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EFFECT OF RAPID THERMAL ANNEALING ON MICROSTRUCTURE AND OPTICAL PROPERTIES OF ZnO NANORODS

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In this work, we have investigated the influence of rapid thermal annealing (RTA) on structural and optical properties of ZnO nanorods synthesized by a mechanochemical reaction route using a planetary ball mill for different reaction time durations. Optical properties of as-grown and RTA-annealed samples are studied by UV−visible absorption and photoluminescence (PL), while structural studies are performed using X-ray diffraction line profile analysis and transmission electron microscopy. X-ray diffraction pattern of each sample is accompanied by characteristic wurtzite peaks of zinc oxide and exhibits the decrease in full width half maxima of the peaks after RTA. Williamson−Hall plot of each pattern is done to correlate the effect of strain of as-synthesized and RTA-treated samples. UV−visible absorption spectra show distinct redshift of excitonic absorption peaks with respect to those of as-synthesized samples. Interestingly, in PL spectra, the broad visible emission peaks observed for as-synthesized samples are eliminated completely for annealed samples. However, some of the constituent peaks in the UV−blue region of the PL spectra redshifted due to the grain growth and strain reduction.

Keywords: Rapid thermal annealing; ZnO; nanorods; photoluminescence.

1. Introduction

ZnO being a direct bandgap (3.37 eV) material accompanied by a high value of exciton binding energy (60 meV) makes it an important optoelectronic material. ZnO nanorods and nanowires have been under intense research attention due to their easy growth process and excellent optical properties. ZnO nanorods have already been used for fabrication of UV nanolasers,[1] and dye sensitized solid-state solar cells.[2] For synthesis of ZnO nanorods, mechanochemical reactions[3] offer certain advantages over other widely used synthesis mechanisms such as hydrothermal synthesis,[4] vapor−liquid−solid,[5] and chemical vapor deposition[6] which involve critical growth mechanisms, high temperatures, and hazardous chemicals. Besides, sizes of nanorods can be controlled by reaction time duration and ball to mass ratio.

Nanorods synthesized by mechanochemical route by ball-milling are sometimes accompanied by structural or morphological defects such as strain, influence of atmosphere, etc. So, it becomes necessary to adopt some mechanism to remove or improve such defects. One such route is to subject samples to thermal annealing. Conventional furnace annealing (CFA) and rapid thermal annealing (RTA) are often used for improving material properties. But RTA provides certain advantages over CFA.[7] Relatively long thermal cycles of CFA may cause certain impurities to activate and they may be diffused into the material under study which is undesirable, whereas in RTA this possibility is much reduced because of its lower thermal cycles, which is of the order of minutes rather than hours of furnace annealing. Therefore, we performed RTA to improve the structural properties of mechanochemically as-synthesized nanorods and study the influence of RTA treatment on the structural and optical properties of ZnO nanorods.

2. Experimental Details

ZnO nanorods are synthesized by a simple and effective mechanochemical reaction route carried out in planetary ball-milling apparatus which involves reaction of starting materials like zinc acetate [$Zn(CH_3COO)_2$], N-acetyl, N, N, N-trimethyl ammonium bromide (CTAB), and sodium hydroxide pellets. Ball-millings are performed for time durations ranging from 30 min to 5 h with a fixed ball to mass ratio of 10:1. The resultant powder product is treated several times with millipore water and alcohol to remove impurities and by-products which is then dried for 2 h at a suitable temperature to get the final product. Each sample is then subjected to RTA (Mila 3000P, ULVAC) for 120 s at temperatures 500°C and 700°C under constant flow of oxygen.

The structural and morphological characterizations of the samples are carried out by X-ray diffractometer with Cu Kα radiation (Bruker D8 advance) and transmission electron microscope (TEM, JEOL JEM 2100). Optical characterizations are performed by UV−visible spectrophotometer (Varian), photoluminescence spectrophotometer (thermo electron) using 325 nm xenon lamp light excitation.

3. Results and Discussion

Figure 1 shows the X-ray diffraction spectra of the as-prepared 2 h mechanochemically synthesized ZnO nanorods and after RTA treatment at various temperatures. With the increase in annealing temperature, the position of the diffraction peaks of ZnO nanorods remains the same, while the intensity of the (101) peak increases with annealing temperature, which indicates an improvement of crystalline quality of the nanorods. We also observed a decrease in full width at half maximum (FWHM) of (101) peak with increase in RTA temperature. The results imply that the nanorods recrystallize during annealing and also show increase in the diameter of the nanorods. From the Williamson−Hall plot[8] of the XRD line profile, we found that nanorod's size gradually increased with increase in RTA temperature (see inset of Fig. 1). But lattice strain gradually decreased, due to stress relaxation of the nanorods. Other RTA-treated ZnO nanorods show similar structural changes.

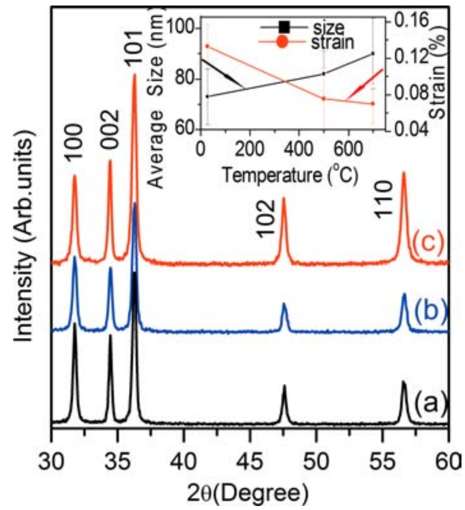

Fig. 1. XRD spectra of the 2 h mechanochemically synthesized ZnO nanorods (a), after RTA at 500°C (b), and 700°C (c). Inset: average nanorods size and lattice strain as a function of RTA temperatures.

Figure 2(a) shows the TEM image of the as-synthesized ZnO nanorods prepared by 2 h mechanochemical reaction. Diameter of the nanorods is in the range of 41−50 nm. Figures 2(b) and 2(c) show the lattice image of as-synthesized and 700°C RTA-treated nanorods, respectively. The HRTEM images indicate that the as-grown nanorods are single crystalline with wurtzite structure and grown along (101) direction. This is consistent with the XRD results. The interplanar spacing in as-grown and RTA-treated nanorods are 2.402 Å, 2.449 Å, and 2.458 Å, respectively. Compared to the as-grown sample, interplanar spacing reaches the reference strain-free (101) interplanar spacing of ZnO (2.476 Å) with the increase in RTA temperature. This shift shows the relaxation of compressive stress caused by ball-milling. Therefore, residual stress can be effectively relaxed by RTA process.

To study the effect of RTA in band gap energy of the nanorods UV−visible absorption measurement

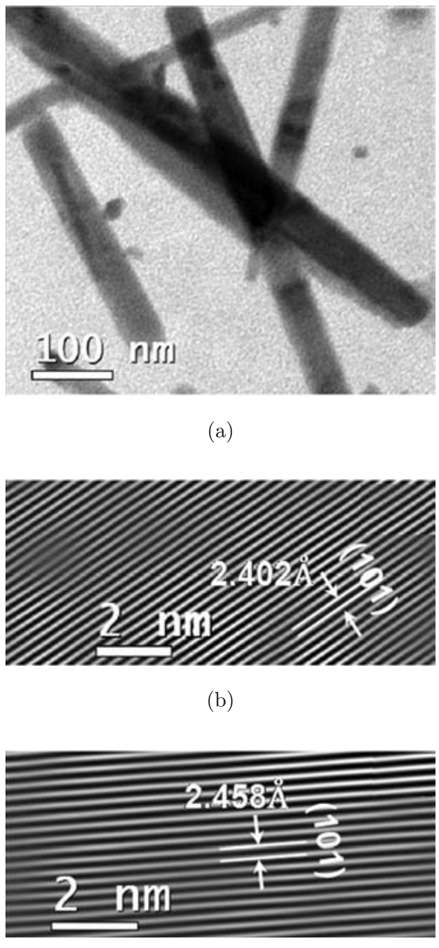

Fig. 2. (a) TEM and (b) HRTEM of as-synthesized and (c) HRTEM of 700°C RTA-treated ZnO nanorods prepared by 2 h mechanochemical reaction.

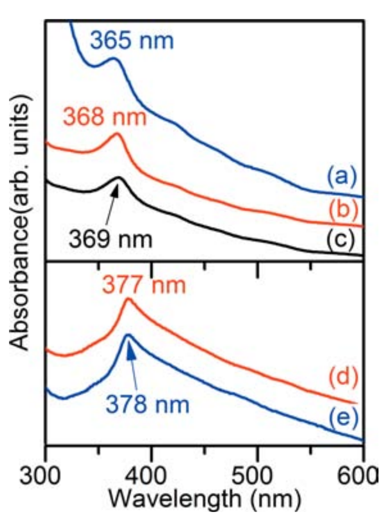

Fig. 3. UV−visible absorption spectra of (a) 5 h, (b) 2 h, and (c) 30 min mechanochemically synthesized ZnO nanorods. Effect of RTA at (d) 500°C and (e) 700°C on the 2 h reacted samples.

was carried out. Figure 3 shows the UV−visible absorption spectra of various as-synthesized nanorods and RTA-treated 2 h milled nanorods. As-synthesized nanorods show blueshift in excitonic absorption peak with increasing milling time due to decrease in size and induced strain during milling process. The excitonic peak shifted from 369 to 365 nm. This blueshift is indicative of the increase in band gap energy of the nanorods. After RTA, with respect to as-synthesized sample, a redshift is observed from all the samples. Two hours milled nanorods show redshift from 368 to 378 nm, which indicate the decrease in band gap energy as the result of recrystallization and strain relaxation of the nanorods.

To understand the change in optical behavior of the RTA-treated ZnO nanorods PL measurements were carried out of as-synthesized and RTA-treated samples. Figure 4 shows room temperature PL spectra of as-synthesized and RTA-treated nanorods prepared by 2 h mechanochemical reaction. Exact peak positions are extracted from the Gaussian line shape fitting to the experimental data. As-synthesized nanorods show three distinct peaks (I−III) in the UV−blue region, and one strong, broad peak (IV) in the visible region. From 2 to 5 h milled nanorods a blueshift in peak I is observed from 379 to 374 nm. This shift is consistent with the UV−visible absorption results and results from the quantum size effect. This UV emission is attributed as bound excitonic recombination.[9] The peak II at

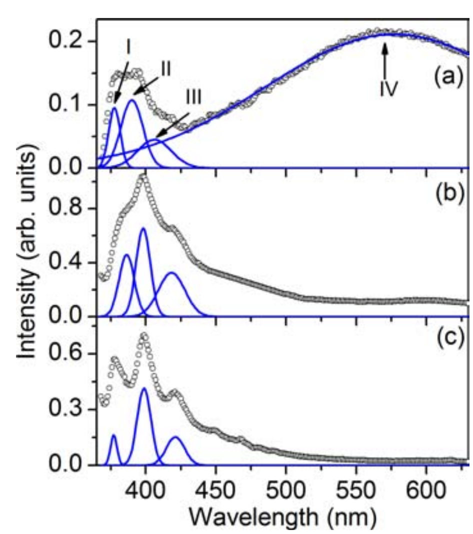

Fig. 4. Room temperature photoluminescence spectra of 2 h mechanochemically synthesized ZnO nanorods (a), after RTA at 500°C (b) and 700°C (c), respectively. Four peaks are fitted with Gaussian line shape (solid line) to the experimental data (symbol).

$\sim$390 nm is likely to be due to band-to-band transition between band tail states.[10] These band tail states are primarily caused by the presence of defects at the surface of the nanorods. The peak III at $\sim$409 nm is caused by the presence of zinc vacancy related defect states as reported by Lin *et al.*[11] The visible peak (IV) at 582 nm is very broad and it is not a bulk defect related emission. It is likely to be related to the atomic disorder at the surface of the nanorods[12] caused by milling-induced lattice strain. RTA-treated nanorods show reduction in intensity of the peak IV as a result of strain relaxation, whereas other three peaks are present in the UV−blue region. Interestingly after RTA treatment peaks II and III are shifted to higher wavelengths. This redshift is increased with increase in RTA temperature. The strain may change the position of the intermediate defect-related states in the band structures. During annealing, nanorods recrystallize and grain growth may take place. This is likely to be responsible for the change in band gap and corresponding redshift in the PL spectra.

4. Conclusions

We have shown the influence of RTA treatment on the structural and optical properties of the mechanochemically prepared ZnO nanorods with various diameters. XRD line profile analyses and TEM results demonstrate an improvement of crystalline quality and relaxation of lattice strain. Emission in the UV−blue region was strongly enhanced by RTA treatment. Various structural defects and strain-related visible emission were much reduced due to RTA. Optical studies show the reduction of structural defects of the ZnO nanorods during RTA treatment. This study demonstrated that the RTA treatment is a useful tool for improving the structure and optical properties of ZnO nanostructures.

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