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Ultraviolet lasing of ZnO whiskers prepared by catalyst-free thermal evaporation

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Abstract

ZnO whiskers were synthesized by vapor transportation via thermal evaporation of ZnO powders in open air. Preferred aligned hexagonal ZnO whiskers with length of 30–40 μm were obtained. Room temperature photoluminescence spectrum of the whiskers exhibits intense ultraviolet excitonic emission and weak defect related visible emission. Optical pumped lasing actions have been observed at 393 nm at room temperature when the excitation intensity exceeds 150 kW/cm^2. Laser cavities are formed in the whiskers between the smooth interfaces of the two ends, which acted as reflectors.

1. Introduction

Recently, zinc oxide (ZnO) has attracted increasing attentions as an optoelectronic material for short wavelength device applications because of its wide band gap of 3.3 eV and high exciton binding energy of 60 meV [1,2]. Efficient excitonic emission is possible at room temperature due to the large exciton binding energy. Optically pumped lasing has been reported in ZnO single crystals [3], polycrystalline [4], heteroepitaxial films [5,6], and ZnO/ZnMgO multiquantum wells [7]. Numerous low dimensional structures of ZnO have been synthesized, such as nanobelts and nanowires [8,9]. Excitonic lasing action has also been demonstrated by Huang et al. [10] in ZnO nanowires prepared by vapor transport process via metal catalysts. ZnO whiskers with diameters larger than that of nanowires have been synthesized by thermal evaporation of zinc containing precursor powders in a suitable ambient. Whiskers generally have a higher crystal quality than nanowires [11,12]. In this Letter, ZnO whiskers were synthesized by a thermal evaporation process in open air. Their optical properties, in particular, ultraviolet lasing behaviors are reported.

2. Experimental

ZnO whiskers were prepared using the method described by Yao et al. [11]. ZnO powder mixed

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with graphite powder with molar ratio of 1:1 was used as a source material. Polished silicon wafers were used as substrates. They were cleaned in sequence by acetone, alcohol and deionized water in an ultrasonic bath. Prior to deposition, the silicon substrate was oxidized in air at 1100 °C in order to form a thin layer of SiO_2. The source material was placed at the closed end of a small quartz tube with a diameter of 2 cm, and the substrate was placed near the open end of the tube. The small quartz tube was then inserted into the center part of a furnace heated to 1050 °C. A temperature gradient between the hot zone, where the graphite–ZnO-powder is located, and the substrate is approximately 400 °C. The distance between the source materials and the region of the ZnO whiskers is around 10 cm.

After 20 min of evaporation, ZnO of different shapes was deposited at different locations on the substrate. No catalysts were added intentionally. The morphologies and structures of the products were characterized by scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (XRD). Photoluminescence (PL) measurements were performed at room temperature. A He–Cd laser, working at the 325 nm line, act as an excitation source. The stimulated lasing was achieved by a frequency tripled Nd:YAG laser (355 nm) at pulsed operation (6 ns, 10 Hz). The pumping beam illuminated on the whiskers at an incident angle 30–40° to the surface of the substrate. The beam is 9 mm in diameter. The emission light of the whiskers was collected from the direction normal to the surface of the substrate.

3. Results and discussion

After the growth, the substrate was coated by a layer of white products (ZnO nanostructures); the shapes of them are very sensitive to temperature as indicated by Yao et al. [11]. We also found that the shapes are also affected by the amount of source material. Under certain conditions, ZnO whiskers can be prepared. The substrate temperature favor the whisker growth is at around 650 °C. Fig. 1 shows a typical SEM image of the whiskers. The whiskers grow along the c-axis with a sharp top surface, and a large part of them are aligned nearly perpendicular to the substrate. The lengths of them are ranging from 30 to 40 μm. The diameters of whiskers vary from several hundreds nm to 1 μm. The diameters of whiskers keep nearly unchanged from the bottom (substrate) to the smooth interfaces at the top. The majority of the whiskers show prismatic shape with hexagonal top surface, while the rest exhibits cylindrical shape. XRD spectrum, as shown in Fig. 2, is acquired with $\theta/2\theta$ scanning mode. The spectrum confirms that the products are ZnO with hexagonal crystal structure, the lattice parameters of them are $a = 0.324$ and $c = 0.521$ nm. The intensity of

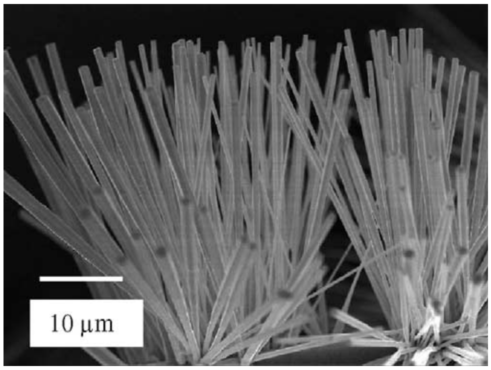

Fig. 1. SEM image of the ZnO whiskers.

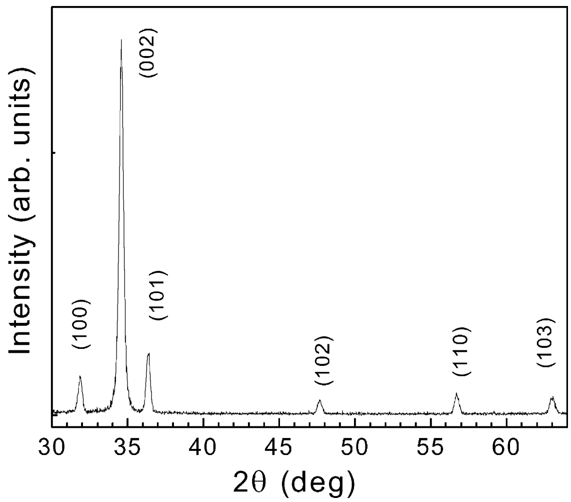

Fig. 2. XRD spectrum of the ZnO whiskers.

(0 0 2) diffraction peak is much stronger than that of other diffraction peaks, which indicates that a large percentage of whiskers are aligned perpendicular to the substrate. Energy dispersive X-ray spectroscopy detects no elements other than zinc and oxygen in the whiskers. All these evidences demonstrate that the growth mechanism of the whiskers is mediated by vapor–solid mechanism, and not the vapor–liquid–solid mechanism that required the existence of metal catalyst [9].

Fig. 3 shows the room temperature PL spectrum of the whiskers. An intense peak appears at ultraviolet (UV) region of the spectrum at around 382 nm, which is attributed to free excitonic emission [2]. Defect related emission band appears in the visible region; its intensity is relatively weak compared with the UV emission. The visible emission is originated from the optical recombination at defect in the ZnO crystal, such as oxygen vacancies or zinc vacancies [13,14]. The surface is also considered to introduce recombination centers and deteriorate the excitonic emission [9,11].

The optical pumped-lasing experiments were carried out at room temperature. At low exciting intensity, a broad emission band is observed. When pumping intensity reaches a value of 150 kW/cm^2, some sharp peaks appear in the spectra, which indicate the onset of stimulated lasing. Fig. 4 shows emission spectra recorded at pumping intensities of (a) 106 kW/cm^2 and (b) 160 kW/cm^2 (c) 213 kW/cm^2. The band position shifts to lower energy as compared to the PL spectrum as shown in Fig. 3. Furthermore, the linewidth of the sharp peaks on the spectrum excited by 213 kW/cm^2 is below 0.2 nm. The stimulated emission in ZnO is generally attributed to two processes, exciton–exciton scattering and electron–hole plasma (EHP) recombination [15]. Investigations carried out by other researchers indicate that the two emissions located at 3.175 and 3.145 eV are exciton–exciton scattering and EHP, respectively [5,6,10]. The emission band obtained here spans between 3.20 and 3.13 eV, so it should be composed of the two kinds of recombination processes; however, the main part seems located at the EHP region.

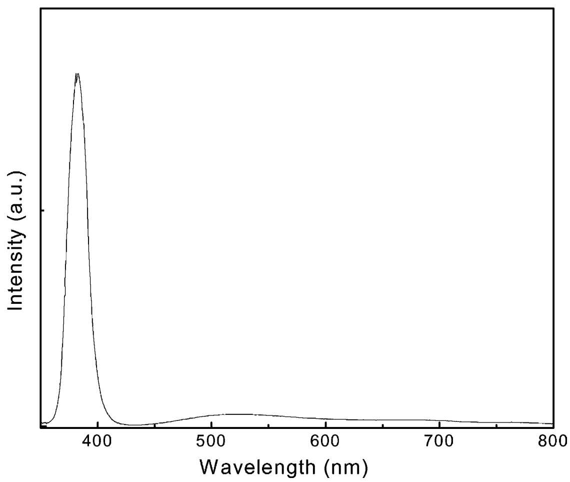

Fig. 3. PL spectrum of the ZnO whiskers at room temperature.

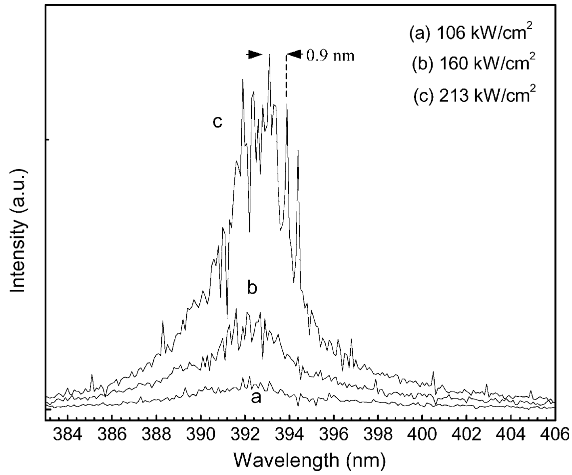

Fig. 4. Spontaneous (a) and stimulated (b and c) emission spectra under different optical pumping power densities.

The sharp peaks observed from Fig. 4 curve (c) can be considered as the Fabry–Perot modes of the ZnO whiskers. Positive optical feedback is occurred between the bottom and the top end interfaces, which is due to the difference in refractive indexes between ZnO, SiO_2 and air. The calculation of the mode spacing for ZnO whiskers with cavity length ~40 μm is found to be 0.9 nm, which is quite close to the measured mode spacing (i.e., ~0.9 nm). However, it is observed from Fig. 4 that the mode spacing is not uniform over the entire spectrum ranging from 0.5 to 1.0 nm. It may be due to the superposition of the optical spectra

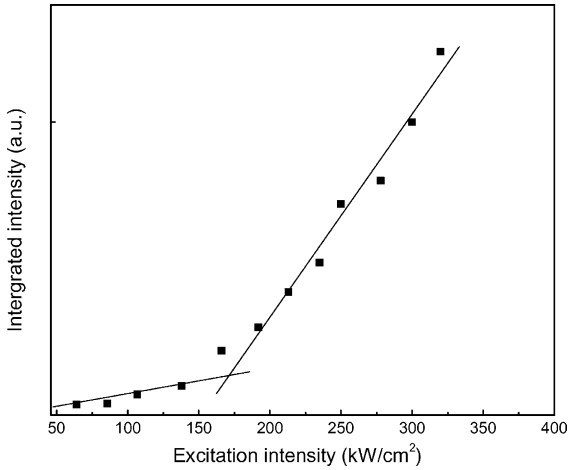

Fig. 5. Integrated PL intensity dependence on pumping intensity.

from ZnO whiskers with different cavity dimensions (i.e., cavity length and diameter). Fig. 5 illustrates the spectrally integrated emission intensity of the ZnO whiskers as a function of excitation intensity. A threshold excitation intensity is observed for the value of above 150 kW/cm^2, the integrated emission intensity increases more quickly as the increase of excitation intensity. It should be noted that the threshold excitation intensity here is the average contribution from the ZnO whiskers with different lengths and diameters within the excitation area of 9 mm in diameter. The threshold value is similar to that of ZnO epilayers deposited by plasma-assisted molecular beam epitaxy [6,16], but much lower than that of polycrystalline ZnO [4]. However, it is higher than that of ZnO/(Mg, Zn)O superlattices and ZnO nanowires [7,10], in these two cases, the stimulated emission is attributed to exciton–exciton scattering. More works are currently underway to investigate if exciton–exciton scattering related lasing could be realized in the ZnO whiskers.

4. Conclusions

In summary, high crystal quality ZnO whiskers were prepared by vapor transport method via thermal evaporation of ZnO powder in open air. Intense free excitonic UV emission is observed in room temperature PL spectrum. The relative intensity of the defect related visible emission is very small. Under optical pumping, a strong stimulated lasing emission is observed in the ZnO whiskers at room temperature. The threshold optical pumped power is about 150 kW/cm^2. The mechanism of lasing emission is attributed to a mixture of exciton–exciton scattering and EHP recombination.

Acknowledgements

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