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Surface plasmonic resonances and enhanced IR spectra in GZO nano-triangle arrays

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ABSTRACT

Ga-doped zinc oxide (GZO) nano-triangle arrays with different doping concentration and sizes were fabricated by nanosphere lithography (NSL) and pulsed laser deposition (PLD) techniques, using GZO targets and polystyrene (PS) spheres. The influences of doping concentration on band gap and optical properties were investigated using ultraviolet-visible spectra and Fourier transform infrared (FTIR) spectra. The surface plasmonic resonance (SPR) peaks of the GZO nano-triangle arrays could be tuned in infrared region by changing the doping concentration. The surface-enhanced infrared spectroscopy (SEIRS) experiments of polymethyl methacrylate (PMMA) films on GZO nano-triangle arrays indicated that the absorption peaks of the PMMA overlapped with the SPR peaks of GZO nano-triangle arrays (on-resonance) could be enhanced. However, the off-resonance peaks of the PMMA could not be enhanced.

1. Introduction

Transparent conducting oxide (TCO) materials play an important role in optoelectronic devices. Most of the previous research on TCOs has been focused on the applications like surface acoustic wave devices, sensors, window materials in solar cells and flat panel displays [1–4]. In recent years, TCO nanoparticles (NPs) have been found to be converted to the plasmonic material which may show SPR peaks in infrared region when appropriately doped [5–7]. The SPR of these TCO NPs can be tuned by adjusting the doping concentration. Like in metallic surface plasmonic nanostructures, localized surface plasmon resonance (LSPR) in TCO nanostructures is helpful in plasmonic gas sensors, surface enhanced Raman scattering application and IR spectra [8,9].

Doped ZnO is a candidate material for applications because of wide band gap, low resistivity, high transparency, nontoxicity, chemical stability, and low cost. Ga-doped ZnO (GZO) have some merits because of close atom radius of and Zn, leading to less strain and local lattice distortion [10–12]. In this paper, the GZO nano-triangle arrays were prepared by NSL and PLD methods. The influences of doping concentration on the SPR properties of the GZO arrays were investigated. Furthermore the SEIRS of PMMA on the GZO arrays were studied for the first time.

2. Experimental

GZO nano-triangle arrays were fabricated on Si(1 0 0) and fused silica substrates by NSL and PLD methods. The substrates used were cleaned in four steps: (1) cleaned in an ultrasonic bath using deionized water and then ethanol for 10 min, (2) etch in 3: 1H_2SO_4:30% H_2O_2 at 80 °C for 1 h, (3) base treatment in 5:1: 1H_2O:NH_4OH:30% H_2O_2 with sonication for 1 h, and (4) cleaned in an ultrasonic bath using deionized water and then ethanol for 10 min. The mask templates of PS were prepared on the cleaned substrates using PS spheres (Duke Scientific Corporation) with diameter of 0.43 μm, 0.82 μm, 1 μm and 1.5 μm as reported in previous paper [13,14].

The GZO arrays were deposited on the template substrates by PLD technique (KrF excimer laser, Lambda Physics) using GZO targets. The GZO targets were fabricated by standard solid-state reaction method. GZO targets were sintered at 1300 °C for 5 h in air atmosphere using prescribed amount of ZnO (99.99%) and Ga_2O_3 (99.99%). The contents in the ceramic GZO targets were 2.9, 5, 7.3, 9.9, and 21.9 wt%, respectively. Then excimer laser (248 nm, 5 Hz, 330 mJ) was focused onto a rotating GZO target at room temperature. High purity oxygen was introduced into the chamber and the pressure maintained at 0.2 Pa during the deposition. After the deposition, the samples were ultrasonicated in alcohol for 30 s to clean the PS spheres. Then the GZO nano-triangle arrays were obtained. In post-deposition annealing treatment the arrays were annealed in oxygen under 300 °C for 1 h. To investigate the SEIRS of PMMA induced by the GZO nano-triangle arrays, PMMA thin

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layers about 50 nm were spun coated onto the GZO arrays.

The surface morphologies of the GZO nano-triangle arrays were measured by atomic force microscope(AFM, Veco NanoScope MultiMode). The UV–visible transmission spectra were performed by UV–visible spectrophotometer (HITACHI U3310). The IR spectra were measured by FTIR spectrometer (Nexus).

3. Results and discussion

The surface images of the GZO nano-triangle arrays prepared with PS spheres of different sizes (0.82 μm, 1.0 μm, 1.5 μm) were shown in Fig. 1(a), (b) and (c), respectively. The figures indicate uniformly distributed arrays. The edge lengths of the nano-triangles were about 240 nm, 310 nm and 500 nm, respectively. Fig. 1 (d) shows the section analysis of the nano-triangle arrays in Fig. 1 (c). The average height of the nano-triangles was about 90 nm.

In order to determine the influences of the doping concentration on the optical band gap of GZO. The optical transmission spectra of GZO deposited at room temperature and post-deposition annealed with different contents were shown in Fig. 2 (a) and (b), respectively. The optical gap energy of GZO (direct interband transition) is given by the following formula [15],

$$\alpha h\nu = B(h\nu - Eg)^{1/2}$$

where B is a constant, α is the absorption coefficient. The optical gap energy (Eg) can be obtained from the intercept of $(\alpha h\nu)^2$ versus $h\nu$. Fig. 2(c) and (d) show curves of $(\alpha h\nu)^2$ versus $h\nu$ for Fig. 2(a) and (b), respectively.

Fig. 2(c) shows that the optical band gap increases from 3.6 to 4.0 eV with increase of Ga. The widening of the band gaps with the increase of is mainly attributed to the Burstein-Moss effect [16]. Fig. 2(b) shows that the transmittance of the annealed samples increased. Fig. 2(d) shows that the optical band gap energy increased after the annealing treatment. These results were in agreement with the previous works [17,18].

The SPR wavelength and intensity of doped TCOs nanoparticles depend on the doping concentration, the size, and shape of the nanoparticles. We investigated the influences of sizes and the doping concentration on the SPR properties of the GZO arrays.

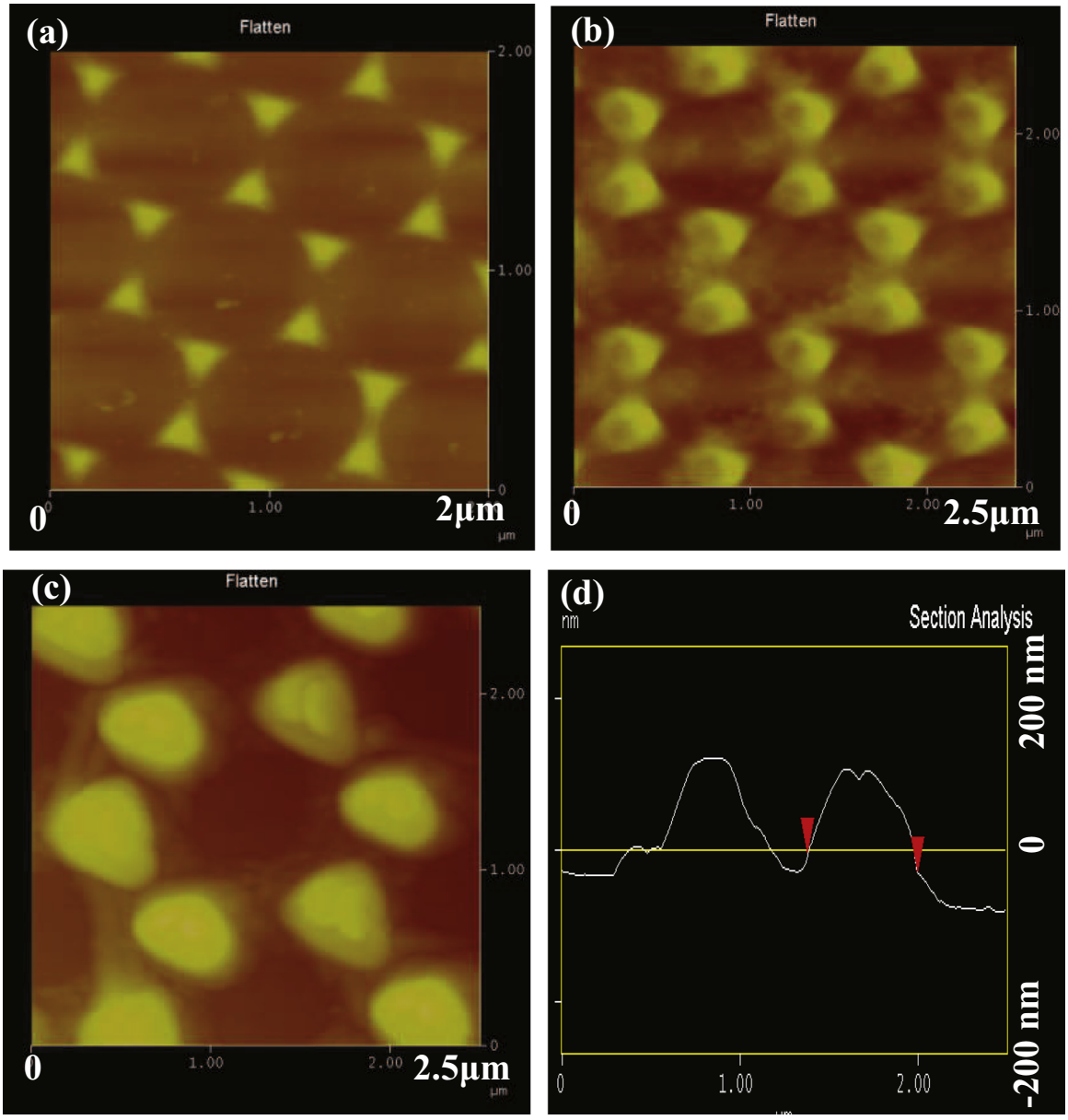

Fig. 1. AFM images of GZO arrays prepared with PS spheres of different diameters (a) 0.82 μm, (b) 1 μm and (c) 1.5 μm. (d) shows the section analysis of the arrays in (c).