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Surface modification of nanostructured ZnS by femtosecond laser pulsing

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ABSTRACT

The surface modification of nanostructured crystalline ZnS by near-infrared femtosecond laser pulses was investigated. A large area nano-grating array was formed on a ZnS surface, with the period and orientation of the nano-gratings depending on the laser wavelength and polarisation direction of the electric field of the light wave, respectively. The nanostructured ZnS surface exhibited the same crystal structure as the polycrystalline ZnS substrate. The photoluminescence (PL) characteristics of ZnS samples were observed to be different before and after laser irradiation when an excitation wavelength above the band-gap energy of ZnS was used. Two additional luminescence peaks were observed to appear in PL spectrum of nanostructured ZnS relative to that of crystalline ZnS. Then, for an excitation wavelength below the band-gap energy, the PL peaks were almost coincident for the two aforementioned ZnS samples; however, the fluorescence lifetime of the nanostructured ZnS sample (2.33 ns) was notably shorter than that of the ZnS crystal sample (10.87 ns).

1. Introduction

In recent years, femtosecond (fs) laser micro- and nanofabrication techniques have garnered great interest because of their potential application in various fields such as micro-optics, micro-machining and micro-fluidics [1–3]. Femtosecond lasers can realise precise material processing owing to their extremely high peak power and minimal thermal effects [4,5]. Using the femtosecond laser direct-writing technique via multi-photon absorption, which can break through the diffraction limit, complex three-dimensional micro- and nanostructures can be prepared within transparent materials [6–8]. Thus, after laser interaction, coherent surface-structuring ripples can be formed on various semiconductor surfaces [9–13]. In many situations, the period of such ripples is close to the wavelength of the incident laser; in particular, periodic ripple structures with a spatial period notably shorter than the irradiating laser wavelength can also be formed after fs laser irradiation on many semiconductor surfaces, such as the surfaces of some III–V group and II–VI group compound semiconductors [14–17]. However, with the formation of periodic nanostructures, the surface of the substrate materials would be substantially destroyed by the strong electric field of the laser, resulting in the formation of laser-induced defects [18–20]. Thus, studies on the behaviour of laser-induced surface modification and defects of II–VI group compound semiconductor surfaces have rarely been reported. We have extended the scope of these investigations to zinc sulphide materials. As a II-VI semiconductor with a wide band-gap energy of 3.66 eV, ZnS is a promising material for optoelectronic applications in the near-ultraviolet spectral region [21]. Low-dimensional ZnS nanostructures, such as nano-crystals, nano-rods and nano-wires, are expected to exhibit excellent optical and optoelectronic performance that differs greatly from that of bulk ZnS [12–24]. In this study, we demonstrated that uniform, planar nano-grating structures can be produced on wide-band-gap ZnS surfaces by femtosecond laser irradiation using a simple scanning technique under appropriate processing conditions. The surface morphologies of the large-area nano-structures are controlled by the laser fluence, polarisation direction of the optical field, and the scanning speed and interval. In addition, the feature sizes of the formed nano-structures can be tuned by varying the irradiation wavelength. The physical properties of the nano-structured surfaces vary greatly, especially the optical properties, as demonstrated by corresponding PL spectra. This nanofabrication technique is simple, efficient, universal and environmentally friendly and holds potential for widespread application in the nano-processing of material surfaces.

2. Experimental details

A polished ZnS sample (an infrared window material prepared by Chemical Vapor Deposition-CVD) was used in this study. A regenerative Ti:sapphire amplifier system with a central

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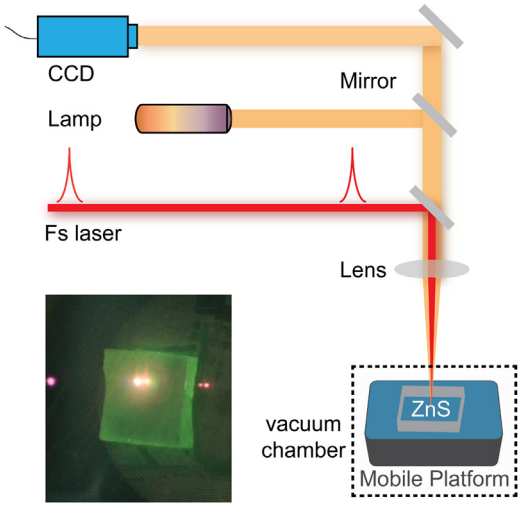

Fig. 1. Femtosecond laser fabrication light path diagram. ZnS samples were loaded into a vacuum chamber with N_2 and positioned with a three-dimensional platform.

wavelength of 800 nm, pulse duration of 120 fs and repetition rate of 1 kHz was used in the experiments to fabricate large-area nanostructures. The output pulse energy of the femtosecond laser was approximately 600 μJ. A spot with an area of approximately $30 \times 30\ \mu m^2$ was projected onto the sample surface with a lens (f = 600 mm). The sample was placed in a three-dimensional micro-positioning stage with the surface perpendicular to the propagation direction of the laser beam. A computer-controlled XY-stage (for the sample) and Z-stage (for the lens) allowed for the precise positioning of the spot on the sample surface and enabled us to scan the surface at 500 μm/s. A variable neutral density filter (NDF) was utilised to adjust the irradiation fluence and the position of the laser spot on the ZnS sample, which was monitored in situ by a CCD camera as shown in Fig. 1. The texturisation of the ZnS surface was carried out in a N_2 atmosphere with a pressure of 5×10^4 Pa. To make the area ablated by focussed laser pulsing flat and uniform, we used a scanning technique. By properly adjusting the interval of two adjacent scanning lines and choosing a suitable scanning speed for the stage, we could produce a large-area, planar nanostructured surface.

Fig. 2(a) shows an SEM image of a ZnS sample surface after a single line scan by a linearly polarised, 800 nm laser. The laser pulse fluence was 17.7 J/m^2, the number of pulses was 200, and the scanning speed was 500 μm/s. To obtain a uniform, large-area surface morphology, a scanning interval of 20 μm was used. An SEM image of the ZnS surface created with these machining parameters is shown in Fig. 2(b); in addition, the $1000 \times 1000\ \mu m^2$ nanostructured surface produced within 100 s is shown in the inset of Fig. 2(b), demonstrating the high efficiency of this nanofabrication technique. Over the entire ablated areas, the uniform and planar nano-gratings were formed with a small of redeposited material. The orientations of the nano-gratings are related to the laser polarisation, as demonstrated by the SEM images shown in Fig. 2(c) and (d). The arranged orientations of the nano-gratings are vertical and horizontal in Fig. 2(c) and (d), respectively, i.e., perpendicular to the direction of the polarised electric field of the laser beam because of that the nano-grating k-vector is parallel to the incident optical electric field [33].

Moreover, in addition to the difference in the polarisation orientations, the laser wavelengths shown in Fig. 2(c) and (d) are different as well: 800 nm and 400 nm (frequency-doubled light), respectively. The periodicities of the gratings are estimated by measuring the mean value of multiple pair spacing between adjacent two nano-gratings. Therefore, the periodicities of the nano-gratings are different: approximately 220 nm and 110 nm for the gratings shown in Fig. 2(c) and (d), respectively. (Here the spacing data are measured by a professional SEM photo tool "Smile view software"). The periodicities of the nano-gratings are dependent on the applied laser wavelength ($\Lambda \sim \lambda/2n$, where Λ is the period of the nano-gratings, λ is the laser wavelength, and n is the refractive index of ZnS [25]). The periodicities obtained from experimental measuring results are more coincident with the theoretical calculation formula of the nano-grating period.

3. Results and discussion

To investigate the crystal structure evolution of the ZnS surfaces after irradiation by femtosecond laser pulses in N_2, the X-Ray Diffraction (XRD) spectra of the ZnS samples were measured

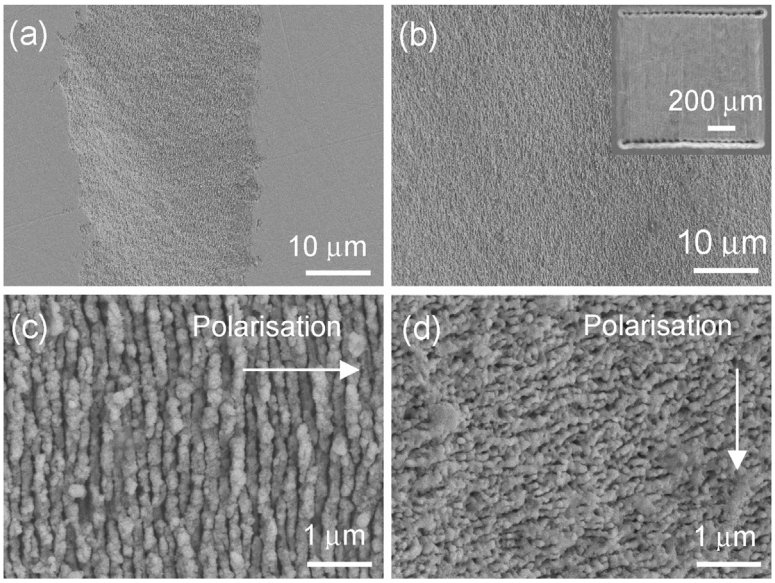

Fig. 2. SEM images of (a) single line scan and (b) large area of ZnS surface. Surface images of ZnS for different (c) wavelengths and (d) polarisations, respectively. Direction of arrow denotes the direction of the polarised electric field of light.