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Highly ordered ZnO nanohole arrays: Fabrication and enhanced two-photon absorption

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ABSTRACT

Highly ordered ZnO nanohole array was synthesized using pulsed laser deposition technique on the prepared template substrate fabricated by nanosphere lithography and reactive ion etching. The linear absorption coefficient around 400 nm of the nanohole array shows a significant increase compared with the corresponding value at 800 nm. The nonlinear absorption properties were investigated by Z-scan method with a femtosecond laser at the wavelength of 800 nm. An obvious enhancement of two-photon absorption is observed and the value is estimated to be 180 cm/GW, which is about 60 times larger than that of ZnO film fabricated under the same conditions. It indicates that the ordered ZnO nanohole array with enhanced two-photon absorption coefficient has a potential application in nonlinear optical devices.

1. Introduction

Patterned-nanostructures of materials have attracted great attention due to their particular properties different from corresponding bulk counterparts. During the past years, various kinds of nanostructures, such as nanowires, nanorings and nanocombs, have been successfully synthesized [1]. Recently, the nanohole array is attractive owing to its potential applications in optics, optoelectronics and templates for fabricating sensors [2–5]. Some techniques, such as electron beam lithography [6], focused-ion-beam etching [7] and soft embossing lithography [8], can be used to fabricate this structure. However, different masks must be fabricated for modifying the nanoholes, which would raise the cost. Nanosphere lithography (NSL) [9] is a versatile, high-throughput and low cost technique to fabricate periodic nanoparticle arrays. Using this method, monolayer polystyrene (PS) nanospheres are arranged onto the substrate by a self-assembly way. Furthermore, reactive ion etching (RIE) [10] has been used to decrease the diameter of the nanosphere without significantly altering the periodicity of the crystalline lattice. The periodicity of the array is identical with the diameter of the PS sphere, and the size of the nanohole is equal to the etched nanosphere. Therefore, NSL in combination with RIE is an effective method to fabricate the nanohole arrays.

ZnO, a multi-functional semiconductor material with a wide band gap ($\sim$3.3 eV) and high exciton binding energy ($\sim$60 meV), has been extensively investigated for its promising applications in numerous optoelectronic devices including UV-emitters, light modulators and nanolasers [11]. Generally, most ZnO optical components require optical excitation with deep-UV coherent light to obtain efficient spontaneous or stimulated emission. However, the short tissue penetration depth and expensive cost for deep-UV excitation sources significantly hinder the photonic applications of ZnO [12]. To circumvent the above limitation, near-infrared (NIR) light is proposed as an alternative approach which is based on nonlinear optical process such as two-photon absorption (TPA) or multi-photon absorption (MPA) [12,13]. In recent years, the studies on TPA by the NIR excitation are much attractive because of its applications in optical limiting, optical imaging and all-optical shutter [14–16]. However, due to the low TPA coefficient of ZnO in NIR region, the pumping efficiency is rather low which would limit the applications in nonlinear optical devices. Therefore, searching for ZnO nanostructures with large TPA in NIR is necessary.

In this work, the highly ordered ZnO array was fabricated using NSL technique in combination with RIE. The nonlinear absorption properties were investigated by Z-scan method [17] with a femtosecond laser at the wavelength of 800 nm. A significant enhancement of TPA in ordered ZnO nanohole array was observed compared with that of the film fabricated under the same conditions, and the mechanism for the enhancement was discussed. The result indicates that the ZnO nanohole array has a potential application in nonlinear photonic devices such as optical limiting, fluorescence imaging and two-photon pumping laser.

2. Experimental details

2.1. Fabrication

The ZnO nanohole arrays were synthesized on fused quartz substrates (10 mm $\times$ 10 mm $\times$ 0.3 mm) at room temperature.

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First, the ZnO ceramic target (30-mm diameter and 3-mm thick) was sintered from high-purity (99.999%) zinc oxide powder for 5 h at 800 °C using the conventional ceramic sintering process. The quartz substrates used here need to be kept in a mixed solution of H_2SO_4 and H_2O_2 for 1 h at 80 °C, followed by ultrasonic cleaning in another solution of $NH_4OH/H_2O_2/H_2O$ for another hour to obtain a clean and hydrophilic surface.

Second, the templates for nanohole array were fabricated on quartz substrates by NSL and RIE methods. The monolayer-packed mask was prepared on the substrates by NSL technique using PS spheres suspension purchased from Duke Scientific Corporation. The diameter of the PS sphere is 820 nm. The details for preparing well-ordered PS mask are described in the reference [18]. The difference is that the mask was lifted up with another clean substrate, making sure that no additional PS spheres were deposited on the monolayer during this process. After drying, the close-packed mask was followed by an RIE process in a mixture of argon and oxygen gases (Ar/O_2 = 10 sccm/35 sccm), causing the PS spheres to shrink while retaining their original crystalline lattice location.

Subsequently, ZnO was deposited on the template substrate by pulsed laser deposition technique at room temperature using a Lambda Physik KrF excimer laser (248 nm, 20 ns, 5 Hz). Pay attention that the template was not heated to prevent the PS spheres from burning up. The vacuum chamber was evacuated to 6×10^{-4} Pa prior to the deposition. During the deposition, the oxygen gas was introduced and was kept for 1.0×10^{-2} Pa. The energy density at the target surface was about 1.5 J/cm^2. In order to avoid fast drilling, the target was mounted onto a rotating holder, 45 mm from the substrate, which was also put onto a rotating holder to improve the uniformity of the film. The deposition time was 10 min. After that, the PS nanospheres were washed away by ultrasonic cleaning in alcohol for about 30 s, leaving behind the nanohole arrays. Finally, the arrays were annealed for 2 h at 600 °C under atmospheric environment to reduce the stress and lattice defects, simultaneously to enhance the crystallinity.

2.2. Characterization

The surface morphology of the PS mask and the ZnO nanohole array was characterized by field emission scanning electron microscope (FE-SEM, Sirion 200). The structure and orientation were investigated by X-ray diffraction (XRD, PANalytical X'Pert PRO). The linear absorption spectrum was measured by the double-beam ultraviolet–visible spectrophotometer (HITACHI U3310) in the wavelength range from 250 nm to 850 nm.

The nonlinear absorption (NLA) properties of the nanohole arrays were measured by Z-scan method with a femtosecond laser system, which consisted of a mode-locked Ti: Sapphire oscillator and a regenerative amplifier (Spitfire, Spectra-Physics, 800 nm, 50 fs, 1 kHz) [19]. The incident laser beam was focused on the tested sample using a 20 cm focal-length converging lens. The sample was mounted on a computer-controlled step-motor and moved along the *Z*-axis, while the transmitted light through the sample and an aperture in the far field was detected by a photodiode (PC20-6, Silicon Sensor GmbH), which was connected to a lock-in amplifier (SR830, Stanford Research System) to improve the signal-to-noise ratio. The radius of the beam waist (ω_0) is calculated to be 30 μm. The Rayleigh length, $z_0 = \pi\omega_0^2/\lambda$, of the beam is about 3.5 mm, much larger than the thickness of either the 0.3 mm-thickness quartz substrate or the array, which is an essential requirement for Z-scan experiments.

3. Results and discussion

3.1. Morphology and structure characterization

The self-assembled PS masks were prepared on the quartz substrates. Then the close-packed nanosphere template was followed by an RIE process to reduce the nanosphere size. Fig. 1(a) presents a FE-SEM top view image of the PS mask after etching. The higher magnification images of the etched mask by top-view (Fig. 1(b)) and cross-section SEM (Fig. 1(c)) show that the nanospheres are etched uniformly. The diameter and height of hemispheroidal PS spheres are estimated to be about 700 nm and 560 nm, respectively.

Fig. 2(a) shows the nearly defect-free ZnO nanohole array grown on the quartz substrate, and a higher magnification image is shown in the inset. The diameter of each nanohole is about 700 nm and the average thickness of the array is determined to be 50 nm. In our measurement, the array is well-ordered in a large scale (about 120 μm × 100 μm). Fig. 2(b) shows the top view image of ZnO film which is fabricated by PLD technique under the same conditions. It can be seen that the ZnO film has a quite uniform surface. The structure properties of the ZnO nanohole arrays and films grown on fused quartz substrate are characterized by XRD, as shown in Fig. 3. The two peaks at $2\theta = 34.4°$ and

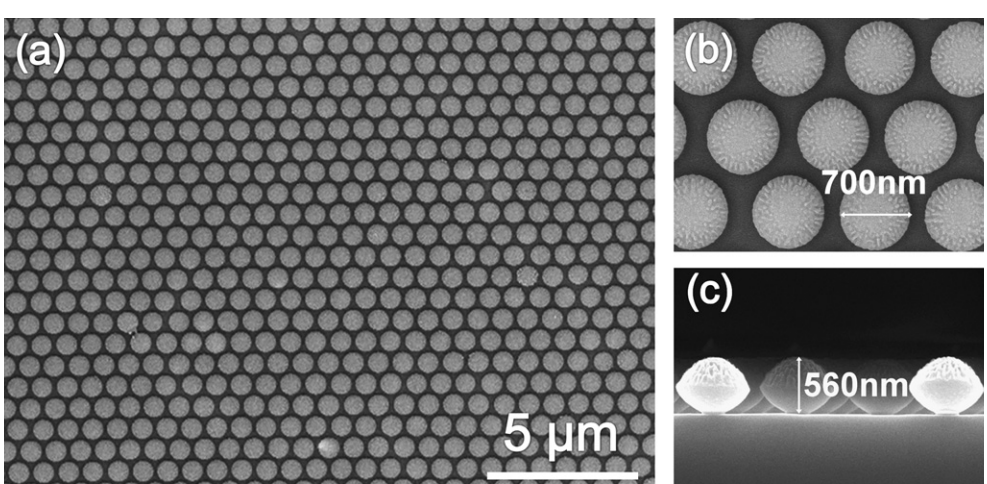

Fig. 1. (a) FE-SEM top-view image of the self-assembled nanosphere template after size reduction using reactive ion etching; (b) a higher magnification image showing a uniform reduction of the spheres; (c) FE-SEM cross-section image of the etched template.