Second harmonic generation in laser ablated zinc oxide thin films

H. Cao,[a] J. Y. Wu, H. C. Ong, J. Y. Dai, and R. P. H. Chang
Materials Research Center, Northwestern University, Evanston, Illinois 60208

(Received 23 April 1998; accepted for publication 1 June 1998)

We have observed large second-order nonlinear optical response from zinc oxide (ZnO) thin films deposited on sapphire substrates by pulsed laser ablation. By comparing the second harmonic signal generated in a series of ZnO films with different crystallinity and thickness, we conclude that a significant part of the second harmonic signal is generated at the grain boundaries and interfaces.
 [S0003-6951(98)03131-3]

There has been much interest in the development of new nonlinear optical materials for potential application in integrated optics.[1] Impressive progress has been made in nonlinear optical waveguides made of $LiNbO_3$, $LiTaO_3$, and KTP.[2–4] However these waveguides are fabricated from expensive single nonlinear optical crystals. Therefore it is desirable to fabricate thin films with large nonlinear optical response.[5,6] In this letter, we report second harmonic generation (SHG) measurement on ZnO thin films deposited on sapphire substrates by pulsed laser ablation. The second order susceptibility $\chi^{(2)}_{zzz}$ was found to be as large as 10 pm/V.

Thin films of (0001) ZnO were deposited on (0001) sapphire substrates by pulsed laser ablation. A detailed description of our growth apparatus and growth procedure have been given elsewhere.[7,8] Briefly, a KrF excimer laser (248 nm, 300 mJ pulse energy, 5 Hz repetition rate) was used to ablate a hot pressed ZnO target in a vacuum chamber with a base pressure of 1×10^{-7} Torr. Films were deposited in an oxygen partial pressure of 1×10^{-4}–1×10^{-3} Torr at substrate temperature of 500–700°.

X-ray diffraction (XRD) measurement and transmission electron microscopy (TEM) have been carried out for structural study of ZnO films. X-ray $\theta/2\theta$ analysis indicates that ZnO films are textured with the *c*-axis oriented perpendicular to the substrate plane. Plan view TEM images show that ZnO films consist of closely-packed grains. The grains appear in irregular shapes rather than in a well-defined hexagonal pattern.

Polarized SHG measurement was performed on ZnO films in the transmission mode. The 1.06 μm output of a *Q*-switched YAG laser (10 Hz repetition rate, 5 ns pulse width) was used as the fundamental beam. To minimize the influence of laser output power fluctuation, the fundamental beam was split into two beams. One beam passed the ZnO film, and the other passed a *Y*-cut quartz plate. The intensity of SHG from the ZnO film and that from the quartz are measured by two identical photomultiplier tubes, and then signal averaged by two identical boxcar integrators. The intensity of the second harmonic signal from the ZnO film was normalized by that from the quartz plate, and thus the effect of laser power fluctuation was eliminated. The sample was mounted on a motorized rotation stage so that the incident angle of the fundamental beam can be continuously varied. The polarization direction of the fundamental beam could be changed by rotating a half-wave plate placed in front of the sample. A low-pass filter was placed after the sample to block the fundamental beam. The polarization of the second harmonic signal was checked by a linear polarizer placed after the filter.

We first measured the second harmonic signal from two ZnO thin films with almost the same thickness (~45 nm) but very different crystallinity. From x-ray diffraction measurement, the full width at half maximum (FWHM) of (0002) ω-rocking curve of sample 1 is 0.15°, indicating high crystallinity of the film. However the FWHM of ω-rocking curve of sample 2 is 0.7°, showing poor crystallinity. Figure 1 shows the intensity of the transmitted second harmonic signal from sample 1 as a function of the incident angle of the fundamental beam. We checked the polarization of the second harmonic signal, and found it is always *p*-polarized no matter the fundamental beam is *p*-polarized or *s*-polarized.

By comparing Figs. 1 and 2, we can see that the SHG intensity from sample 2 is almost twice larger than that from sample 1, although those two films have almost the same thickness. This suggests that the second harmonic signal is

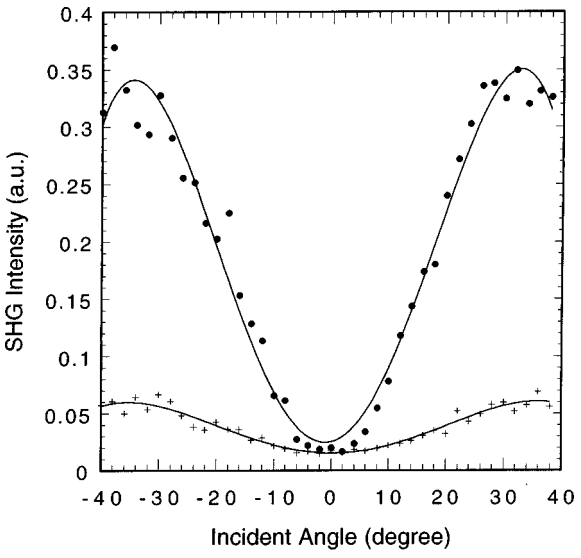

FIG. 1. Measured transmitted second harmonic intensity from sample 1 as a function of the incident angle of the fundamental beam, when the fundamental beam is *s*-polarized (crosses), and *p*-polarized (closed circles), respectively. The solid curves correspond to theoretical fitting.

[a]Electronic mail: h-cao@nwu.edu

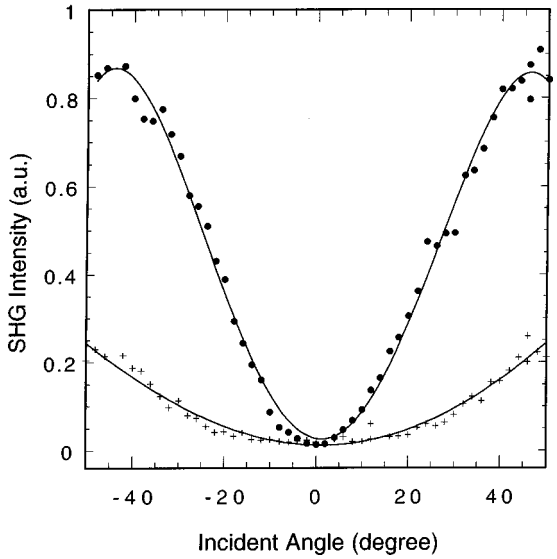

FIG. 2. Measured transmitted second harmonic intensity from sample 2 as a function of the incident angle of the fundamental beam, when the fundamental beam is *s*-polarized (crosses), and *p*-polarized (closed circles), respectively. The solid curves correspond to theoretical fitting.

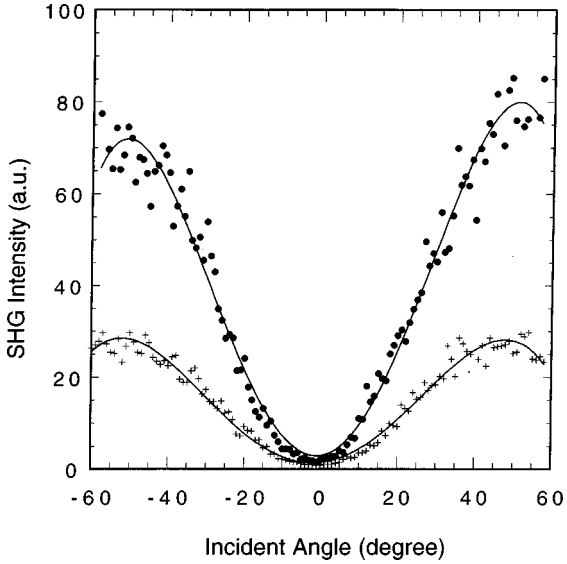

FIG. 3. Measured SHG intensities from two thicker ZnO films as a function of the incident angle of the fundamental beam, when the fundamental beam is *p*-polarized. The FWHM of ω-rocking curves of those two films are 0.1° (crosses), and 0.26° (closed circles), respectively.

generated not only inside crystallites, but also at grain boundaries.

We have modeled our sample as a four-layer system: air-film-substrate-air. Absorption at both fundamental and second harmonic frequency is negligible since the photon energies at those frequencies are much smaller than the band-gap energy of ZnO. The transmitted second harmonic intensity $I_{2\omega}$ as a function of the incident angle θ of the fundamental beam can be written as[9]

$$I_{2\omega}(\theta)=\frac{128\pi^3}{cA}\frac{(t_{af}^{1\gamma})^4(t_{fs}^{2p})^2(t_{sa}^{2p})^2}{(n_{2\omega}\cos\theta_{2\omega})^2}\times I_\omega^2\left(\frac{2\pi L}{\lambda}\right)^2(\chi_{\text{eff}}^{(2)})^2\frac{\sin^2\Phi}{\Phi^2}, \tag{1}$$

where A is the area of the incident beam spot, I_ω is the intensity of the incident fundamental beam, L is the film thickness, n_ω ($n_{2\omega}$) is the refractive index at the fundamental (second harmonic) frequency in the ZnO film, and θ_ω ($\theta_{2\omega}$) is determined by $\sin\theta=n_\omega\sin\theta_\omega$ ($\sin\theta=n_{2\omega}\sin\theta_{2\omega}$). Φ corresponds to the coherence length

$$\Phi=\frac{2\pi L}{\lambda}(n_\omega\cos\theta_\omega-n_{2\omega}\cos\theta_{2\omega}). \tag{2}$$

$t_{af}^{1\gamma}$ represents the transmission coefficient of the fundamental beam from air to the ZnO film, and γ indicates the polarization direction. t_{fs}^{2p} and t_{sa}^{2p} represent the transmission coefficients of the second harmonic beam from the ZnO film to the substrate and from the substrate to the air, respectively. Note the second harmonic beam is always *p*-polarized.

$\chi_{\text{eff}}^{(2)}$ in Eq. (1) represents the effective second order susceptibility. Since ZnO has the hexagonal close packed (hcp) structure, with the 6 mm symmetry, individual crystallite should have only four independent nonzero components of the second order susceptibility tensor: $\chi_{xzx}^{(2)}=\chi_{yzy}^{(2)}$, $\chi_{xxz}^{(2)}=\chi_{yyz}^{(2)}$, $\chi_{zxx}^{(2)}=\chi_{zyy}^{(2)}$, and $\chi_{zzz}^{(2)}$, where the coordinates correspond to the crystal axes of individual crystallite. When the frequencies involved are far from resonances, Kleinman's symmetry condition can be applied to further reduce the number of independent components to two: $\chi_{xzx}^{(2)}=\chi_{yzy}^{(2)}=\chi_{xxz}^{(2)}=\chi_{yyz}^{(2)}=\chi_{zxx}^{(2)}=\chi_{zyy}^{(2)}$ and $\chi_{zzz}^{(2)}$. Assuming that individual crystallite average to a texture axis, the tensorial property of the ZnO film (including all the crystallites and the grain boundaries) is equivalent to that of an isotropic uniaxial medium. This assumption is supported by the experimental observation that the SHG signal is always *p*-polarized no matter the fundamental beam is *s*-polarized or *p*-polarized. Therefore when the fundamental beam is *s*-polarized,

$$\chi_{\text{eff}}^{(2)}=\chi_{zxx}^{(2)}\sin\theta_{2\omega}. \tag{3}$$

When the fundamental beam is *p*-polarized,

$$\chi_{\text{eff}}^{(2)}=\chi_{zxx}^{(2)}(\cos\theta_{2\omega}\sin 2\theta_\omega+\sin\theta_{2\omega}\cos^2\theta_\omega)+\chi_{zzz}^{(2)}\sin\theta_{2\omega}\sin^2\theta_\omega. \tag{4}$$

To deduce the values of $\chi^{(2)}$ for the ZnO film from Eq. (1), we need to know the value of I_ω^2/A. To get it, we replaced the ZnO film with a *Y*-cut quartz plate, and measured its second harmonic intensity as a function of the incident angle of the fundamental beam. Since $\chi^{(2)}$ is known for quartz, we can deduce the value of I_ω^2/A. After substituting it into Eq. (1), we curve-fit the data in Figs. 1 and 2 to deduce the values of $\chi_{\text{eff}}^{(2)}$. Then using Eq. (3) and Eq. (4), we deduced the values of $\chi_{zxx}^{(2)}$ and $\chi_{zzz}^{(2)}$. For sample 1, we got $\chi_{zxx}^{(2)}\simeq 2$ pm/V, and $\chi_{zzz}^{(2)}\simeq 10.8$ pm/V. For sample 2, we deduced $\chi_{zxx}^{(2)}\simeq 3.6$ pm/V, and $\chi_{zzz}^{(2)}\simeq 13.4$ pm/V. These results indicate that the ZnO films have large second order nonlinear optical response. Furthermore, the ZnO film with lower crystallinity has larger second order optical nonlinear response than the film with higher crystallinity.

Finally we measured two thicker films of ZnO. The thickness of both films is about 235 nm. The FWHM of (0002) ω-rocking curves of those two films are 0.1° and 0.26°, respectively. Figure 3 shows the measured second har-

monic signal from those two samples as a function of the incident angle of the fundamental beam, when the fundamental beam is *p*-polarized. We found the film with lower crystallinity generates stronger second harmonic signal than the film with higher crystallinity, consistent with our result on thinner films. For the film with higher crystallinity, we deduced $\chi^{(2)}_{zxx} \simeq 1.0$ pm/V, and $\chi^{(2)}_{zzz} \simeq 4.1$ pm/V. For the film with lower crystallinity, we deduced $\chi^{(2)}_{zxx} \simeq 1.4$ pm/V, and $\chi^{(2)}_{zzz} \simeq 8.8$ pm/V. Hence the values of $\chi^{(2)}$ for the thicker films are smaller than those from the thinner films. This indicates that part of the second harmonic signal is generated at interfaces.

In conclusion, we have measured the second harmonic signal from ZnO thin films deposited on sapphire substrates by pulsed laser ablation. The ZnO films show large second order nonlinear optical response: the second order susceptibility $\chi^{(2)}_{zzz}$ can be as large as 10 pm/V. In addition, by comparing the second harmonic signal generated from films with different crystallinity and thickness, we conclude that a significant part of the second harmonic signal is generated at grain boundaries and interfaces. However, the effect of grain boundaries and interfaces on SHG is not well understood and requires further study.

This work was supported by the MRSEC program of the National Science Foundation (DMR-9632472) at the Materials Research Center of Northwestern University.

[1] M. M. Fejer, Phys. Today **47**, 25 (1994).
[2] J. D. Bierlein, D. B. Laubacher, J. B. Brown, and C. J. van der Poel, Appl. Phys. Lett. **56**, 1727 (1987).
[3] E. J. Lim, M. M. Fejer, R. L. Byer, and W. J. Kozlovsky, Electron. Lett. **25**, 731 (1989).
[4] T. Doumuki, H. Tamada, and M. Saitoh, Appl. Phys. Lett. **65**, 2519 (1994).
[5] W. P. Lin, P. M. Lundquist, G. K. Wong, E. D. Rippert, and J. B. Ketterson, Appl. Phys. Lett. **63**, 2875 (1993).
[6] P. M. Lundquist, H. C. Ong, W. P. Lin, R. P. H. Chang, J. B. Ketterson, and G. K. Wong, Appl. Phys. Lett. **67**, 2919 (1995).
[7] H. C. Ong and R. P. H. Chang, Phys. Rev. B **55**, 13213 (1997).
[8] P. L. Washington, H. C. Ong, J. Y. Dai, and R. P. H. Chang, Appl. Phys. Lett.
[9] P. D. Maker, R. W. Terhune, M. Nisenhoff, and C. M. Savage, Phys. Rev. Lett. **8**, 121 (1962).