Influences of KrF laser irradiation on the structure and luminescence of ZnO single crystal*

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In this paper, we investigate the laser irradiation of ZnO single crystals and its influence on photoluminescence. Our study shows that the photoluminescence of ZnO single crystals strongly depends on surface morphologies. The ultraviolet emissions of laser treated-ZnO under 200 mJ/cm^2 become stronger, whereas for those deteriorated by irradiation above 200 mJ/cm^2, the green emissions centred at 2.53 eV are significantly enhanced with a red-shift to 2.19 eV, probably due to the changes in the charge states of the defects. Enhanced yellow-green emissions are well resolved into four peaks at around 1.98, 2.19, 2.36, and 2.53 eV due to a shallow irradiation depth. Possible origins are proposed and discussed.

Keywords: laser irradiation, ZnO single crystal, photoluminescence

PACC: 7855D, 7280E

1. Introduction

Zinc oxide (ZnO) has attracted much attention recently because of their fundamental physics and the potential applications in ultraviolet (UV) and blue optical devices.[1−3] Generally, ZnO usually exhibits two photoluminescence (PL) bands: near band edge (NBE) excitonic UV emission and defect related deep band emission (DBE) in the visible range.[4−6] The latter band is commonly observed on the oxygen deficient ZnO samples prepared by different growth techniques. The origin of the NBE around 3.28 eV is well known to be excitonic related recombination,[4,5] whereas that of the DBE remains unknown, and various mechanisms including intrinsic defects and extrinsic impurities have been proposed.[7−16] The variation of green emissions with the changes in the charge states of oxygen vacancies, which strongly depends on the surface morphology and grain structures, has been reported.[7,9,10,15] Owing to the complexity of the ZnO microstructure, many properties of defect-related luminescence remain unclear which requires further systematic studies.

Many studies have been devoted to the influence of the surface morphology on the PL properties of GaN through the modification of the sample surface state by means of laser irradiation.[17−19] However, the similar studies on ZnO single crystal through laser irradiation at different energy densities are rare which is the main objective of the present work. We also propose the possible transition processes for green emissions on the basis of the grain boundary defect model.

2. Experiment

The samples used here were high quality single crystal ZnO obtained by a hydrothermal growth method. PL spectra were obtained on a series of (0001) ZnO single crystals irradiated by a 248-nm KrF excimer laser with a repetition rate of 4 Hz and with various laser energy densities from 100 to 600 mJ/cm^2 as described in Ref. [20]. The measurements were performed by a SPEX 1403 RAMANLOG system at room temperature (RT), using the 325-nm line of a He–Cd laser as the excitation source. The crystalline structures and the surface morphology of the irradiated samples were examined by x-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively.

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3. Results and discussions

Figure 1 presents the PL spectra for six samples irradiated at different laser energy densities labeled as n1 to n6. All spectra show stronger UV emission around 3.28 eV due to the free-excitonic emission at room temperature, and a broad asymmetric DBE band between 1.8 eV and 2.6 eV. It can be seen from Fig. 1 that after laser irradiation, the UV emission intensity increases with the laser energy density up to a maximum of 200 mJ/cm^2, having the strongest intensity with the narrowest full width at half maximum (FWHM). The intensity ratios for UV emission band to DBE band are 27.4 and 44.72 for the samples n1 and n3 irradiated at 0 and 200 mJ/cm^2, respectively. It is worth while emphasizing here that too high laser fluence will induce surface damage probably due to laser ablation of the sample surface, and production of structural defects, leading to a reduction in the UV emission intensity [Fig. 1 (n4–n6)]. Similar phenomena are observed for GaN films.[17−19]

Figures 2(a) and 2(b) show the DBE spectra of the samples n1–n3 irradiated at 0, 100 and 200 mJ/cm^2, and those of the samples n4 to n6 irradiated at 300, 450 and 600 mJ/cm^2, respectively. These spectra all show an asymmetric broad band in the green range, but with their intensities different from each other. For better interpretation, using Lorentzian curves to best fit such broad DBE, overall three individual emission peaks for the samples n1 to n3 and four individual emission peaks for the samples n4 to n6 are found to be centred at 1.98, 2.19, 2.36 and 2.53 eV and labeled as B1, B2, B3, and B4, respectively [Figs. 2(a) and 2(b)], in which all the positions are consistent with previous studies.[5−7] They all emphasized that the origin of the peaks around 2.35 and 2.53 eV are attributed to V_{Zn}-, and V_O-related defects, respectively, but for those around 2.0 eV, different mechanisms were proposed. Børseth *et al.*[5] attributed the yellow emission at 2.17 eV to Li related impurities, whereas Roro *et al.*[6] did the peak around 2.0 eV to the level of the oxygen vacancy ($V_O^{+/0}$).

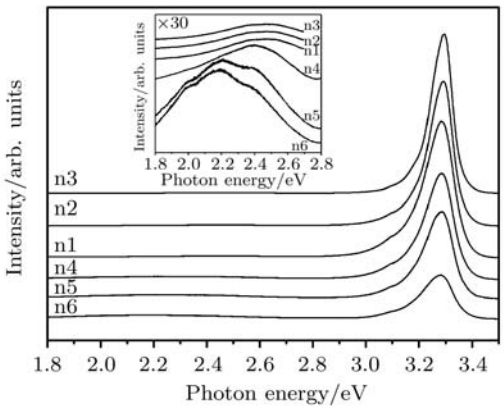


Fig. 1. PL spectra of ZnO single crystals irradiated at different laser energy densities (E_i), n1 for un-irradiated sample, and E_i = 100, 200, 300, 450, and 600 mJ/cm^2, respectively for n2 to n6.

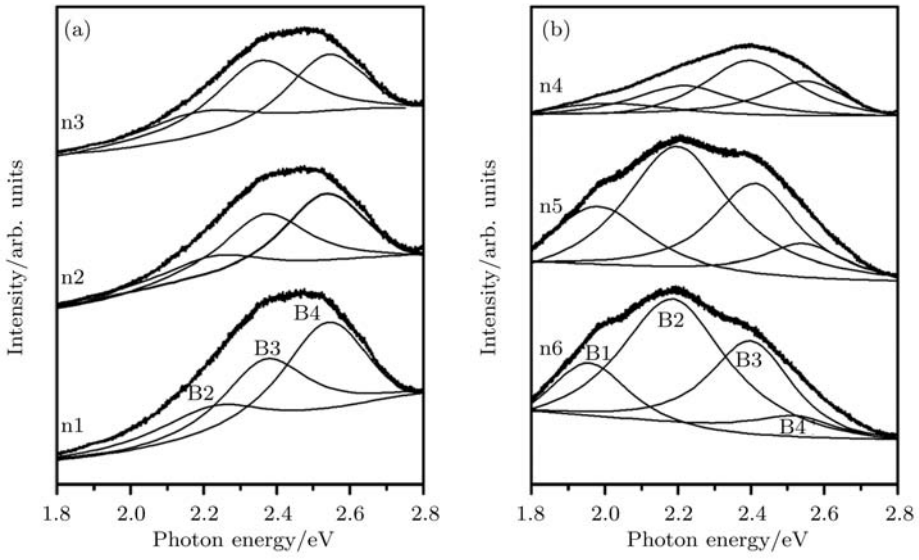


Fig. 2. (a) Room temperature green luminescence of the ZnO single crystals irradiated at different laser fluences (n1–n3), and (b) room temperature yellow-green luminescence of the ZnO single crystals irradiated at different laser fluences (n4–n6). Each of the spectra is composed of the peaks, labeled as B1, B2, B3, and B4.

Garces *et al.* found that excimer laser irradiation on GaN surface under appropriate conditions can induce the interdiffusion of surface atoms and eliminate oxygen vacancies, leading to the increase in PL intensity.[16] In our experiments, when the samples are irradiated under appropriate laser energy in air, some oxygen atoms can be adsorbed onto the surface via occupying those positions of oxygen vacancies. The surface of the laser treated-ZnO becomes more stoichiometric with the reduction of the oxygen vacancies. From Fig. 2(a), a sharp feature of the three peaks shows that although the absolute intensity decreases from samples n1 to n3, the relative integrated intensity ratios of B4/B3 have different values of 0.65, 0.92, and 1.17, while the values of B2/B3 remain constant at around 2.9±0.2 for samples n1, n2 and n3, respectively. We conclude that the emission intensity of B4 is highly sensitive to the variation of oxygen vacancies at the crystal surface, indicating that the intrinsic defects are reduced within the sample surface by this laser irradiation method to enhance the luminous efficiency of the UV band. It can be seen from Fig. 2(b) that the relative integrated intensities of DBE band for sample n6 reaches a maximum at 600 mJ/cm^2, being about 5.5 times as that at 200 mJ/cm^2, and the intensities of the peaks show significant changes from one sample to another, probably due to variations in local environments of the defect centres. Among the six samples n1–n6, sample n1 has the highest green emission peak (B4) at 2.53 eV, and its intensity gradually decreases to such an extent, as the laser fluence increases, that its shoulder broadens to the green emission peak (B3) at around 2.36 eV in sample n6. Except for the emission peak B4, all the other peaks, B1 around 1.98 eV, B2 around 2.19 eV, B3 around 2.36 eV, become more intense and sharper when undergoing laser irradiation, as compared with those of sample n1, and B2 attains the maximum intensity for the laser fluence 600 mJ/cm^2. According to the previous literature,[21,22] the emission peak at 1.94 eV in ZnO films, corresponding to the position of B1 in our present observation, was reported to be attributed to deep acceptor oxygen interstitial. In addition, if the origin of the B2 peak around 2.19 eV actually comes from the impurities, its intensity will strongly depend on the impurity concentration, and without any obvious changes when subjected to such a strong laser fluence, which do not agree with those of our present study. Hence, it is strongly believed that the presence of the peak around 2.19 eV is originated from intrinsic defect rather than from impurities.

Gupta *et al.*[15] proposed that the charge states of the defects strongly depend on the surface morphology and grain structure in the grain boundary defect model. It is known that nano-size particles with different grain boundaries agglomerate each other together, and polycrystalline films of several hundreds nanometer thick are composed of large numbers of crystallites linked by grain boundaries. ZnO materials prepared by different growth techniques may have different grain sizes and grain structure in different samples. Generally, an intense and board emission in the visible range from 1.8–2.5 eV has been observed, especially for those of nano-size particles or polycrystalline ZnO films prepared by different techniques, with the shape and position of the band varying significantly with surface morphology and grain structure.[9,10] Hence, the emission associated with native defects in the undoped ZnO such as interstitial zinc,[15] oxygen vacancies[5,6,11] and interstitial oxygen[8] or zinc vacancies[13,14] in the DBE signal is not well resolved to attribute to the competition of the different charge states of the defects around the grain boundary each other. Since laser irradiation is an effective method for modifying the surface state of the sample,[16,17] in our experiment, we took the surface morphologies of the irradiated samples by SEM [Figs. 3(a) and 3(b)]. Take sample n4 under 300 mJ/cm^2 irradiation as an example, cracks of micrometer in size can be clearly observed on its surface [Fig. 3(a)]. This appearance suggests that tensile stress develops over the irradiated layer during irradiating, and closely relates to local changes in stoichiometry over the near-surface region. For sample n6 irradiated under 600 mJ/cm^2, however, laser ablation effect occurs and a layer of misoriented polygonal grains is generated on the surface cracks, with different grain sizes ranging from several tens up to 200 nm [Fig. 3(b)], overall creating a very rough surface. Recently, Ye *et al.*[7] made an attempt to combine the grain boundary defect model with those reported by Vanheusden *et al.*[9] and Dijken *et al.*[12] in order to interpret the correlation between yellow–green luminescence bands at 2.2 eV and 2.5 eV and the morphology of ZnO films. They ascribed the variation of the relative intensity between the emission peak at 2.2 eV and

other peak at 2.5 eV to changes in the charge state of oxygen vacancies. They showed that when the surface is covered by rough and large discrete islands, band bending can be ignored due to the relatively large bulk of the grains. Hence, most of the oxygen vacancies will be in V_O^+ state upon photo-excitation and lead to the appearance of the green emission around 2.5 eV.[9] In contrast, when the film consists of small closed-packed grains, most of the oxygen vacancies will be in V_O^{++} state, by trapping a hole from the grain surface, due to the small difference between the depletion width and actual grain size, and leads to the appearance of yellow emission peak around 2.2 eV.[12] However, in our studies, the broad DBE band with an asymmetric broadening and a redshift luminescent peak corresponds to the increasing intrinsic defects and nanocrystallization with increasing laser fluence, respectively, which overall agree well with those observed by SEM. Compared with the DBE band from the nano-size particles or the polycrystalline ZnO films,[5−15] our results not only agree with those reported by others,[5−15] but also are improved to such an extent that enhanced yellow–green emission bands are well resolved into four peaks at around 1.98, 2.19, 2.36, and 2.53 eV due to a shallow irradiation depth. According to the results, relative integrated intensity ratios of B2/B4 are obtained, having different values of 1.37, 6.83, and 12.1 for samples n4, n5 and n6, respectively. As shown in Fig. 2(b), the position of the green peak depends strongly on the laser fluence. A red shift of 0.34 eV is observed for the sample n6 irradiated at 600 mJ/cm^2 compared to the un-irradiated sample n1. It also shows that the intensity between B4 and B2 changes with laser fluence, and can be explained by converting most of V_0^+ into V_0^{++} state in small nanograins. Further investigations are required to conclusively confirm these suggestions.

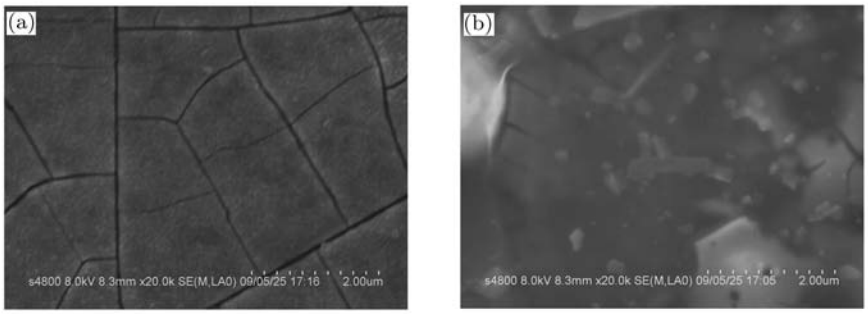


Fig. 3. SEM images of the surface morphology of ZnO samples irradiated at different laser energy densities: (a) 300 mJ/cm^2 and (b) 600 mJ/cm^2, respectively.

4. Conclusion

In summary, the PL of ZnO single crystals irradiated at different laser energy densities are systematically investigated. Our results show that, through the laser irradiation, both UV and visible emissions strongly depend on surface morphologies. At laser density 200 mJ/cm^2, the strongest UV emission spectrum is obtained, while, above such a critical density, the green emission centred at 2.35 eV are significantly enhanced with a red shift to 2.19 eV. Four different peaks in the DBE band have also been identified, and centred at 1.98, 2.19, 2.36, and 2.53 eV, respectively, and such results have been interpreted in terms of oxygen interstitial (O_i), double ionized oxygen vacancy (V_O^{++}), zinc vacancy (V_{Zn}), and single ionized oxygen vacancy (V_O^+)-related transitions.

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