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Third-harmonic generation from ZnO films deposited by MOCVD

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ABSTRACT Third-harmonic generation (THG) was studied from ZnO thin film deposited by the metalorganic chemical vapor deposition (MOCVD) technique on sapphire substrates at different temperatures. A strong THG signal was obtained from the film deposited at an appropriate temperature. The dependence of THG on the deposition temperatures was discussed. A third-order susceptibility $\chi^{(3)} = 3.77 \times 10^{-12}$ esu was deduced for a film deposited at 250 °C. This value is similar to that observed from ZnO nanocrystalline films fabricated by pulse-laser deposition (PLD). We conclude that film structure and the crystalline quality is main factors determined the THG in the film.

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1 Introduction

Wide band gap materials are attracting more attention for their potential application in optical devices [1, 2]. These materials can be used to develop laser diodes and the other optoelectronic devices. In the fields of electro-optic and integrated optical devices, there is an intense requirement in the development of thin films of materials with large nonlinear optical response. Many efforts have been made in nonlinear optical waveguides made of $LiNbO_3$, $LiTaO_3$, and KTP [3, 4]. However, it is necessary to fabricate them with expensive single crystals. Also the integrated ability was limited. Therefore, it is imperative to develop a new material with large nonlinear optics response and small size that can be integrated for the application. GaN and SiC have been used for blue or shorter wavelength emitting diodes (LEDs).

Recently, II-VI semiconductor material ZnO has been widely investigated in many fields from film growth to optical properties [5–7]. Like GaN, ZnO has a wide band gap energy of 3.37 eV at room temperature. The extremely high melting point around 2300 K suggest that the optical damage threshold of ZnO may be higher than those of many common nonlinear (NLO) materials. It is regarded as a good candidate material in green, blue or shorter wavelength LED. The second harmonic generation (SHG) of ZnO thin film has been reported and the second order susceptibility $\chi^{(2)}$ has been measured [6, 7]. However, most of the nonlinear optical devices are concerned with the third order optical susceptibility $\chi^{(3)}$ like optical limiting, optical switches, bistable and modulators to function. The primary advantage of THG is, that because of the high frequencies involved, it can probes purely coherent, electronic nonlinearity [8, 9]. THG is not sensitive to thermal response. But little work has been done with ZnO film in THG. For ZnO bulk crystal, the refractive index n_2 or $\chi^{(3)}$ was measured about 2.3×10^{-12} esu or 1.2×10^{-13} esu (for $\lambda = 1.06\,\mu m$). It is prefigured that nonlinear optical susceptibility of ZnO will be affected by the nanocrystal structure. G. Petrov reported the third harmonic generation (THG) in ZnO film grown by PLD on fused silica substrate with fundamental wavelength 1.2–1.3 μm. Here we will report on THG in films deposited at different temperatures by metalorganic chemical vapor deposition (MOCVD). We will investigate the dependence of the THG on the deposition temperatures in the ZnO films.

2 Film fabrication and characterization

Up to now, several techniques have been used to grow ZnO film; e.g., molecular beam epitaxy methods (MBE), metalorganic chemical vapor deposition (MOCVD), pulse-laser deposition (PLD) and sputtering. Among these methods, MOCVD technology is particularly interesting not only because it leads to high-quality films, but also because it is applicable to industrial mass-production. In an epitaxial film, it is necessary that all the unit cells have the same in-plane (and then along the growth direction, too) orientations. MOCVD technique can lead to epitaxial growth of many kinds of semiconductor materials such as GaAs, InP, GaN, and ZnO. Moreover, we have shown that Zn-polarity ZnO films, which are considered to be superior to O-polarity ZnO films toward realization of *p*-type ZnO, are easily obtained by MOCVD, indicating the importance of this technique. The properties of the films are known to be strongly dependent on the growth parameters such as temperature, rate, and pressure. Here growth temperature is one of the most important parameters that determine the quality of epitaxial films. However, there are only a few reports on the temperature dependence of

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the properties of ZnO epitaxial films grown by MOCVD and the effects of growth temperatures on the crystalline, optical and surface properties of ZnO films are still not fully investigated. Park et al. reported the growth of ZnO on $Al_2O_3(0001)$ substrates at temperatures of 250–550 °C. From the dependence on growth temperature of half width (FWHM) values of rocking curves, they found the optimized growth temperature of ZnO was 500 °C. Gorla et al. reported the growth of ZnO epitaxial films on $Al_2O_3(01\bar{1}2)$ (R-sapphire) substrates. Recently, we reported the growth of ZnO films at even lower temperatures of 150–300 °C on sapphire(0001) substrates by MOCVD [11]. Epitaxial growth was obtained down to 200 °C and acceptor-related emission peaks were observed from these films. Here the films were deposited at different temperatures range from 200 to 500 °C.

X-ray diffraction (XRD) machine was used to characterize the crystalline quality, by measuring the rocking curve, and the epitaxial relationship, by measuring the Φ scan. Figure 1 shows the Φ scans of the ZnO$\{11\bar{2}2\}$ family of planes grown at different temperatures together with the Φ scan of the $\{11\bar{2}6\}$ family of planes of the Al_2O_3 substrate. The sixfold symmetry unambiguously demonstrates that the film was grown epitaxially.

Surface morphologies were investigated by using a scanning electron microscope (SEM). The result was shown in Fig. 2. The surface morphology changes with the temperature significantly.

From Figs. 1 and 2 we know the film crystalline quality dependence on the deposition temperature. At higher growth temperature, the films have a good crystalline structure. The surface morphology changes with the growth temperature significantly. For $T_g \leq 250$ °C, smooth surfaces without grain formations (Fig. 2a and b) were observed. However, cracks were also observed for the film deposited at 250 °C indicating existence of internal stresses in the film. On the other hand, the film grown at 300 °C exhibited a rough surface with hexagonal grains (Fig. 2c). The lateral grain size is estimated to be 0.5–1 μm. At further higher growth temperatures, column growth with formations of rods was observed clearly at 350 °C (Fig. 2d and h). The diameters of the rods were 0.1–0.3 μm.

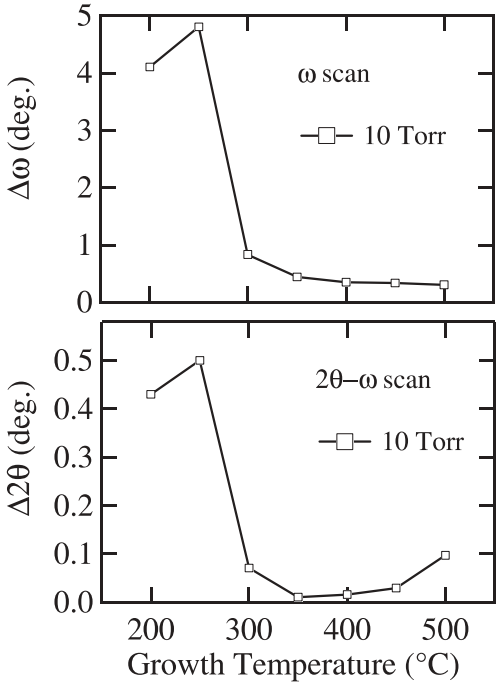

FIGURE 1 FWHM values of 2θ–ω and ω scans of the (0002) crystal plane of ZnO films as a function of growth temperature

3 THG experiment

THG properties were studied for fundamental wavelength at 1.06 μm from a Q-switch Nd : YAG laser (LOTIS: LS-2138) with 15 ns, repetition 50 Hz. The measurement was set up in the transmission mode. The power and the polarization of 1.06 μm fundamental beam can be adjusted by rotating a half wave plate (HWP) put between of two polarizers. The fundamental power was measured with a power meter (Newport 1835C). THG signal is collected by a quartz lens (focal length 10 cm) then was redirected into spectrometer connected a CCD detector for spectra measurement. The intensity of the THG signal is measured by photomultiplier tube and then averaged by boxcar integrator. In order to increase the fundamental beam intensity, a quartz lens with 30 cm focal length was used to focus the beam. The film was mounted on a step-motorized rotating stage so that the incident angle of the fundamental beam can be continuously varied. An appropriate filter was used to block the fundamental beam. The polarization of the THG was checked with a polarizer placed behind the filter.

THG is a third order nonlinear process in which the fundamental beam at wavelength λ interacts with nonlinear medium and another beam at wavelength (λ/3) can be obtained. For a thin film, the thickness is much less than confocal parameter b of fundamental beam. In this case, the intensity of THG signal can be expressed as [12]

$$I_{3\omega} = \frac{64\pi^4}{c^2}\left[A\chi^{(3)}\right]^2 (I_\omega)^3 f_a,$$

$$f_a = \frac{\left\{\left[1-\exp(-\alpha_{3\omega}d/2)\right]^2 + (\Delta\psi)^2\exp(-\alpha_{3\omega}d/2)\right\}}{\left[(n_{3\omega}^2 - n_\omega^2 - k_{3\omega}^2)^2 + (2n_{3\omega}k_{3\omega})^2\right]} \tag{1}$$

where $\chi^{(3)}$ is third-order nonlinear susceptibility, d is the thickness of film, $n_\omega(n_{3\omega})$ is the real part of the refractive index for the fundamental (third harmonic) frequency, $\alpha_{3\omega}$ is the linear absorption coefficient, A is an empirical factor that depends on the experimental geometry, $k_{3\omega}$ the imaginary of the refractive index for third harmonic frequency, c is light speed, $\Delta\psi$ is the wave vector mismatch between the fundamental and THG beam in film, and I_ω is the intensity of the fundamental beam. If the absorption is neglected, $I_{3\omega}$ will be proportional to the fundamental beam intensity ($I_\omega)^3$ The intensity of THG generated from the films, with a thickness of about 1.2 μm, at different temperatures dependent on the fundamental beam intensity were shown on the Fig. 3. The results conforming to the intensity of THG are proportional to the third power of the fundamental beam intensity. In our experiments, the film was put at the lens focus point, where the

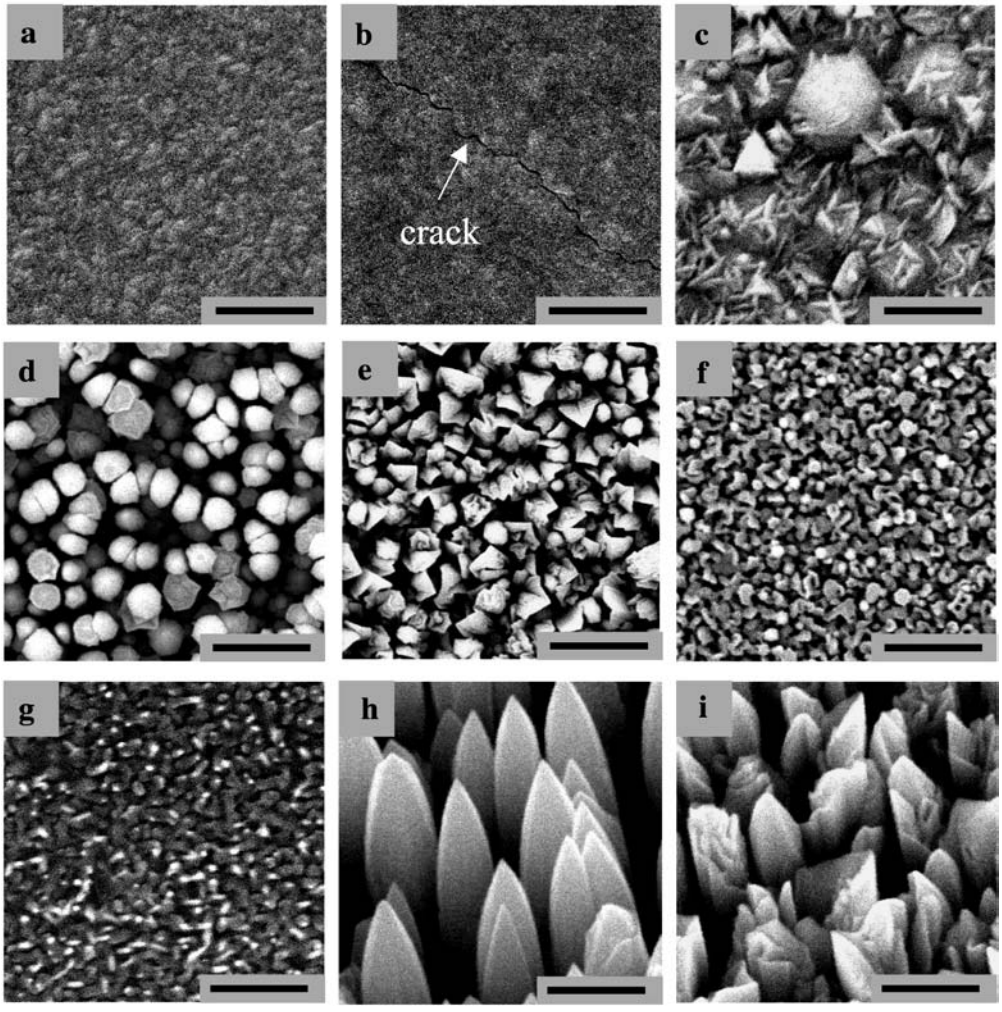

FIGURE 2 **a** to **g**: Surface SEM images of the ZnO films grown at 200 to 500 °C with an interval of 50 °C. Smooth surfaces at $T_g \leq 250$ °C, facet- and column-growth at $T_g = 300$–450 °C, and fine-grain surfaces at even higher growth temperatures. Cracks were observed from the film grown at $T_g \leq 250$ °C. **h** and **i**: The enlarged SEM surface images of the films grown at 350 °C and 400 °C taken with an inclination angle of 30°. The *bars* indicate 1 μm in length from **a** to **f** and 0.5 μm from **g** to **i**

beam spot is about 100 μm in the radius. When the power of the fundamental beam is higher than 100 mW (2 mJ/pulse or 0.42 GW/cm^2), the film was damaged.

The results indicate that THG are dependent on the deposition temperature. The THG signal increases with increasing growth temperature (showed in Fig. 3, 200 °C, 300 °C and 400 °C). That means the THG signal is dependent on the crystalline quality. But, in our experiments, the strongest THG signal was observed from the film grown at 250 °C. The reasons can be explained as following. First, the film has a poor crystalline but the surface of the film, which is shown in Fig. 2, is smooth. The scattering of the fundamental beam is lower than that from the other films. Second, as shown in Fig. 1, this film consists of two kinds of unit cells with different in-plane orientations which twist 30° from each other. The film structure is believed to be tightly correlated with the nonlinearity. In a perfect film, the unit cells have the same in-plane orientations for the whole film. When the in-plane orientations are different, the atomic bounds between neighboring unit cells will deviate from their equilibrium positions. This may cause dandling bounds at the interfaces of different unit cells, which results in extra carriers in the film. The higher carrier density can enhance the nonlinearity. Similarly, a stronger THG signal can be expected in ZnO films grown at 250 °C.

We have checked the polarization of the THG and found that the polarization of THG is always same as the fundamental beam. This point is different from the SHG where the polarization is always *p*-polarization no matter the fundamental beam is *p*-polarization or *s*- polarization. In order to conform, the THG really comes from the film, replacing the film with the Al_2O_3 (0001) substrates at the same condition, we did not get any THG even at a higher fundamental beam intensity level.

Using the film deposited at 250 °C, the dependence of THG on the polarization of the fundamental beam was shown in the Fig. 4. The result indicted *p*-polarized fundamental beam gives a larger THG than *s*-polarized. But the difference between *p*-polarization and *s*-polarization is not so large compared to the SHG where *p*-polarization fundamental beam gives a much larger SHG than the *s*-polarization.

In order to investigate the order of magnitude of the nonlinear susceptibility $\chi^{(3)}$, microscope slide was used as a reference material. The refractive index and third-order susceptibility $\chi^{(3)}$ are considered as real, and the phase of $\chi^{(3)}$ relative to the substrate is ignored. The $\chi^{(3)}$ can be expressed as [12]

$$\chi^{(3)} = \chi_s^{(3)} \left(\frac{2}{\pi}\right) \left(\frac{l_{c,s}}{l}\right) \left(\frac{I_{3\omega}}{I_{3\omega,s}}\right)^{1/2} \tag{2}$$

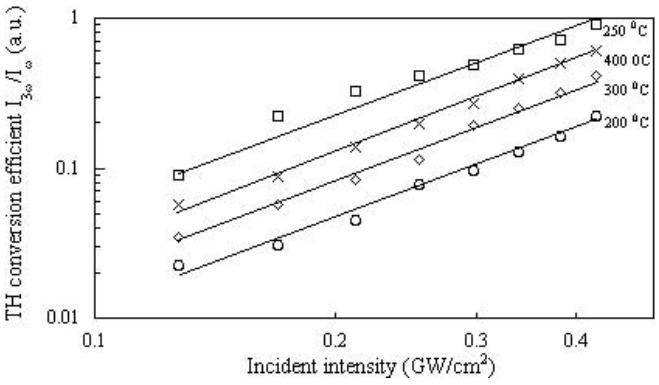

FIGURE 3 Measured conversion efficient $I_{3\omega}/I_\omega$ as a function of the intensity of incident fundamental beam I_ω^2

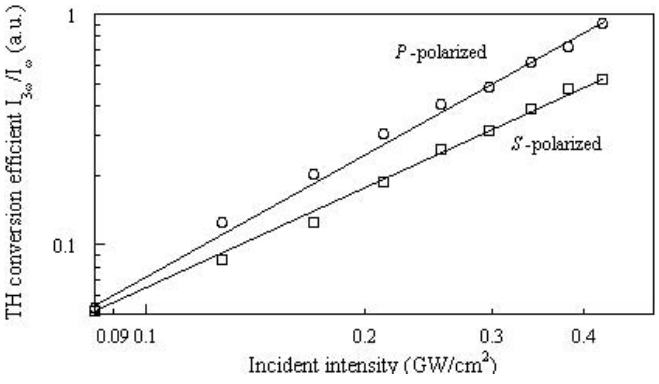

FIGURE 4 Measured conversion efficient $I_{3\omega}/I_\omega$ as a function of the intensity of incident fundamental beam I_ω^2 when the fundamental beam is *p*-polarized, and *s*-polarized, respectively.

Where the $I_{3\omega}$ is the THG intensity, the suffix *s* refers to the reference material. $L_{c,s}$ is the coherence length of microscope slide which is about 17.69 μm. The $\chi_s^{(3)} = 4.38 \times 10^{-14}$ esu.

Using (2), we can deduce the value of $\chi^{(3)}$ to be 3.77×10^{-12} esu which is larger than that of ZnO bulk crystal (1.2×10^{-13} esu). We have completed the SHG experiments that will be reported elsewhere, The second order susceptibility tensor $\chi_{zzz}^{(2)} = 9.2$ pm/V was deduced for a film deposited at 250 °C. Both of them conform that nanostructure film have an efficient nonlinear properties.

4 Conclusion

In conclusion, THG in MOCVD thin films of ZnO deposited at different temperatures was studied. It was found that the THG of the film was dependent on the deposited temperature. Normally, for the films deposited at higher temperature, the THG will be large. But a special deposition temperature was found where the THG is higher than others. The polarization of the THG was found to be same as the fundamental beam. For a film deposited at 250 °C, the $\chi^{(3)} = 3.77 \times 10^{-12}$ esu is obtained.

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