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Effect of KrF excimer laser irradiation on the surface changes and photoelectric properties of ZnO single crystal

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A B S T R A C T

In this paper, the effect of KrF pulsed excimer laser irradiation on the structural, surface morphology, photoluminescence and electrical properties of ZnO single crystal was investigated. Compared to the as-grown sample, at an irradiation energy density of 257 mJ/cm^2, the ZnO single crystal exhibits a series of phenomenon: XRD and Raman results show that the crystallization of ZnO quality change slightly, resistivity is decreased by two orders of magnitude, carrier concentration is increased by one order of magnitude. After laser irradiation, the surface shows some strip lines and no cracks. Formula calculation and simulation results show that the stripes are not caused by surface melting. We speculate that these stripes are caused by the precipitation of ZnO material inside to the surface. Due to the reduction of oxygen vacancies, UV emission has been enhanced and visible emission has been declined after irradiation. After the laser irradiation, the visible light of ZnO surface can be regulated. The experimental results show that KrF laser irradiation could effectively improve the optical and electrical properties of ZnO single crystal, which is important for the application of high performance of emitting optoelectronic devices.

1. Introduction

ZnO single crystal has been widely studied due to its wide band gap (3.3 eV) and high exciton binding energy (60 meV). Therefore, ZnO has good prospects in the field of optoelectronic devices. [1], sensors [2] and spintronics [3]. Modern optoelectronic devices typically require a material with an excellent electrical and optical properties. However, as an n-type semiconductor, as-grown ZnO single crystal normally has many natural defects, such as oxygen vacancies, zinc interstitial etc. [4–7]. These defects are not conducive to the optical and electrical properties of ZnO. As a versatile tool capable of improving functional properties, laser irradiation has attracted considerable attention recently [8–11]. Aoki et al. first reported the KrF excimer laser induced decrease in UV emission intensity of single crystal ZnO wafers [12]. Oh et al. studied the improvement in electrical conductivity of single crystal n-type ZnO after laser irradiation, leading to the formation of a high quality ZnO-based Ohmic contact [13,14]. Zhao et al. found that the irradiated ZnO films exhibited a series of desirable properties: UV emission is distinctly higher, resistivity is decreased by three orders of magnitude [15]. Schneider et al. investigated the structural modifications of ZnO single crystals that were created by the irradiation with femtosecond laser [16]. However, there are few reports about the details of excimer laser irradiation on electrical and photoluminescence properties of ZnO single crystal. In this paper, ZnO single crystals were irradiated by a KrF excimer laser with a wavelength of 248 nm in the air. The effect of laser irradiation on the photoluminescence, electrical properties and structure of ZnO single crystals were investigated in detail.

2. Experiment

ZnO single crystals were purchased from MTI Corporation. The samples were grown by hydrothermal method. The quality of the purchased single crystal ZnO has been shown in our another paper [17]. The size of ZnO single crystal is 5 × 5 × 0.5 mm. ZnO single crystal was single-sided polishing [18]. The laser irradiation experiment was performed at room temperature in ambient air by using KrF excimer laser with a wavelength of 248 nm and a laser

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frequency of 1 Hz. The laser energy density was set to be 257 mJ/cm^2. The surface morphology of the irradiated samples were examined by scanning electron microscope (SEM, JEOLJSM 6500F). X-ray diffraction (XRD, D8 ADVANCE) and Raman spectra (HORIBA T64000) were applied to access the structural quality of ZnO. The electrical conductivity of the as-irradiated single crystals was measured by a Hall system (ACCENT HL5500). The photoluminescence spectra were carried out by using the He–Cd laser with a wavelength of 325 nm. All the spectra were recorded at room temperature.

3. Results and discussions

XRD is employed to examine the crystal structure of ZnO samples. Fig. 1 shows the XRD of as-grown and as-irradiated ZnO crystal. The as-irradiated sample was dispose by laser with a pulse count of ~5600. It distinctly shows that the predominant (002) and (004) ZnO peaks at 34.4° and 72.5°, respectively. The dominance of the (002) and (004) peaks indicate that ZnO single crystal highly textured c-axis-oriented growth and the wurtzite structure. After irradiation, these two peaks exhibit no significant deviation. The full widths at half-maximum (FWHM) of ZnO (002) peak is 0.08° and 0.22° for the as-grown and as-irradiated ZnO, respectively. It means that the crystallization of ZnO single crystal deteriorated slightly after irradiation. However, due to the small FHWM value, the as-irradiated ZnO still has a high crystallization.

Fig. 2 (a) shows the Raman spectra of ZnO single crystals. The as-irradiated ZnO was dispose by laser with a pulse count of ~5600. All spectra show three peaks: 99, 333 and 437 cm^{-1}. The peaks at 99 and 437 cm^{-1} are ascribed to the two non-polar optical phonons modes, E_2(low) and E_2(high), respectively. It is well known that E_2(low) and E_2(high) mode are related to the vibration of Zn and O atoms indicative of the wurtzite phase formation, respectively [19,20]. The 333 cm^{-1} peak is due to multi-phonon processes [21]. These three peaks of ZnO single crystal show no shift after laser irradiation. Table 1 shows the full widths at half maximum (FWHM) of as-grown and as-irradiated ZnO. The value of FWHM of E_2(low) and E_2(high) change slightly after irradiation, which means that the crystallization of ZnO single crystal quality changed little after laser irradiation. This result is consistent with the XRD.

Fig. 3 (a) and (b) show the surface morphology of as-grown and as-irradiated ZnO single crystal, respectively. It can be seen that the

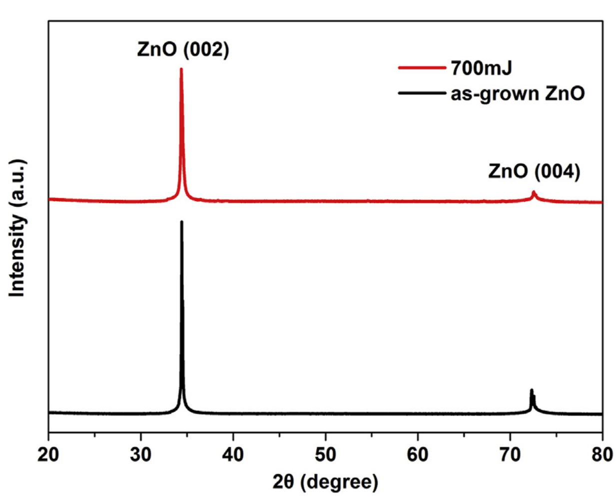

Fig. 1. X-ray diffraction of as-grown (black line) and as-irradiated (red line) ZnO single crystal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

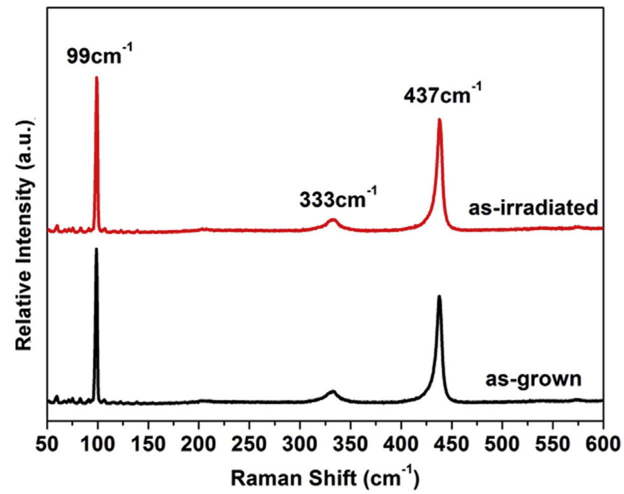

Fig. 2. The Raman spectra of as-grown (black line) and as-irradiated (red line) ZnO single crystal. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
The full widths at half maximum (FWHM) of E_2(low) and E_2(high) of as-grown and as-irradiated ZnO single crystal.

	E_2(low) (cm^{-1})	E_2(high) (cm^{-1})
as-grown	2.1	6.4
as-irradiated	2.1	6.5

as-grown ZnO single crystal surface is very smooth. The ZnO surface shows some strip lines after irradiation. There are no cracks on the as-irradiated sample surface. Khan et al. used 193 nm excimer laser to irradiate single crystal ZnO at room temperature. They found that gray to nearly black colored material appeared in the irradiated laser spot. They speculated that the coloration was due to high densities of metallic Zn nano particles growing on the exposed surface of the crystal [22]. A constant rate of energy input equal to the pulse energy per unit area J (J/cm^2) divided by the nominal pulse width τ (20 ns) will produce a temperature change at the surface given by Ref. [23].

$$\Delta T = \frac{2(1-R)J}{k}\left(\frac{\alpha}{\pi\tau}\right)^{\frac{1}{2}} \tag{1}$$

where k is the thermal conductivity (about 1 W cm^{-1} K^{-1}, depending on sample treatment [24]), α is the thermal diffusivity (about 0.08 cm^2/s [25]), and R is the reflectivity of ZnO at 248 nm (about 0.2). When the laser fluence is 257 mJ/cm^2, where the calculated temperature change from Equation (1) is about 191 °C. Thus, the peak surface temperature during the laser pulse at 257 mJ/cm^2 is about 218 °C. On the other hand, we simulate the temperature changes on the surface of the ZnO crystal irradiated by laser. Fig. 4 (a) is a schematic diagram of radiation model. In our experiment, we used a 16 × 16 lens array to obtain a relative uniform spot. So the distribution of the laser energy on the sample surface was relatively uniform. The heating of material by laser light can be expressed by

$$\frac{\partial T}{\partial t} = \frac{\alpha}{\rho \cdot C_p} I(x,t) + \frac{1}{\rho \cdot C_p}\frac{\partial}{\partial x}\left(\kappa \frac{\partial T}{\partial x}\right) \tag{2}$$

Where *I(x,t)* is the power density of the laser light at depth x and time t, T is the temperature, and ρ, C_p, κ, and α are the density,