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갈륨 도핑된 ZnO 나노와이어의 합성과 구조적 광학적 특성 분석

김창은, 안병두, 전경아, 손효정, 김건희, 이상렬
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Structural and optical properties of Ga-doped ZnO nanowires synthesized by pulsed laser deposition in furnace

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Abstract - Ga-doped ZnO nanowires have been synthesized by pulsed laser deposition (PLD) in furnace on gold coated (0001) sapphire substrates. The effect of repetition rate on structural and optical properties of Ga-doped ZnO nanowires are investigated. By controlling repetition rate, the diameter of nanowires is varied between about 60 and 100 nm, and the length of nanowires is varied between about 2 and 4 um. The X-ray diffraction (XRD) reveals the structural defects induced by the Ga doping. The room temperature photoluminescence (PL) spectra of Ga-doped ZnO nanowires show strong UV emission between 382.394 and 385.279 nm with negligible visible emission.

1. Introduction

Nanosize one-dimensional (1D) materials have stimulated great interest due to their importance for novel physical properties and potential application in nanodevices.[1] ZnO is a promising material applied to optical devices, solar cell, gas sensor, and biosensor, because ZnO is a wide band gap compound II-VI semiconductor that has a direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature and is photoelectric, gas-sensitive, and biocompatible.[2]
For practical device application, doping of nanostructure is an important issue. Controllable doping of 1D semiconductor nanostructure realize nanosize electronic and photonic device. Zhong et al.[3] reported the enhanced electronic properties of ZnO nanowires due to Ga doping and Geng et al.[4] reported the optical properties of ZnO nanowires doped with S. However synthesis of ZnO nanowires doped with dopants have been reported by using VLS method, MOCVD, chemical vapor deposition, electrochemical method except PLD.
In this letter, we report that Ga-doped ZnO nanowire are synthesized by PLD in furnace on the Au coated (0001) sapphire. We have fabricated the Ga-doped ZnO nanowires of different diameters in a controllable way and structural, and optical properties of the Ga-doped ZnO nanowires on repetition rate are investigated.

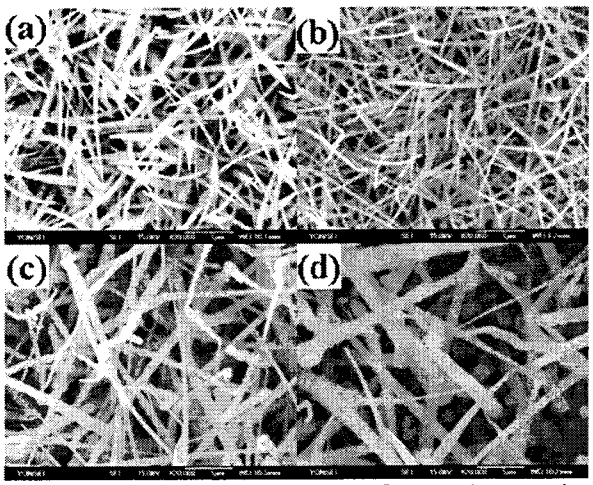
2. Experimental

Ga-doped ZnO nanowires are grown by PLDin furnace. The target in this experiment are synthesized using high purity of ZnO (99.999 %) and 3wt. % Ga_2O_3(99.99 %) powders by a conventional ceramic powder process. The deposition furnace is evacuated by a rotary pump yielding pressures of 1×10^{-3} Torr. After evacuating the furnace, the deposition pressure of furnace is maintained at 1 Torr by Ar (99.999 %) gas flowing at 50 sccm. The substrate is a c-sapphire and Au is coated on the substrate with 10nm thickness by thermal evaporation. The target-substrate distance is fixed to be 20 mm. The temperature of substrates is hold at 800 °Cduring synthesizing of the nanowires. The target is ablated with Nd:YAG laser (355 nm) at a laser fluency of 3 Jcm^{-2}. Different repetition rates (1-10Hz) have been used to investigate their effect on the nanowire growth. To apply same laser pulses, the 18,000 laser pulses are kept for different repetition rates by controlling deposition time.
The morphology of the as-deposited products is observed wit hfield emission scanning electron microscopy (FE-SEM). The str uctural properties of nanowires are examined with XRD where a Ni-filtered K_α (λ= 1.54056Å) is used. The optical properties are an alyzed by photoluminescence (PL) with a He-Cd laser (325 nm, o utpower of 20 mW) as a light source at room temperature.

3. Result and discussion

3.1 Morphological property

The morphological characteristic of Ga-doped ZnO nanowires has been investigated with FE-SEM. Figure 1 show the different shapes of Ga-doped ZnO nanowires with repetition rate variation. These images clearly demonstrate that the repetition rate of laser affects the growth of Ga-doped ZnO nanowires. When the repetition rate is 10 Hz, the length of nanowires is in the range from 1 to 2 um, as shown Fig. 1(a). As the repetition rate decreases to 5, 2, and 1 Hz, the length of nanowires increases to 2.6, 3, 4 um. The diameter of nanowires is not in inverse proportion to repetition rate. When the repetition rate is 5 Hz, the nanowires have a more uniform size of 50-70 nm, as shown Fig. 1(b). In other repetition rates, the diameter of nanowires is in the range from 40 to 180 nm. The average diameters of sample 1, 2, 3 and 4 are 80, 60, 80, 100 nm. The repetition rate control the flux of plume, and the flux of plume control the growth of nanowires. Therefore the repetition rate affects the growth rates of the nanowires. While the surface of ZnO nanowires grown by PLD is uniform,[2] and independent of repetition rate, the Ga-doped ZnO nanowires synthesized by PLD in this experiment have stacked morphology. Therefore we conclude that the stacked characteristic of nanowires is affected by Ga.

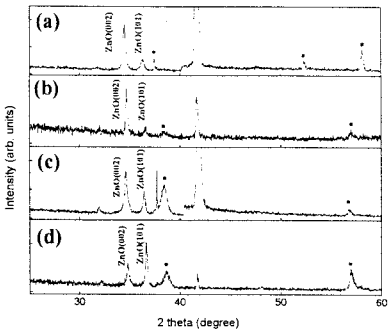


<Fig. 1> SEM images of Ga-doped ZnO nanowires synthesized at (a) 10Hz, (b) 5Hz, (c)2Hz, and (d)1 Hz.

3.2 Structural property

Figure 2 shows the XRD patterns of Ga-doped ZnO nanowires. All diffraction peaks in Fig.2 match the hexagonal ZnO structure. While Au peaks are detected in some samples, no phases such as Ga_2O_3 or $ZnGa_2O_4$ are detected. The (0002) peak of ZnO nanowires have been reported at 34.4, (0002) peak of Ga-doped ZnO nanowires are detected at between 34.5° and 34.8°.
According to Bragg rule, as the (0002) peak shift to higher angles, the c-axis lattice constant decreases. In Ga-doped ZnO nanowires, the calculated c-axis lattice constant are between 2.5975Å and 2.5758Å and decreased by from 0.28% to 1.11%

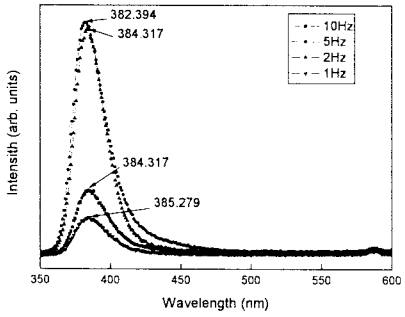
compared to 2.6048Å,[2] c-axis lattice constant of ZnO nanowires. Because the radius of Ga^{3+} ion in the ZnO wurtzite structure is 0.61Å and smaller than 0.74Å of Zn^{2+} ion, Ga^{3+} ion substituted in Zn^{2+} sites could shrink the lattice parameter. Therefore Ga dopant causes the structural defects of ZnO nanostructures. The (0002) peak shift of ZnO nanowires doped with In, and Sn have been reported.[5]



<Fig. 2.>. X-ray diffraction patterns of Ga-doped ZnO nanowires synthesized at (a) 10Hz, (b) 5Hz, (c) 2Hz, and (d) 1Hz. (■ : diffraction peak position of Au)

3.3 Optical property

Figure 3 shows the room temperature PL spectra of Ga-doped ZnO nanowires. Curve 1 is for the Ga-doped ZnO nanowires with repetition rate of 10Hz, curves 2, 3, and 4 correspond to Ga-doped ZnO nanowires with repetition rate of 5, 2, and 1 Hz. The PL spectraof Ga-doped ZnO nanowires exhibit a strong UV emission peak at 384.318 nm, 382.394 nm, 384.318 nm, and 385.279nm corresponding to the near band edge peak. And the PL full width at half magnitude (FWHM) values of samples at peaks are calculated to be 0.257 eV, 0.241 eV, 0.220 eV, and 0.277 eV. The PL spectraof ZnO nanowires is reported that UV peak is at 379 nm or 380 nm, corresponding to the near band edge peak originated from the recombination of the free exicitons of ZnO, with FWHM of 0.11~0.12eV.[2] In this experiment, PL peaks are at between 382 ~ 385 nm with FWHM of 0.220 to 0.277 eV. The redshift of peak positions and broadening of FWHM mean that ZnO nanowires are doped with Ga. As ZnO nanowires are highly doped with Ga, many body effects of free carriers which lower the electron energies may lead to bandgap narrowing. And the broadening may be caused by the potential fluctuation of Ga dopant in nanowires and/or the dopant-related defects in the nanowire crystalline structure. A similar shift of peak and broadening of FWHM in PL spectra in Ga doped ZnO nanowire are reported by Zhong et al.[3]

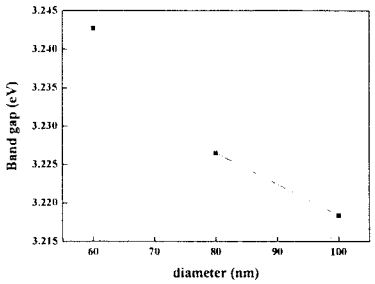


<Fig. 3.> PL spectra of Ga-doped ZnO nanowires synthesized at 10Hz, 5Hz, 2Hz, and 1Hz.

3.4 PL shift

Figure 4 shows the bandgap of Ga-doped ZnO nanowires obtained from PL spectra in Fig.2 is inverse proportional to diameter. Chen et al. report that blueshift of cathodeluminescence(CL) emission spectra of ZnO nanorods with diameters beyond quantum confinement regime.[6] According to their report, the CL shift, ΔE_g, is expressed as $\Delta E_g(shift) = -0.006 + 3.71119(1/d)$, where ΔE_g represent the difference between CL emission energy and the bulk bandgap of ZnO nanorods. The average diameters of Ga-doped ZnO nanowires are 80, 60, 80, 100 nm.

As the equation apply to PL shift of Ga-doped ZnO nanowires, the ΔE_g of Ga-doped ZnO nanowires are 0.04038, 0.05585, 0.04038, and 0.03111. The calculated difference between Ga-doped ZnO nanowires synthesized at 5Hz and 10Hz (or 2Hz) is 0.01547 and comparable to 0.0162, which is a gap of PL peak between 3.2427 and 3.2265 eV. And the calculated difference between Ga-doped ZnO nanowires synthesized at 5Hz and 1Hz is 0.02474 and comparable to 0.0243, which is a gap of PL peak between 3.2427 and 3.2184 eV. The blueshift of UV peak of PL by the decrease of diameter of nanowires is caused by the surface resonance effect for the relatively high surface to volume ratio of Ga-doped ZnO nanowires[6]



<Fig. 4.> Bandgap energy of Ga-doped ZnO nanowires synthesized at various diameter.

4. Conclusion

In this study, synthesis of Ga-doped ZnO nanowire using Ga_2O_3 as dopant by PLD in furnace and structural and optical properties of Ga-doped ZnO nanowire are reported on repetition rate. The diameter and length of nanowires are affected by repetition rate. The surfacecharacteristic of morphology is considered to be affected by Ga. The XRD patterns show that the XRD peak shift, indicating that the Ga doping causes the structural defects of ZnO nanowires. In PL spectra of nanowires, the redshift of UV peak from 380 nm to 382, 385 nm demonstrate bandgap narrowing due to many body effects of free carriers caused by Ga doping, and the difference of peak shifts is owing to surface resonant effect of nanowires with the different diameter. We suggest that 1D ZnO nanowires are doped using PLD method.

Acknowledgement

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