Growth-controlled and laser-induced nanostructures in thin nonlinear-optical ZnO layers

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Abstract

Nanocrystalline ZnO layers for nonlinear-optical applications were obtained with spray pyrolysis and pulsed laser deposition. Crystal orientations, size and structure of nanocrystallites were controlled by process parameters. With optimized layers, high-efficiency second harmonic generation at normal incidence was demonstrated which enables a spatially resolved diagnostics of ultrashort pulses. By testing the damage risk it was found that nonlinear absorption channels appear at high power density depending on nanoscale properties. Periodic nanostructures were obtained by self-organization processes under strong focusing conditions. The phenomenon is explained by laser-induced periodic surface structuring (LIPSS) via intra-layer interference of scattered waves.

Introduction

ZnO is presently within the focus of numerous activities in semiconductor physics, magnetooptics, solar technology, or biochemistry [1]. As a wide band-gap material, it is interesting for short-wavelength optoelectronic devices. Other important fields of applications arise from exploiting the nonlinear optical features of ZnO [2-3]. The large electrooptical

constants cause considerably high nonlinear susceptibility coefficients which enable for the implementation of efficient frequency converters for laser diagnostics and optical processing, e.g. spatially resolved autocorrelators for ultrafast pulses [4-5]. The motivation to apply nanocrystalline SHG layers was to overcome typical phase matching restrictions, to reduce the dispersion, to enhance the efficiency and to realize compact systems with composite structures of multiple functionality. Here, the growth and structuring conditions of ultrathin layers of adapted crystalline orientation have to be well controlled. Because of high transmitted intensities in nonlinear regime, laser-induced damage is an essential limiting factor. Experimental findings indicate, however, that laser-induced spontaneous structuring processes can otherwise be the key to the generation of extremely small periodic structures (down to the few-hundred-nanometer scale) in this class of materials. Here we report on the formation of growth- and laser-induced nanostructures in ZnO layers deposited with spray pyrolysis and pulsed laser deposition (PLD).

Structure and laser-modification of nanolayers deposited by spray pyrolysis

Classical and advanced spray pyrolytical procedures were used to fabricate ZnO nanolayers on amorphous and crystalline substrates (glass, fused silica, alumina, sapphire, MgO, Ag and Al [4-5]). The thickness range of the layers was varied between 100 and 800 nm. Shape and size distributions of nanocrystals were directly coupled to the deposition parameters (substrate temperature and post-deposition tempering regime, flow rates, concentrations, gas atmosphere etc.). However it was found, that the three-dimensional crystallite structure is not directly represented by the surface patterns so that grain size and film thickness data have to be analyzed in combined reconstruction models. In this way, correlations between film structure and nonlinear-optical parameters could be indicated. The elements of the nonlinear susceptibility tensor were found to preferentially be determined by the crystal axis orientation. In most cases, nanocrystalline films of c-axis orientation were obtained which can be applied to SHG only at oblique incidence angles (about 45°) [4]. In the exceptional case of r-plane sapphire substrates, a-axis layers of much higher nonlinear susceptibility were deposited, which allow for much higher nonlinear efficiency in laser-optical devices, as the

laser beam easily can be aligned with its E-vector parallel to the crystallite's c-axes compared to high crossing angles in ZnO c-axis orientation [5]. Fig. 1 shows a part of the surface profile of an optimized layer detected by a scanning electron microscope. The a-axis-type ZnO nanolayer consists of growth-induced scale-type nanocrystalline substructures. It can be shown that in appropriate parameter windows, size, orientation and shape distribution functions of the nanocrystals contain quasi-regular spatial frequency components which can be classified by a Fourier analysis of texture data. In the shown example, spatial frequencies of 2-4 μm^{-1} in low-frequency direction and 6-17 μm^{-1} in high-frequency direction were found. The nanoscale surface structure significantly influences the optical performance of the layers in a complex way (scattering, waveguiding, interference, surface-enhanced nonlinear effects, near field phenomena). Because of the contribution of these effects to losses as well as material modification and damage, the interaction of selected layers with laser beams was studied under realistic conditions. In spatially resolving pulse diagnostics, the 2D second order autocorrelation function of a wavepacket is obtained by splitting the laser beam into an array of pseudo-nondiffracting sub-beams and replacing the photodetector of a conventional collinear autocorrelator setup by a CCD matrix [6]. In the experiment, the beam of an amplified Ti:sapphire laser (pulse duration 35 fs, maximum average power 800 mW, repetition rate 1 kHz, center wavelength 790 nm) was transformed by a thin-film microaxicon array (fused silica on silica, hexagonal, 405 mm pitch) into multiple Bessel-like beams of fringe-like structure [6]. Fig. 2 shows a microscope image of a corresponding SHG pattern generated at normal incidence in an a-axis ZnO layer on sapphire. The intensity profile of each sub-beam can be approximated by the square of the $zero^{th}$ order Bessel function. At high pulse power, patterns of material modification were generated which reflect the fringe geometry of the Bessel-like beams very well (inset in Fig. 2). The corresponding local intensities exceeded estimated values of $I = 1.5 \times 10^{12}$ W/cm^2 in the 4^{th} fringes and 3×10^{13} W/cm^2 in the central lobes. However, a careful analysis of the damaged zones shows that the most structural changes are induced in the outer fringes so that a parameter window for the most efficient damage has to be assumed. One possible

explanation is the intensity dependent conversion of the fundamental wavelength to the second harmonic thus opening a loss channel for the fundamental. Near the damage threshold, the process should react very sensitive on even small intensity variations. From recent publications it is further known that near infrared SHG in ZnO at room temperature competes to three-photon excitation depending on the wavelength [7]. Therefore, further studies of multiphoton absorption and damage mechanisms are necessary.

Structure and laser-modification of nanolayers deposited by PLD

A second method -the pulsed laser deposition (PLD) method- was also used to deposit ZnO nanolayers on either *a*- or *c*-plane (5 mm x 5 mm) epi-ready sapphire substrates [8,9]. The ablation laser was a frequency-quadrupled (266 nm) Nd:YAG laser, operated at a repetition rate of 10 Hz, with a fluence of 5 Jcm^{-2} on a 5N-pure ZnO ceramic target. Oxygen gas was introduced in the growth chamber at a constant rate of 30 sccm, producing a constant ambient pressure of 10 Pa, while the substrate temperature was fixed at 650 °C. 4,800 laser shots were used in each case, producing ZnO film thicknesses on the order of 500 nm. All the films were annealed *in situ*, after growth, in a static oxygen pressure of 500 Pa. X-ray diffraction (XRD) experiments (θ-2θ and ϕ-scans) showed that all the films were textured with the (0002) orientation and had (0002) rocking-curve widths of 0.27 deg. and 0.33 deg. on *a*- and *c*-sapphire, respectively. Furthermore, all films presented the known epitaxial relations to their respective substrate [8,9]. Scanning electron microscope (SEM) images showed that all the films grown in the above conditions appear smooth and devoid of micro-cracks (Fig. 3).

Laser damage investigations were performed by focusing the beam of the Ti:sapphire laser amplifier after passing 2.5 m in air with a plano-convex glass lens of about f = 5 cm onto the surface of the layers (initial pulse duration 35 fs, average power 400 mW, repetition rate 1 kHz, center wavelength 790 nm). Here, peak intensities of >

10^{14} W/cm^2 were obtained. Regular and quasi-random patterns were generated in the material (Figs. 4 and 5). The regular patterns are interpreted to result from laser-induced periodic surface structuring (LIPSS) [10-12] which is explained by interference of counter-propagating waves generated by scattering at the surface. If we assume the refractive index for the center wavelength of 790 nm to be n = 1.87 according to Sellmeier data [13], the minimum accessible spatial period for the linear-optical interference would be near 200 nm ($\lambda/2n$). In the experiments, we found periods of 740-750 nm and 330-400 nm. The intra-layer interference was obviously influenced by nonlinear index changes to smaller values (Kerr effect). Furthermore, it is known from laser written gratings in ZnO that an intensity dependence of refraction can be caused by the generation of electron-hole plasmas [14]. The complex process has still to be investigated in detail by high-resolution flux-dependent spectroscopic measurements.

Conclusions

Nanocrystalline ZnO layers for nonlinear optical applications were deposited by spray pyrolysis and pulsed laser deposition. Specific nonlinear and self-organized damage phenomena were found which have to be taken into account as limiting factors for processor design. To the best of our knowledge, the formation of laser-induced periodic surface structures (LIPSS) in ZnO was demonstrated for the first time and promises new nanooptical applications. Grating periods down to 750-760 nm and quasi-random structures with feature sizes between 300 and 400 nm were observed. The understanding of nonlinear contributions to the interference in self-structuring of nanolayers is subject of further studies.

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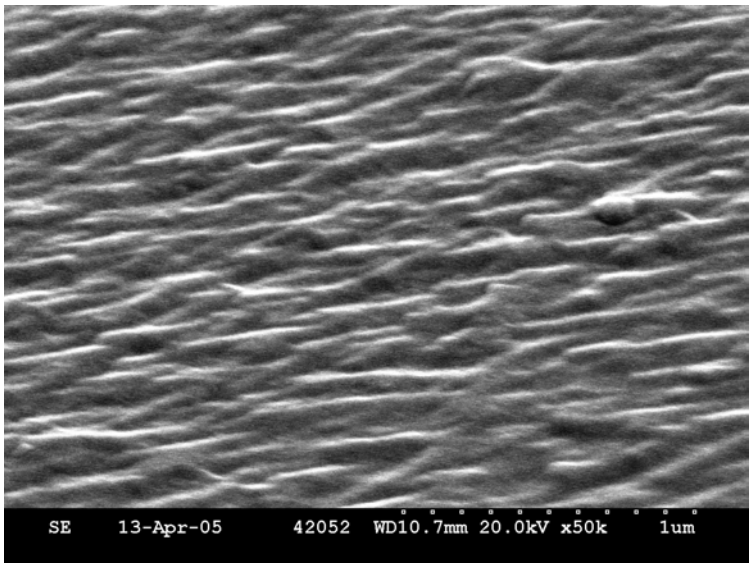

Fig. 1: Nanocrystalline structure of an a-axis ZnO layer deposited by spray pyrolysis on r-plane sapphire substrate (detected with SEM).

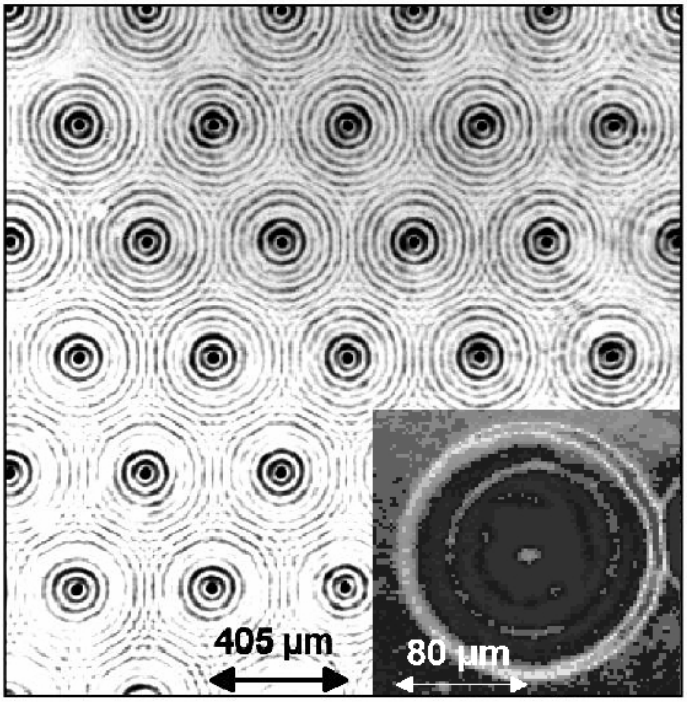

Fig. 2: Second harmonic generation in an a-axis ZnO-nanolayer on sapphire at structured illumination with Bessel-like beams shaped from a Ti:sapphire laser beam after magnifying with a microscope and imaging on a CCD camera (laser: pulse duration 35 fs, center wavelength 790 nm; SHG: center wavelength 395 nm). To improve the visualization, the gray scale was inverted (black: maximum, white: minimum intensity). Inset: Fringe-shaped laser damage zone.

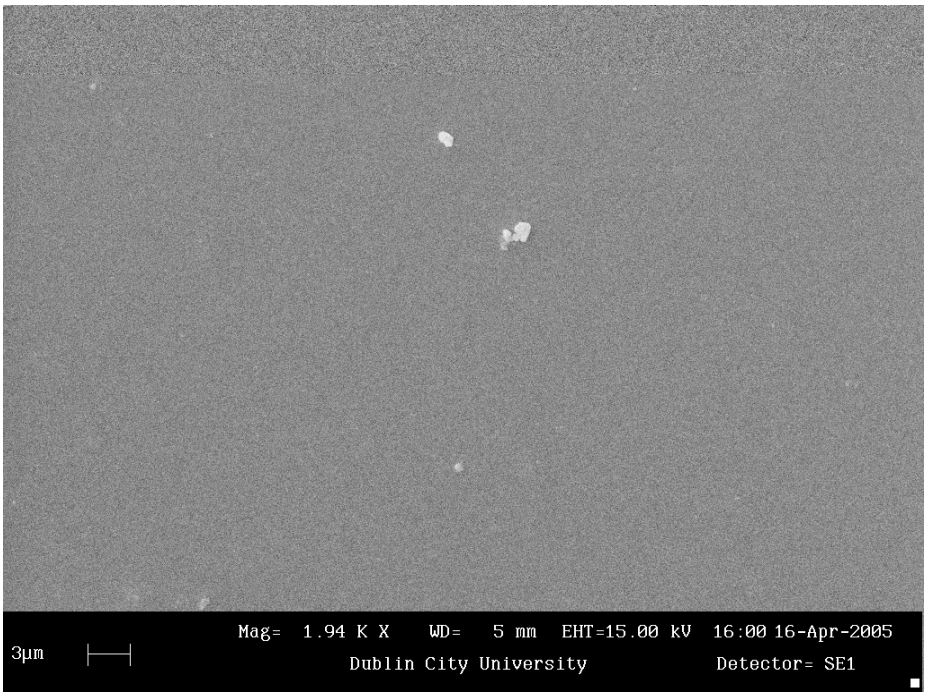

Fig. 3: PLD-generated smooth c-axis ZnO-film of about 500 nm thickness on a-axis substrate (detected with SEM).

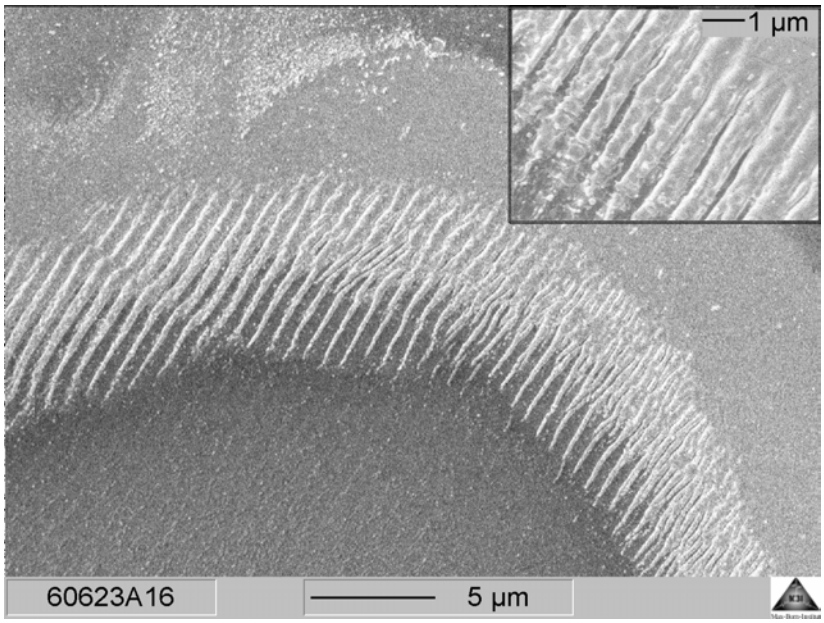

Fig. 4: Laser-induced periodic surface structures (LIPSS) in PLD-generated ZnO (detected with SEM). Spatial transitions from quasi-periodic patterns with periods about 750-760 nm to higher-frequency random patterns with pitches in 300-400 nm range were observed (see Fig. 5). Inset: Part of the structure at higher magnification.

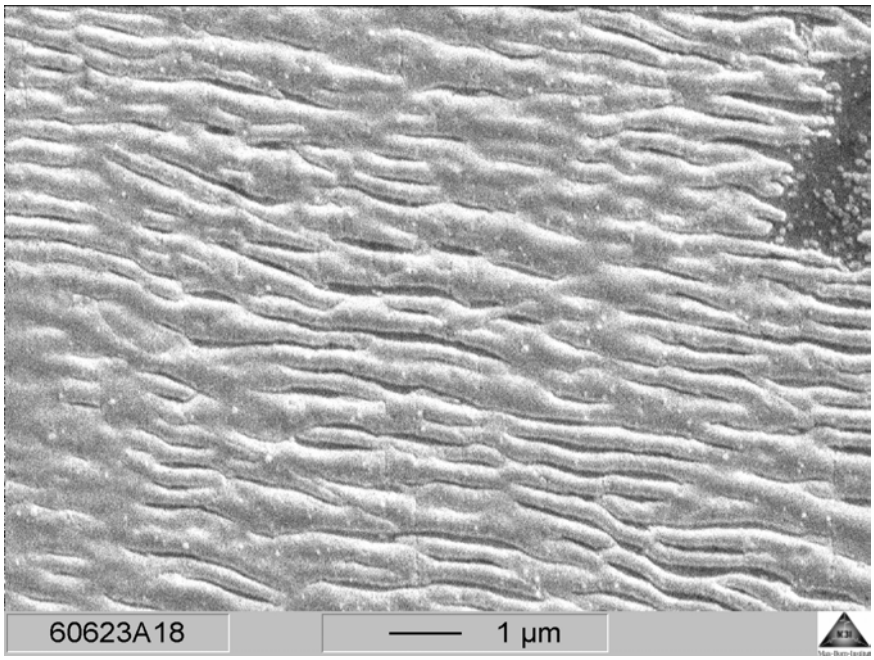

Fig. 5: Quasi-random patterns with sub-400 µm features and local periodicities written with a focused Ti:sapphire laser in a-axis ZnO (detected with SEM).