Hydrothermal Growth and Characteristics of ZnO Nanorods on *R*-plane Sapphire Substrates

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초 록: ZnO nanorods were grown on *R*-plane sapphire substrates with the seed layers annealed at different temperature. The effects of annealing temperature for the seed layers on the properties of the ZnO nanorods were investigated by scanning electron microscopy, X-ray diffraction, UV-visible spectroscopy, and photoluminescence. For the as-prepared seed layers, the ZnO nanorods and the ZnO nanosheets were observed. Only the ZnO nanorods were grown as the annealing temperature was above 700 °C. The optical transmittance in the UV region was almost zero while that in the visible region was gradually increased as the annealing temperature increased to 700 °C. The optical band gap of the ZnO nanorods was increased as the annealing temperature increased to 700°C. In the visible region, the refractive index was decreased with increasing the wavelength, and the extinction coefficient was decreased as the annealing temperature increased to 700°C. The non-linear exciton radiative life time of the FX emission peak was established by cubic equation. The values of Varshni's empirical equation fitting parameters were $a = 4 \times 10^{-3}$ eV/K, $\beta = 1 \times 10^{4}$K, and $E_g(0)$=3.335eV and the activation energy was found to be about 94.6 meV.

1. 서론

Over the last several years, great progress has been reported in growth of ZnO nanostructures, such as nanowires, nanorods, nanobelts, nanotubes, and nanoneedles. These ZnO nanostructures show unique properties that can be applied to short-wavelength light emitting diodes, roomtemperature (RT) ultra-violet (UV) lasing diodes, solar cells, and piezoelectric and optoelectronic devices. It is difficult to obtain well-aligned ZnO nanostructures on silicon substrates because the formation of an interfacial layer and large lattice misfit. Interestingly, *c*-plane sapphire over comes some of the limitations arising from the above substrates. On the other hand, ZnO nanostructures on *R*-plane sapphire have an advantage for the fabrication of the next generation sensor and detectors in the form of surface acoustic wave devices due to higher electromechanical coupling. Recently, a few reports have been published for the growth of ZnO thin films on *R*-plane sapphires, but the synthesis of ZnO nanostructures on *R*-plane sapphire has not been well explored. In this work, ZnO nanorods on *R*-plane sapphire substrates with ZnO seed layers annealed at different temperature were grown by hydrothermal method. The effects of annealing temperature for the ZnO seed layers on the structural and optical properties of the ZnO nanorods were investigated.

2. 본론

Fig. 1 shows SEM images of the ZnO nanorods grown on the seed layers annealed at different temperatures. For the as-prepared seed layers, the ZnO nanorods and the ZnO nanosheets were observed. Li *et al.*[1)] and Cao and Cai[2)] reported control of the shape between nanorod and nanosheets by change in the concentration of aqueous solutions. The growth rate along *c*-axis direction could be reduced because adsorption of the superfluous OH^- ions was easily happen and finally lead to the formation of nanosheets[1)]. This implies that the as-prepared seed layers could not provide stable conditions for the growth of the ZnO along *c*-axis over whole the surface. However, the number of the ZnO nanosheets was decreased as the seed layers were annealed at 600 °C. Eventually, only the ZnO nanorods were grown by increase in the annealing temperature. The diameter of the ZnO nanorods was also increased with increasing the annealing temperature to 700 °C.

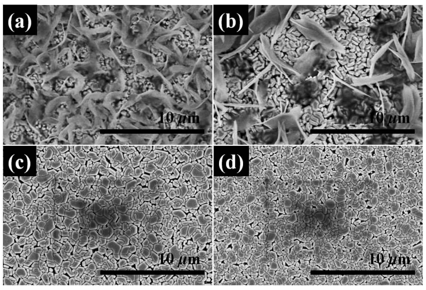

Fig. 1. SEM images of the ZnO nanorods grown on the seed layers annealed at different temperatures of (a) as-prepared, (b) 600, (c) 700, and (d) 800 °C.

Only the ZnO (002) and ZnO (004) diffraction peaks of hexagonal wurtzite are observed in all the ZnO nanordos, indicating that all the ZnO nanorods exhibit (002) preferential orientations with the *c*-axis perpendicular to the substrate surface and have strong textures. The full width at half maximum (FWHM) of the ZnO (002) diffraction peak is closely related to both average grain size and crystal quality. A narrower FWHM and a larger grain size imply a better crystal quality. The FWHM is correlated with the average grain size by the Scherrer equation. The average grain size of the ZnO nanorods was increased from 84 to 94 nm with increasing the annealing temperature to 700 °C, which indicates that the crystal quality of the ZnO nanorods was enhanced. However, the average grain size was decreased again by further increase in the annealing temperature. With increasing the annealing temperature, the bond length was decreased from 1.953 to 1.949 Å.

At the below the absorption edge around 375 nm, the optical transmittance was almost zero because the ZnO nanorods was thick (approximately 2 μm). The optical transmittance in visible region was gradually increased as the annealing temperature increased to 700 °C. With the further increase in the annealing temperature, the optical transmittance in visible region was decreased again. the optical band gap E_g was increased from 3.276 to 3.288 eV as the annealing temperature increased to 700 °C. On the other hand, the Urbach energy E_U was decreased from 59.5 to 47.2 meV as the annealing temperature increased to 700 °C. It was found that the annealing temperature was responsible for the width of localized states in the optical band gap of the ZnO nanorods, and consequently, the optical band gap was increased.

Two emission peaks were observed from the ZnO nanorods. One is the strong near-band-edge emission (NBE) at 3.3 eV generated by exciton recombination. The other is the weak deep-level emission (DLE) around 2.2 eV (green emission) caused by oxygen vacancies. The FWHM of NBE peak from the ZnO nanorods was decreased from 139 to 129 meV with increasing the annealing temperature to 700°C. However, the FWHM was slightly increased again by further increase in the annealing temperature. The narrower FWHM of the NBE and the weak DEL peak of the ZnO nanorods grown on seed layers annealed at 700 °C were observed, which was due to enhancement of the crystal quality.

3. 결론

The ZnO nanorods were grown on *R*-plane sapphire substrates with the seed layers annealed at different temperature. The ZnO nanorods and the ZnO nanosheets were observed for the as-prepared seed layers. Only the ZnO nanorods were grown as the annealing temperature was above 700 °C. The density and structural properties of the ZnO nanorods were enhanced when the seed layers annealed at 700 °C. The optical transmittance in the UV region was almost zero while that in the visible region was gradually increased as the annealing temperature increased to 700 °C. The optical band gap of the ZnO nanorods was increased as the annealing temperature increased to 700 °C. In the visible region, the refractive index was decreased with increasing the wavelength, and the extinction coefficient was decreased as the annealing temperature increased to 700 °C. The non-linear exciton radiative lifetime of the FX emission peak was established by cubic equation. The values of Varshni's empirical equation fitting parameters were $a = 4 \times 10^{-3}$ eV/K, $\beta = 1 \times 10^{4}$ K, and $E_g(0) = 3.335$ eVand the activation energy was found to be about 94.6 meV.

참고문헌

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