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Research Article

Fluorescent Properties of ZnO Nanostructures Fabricated by Hydrothermal Method

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ZnO nanorods with mean diameter 200 nm on different substrates were fabricated by hydrothermal method. Fluorescent properties of fabricated ZnO nanorods were researched by both linear and nonlinear excitation using femtosecond lasers. The damage threshold of productions on Si substrate irradiated under intense femtosecond pulses was found much higher than that on Zn plate. Raman spectrum was also applied to investigate relative optical properties. The A_{1L} optical mode was found to be important to the fluorescent properties of ZnO materials.

1. Introduction

ZnO is a kind of II-VI compound wide band gap semiconductor with a direct band gap of 3.37 eV and a large exciton binding energy about 60 meV at room temperature, which makes it a potential candidate for the room temperature ultraviolet (UV) laser diodes [1, 2]. Researches on the fabrication of ZnO materials show that different kinds of nanostructures can be got through controlling fabrication methods or conditions [3–5]. Among the fabrication methods, hydrothermal has been found to be economical and flexible to realize various kinds of nanostructures such as nanorods and nanoflowers [6–9]. Most of the researches about hydrothermal fabrication were focused on the relationship between fabrication conditions and the configuration of the productions [10–13]. Special investigations on the effects of fabrication conditions on the optical properties of ZnO nanostructures are meaningful. But as far as we know, these researches are still few.

Besides, owing to the development of laser technology, the emergence of ultrafast laser, especially the femtosecond (fs) laser source with low repetition rate, makes it possible to get extremely intense field above TW/cm^2 which ensures us to explore the interaction between condensed matters and intense field. Recently, researches on the nonlinear excitation of ZnO with intense laser pulses have been done, and the nonlinear properties, especially the basic mechanisms of multiphoton absorption-induced fluorescent emission in ZnO, are proven to be meaningful [14–20]. This calls for the ZnO materials with high quality that is stable under the intense field of ultrafast pulses [21]. However, most of the ZnO materials used in these experiments are fabricated by molecular beam epitaxy (MBE), metal-organic chemical vapor deposition (MOCVD), or magnetron sputtering [22–25]. Special researches on the fluorescent properties of hydrothermal ZnO are quite few.

In this paper, we fabricated ZnO nanorods with mean diameter 200 nm on different substrates through hydrothermal at 90°C. The fabrication conditions including the concentrations of reactants, PH value, and substrate properties on the fluorescent properties of the productions were discussed by applying Raman spectra and fluorescent spectra under linear and nonlinear excitation conditions.

2. Experimental

The details of the fabrication of ZnO materials are as follows. The Si or Zn plate substrates were first precleaned by

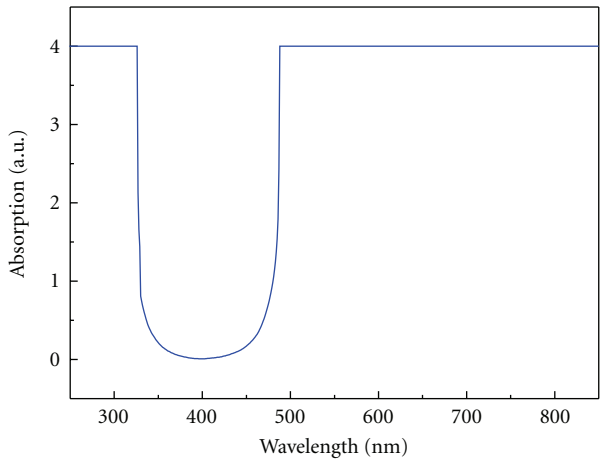

Figure 1: Absorption spectrum of the blue glass used in the measurement of fluorescent spectra under nonlinear excitation.

ultrasonic. Then, the reactant solution with zinc chloride solution (0.1 M) and ammonia used to adjust the PH value were mixed, round, and poured into a Teflon vessel. After the substrates were put into it, the vessel was heated to 90°C for 4 hours and then cooled down naturally; the products were washed with deionized water for several times and dried. Scanning electron microscopy (SEM) was introduced to characterize the products. The main reactions occurred in the vessel can be expressed as follows [9]:

$$Zn^{2+} + 4NH_3 \cdot H_2O \longrightarrow Zn(NH_3)_4^{2+} + 4H_2O \quad (1)$$

$$Zn(NH_3)_4^{2+} + 2OH^- \longrightarrow ZnO + 4NH_3\uparrow + H_2 \quad (2)$$

The fluorescent properties of fabricated nanostructures were recorded when the productions were excited by Xe lamp at 327 nm. The nonlinear excitation laser source used in this experiment was a Ti : sapphire laser (Spectra-Physics, Spitfire) operating at repetition rate of 1 kHz with output pulses centred around 800 nm and full width at half maximum of 150 fs. The nonlinear fluorescent spectra were recorded by a spectrometer with a blue glass placed in front to filter the excitation laser. The absorption spectrum of the blue glass is shown in Figure 1. The Raman spectra were recorded by a Raman spectrometer with an argon laser at 514.5 nm as the excitation source.

3. Results and Discussion

Figure 2(a) illustrates the products on the Zn plate when the content of the zinc chloride is 0.1 M and PH value is 11 in the reactant solution. The productions show nanorods with the mean diameter about 200 nm from the SEM image. And they form balls with the size in micrometer. We investigated the effects of reactant solution by changing the content of zinc chloride or PH value. When the content of the zinc chloride decreased, the amount of the products decreased accordingly. Figure 2(b) shows the SEM image of the products when the content of the zinc chloride is 0.07 M. No nanostructures were found on the substrate. According to (1) and (2), when the concentration of zinc chloride is low, the reactions move to the left which means that ZnO cannot be formed in this condition.

The optical properties of the productions were first researched by fluorescent spectra under linear excitation. Figure 3 is the fluorescent spectra of fabricated nanostructures on Zn substrate with different PH values of the reactant solution excited at 327 nm. The intense peak at near the ultraviolet region corresponds to the band-edge emission of ZnO which indicates that the nanostructures produced were ZnO. Usually, there is a broad peak at around 550 nm in the fluorescent spectra of the hydrothermal fabricated ZnO material which is caused by defects induced in the fabrication process [26–29]. Compared with the UV emission, this peak is weak in the fluorescent spectra especially when the PH value of the reactant solution is 11 as shown in the blue line in Figure 3, implying good optical properties of the fabricated ZnO under this condition. When the PH value of the solution increased further, too much OH^- in the reactant solution may cause defects in the ZnO which can be expressed as follows:

$$ZnO + 2OH^- \longrightarrow (ZnO_2)^{2-} + H_2O \quad (3)$$

The fluorescent spectrum of the products fabricated under PH value of 12 on Zn plate is shown in the red dashed line in Figure 3. The broad peak around 550 nm enhances evidently which confirms the supposition above. The remaining $(ZnO_2)^{2-}$ due to the incomplete cleaning step may also be another origin of this broad peak in the fluorescent spectra.

The fluorescent properties under nonlinear excitation conditions were investigated applying femtosecond pulses. The productions on Zn plate were found unstable under the intense excitation field, and no fluorescent spectrum was recorded under our experimental conditions. Figure 4 shows the fluorescent spectrum of the productions on Si plate irradiated under 800 nm femtosecond pulses. The peak at 400 nm was found moving together with the tuning of the excitation laser, and it kept locating at just half of the wavelength of the excitation laser. It was attributed to the second harmonic signal (SHG) of the excitation laser. The peak at the blue side of the SHG is the band-edge emission of ZnO which is mainly caused by the exciton-exciton collision or the recombination of the electron-hole plasma (EHP) [21]. This peak increased quite prominently compared with SHG, and the spectral width of this peak decreased to only 2 nm when the excitation intensity reached 0.2 TW/cm^2, indicating that stimulated emission emerged under this excitation condition. This shows that we fabricated ZnO nanorods through hydrothermal with high quality that can realize stimulated emissions at room temperature under intense nonlinear excitation. The experimental results show that the damage threshold of ZnO nanorods irradiated under intense femtosecond pulses fabricated on Si substrate is much higher than that on Zn plate which is considered relative to the surface properties of the substrates for the surface

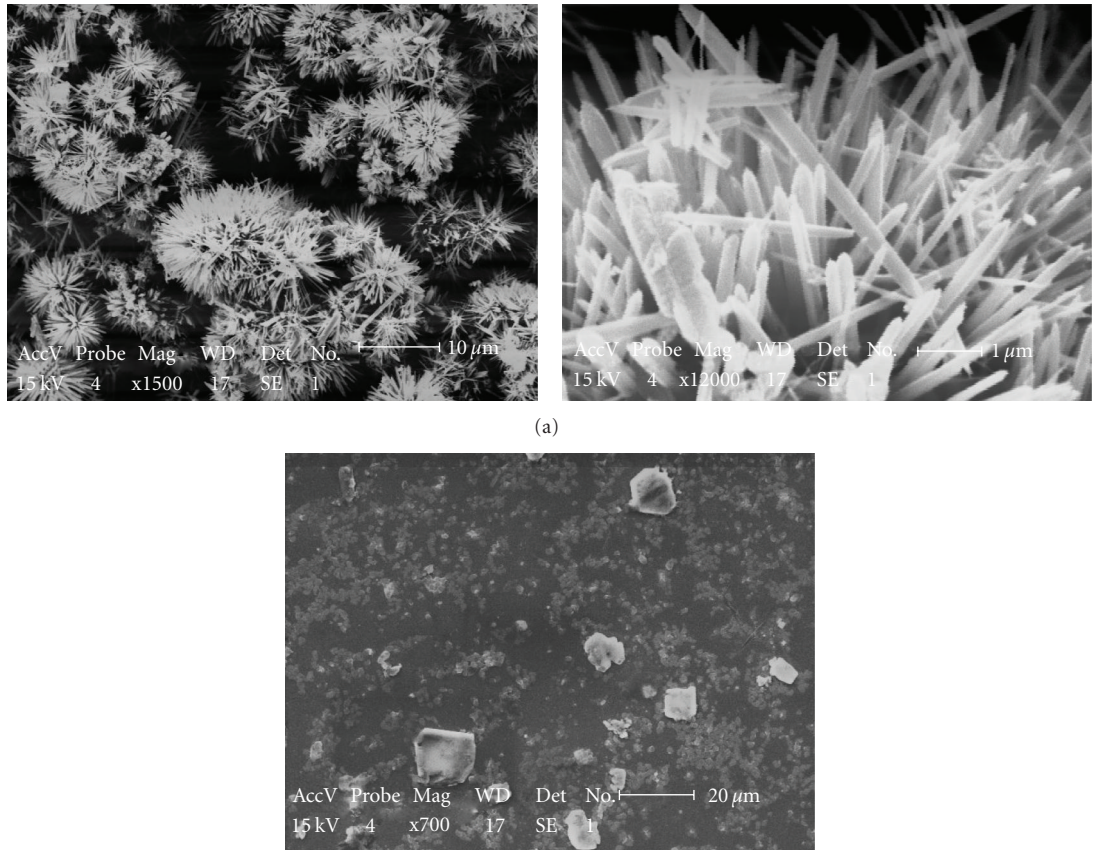

FIGURE 2: (a) SEM images of ZnO nanostructures on Zn substrate with different scales when the Zn^{2+} content is 0.1 M. (b) SEM image of fabricated ZnO on Zn substrate fabricated by hydrothermal method with low Zn^{2+} content 0.07 M.

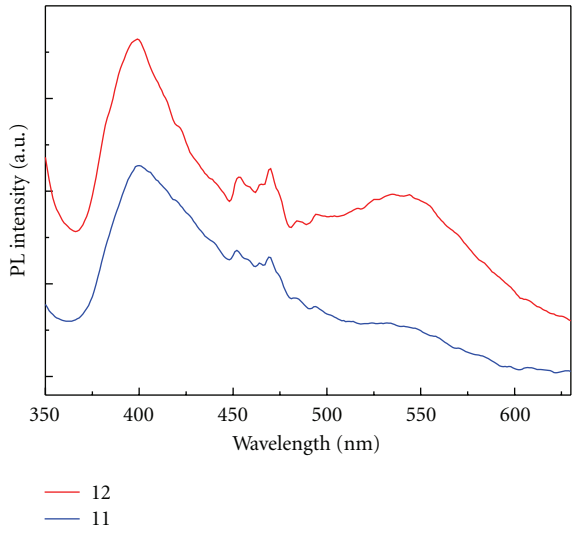

FIGURE 3: Fluorescent spectra of ZnO nanostructures fabricated with different PH values on Zn substrate excited at 327 nm (the red curve is moved upwards).

of the Si plate was much glazed than that of the Zn plate used in the experiment and the substrate softened when Zn is heated above 90°C, because both Si and ZnO are cubic crystal structure, however, Zn is hexagonal crystal structure. The difference in their crystal structures is another reason that Si substrate benefits the formation of ZnO with high quality.

To further investigate the optical properties of ZnO on different substrates, we measured the Raman spectra of the ZnO nanostructures as shown in Figure 5 with the red and blue line responses to the result of products on Si and Zn plate, respectively. There are several Raman peaks in the region of 50–1400 cm^{-1}. The obvious sharp peaks at 100 and 438 cm^{-1} correspond to E_2 mode which confirm the formation of ZnO, the wide peak around 1140 cm^{-1} is A_1 mode, while the relative weak peak at 331 and 378 cm^{-1} corresponds to A_1 and A_{1T} mode, respectively [30]. Compared with that on Zn substrate, the A_{1L} mode which locates at 576 cm^{-1} only emerges in the case of Si as substrate. Considering the results under nonlinear excitation, we regard that the A_{1L} optical mode is important to the fluorescent properties of ZnO materials. Compared with transverse optical modes, the coupling between longitudinal optical modes and electromagnetic field is more efficient especially for low-order optical modes [31]. This is why A_{1L} optical mode is important to the fluorescent properties of productions. The experimental results show that Si substrate benefits the formation of A_{1L} optical mode compared with Zn plate.

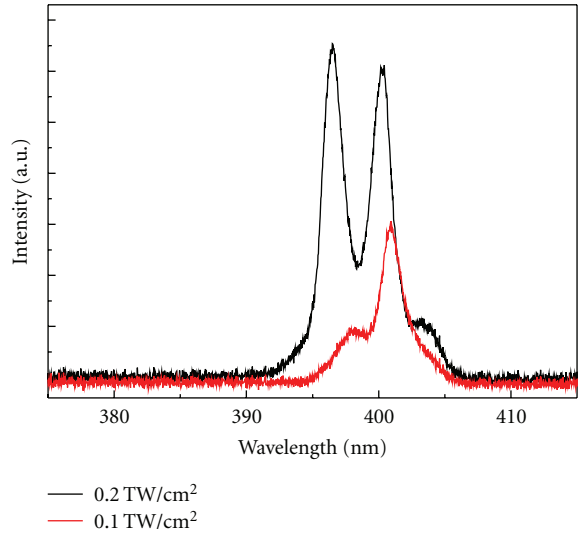

Figure 4: Fluorescent spectrum of fabricated ZnO nanostructure on Si substrate excited at 800 nm applying femtosecond pulses under different excitation intensities.

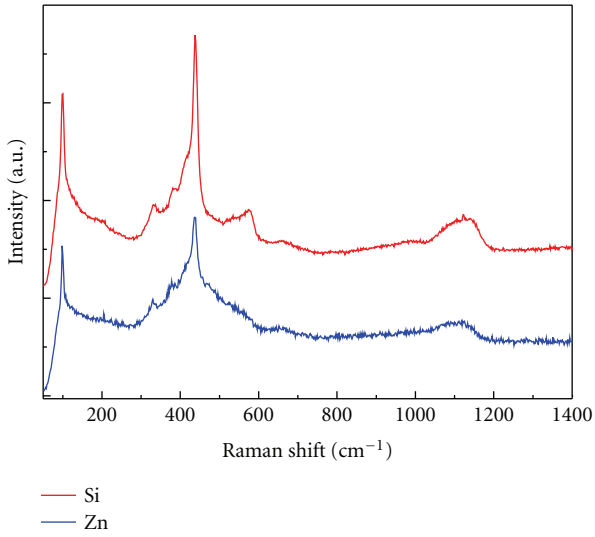

Figure 5: Raman spectra of fabricated ZnO nanostructures on Si and Zn substrates (the red curve is moved upwards).

4. Conclusions

In summary, ZnO nanorods have been fabricated by hydrothermal method on Zn and Si substrates. The effects of fabrication conditions including the concentrations of reactants, PH value, and substrates on the fluorescent properties of fabricated ZnO material have been researched. The optimized fabrication conditions were found, and stimulated emissions in the hydrothermal fabricated ZnO nanorods were realized at room temperature under intense nonlinear excitation. The A_{1L} optical mode was found important to the fluorescent properties of ZnO materials by analyzing the Raman spectra of the productions on Si and Zn substrates.

Acknowledgments

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