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Frequency doubling and autocorrelation studies of 20-fs pulses using polycrystalline zinc oxide thin films

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Abstract. We demonstrate the potential of thin ZnO films for frequency doubling and autocorrelation measurements of ultrashort laser pulses. Using a spray pyrolysis technique, ZnO films of submicron thickness were deposited on glass substrates. Such thin films show an effective second-order nonlinearity larger than that of beta-barium borate and negligible group velocity dispersion for input wavelengths around 800 nm. Autocorrelation measurements performed with 20-fs pulses from an 88-MHz modelocked Ti:sapphire laser show a nonresonant, instantaneous nonlinear response of the material and a dynamic signal range of two orders of magnitude for average input powers down to 10 mW.

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In recent years, ultrashort pulses of sub-50-fs duration have become available in a wide wavelength range and have found numerous applications in physics, chemistry and biology [1]. Characterization of the temporal properties, i.e. the width and shape of the temporal envelopes and the phase of the electric field, is mandatory both in generating and in using such extremely short pulses. For this purpose, a number of nonlinear techniques have been developed, among them autocorrelation and crosscorrelation measurements as well as frequency-resolved optical gating (FROG). In general, such methods are based on phase-matched nonlinear optical interactions and, thus, require a nonlinear medium of a sufficiently high second- and/or third-order optical nonlinearity. Furthermore, the response time of the nonlinear medium has to be short compared to the pulse duration, and the distortion of the pulse envelopes by group velocity dispersion in the nonlinear medium has to be minimized. The latter requirement limits the maximum possible interaction length in most nonlinear crystals to values below 100 μm [2, 3], which is a difficult range of crystal thickness to prepare.

Thin films of organic or inorganic materials represent a class of nonlinear materials in which a non-phase-matched nonlinear process has been exploited for pulse characterization with negligible group velocity mismatch. Thin organic films, e.g. polycrystalline pentacene films or dye molecules embedded in a poled polymer film, have been used successfully for pulse characterization by autocorrelation and FROG measurements [4, 5]. Under nonresonant conditions, i.e. in the transparency range of the materials, the macroscopic nonlinearity shows an instantaneous response, whereas nonlinear polarizations created on molecular resonances show a finite phase relaxation time, leading to a systematic temporal broadening of the nonlinear response [5]. This problem and the sometimes limited photochemical and photothermal stability have prevented wide-spread application of these molecular materials so far. Here, inorganic thin films with a higher nonlinearity and a wide transparency range should be useful. For instance, nonlinear materials such as the wide-gap semiconductor ZnO have attracted attention for application in integrated optics [6]. Very recently, the nonlinearity of sputtered ZnO films on sapphire substrates was investigated with nanosecond pulses in the near-infrared [7].

In this article, we report on a study of the second-order nonlinearity of thin polycrystalline ZnO films using 20 fs pulses. Layers of submicron thickness were prepared on glass substrates by spray pyrolysis. For an optimal choice of sample orientation and input beam polarization, effective second-order nonlinearities larger than those of beta-barium-borate (BBO) were measured. Autocorrelation studies of 20-fs pulses performed with the ZnO films show a nonresonant, instantaneous nonlinear response and a high dynamic range of two orders of magnitude in the correlation signal for input powers down to 10 mW.

1 Experimental

1.1 Preparation and characterization of ZnO *films*

Thin undoped ZnO films were made by an optimized spray pyrolysis process on flat glass substrates. Aqueous solutions

of zinc salts were sprayed on heated substrates. Based on previous results [8], we were able to improve the homogeneity and to tailor the morphology of the films to match our demands. Using substrate temperatures > 750 K and slow solution rates, conditions suitable for crystal growth were achieved. The films prepared under different growth conditions were analyzed by plane-view scanning electron microscopy. The micrograph of a sample showing a morphology that is optimal for second-harmonic generation (SHG), is shown in Fig. 1a. It displays a large homogeneity and a microcrystal size on a 200-nm scale. In addition, X-ray diffraction analysis on such samples, as shown in Fig. 1b, demonstrates the preferred [002] orientation of the microcrystals, i.e. the *c* axis of the underlying hexagonal wurzite structure is oriented normal to the substrate surface. The thicknesses of the films were measured with a TENCOR 10 profile meter and had values between 0.1 and 1.5 μm.

1.2 Second-harmonic generation

Second-harmonic generation was studied with the self-mode-locked Ti:sapphire laser described in [9]. This system provides nearly Fourier-limited pulses of 20 fs in duration at a center wavelength of 830 nm. The average output power and the repetition rate have values of about 300 mW and 88 MHz, respectively. In order to pre-compensate for the dispersion of the subsequent optical elements, the pulses travel through a two-prism compressor. Second-harmonic generation was studied in a setup for noncollinear autocorrelation measurements. Two beams were obtained from a beamsplitter and focussed onto the thin film with a lens of 100 mm focal length, resulting in a spot diameter of about 40 μm. The second-harmonic signals originating either from the individual input beams or from their superposition (autocorrelation signal) were detected in transmission. They were separated from the fundamental with a filter (Schott BG 39) and an aperture and detected with a standard photomultiplier (Hamamatsu R212) connected to a lock-in amplifier.

The thin-film sample was mounted on a rotation stage to allow for a variation of the angle of incidence. The incident polarization was selected with a half-wave plate and polarizer in front of the focussing lens, and the polarization of the second harmonic was analyzed with a polarizer in front of the photomultiplier.

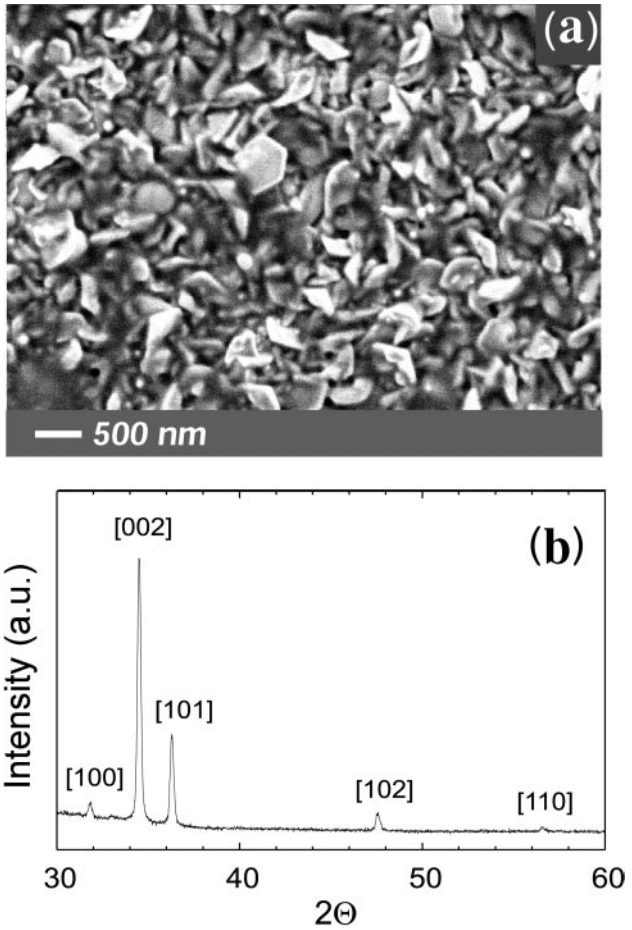

Fig. 1. a Scanning electron micrograph of an undoped ZnO film of thickness $l = 0.85$ μm. **b** The corresponding X-ray diffraction pattern revealing a predominant *c*-axis orientation of the hexagonal crystallites

2 Results and discussion

Second-harmonic generation of the 20-fs pulses was performed on ZnO films of different crystallinity and thicknesses ranging from 0.1 to 1.5 μm. The contribution of the glass substrate to the SHG signal was checked separately and found to be negligible. Absorption at the photon energy of both the fundamental ($E_{\mathrm{ph}} = 1.49$ eV) and second harmonic ($E_{\mathrm{ph}} = 2.98$ eV) is negligible, as both are well below the ZnO bandgap of around $E_{\mathrm{gap}} = 3.35$ eV. Detailed information on the transmission spectra of the ZnO films can be found in [8].

We first present results for a single input beam at the fundamental. Figure 2 shows the dependence of the second-harmonic intensity generated in an 0.85-μm-thick undoped ZnO film as a function of the angle of incidence for s-polarized (open circles) and p-polarized (filled circles) fundamental beams. In both cases, one finds a similar angular dependence with a maximum signal for about 45°. For p-polarization, the signal is approximately five times higher than for s-polarization. The polarization of the second-harmonic signal was found to be always p-oriented, independently of the incident beam polarization. The observed angular dependence is related to the symmetry of the nonlinear tensor of the underlying hexagonal crystal structure and the preferred *c*-axis orientation of the microcrystals. However, even a slightly broadened but symmetric distribution of crystallite orientations (see Fig. 1b) leads to the observed signal minimum at $\Theta = 0°$.

The inset of Fig. 2 shows the second-harmonic signal from the same sample plotted versus the average incident power. These data taken over four orders of magnitude in second-harmonic power clearly demonstrate the quadratic power law expected for second-harmonic generation. A value of 130 mW in fundamental power corresponding to a peak intensity of 5×10^9 W/cm^2 on the sample results in a conversion efficiency to the second harmonic of about 2×10^{-5}.

To estimate the absolute value of the effective second-order nonlinearity d_{eff} of the films, we compared the second-harmonic intensities generated for identical input intensities in ZnO films of different thicknesses and in a 100-μm-

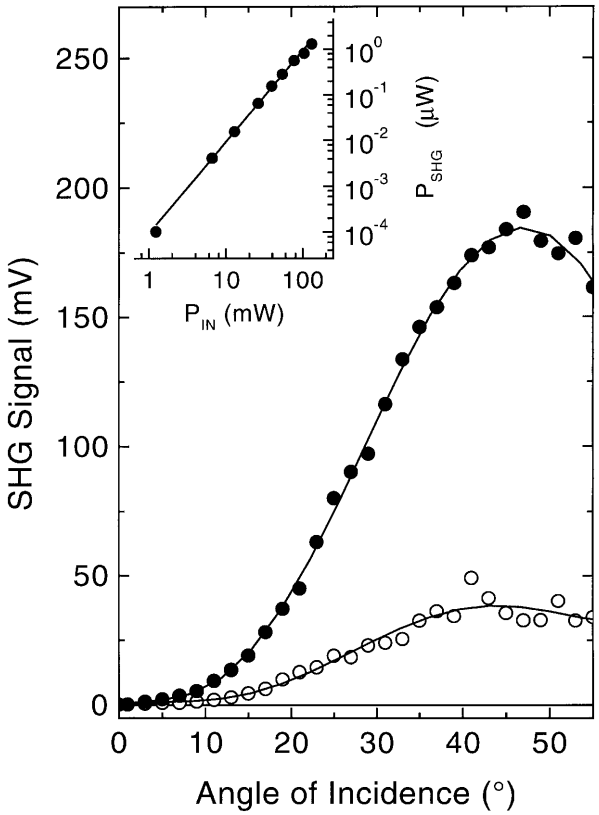

Fig. 2. Second-harmonic intensity from a 0.85-μm-thick ZnO film as a function of the incident angle of the fundamental beam. *Open circles*: s-polarized fundamental. *Filled circles*: p-polarized. *Solid lines*: guide to the eye. Insert: Dependence of the second-harmonic power (P_{SHG}) on the average power P_{IN} of the p-polarized beam for angle of incidence $\Theta = 43°$ (*filled circles*). The experimental data follow a quadratic power law (*solid line*)

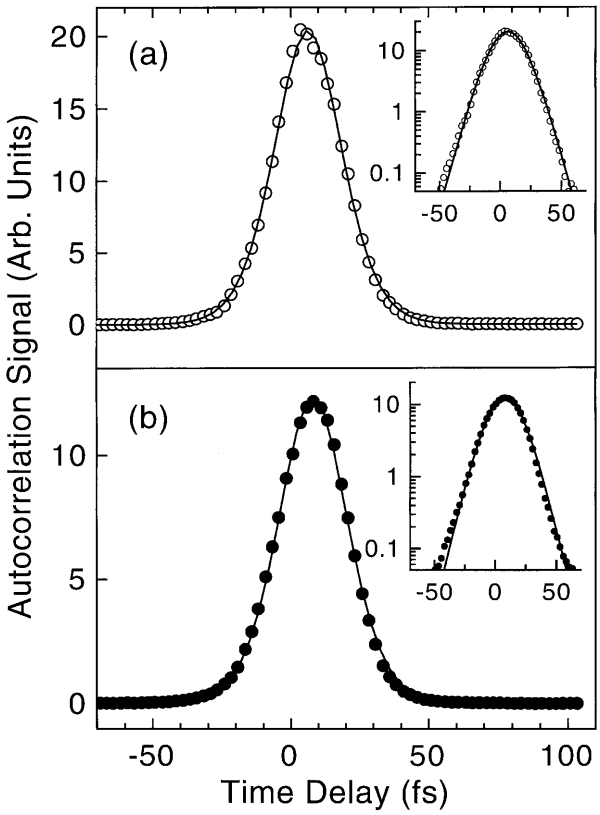

Fig. 3a,b. Intensity autocorrelation on linear and logarithmic scales of 19-fs pulses centered around $\lambda = 830$ nm recorded under identical conditions: **a** measured with a 100-μm-thick BBO crystal with type-I phasematching, **b** signal from a 0.85-μm-thick ZnO layer with p-polarized fundamental beam and $P_{\mathrm{IN}} = 13$ mW. A sech^2 fit to the signals gives a pulse duration of 19 fs (FWHM) in both cases (*solid lines*)

thick BBO crystal. Using the standard expression for SHG under small signal conditions [10], i.e. a quadratic dependence of the second-harmonic intensity on both the intensity of the fundamental and $d_{\mathrm{eff}} \times l$ (l, thickness of the nonlinear medium), we find $d_{\mathrm{eff}} \cong 5 \times d_{\mathrm{eff}}(\mathrm{BBO}) = 10\,\mathrm{pm/V}$ at the optimal angle of incidence.

In an additional series of measurements, we investigated the influence of the film parameters on second-harmonic generation. Films with thicknesses larger than 1 μm generate weaker second-harmonic signals for identical input intensities as a result of increased scattering of both the fundamental and the second-harmonic beams in the films, which results in a reduced efficiency of the nonlinear process and less SHG signal being detected in the fixed solid angle. A systematic dependence of the conversion efficiency on different crystallinity or doping of the films was not observed. It should be noted that even for input intensities in the range of $\mathrm{GW/cm^2}$ no structural change or damage of the films occurred.

Results of the autocorrelation studies are presented in Fig. 3. The prism compressor was adjusted for minimal pulse duration in the nonlinear medium, which was either a type-I-phasematched BBO crystal (100 μm thick) or a ZnO film. The autocorrelation traces in Fig. 3a were measured with the BBO crystal and show the sum frequency signal on a linear and a logarithmic scale versus the delay time between the two input pulses. In Fig. 3b, we present autocorrelation traces measured with the 0.85-μm-thick ZnO film and p-polarized input pulses. With an incident power at the fundamental as low as 13 mW, autocorrelation traces are easily measured over a dynamic range of more than two orders of magnitude, demonstrating the favorable nonlinear properties of the ZnO films for this application. Within the experimental accuracy, the traces measured with the films agree with those from the BBO crystal, giving a pulse duration of 19 fs (FWHM) for a sech^2-shaped temporal pulse envelope. This result demonstrates negligible group velocity dispersion in the thin film and a quasi-instantaneous nonlinear response of the ZnO material even on a time scale as short as 20 fs, which is expected for nonresonant second-order nonlinearity.

3 Conclusions

We have demonstrated the highly favorable properties of ZnO films of submicron thickness for second-order frequency conversion of ultrashort optical pulses. Polycrystalline ZnO films prepared with the spray pyrolysis method show a large second-order nonlinearity $d_{\mathrm{eff}} \approx 10\,\mathrm{pm/V}$, about 5 times larger than that of BBO. The strong nonlinearity and the negligible group velocity dispersion within the submicron interaction length make this material very interesting for correlation studies of extremely short pulses. This was demonstrated in autocorrelation measurements with 20 fs pulses from a Ti:sapphire laser performed at an average power of the

fundamental down to about 10 mW. We envisage application of this material for correlation studies and/or frequency-resolved optical gating at other wavelengths and even shorter pulse durations.

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