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Influence of Annealing on Optical Properties of ZnO Nanorods Obtained by the Microwave-Assisted Hydrothermal Process

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Optical properties of ZnO nanorods (of different sizes, grown on two different substrates) are investigated. Nanorods were grown using microwave-assisted hydrothermal process on gallium nitride or silicon substrate. To initiate nanorods growth on a silicon substrate ZnO nucleation layer was used. ZnO nanoseeds were deposited by atomic layer deposition. For GaN substrate an epitaxial relation was observed. For both substrates nanorods show a hexagonal structure, expected for wurtzite ZnO. Results of nanorods annealing are discussed.

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1. Introduction

Metal oxides are currently intensively studied due to several new applications, such as in photovoltaics [1, 2], in electronics (including transparent electronics [3, 4]) [5], in hybrid structures [6], in biology and medicine [7]. Among them, zinc oxide is one of the most studied materials. This is due to its unique properties, such as transparency and possibility of doping in a wide range of carriers (electrons) concentrations [8, 9]. Importantly, metallic-like conductivity of ZnO can be achieved [10]. Regarding optical properties, ZnO is a wide gap semiconductor with a band gap energy of 3.3–3.6 eV, depending on temperature [9]. That is comparable to the energy gap of gallium nitride.

Zinc oxide interacts with a range of gases, such as nitrogen dioxide, ammonia, and hydrogen by modification of physico-chemical properties due to surface processes. Thus, sensor sensitivity increases with an increasing ratio of surface area to a volume of a sample. This is why ZnO nanorods and ZnO nanoparticles can be used in a sensor technology. ZnO nanostructures can crystallize in various forms, such as: nanowires, nanotubes, nanorods, nanoflowers [11, 12].

2. Experimental details

In the present work we investigate ZnO nanorods obtained by a hydrothermal method. This growth method allows preparation of various forms of nanomaterials [13]. It is based on homogeneous or heterogeneous aqueous phase reactions. Hydrothermal processes are generally slow reactions. However, by manipulating the parameters of the process, such as pressure, temperature, and pH of the solution used, we greatly accelerated the growth process [14]. This was possible by the use of the microwave-assisted hydrothermal process, due to a short warm-up time to the temperature of crystallization. In the process developed by us a steel reactor, used in "classical" hydrothermal process, is replaced by a teflon reaction container, located in an external metal system. By eliminating contact with metal container and with metal heating elements (microwaves are used) one can obtain purer products.

The optimal growth conditions were selected, based on the results presented in Ref. [14]. ZnO nanorods were grown on two types of substrates — on a silicon and on a gallium nitride. Prior to growth of nanorods on Si substrate ZnO nanoseeds were prepared to serve as nucleation centers. For deposition of nanoseeds we applied atomic layer deposition (ALD) method. The seeds have been deposited at 100 °C using 13 ALD cycles. Slightly different growth conditions were selected depending on a substrate used. For a silicon substrate we used pH values of 7.6 and 8, and for gallium nitride — 6.75 and 7.5.

A growth mixture (solution) consisted of zinc acetate dissolved in deionized water. Solution with a concentration of 0.4 M was prepared with a starting pH value of 6.75. A higher pH value (increased from 6.75 up to 8) was obtained by precipitation with a sodium hydroxide. We set the following growth parameters: temperature — 55–65 °C, pressure of 1–2 atm, microwave power — 500 W, heating time — 4 min, pause — 5 s, cooling time — 6 min.

The so-prepared samples were post-growth annealed in three different temperatures: 200 °C, 400 °C, and 800 °C in the presence of two different gases: nitrogen and oxygen. The annealing process was carried out in a rapid thermal process (RTP) oven. For as-grown ZnO bulk samples post-growth annealing results in photoluminescence (PL) enhancement, which is related to elimination of deep defects, material purification (due to defects outdiffusion), or defects compensation. For nanorods we expected similar results. For evaluation of light emission properties we use in the present work PL collected by SOLAR CM 2203 spectrofluorimeter.

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3. Results and discussion

The as-grown ZnO nanorods have a hexagonal form related to their wurtzite structure (see Figs. 1 and 2). Orientation and size of nanorods depends on a substrate, used pH value of the solution, and Zn concentration [14]. For silicon a substrate orientation has no effect on nanorods grown. Nanorods are misoriented, as already reported [14]. Size of these nanorods depends on pH value used in the growth process. Nanorods grown at pH = 8 have smaller sizes than those grown at pH = 7.6.

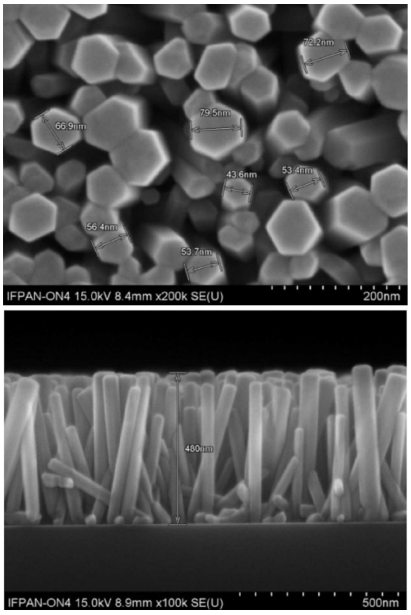

Fig. 1. SEM images of ZnO nanorods grown on a silicon substrate at pH of 8.

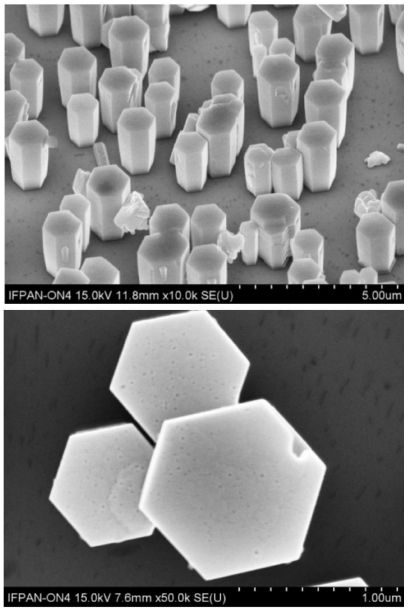

Fig. 2. SEM images of ZnO nanorods grown on a GaN substrate at pH of 7.6.

For a GaN substrate (GaN/Al_2O_3 template) nanorods are oriented. In this case epitaxial growth conditions are achieved. Nanorods grow with *c*-axis normal to a substrate and with in-plane axes aligned with underlying GaN substrate (Fig. 2).

Results of PL investigations of as-grown ZnO/Si nanorods (i.e. deposited on a Si substrate) are shown in Fig. 3. This figure also shows the results of post-growth annealing. As annealing temperature increases, the PL intensity changes, both rises and decreases. Such intensity changes are observed only for the band edge emission of an excitonic origin. Even though the PL line is broad, from its spectral position we can tentatively attribute this line to donor bound excitonic (DBE) transition (dominant at low temperature), and free excitonic and free-to-bound transitions (dominant at room temperature). For samples annealed at 200 °C PL intensity of the band edge emission increases (by a factor of two). However, at the two higher annealing temperatures a significant decrease of the PL intensity is observed. In Fig. 3 we show results obtained for samples grown at pH= 8. But these results are independent of pH value used during the growth.

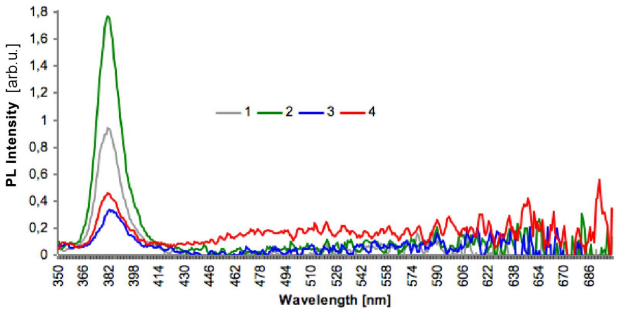

Fig. 3. PL of ZnO nanorods deposited on Si at pH = 8, as-grown or annealed in the presence of nitrogen. 1 — no annealing, 2 — annealed at 200 °C, 3 — annealed at 400 °C, 4 — annealed at 800 °C.

The initial increase of PL intensity is most likely associated with the preliminary purification of nanorods surfaces from remains of the growth precursors, which can act as centers of nonradiative recombination. Surprisingly, the origin of PL emission spectrum is independent of the annealing temperature. For samples annealed at three different temperatures PL is dominated by the band-edge processes. No deep-defects related emission is observed. Thus, the observed reduction of the edge emission intensity, observed at the higher annealing temperatures, cannot be explained by creation of deep defects. Moreover, X-ray diffraction (XRD) investigations (not discussed here) do not show changes of samples crystallinity upon the annealing. High crystallographic quality of nanorods is observed even for as-grown samples [14]. We can tentatively propose that the observed reduction of band edge emission can be due to out-diffusion of some donor centers from samples, caused

by a post-growth annealing. However, further investigations are necessary to explain the observed emission evolution upon the annealing.

Very different situation is found for ZnO samples grown on a GaN substrate. At first, we expected that such samples, grown with an epitaxial relation to a substrate, should be of a higher crystallographic quality. Thus, these samples should show an increased emission intensity. This is not confirmed by the present results. The band edge emission is very weak, while intense emission bands associated with ZnO deep defects are observed (see Fig. 4). Post-growth annealing enhances both bands, but mostly the one (ones) due to deep defects. We obtained slightly different results after annealing in the presence of air or nitrogen, indicating that different types of deep defects are formed. These may be due to oxygen vacancies, oxygen atoms in interstitial sites or due to complexes involving an interstitial zinc [15]. Once more substrate used and not pH value determines the PL properties.

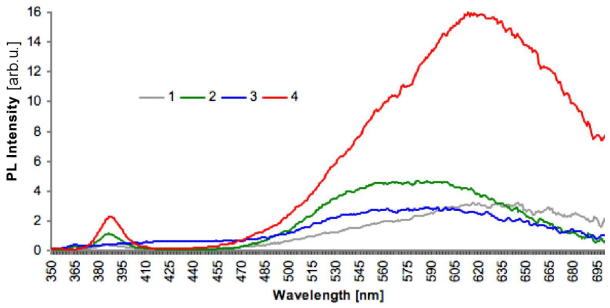

Fig. 4. PL of ZnO nanorods grown on GaN template at pH = 7.6, as-grown or annealed in the presence of nitrogen. 1 — no annealing, 2 — annealed at 400 °C, 3 — annealed at 200 °C, 4 — annealed at 800 °C.

Fact that quite different PL results are obtained is puzzling, since previous TEM investigations (see Ref. [14]) show a high crystallographic quality of both types of nanorods. We can only speculate why so different results are obtained. In the case of epitaxial growth a lattice misfit between ZnO and GaN may result in a built-in strain. This in turn may affect creation of lattice defects, especially of vacancies and interstitials. However, further investigations are required to explain such unexpected PL results.

4. Conclusions

PL emission spectra of ZnO nanorods grown on silicon and GaN substrates vary not only in intensity, but also in a shape. Nanorods grown on Si are not defected, they show dominant band edge emission. The ones grown on a GaN substrate, also with a high crystallographic quality, show very different light emission. The presence of deep defects (resulting in strong defect-related emission) can be caused by a built-in stress, which results from the lattice mismatch between GaN and ZnO.

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