Large second harmonic response in ZnO thin films

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The second-order susceptibilities in the ZnO films have been studied systematically. In very thin films, we observe an enhancement of second-order susceptibilities, which is larger than that of single-crystal ZnO. It was also observed that the second-order susceptibilities for ZnO films depend on the thickness but not on the film growth technique used (reactive sputtering or plasma-enhanced chemical vapor deposition). We suggest a mechanism to explain the reduction in the second-order susceptibilities of the thicker films. © 2002 American Institute of Physics.

In recent years, wide-gap semiconductors have been subjected to extensive studies because of the rising interest in the development of new nonlinear optical materials for potential applications in integrated optics. Impressive progress has been made in fabricating nonlinear optical waveguides from nonlinear optical single crystals like LiNbO$_3$, KTP and LiTaO$_3$. However, such crystals tend to be rather expensive. Efforts have also involved ZnSe and GaN based semiconductor heterostructures; these efforts have resulted in the demonstration of room-temperature blue and green laser diodes. ZnO has a room-temperature band gap of 3.3 eV, combined with high exciton gain and large exciton binding energy. As a candidate for ultraviolet optoelectronic device applications, the nonlinear properties of ZnO are attractive. In this work, we report a systematic study of second-harmonic (SH) generation as a function of the film thickness. Surprisingly, for very thin films a $\chi^{(2)}$ as large as 18 pm/V is obtained which is larger than the value for bulk single-crystal ZnO.

Thin films were deposited using two different approaches. In the first approach, deposition was carried out on fused silica substrates by reactive, pulsed-direct-current sputtering at a temperature of 250°C. A 99.99% pure zinc target (purchased from Goodfellow Co., PA) was used and the chamber gas environment during sputtering consisted of 8 mTorr argon with the oxygen partial pressure fixed at 0.8 mTorr. The substrates were radiantly heated from the back side. The resulting films were all (0001) oriented (with the c axis perpendicular to the film surface), as determined by $\theta/2\theta$ x-ray electron diffraction (XRD). The width of the XRD curves and rocking curves were less than 0.5°. These samples were also examined with a scanning electron microscope (SEM). The SEM images show that the grains are randomly distributed in size and roughly hexagonal in shape.

We also studied films deposited on the (0001) oriented sapphire substrates by plasma-enhanced chemical vapor deposition (PECVD). The Zn precursor was diethyl zinc, and the film growth took place in an oxygen plasma at a pressure of 3 mTorr.

The second-order susceptibility was determined by measuring the angular dependent SH signal using the setup described elsewhere. We used two polarizers and a half-wave plate to adjust the incident intensity. Another half-wave plate in front of the sample was used to adjust the polarization of the fundamental beam. The sample was mounted on a computer-controlled rotation stage. We also used another polarizer behind the sample to check the polarization of the output SH signal. Two filters were used to eliminate the fundamental frequency in both the signal branch and reference branch. We used the 1.064 μm beam generated by a Nd:YAG laser. The SH signal was measured with a photomultiplier tube and compared with a SH reference beam generated by a y-cut quartz plate. The signals in both branches were detected by identical photo-multiplier tubes followed by boxcar integrators, the outputs of which were digitized and fed into the computer.

The second-order susceptibility of thin films can be expressed as:

$$P_{2\omega}/P_\omega = \frac{512 \pi^5}{c \lambda^2} \frac{t_1^2 t_2 f^2_{2\omega}}{n_{2\omega}^2 \cos^2 \theta_{2\omega}} \left( \frac{P_\omega}{A} \right) (d_{eff})^2 \sin^2(\phi) \frac{\sin^2(\theta)}{\phi^2},$$

where $\phi = 2 \pi l/\lambda (n_{\omega} \cos \theta_{\omega} - n_{2\omega} \cos \theta_{2\omega})$ is the phase angle, $P_{2\omega}$ and $P_\omega$ are the intensities and $t_1$, $t_2$ and $f_{2\omega}$ are the fundamental and SH Fresnel transmission coefficients (for the air–film, film–substrate and substrate–air interfaces) and the angle $\theta_{2\omega}$ is given by Snell’s law, $\sin \theta = n_{\omega} \sin \theta_{\omega} = n_{2\omega} \sin \theta_{2\omega}$. In the Kleinman approximation, the second-order susceptibility tensor of hexagonal ZnO can be described by two independent components $\chi_{31}^{(2)}$ and $\chi_{33}^{(2)}$. The effective susceptibility, $d_{eff}$, can be calculated from the two independent components of $\chi^{(2)}$ and the incident angle.

In our experiment, both the fundamental and SH beams were $p$ polarized. The effective susceptibility is:
The two different methods give essentially the same SH response; i.e., the observed second-order susceptibility is not highly dependent on the deposition technique. Note the samples made by PECVD were deposited on the sapphire substrate. Our observation that the SH signal output is not highly dependent on the deposition method or substrate material suggests that the films can be used for a variety of applications, because of the insensitivity to production details.

The data were fitted to the theoretical expressions to obtain the two components of the second-order susceptibility tensor. Figure 1 shows the fitted curve for a 272 nm thick ZnO film. We systematically studied films with thicknesses between 5.3 and 350 nm (the thickness was measured by a “Tencor 200” profile finder). The ratios of two components of the second-order susceptibility do not show any systematic dependence on the film thickness. They vary from $X_{31}^{(2)}/X_{33}^{(2)} = -0.3369$ for the 47 nm film to $X_{31}^{(2)}/X_{33}^{(2)} = 0.2406$ for the 150 nm film. The mean value is $X_{31}^{(2)}/X_{33}^{(2)} = 0.2699$, with a standard deviation of 0.02. However, the absolute values of these components decrease with the thickness. For thinner films, it can be as large as $X_{33}^{(2)} = 17.89 \text{ pm/V}$ for the 44.2 nm film and drops to $X_{33}^{(2)} = 8.70 \text{ pm/V}$ for the 343.5 nm film. The larger component of the susceptibility, $X_{33}^{(2)}$, versus film thickness is shown in Fig. 2. When the film is very thin, $X_{33}^{(2)}$ is somewhat larger than the bulk value, but as the film becomes thicker, $X_{33}^{(2)}$ drops.

SH measurements on laser ablated films were studied earlier, by Cao et al., although the maximum $X_{33}^{(2)}$ reported was somewhat different (18 pm/V vs 13.4 pm/V). To further explore the effects of film thickness, we also measured some samples prepared by PECVD. The films made by the two different methods give essentially the same SH response; i.e., the observed second-order susceptibility is not highly dependent on the deposition technique. Note the samples made by PECVD were deposited on the sapphire substrates. Our observation that the SH signal output is not dependent on the deposition method or substrate material suggests that the films can be used for a variety of applications, because of the insensitivity to production details.

From the data shown in Fig. 2, we note that the thinnest film has a second-order susceptibility higher than the bulk material, $X_{33}^{(2)} = 14.31 \pm 0.4 \text{ pm/V}$. ZnO has the hexagonal wurtzite structure, which during growth along the c axis may have two different stacking sequences, which are indistinguishable by ordinary XRD experiment, as pictured in Fig. 3. It is natural to expect two limiting growth behaviors on an unpolished substrate. One is that grains growing with both sequences nucleate with the same probability at the substrate surface, after which they continue to grow with these orientations. However, by introducing a stacking fault, a grain may, with some probability, flip to the other stacking sequence. The second limiting case is that the grains all nucleate with the same orientation after which flipping sets in. In our case, it appears that the second behavior occurs. The probability of the flipping is expected to be proportional to the total thickness, approaching unity for a thick film. From the crystal symmetry, we know that a second-order susceptibility can only exist in a crystal lacking inversion symmetry. Though both the “up” and “down” structures do not have inversion symmetry by themselves, the “layered” structure, made up from stacks of the up and down layers, will lose some of its polarization. As a result, the thinner films will be better oriented than the thicker films, resulting in a larger effective second-order susceptibility. Although the introduction of stacking faults will tend to reduce the effective susceptibility of thicker films, a thick film may still approach some asymptotic effective susceptibility owing to a different flipping probability (or sticking coefficient) associated with
the two polar surfaces during growth. Although we have not investigated it, the effective piezoelectric response would also be expected to fall off with increasing film thickness.\textsuperscript{14}

For the very thin ZnO films, the polar axis appears to be well oriented; hence, these give the strongest SH generation. Curiously, the SH in very thin films is somewhat stronger than in a single crystal. Whether the structure of typical single crystals are made up of only a single orientation or contains some combination of both needs further study. However, film deposition is much easier than making single crystals and films are more easily integrated into devices. The enhancement in the very thin films is very encouraging. The insensitivity of the film growth to the deposition technique enhances the utility of ZnO films for various applications.

The second-order susceptibilities observed in the very thin ZnO films are enhanced and can be larger than that of single crystal ZnO. However, the second-order susceptibilities for ZnO thin films depend on their thickness but were observed to have the same behavior independent of whether they were prepared by sputtering or PECVD. The reduction in the second-order susceptibilities of thick film can be explained by the model in which the polar axis, which is initially aligned with respect to the substrate, flips as the film thickens.

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\textsuperscript{2}P. M. Verghese and D. R. Clarke, J. Appl. Phys. 87, 4430 (2000).
\textsuperscript{12}Films measured by these authors which had higher $\chi^{(2)}_{33}$ values also had larger rocking curve widths. If one assumes the rocking curve was dominated by grain size (usually determined by the $\theta$-2$\theta$ width), one might conclude that any enhancements come from a surface mechanism. However, in both our case and theirs, dense films are being studied where the variation in material properties in passing from grain to grain are minimal, suggesting a small surface contribution.
\textsuperscript{14}Measurements were made on our samples with both sides facing the laser; no difference of the output SH signals was expected and none was observed, in either the thinner or the thicker films.