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NEAR-BAND-EDGE EMISSION OF MECHANICALLY MILLED AND THERMALLY ANNEALED ZnO:Ge PARTICLES[**]

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This paper reports a novel way for the synthesis of Ge doped ZnO particles by a mechanically milled Ge and ZnO powder mixture (ZnO:Ge) followed by thermal annealing in Ar + 5%H_2 to achieve near-band-edge (NBE) emission of ZnO with controllable intensities. The Ge doped ZnO particles were synthesized by mechanical milling of a ZnO and Ge powder mixture up to 50 h in particularly, using different ZnO:Ge ratios and annealing temperatures. The Ge doped ZnO particles were observed to have a rounded morphology with a diameter of ~500 nm when an annealing temperature of 1000°C was used. The Ge doped ZnO particles showed NBE emission of ~380 nm with a suppressed visible band of ~500 nm as a function of the Ge content and annealing temperatures. These results suggest that the current method is very useful for synthesis of Ge doped ZnO particles to obtain NBE emission, which is of particular importance for potential application in the optoelectronic and UV detector field.

Keywords: *luminescence, ZnO, near-band-edge emission, UV-light.*

ИЗЛУЧЕНИЕ ВБЛИЗИ КРАЯ ПОЛОСЫ ПОГЛОЩЕНИЯ МЕХАНИЧЕСКИ ИЗМЕЛЬЧЕННЫХ И ТЕРМИЧЕСКИ ОТОЖЖЕННЫХ ЧАСТИЦ ZnO:Ge

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Предложен способ синтеза частиц ZnO, легированных Ge, путем механического измельчения порошкообразной смеси Ge и ZnO (ZnO:Ge) с последующим термическим отжигом в атмосфере Ar+5% H_2 для достижения контролируемого излучения ZnO вблизи границы полосы поглощения. Частицы ZnO:Ge получены механическим измельчением смеси порошка ZnO и Ge в течение 50 ч. Использованы различные соотношения ZnO/Ge и температуры отжига. Установлено, что при

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температуре отжига 1000°C частицы ZnO:Ge имеют округлую форму с диаметром ~500 нм. В зависимости от содержания Ge и температуры отжига частицы ZnO, легированные Ge, обнаруживают излучение на длине волны 380 нм с подавлением видимой полосы ~500 нм.

Ключевые слова: *люминесценция, ZnO, излучение вблизи края полосы поглощения, УФ излучение.*

Introduction. Zinc oxide (ZnO) particles are of interest because of their direct wide band gap of about 3.37 eV, large exciton binding energy (60 meV), chemical stability, transparency, and a cost-effective method of synthesis [1, 2]. The luminescence of ZnO demonstrates two typical emission bands: a green visible emission assigned as deep-level emission (DLE), related to the structure defects, and an ultraviolet near-band-edge emission (NBE), originating from the recombination of free excitons [3–5]. Tailoring the NBE of ZnO particles is of special interest for the optical research community. Considerable effort has been made to tailor the light emission of ZnO particles by controlling the microstructure [6, 7] and incorporation of its materials with dopants [8, 9].

Germanium is a suitable dopant for ZnO. Owing to a small difference between Ge (0.53 Å) and Zn (0.74 Å) ionic radii, the probability of the Ge ion replacing the Zn ion vacancy is large [10]. Ge doping into ZnO via sputtering and atomic layer deposition (ALD) is reported to give NBE emission [11, 12]. Although the light emission of ZnO particles is widely investigated, there are only a few reports related to controlling the light emission of ZnO particles [13, 14]. In particular, to our knowledge there are no reports on the NBE light emission of ZnO particles obtained by simple mechanical milling followed by thermal annealing for optoelectronic applications. In this paper, we propose a novel method for controlling the NBE light emission of ZnO doped with Ge, achieved by mechanically milling a ZnO:Ge powder mixture followed by thermal annealing in Ar + 5% H_2. This method provides a simple, cost-effective, and green synthesis of Ge-doped ZnO particles. These particles exhibit strong NBE emission with suppressed visible green emission, which is of great interest for optoelectronic and UV detectors. The microstructure and crystal structure of Ge-doped ZnO are characterized by field emission scanning electron microscopy (FE-SEM, JEOL, JSM-7600F, JEOL Techniques) and X-ray diffraction (XRD, D8 Advance, Bruker), respectively. The light emission of particles is also determined by a photoluminescence spectrometer (NANO LOG spectrofluorometer, Horiba).

Experimental procedure. ZnO and Ge-doped ZnO particles were prepared by mechanical milling of ZnO and a (Ge, ZnO) powder mixture using a Fritsch (Gemany) instrument equipped with a hardened steel vial and 5 mm diameter balls. Prior to the mechanical milling of the ZnO:Ge powder mixture, 15 g of ZnO particles were added with a various amount of Ge powder (0.2, 0.5, 0.8 g), denoted as ZnO:0.2Ge, ZnO:0.5Ge, and ZnO:0.8Ge, respectively in order to control the microstructure and luminescent properties of ZnO:Ge. The Ge-doped ZnO particles were synthesized by the milling method at a fixed rotation speed of 2000 rpm/min and a milling time of up to 50 h. For the thermal annealing process, the milled ZnO:Ge powders in a ceramic boat were placed in the middle of a horizontal quartz tube inside the muffle furnace (Nabertherm, Germany). Then the temperature of the furnace was changed; the annealing temperature was 900°, 1000°, 1100°, and 1200°C under Ar + 5% H_2 atmosphere for 1 h. After that, the system was cooled to room temperature naturally. For comparison, pure ZnO particles were also milled and annealed at 1000°C. The crystalline structures of the Ge-doped ZnO particles were characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The microstructure and chemical composition of the ZnO:Ge particles were determined by field emission scanning electron microscopy (JEOL, JSM-7600F, JEOL Techniques, Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDS, Gatan, UK). Room temperature photoluminescence (PL) tests were performed with an excitation wavelength of 325 nm. A NANO LOG spectrofluorometer (Horiba, USA) equipped with a 450 W Xe arc lamp and double excitation monochromators were used. The PL spectra were recorded automatically during the measurements.

Results and discussion. Figure 1 shows typical XRD patterns of the ZnO and ZnO:Ge particles synthesized by mechanical milling followed by thermal annealing at 900–1200°C. The ZnO particles showed several strong peaks at 2θ = 31.8.2, 34.4, 36.1, 47.4, 56.6, 63.0, 67.2, 68.0, and 69.2°, which corresponded well to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes of the crystalline hexagonal wurtzite ZnO phase (JCPDS 36-1451). On the other hand, as annealed at 900°C, the ZnO:Ge particle showed peaks of the hexagonal wurtzite structured ZnO with additional peaks at 21.52, 24.92, 30.76, and 32.97° corresponding to the (300), (220), (113), and (410) planes of the crystalline rhombohedral Zn_2GeO_4 (JCPDS 11-0687). If the annealing temperatures increased up to 1000–1200°C, the intensities peaks of ZnO significantly increased while the peaks assigned to the Zn_2GeO_4 phase decreased. For the annealing temperature of

1200°C, the peaks of the Zn_2GeO_4 phase were not detected in the Ge-doped ZnO samples, which could be due to the Zn_2GeO_4 evaporation under the high temperature.

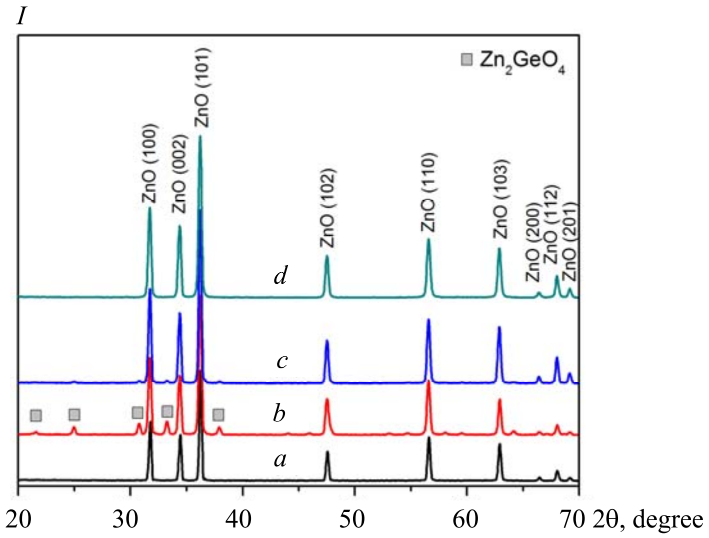

Fig. 1. XRD patterns of ZnO (a) and ZnO:0.8Ge (b–d) particles prepared by thermal mechanical milling followed by thermal annealing: 900 (a, b), 1000 (c), and 1200°C (d).

The microstructures and chemical composition of mechanically milled ZnO and ZnO:Ge annealed at 900–1200°C were examined by SEM, as shown in Fig. 2. The ZnO specimens annealed at 1000°C showed a rounded form with a diameter of ~400 nm (Fig. 2a). The ZnO:Ge annealed at 1000°C also showed rounded a form with a diameter of ~500 nm (Fig. 2b). When the annealing temperature increased to 1100°C, the specimens still displayed a rounded morphology of particles with a diameter of 1 µm (Fig. 2c). The evidence of increasing particle sizes became clearer as the annealing temperature increased up to 1200°C (Fig. 2d). The increase of the particle size indicated that the crystallinity of the specimens was increased [15, 16]. The representative chemical composition of the milled ZnO:Ge specimen was characterized by EDS, as shown in Fig. 2e. Peaks corresponding to the Ge, oxygen, and Zn elements were observed. In addition, the calculated atomic content of the Ge was ~1%, which suggested the successful doping of Ge into ZnO.

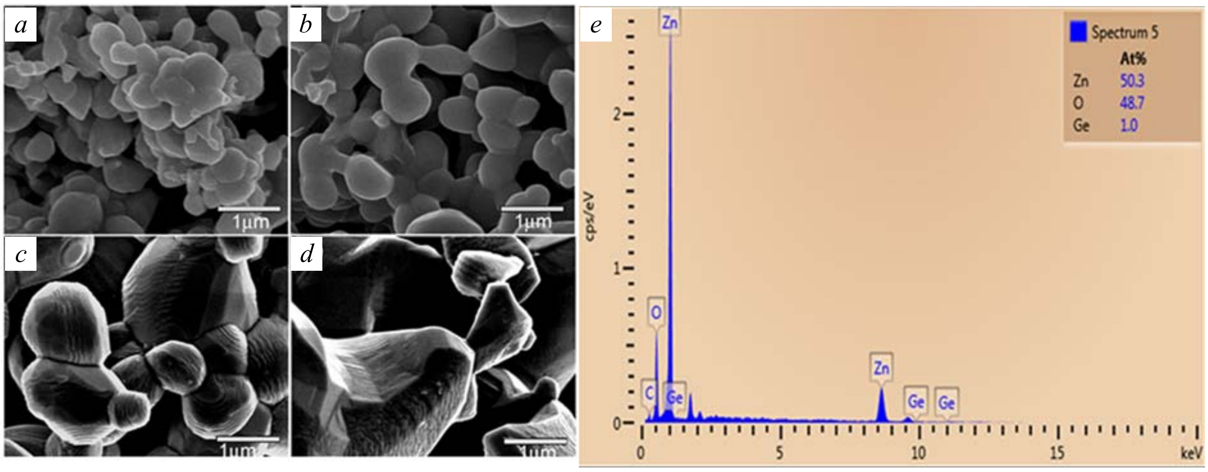

Fig. 2. Microanalysis of the mechanical milled ZnO (a) and ZnO:0.8Ge (b–d) particles (1000 (a, b), 1100 (c), and 1200°C (d)) and EDS analysis of ZnO:0.8Ge particles annealed at 1000°C (e).

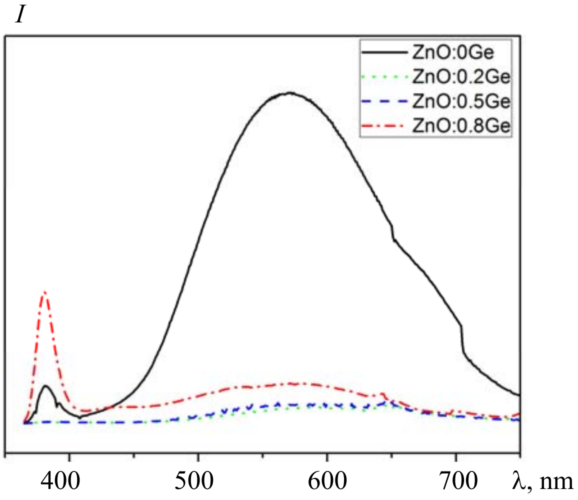

Fig. 3. Luminescence spectra of mechanical derived ZnO:Ge nanoparticles without thermal annealing.

Figure 3 shows the emission spectra of milled pure ZnO and ZnO: Ge nanoparticles with various Ge concentrations at 325 nm. The pure ZnO showed typical luminescent properties of ZnO with NBE emission of ~380 nm and strong visible emission peaks appearing at ~500 nm with the broad band spectrum. The ZnO:Ge also showed two band emission of ZnO different from pure ZnO. Interestingly, as the Ge concentration of 0.8 g (ZnO:0.8Ge) was used, the PL signal showed a dominant band of the NBE emission of ~380 nm with a low band of ~500 nm. Meanwhile, NBE emission intensities of the specimens increased with increasing the Ge amount in the mechanical milling. This significant enhancement of the NBE emission was mainly attributed to the achievement of Ge doping into ZnO, which can be explained by the increase in the ZnO crystalline structure and reduction of defects. So, the ZnO with a doping concentration of 0.8 g Ge was used for further characterizations.

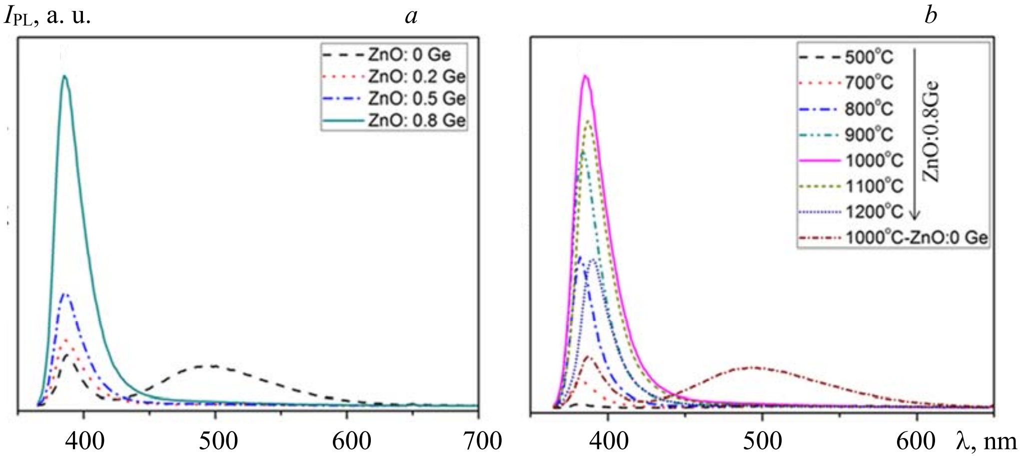

Fig. 4. Luminescence spectra of mechanical derived ZnO:Ge nanoparticles: a) effect of Ge content on the luminescence of ZnO:Ge particles annealed at 1000°C, b) effect of annealed temperatures on the light emission of ZnO:0.8Ge.

Figure 4a shows the emission spectra of ZnO and ZnO:Ge nanoparticles annealed at 1000°C and monitored at 325 nm. The ZnO showed typical luminescent properties of ZnO with the NBE emission of ~380 nm and strong visible emission peaks appearing at ~500 nm with a broad band spectrum. However, all PL signals of ZnO:Ge showed NBE emission of ~380 nm with a suppressed broad band of ~500 nm. Meanwhile, PL intensities of the ZnO:Ge specimens increased with increasing Ge amount in the annealed ZnO:Ge. When the Ge amount reaches 0.8 g, they achieve the maximum value. Although the ZnO:Ge mixture was used in the annealing process, only ZnO light emission was observed without any signal from the Ge specimens. This suggests that Ge links to the phonon coupling in ZnO, thereby stabilizing of the PL NBE [17]. Thus, the Ge content of 0.8 g in the milled ZnO:Ge powder mixture (ZnO:0.8Ge) was used for further characterizations of the luminescent properties. Figure 4b shows the emission spectra of ZnO:Ge under different temperatures at 325 nm. Similarly, the ZnO:Ge specimens showed NBE emission at ~380 nm. One can see that the luminescent intensity of ZnO:Ge specimens increased with increasing annealing temperatures. When the annealing temperature was 1000°C, they reached the maximum value. Thus, under high temperature, one can obtain a well-crystallized structure as well as create a significant amount, of defects resulting in the appearance of visible light at 500 nm (as for the case of ZnO) [18, 19]. It should be noted that the visible emission band ~500 nm was not detected even when ZnO:Ge was annealed at 1200°C, which differed from the previous reports showing both the NBE and visible emission bands [13]. Similarly, Kokin et al. demonstrated that the method of lithium doping into ZnO, followed by thermal annealing, permits one to improve the crystalline structure of ZnO, resulting in the achievement of NBE emission [20]. The typical emission of ZnO:Ge observed by us can be attributed to the appearance of well crystallized ZnO during thermal annealing of the milled ZnO:Ge in the Ar + 5% H_2 atmosphere. Thus, for observation of NBE emission we propose a simple synthesis method of milled ZnO:Ge. Its application can decrease the cost of ZnO devices.

Conclusion. Herein, we demonstrated that the near-band-edge light emission of the milled ZnO:Ge coupled with thermal annealing could be obtained. In particular, the microstructure of ZnO:Ge particles were controlled by thermal annealing temperatures. The luminescence of ZnO:Ge particles with a thermal annealing temperature of 1000°C displayed the strongest band at 380 nm with a suppressed visible band of ~500 nm with controllable near-band-edge intensities. This suggests that the present method is very useful to obtain near-band-edge emission, which is important for designing optoelectronic devices and UV detectors.

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