to adjust and analyze the polarization directions of the incidence laser beam and the generated SH radiation, respectively [13].

3. Results and discussion

The nonlinear susceptibility for SHG of ZnO (point group: 6mm) can be written as a matrix $[d_{ij}]$ with five nonzero components and three independent components: d_{31}=d_{32}, d_{15}=d_{24} and

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d_{33}. Considering only the c-domains of ZnO film, we can write the reflected s-polarized SH field $E_s^{2\omega}$ and p-polarized SH field $E_p^{2\omega}$ as following [13]

$$E_s^{2\varpi} /(S_s(E^{\omega})^2) = -2d_{15} f_s t_s t_p \cos\varphi \sin\varphi , \tag{1a}$$

$$E_p^{2\varpi} /(S_p(E^{\omega})^2) = (d_{31} f_c^2 F_s + d_{33} f_s^2 F_s - 2d_{15} f_c f_s F_c) t_p^2 \sin\varphi^2 + d_{31} F_s t_s^2 \cos\varphi^2 . \tag{1b}$$

Here, E^{ω} is the amplitude of the fundamental field; $S_{(s,p)}$ are the scaling factors for the s-polarized and p- polarized SH fields, respectively; φ is polarization angle of the incident fundamental field with respect to the direction of s polarization; $t_{(s,p)}$ are the Fresnel transmission coefficients for the s-polarized and p-polarized fundamental beams incident from vacuum to ZnO film; $f_{(s,c)}$ and $F_{(s,c)}$ are the sine and cosine values of the corresponding refraction angles in the film for the fundamental and SH wavelengths, respectively. Therefore, the reflective s- and p- polarized SH intensities can be fitted via:

$$I_s^{2\omega} = (c_s \cos\varphi \sin\varphi)^2 , \tag{2a}$$

$$I_p^{2\omega} = (a_p \cos\varphi^2 + b_p \sin\varphi^2)^2 , \tag{2b}$$

where c_s, a_p and b_p are the fitting parameters. Comparing the coefficients of Eq. (1b) and Eq. (2b), we obtain a linear equation for the ratios of d_{ij} as:

$$\left(\frac{d_{33}}{d_{31}}\right) - 2\frac{f_c F_c}{f_s F_s}\left(\frac{d_{15}}{d_{31}}\right) = \frac{t_s^2}{f_s^2 t_p^2}\left(\frac{b_p}{a_p}\right) - \frac{f_c^2}{f_s^2} . \tag{3}$$

Since the ratio b_p/a_p and the Fresnel factors of $f_{(s,c)}$, $F_{(s,c)}$, and $t_{(s,p)}$ strongly depend on the incidence angle, we can set up two linear equations in the form of Eq. (3) by measuring SHG with two different incidence angles. From these two equations, the ratios of d_{33}/d_{31} and d_{15}/d_{31} can be solved. Although the s-polarized SHG described by Eq. (1a) and Eq. (2a) is not used to derive Eq. (3), it is helpful for us to verify the c-domains in ZnO films. Its polarization diagram presents a unique characteristic with the equal maximum under the incidences of 45° and 135° mixedly polarized fundamental beams.

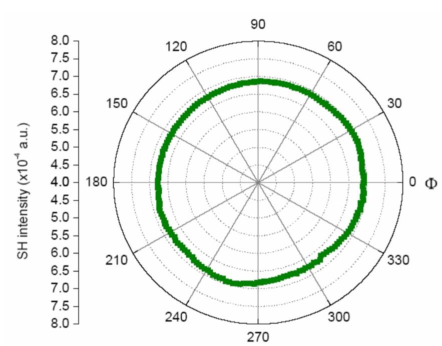

Fig. 2. Φ-dependence of SH intensity under the configuration of P_{in}-P_{out}.

SH fields were analyzed by rotating the polarizer. We find that the p-polarized SH fields are always dominant regardless of the polarization of the fundamental beam. The strongest SHG occurs under the polarization configuration of P_{in}-P_{out}. To investigate the domain distribution in the film, we measured the SH intensity under this configuration as a function of the azimuthal angle Φ by rotating the film along its surface normal under the incidence of 45°. As shown in Fig. 2, the SH intensities were found to be isotropic about this kind of rotation with the intensity's fluctuation less than 4%. This result is very important because it has the

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following implications: a) Considering that sapphire has a lower symmetry (point group: 3m) than that of ZnO, we should expect that the SH intensity generated by sapphire has a six-fold symmetry (~$\cos^2(3\Phi)$ or $\sin^2(3\Phi)$) about the azimuthal rotation [14]. However, this six-fold symmetry was not observed in our measurement. The isotropic SH intensity about the azimuthal angle indicates that the contribution to the SH signal from sapphire is negligible. b) The measured isotropy about the azimuthal angle is only consistent with the symmetry of c-domain in ZnO film. The six-fold rotation axis along the film's normal in c-domain leads to the isotropy (the third-rank nonlinear susceptibility will be isotropic about the four-fold or higher rotation axis) [14]. It confirms that only c-domains exist in this film and the c-domains are well aligned, which is assumed in calculating the ratios of the susceptibility components.

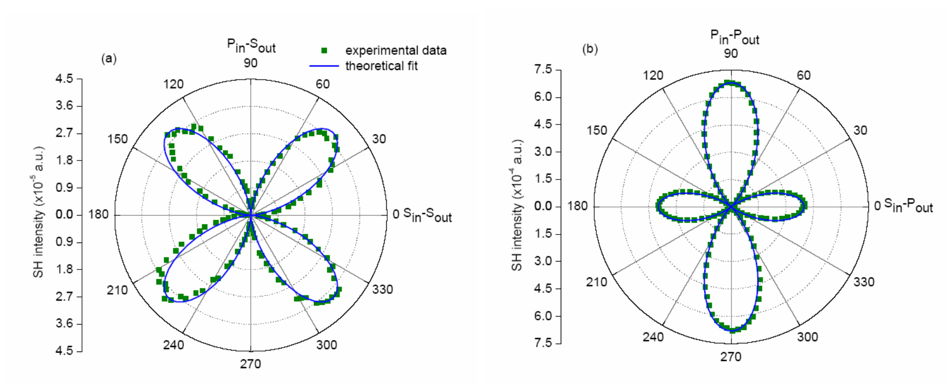

Fig. 3. s-polarized (a) and p-polarized (b) SH intensities as a function of the polarization angle φ of the fundamental beam with the incidence angle 45°. Filled squares correspond to the experimental data and solid lines correspond to the theoretical fits.

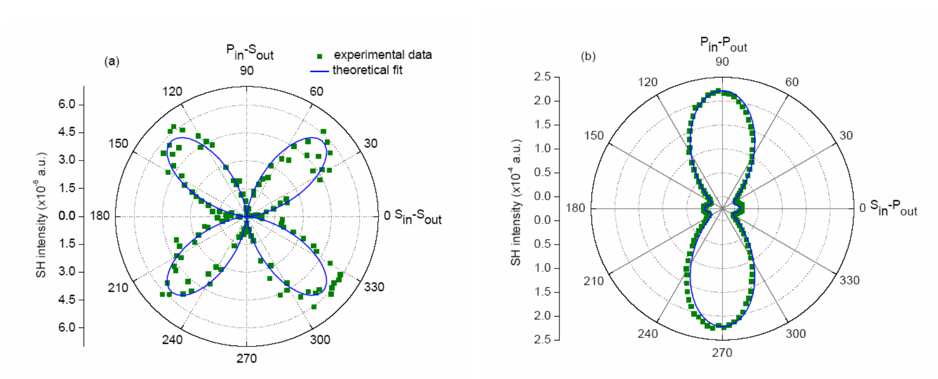

Fig. 4. s-polarized (a) and p-polarized (b) SH intensities as a function of the polarization angle φ of the fundamental beam with the incidence angle 20.4°. Filled squares correspond to the experimental data and solid lines correspond to the theoretical fits.

Figures 3a and 3b show the s- and p- polarized SH intensities under the incidence of 45° as the function of φ, respectively. The s-polarized SH intensity, as shown in Fig. 3a, presents a nearly equal maximum at φ=45° and φ=135°, which can be well fitted via Eq. (2a) with c_s=0.01242. Again, as discussed above, it indicates the well-aligned c-domains in the film. The p-polarized SH intensity in Fig. 3b is fitted by Eq. (2b) with a_p=0.01997 and b_p=-0.02608. Figures 4a and 4b show the same measurements with a different incidence angle of 20.4°. The fitting parameters are c_s=0.00478, a_p=0.00351 and b_p=-0.0149. To solve d_{33}/d_{31} and d_{15}/d_{31}, the linear refraction indices at the fundamental (n) and the SH (N) wavelengths have to be obtained to calculate the various Fresnel factors. We take the values of n=1.9407 at 810 nm and N=2.1708 at 405 nm [11]. Following the procedures described before, we obtain

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d_{33}/d_{31}=25.6 and d_{15}/d_{31}=2.72. The result shows that d_{33} is the dominant component of the nonlinear susceptibility tensor. It also indicates the deviation from Kleinman's symmetry (d_{15}=d_{31}) in our Al:ZnO film at the fundamental wavelength of 810 nm. This is expected because the SH wavelength (405 nm) is near resonance (~3.28 eV band gap for our film measured by PL spectrum) and certain absorption occurs at this wavelength.

To calibrate the system, we replaced ZnO film with a Z-cut quartz plate and orientated quartz $[10\bar{1}0]$ perpendicular to the incidence plane. We measured the SH intensity $I_{(s-s)}^{quartz}$ of quartz plate under the polarization configuration of S_{in}-S_{out} with respect to the SH intensity $I_{(s-p)}^{ZnO}$ of ZnO film measured under the polarization configuration of S_{in}-P_{out}. The absolute value of d_{31} for ZnO film is calculated via the equation:

$$d_{31}^{ZnO} = \left(\frac{I_{(s-p)}^{ZnO}}{I_{(s-s)}^{quartz}} \right)^{1/2} \left(\frac{t_s^{quartz}}{t_s^{ZnO}} \right)^2 \left| \frac{S_s^{quartz}}{S_p^{ZnO}} \right| \left(\frac{d_{11}^{quartz}}{F_s^{ZnO}} \right), \tag{4}$$

where the notations have the same meanings as Eq. (1) with the superscripts to identify the film and quartz. The ratio between the scaling factors can be calculated by

$$\left| \frac{S_s^{quartz}}{S_p^{ZnO}} \right| = \frac{W^{ZnO}(W^{ZnO}+2w^{ZnO})}{W^{quartz}(W^{quartz}+2w^{quartz})} \left(\frac{T_s^{quartz}}{T_p^{ZnO}} \right) \left| 1-\exp(i\frac{D}{W^{ZnO}+2w^{ZnO}}) \right|^{-1} \tag{5}$$

Here, D is the film's thickness; $T_{(s,p)}$ are the Fresnel transmission coefficients for the s- and p-polarized SH waves from the nonlinear medium to vacuum; W and w are the components of the wave vectors of SH and fundamental waves in the nonlinear medium along surface normal, respectively [13,15]. The calibration shows that d_{15}=0.35 pm/V, d_{31}=0.13 pm/V and d_{33}=3.27 pm/V. The values of d_{ij} are smaller than that measured by Maker fringes technique for ZnO film on sapphire at 1064 nm [10] even without considering the possible enhancement near the resonance. It is most likely due to our technique excluding the SH signal from sapphire. The over-estimate by Maker fringes technique for ZnO on sapphire is also evidenced by the fact that the smaller nonlinear response was observed by Maker fringes techniques for ZnO film on non-polar glass [9]. The overestimate is more serious for the small components d_{31} and d_{15} because their values are comparable to sapphire [16].

4. Conclusions

In conclusion, the reflective SHG of the epitaxial Al:ZnO film grown on (0001) sapphire was investigated at the near-resonant SH wavelength (405 nm). We conclude that the film has pure and well-aligned c-domains with the ratios of d_{33}/d_{31}=25.6 and d_{15}/d_{31}=2.72. It indicates that d_{33} is the dominant component of the susceptibility tensor and Kleinman"s symmetry is broken due to the absorption at the SH wavelength. The absolute values of d_{ij} were calibrated, using the Z-cut quartz, to be d_{15}=0.35 pm/V, d_{31}=0.13 pm/V and d_{33}=3.27 pm/V, which indicates a possible overestimate of the nonlinear susceptibility in the conventional Maker fringes technique.

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