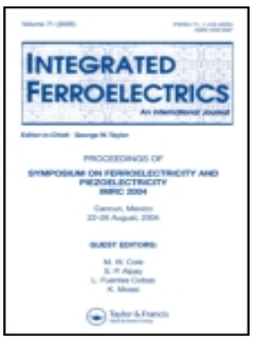

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The formation and characteristics of ZnO/AlN and ZnO/AlN/ZnO core-shell nanowires

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ABSTRACT

In this work, we fabricate the p-type ZnO/AlN/ZnO core-shell nanowire arrays on Al2O3 substrate. The SEM images show the core-shell structure and the connection phenomenon appeared during the deposition process. The XRD results show a better crystal quality after annealing. The sample exhibits some unique properties after annealing treatment. Including the improvement of crystal quality and the shift of the PL emission peak. The low temperture PL spectra show a neutral acceptor bound exciton (A0X) emission (at 3.355 eV), and the emission at 3.325 eV is ascribe to the free electron to the acceptor transition (FA). The calculated result is found in good coincidence with the experiment.

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ZnO; core-shell structures; PL

1. Introduction

Zinc oxide is a direct band gap semiconductor with a wide-band gap (3.37 eV) and large exciton binding energy (60 meV), which is suitable for the development of efficient blue and UV optoelectronic devices. [1–3] However, durable p-type ZnO is the key problem for ZnO based devices. ZnO is intrinsically n-type material, many research effort have been aimed in fabricating p-type ZnO. Considerable works have been reported on the doping of ZnO with several dopants to tailor its electrical and optical properties by different methods. [4–6] But reproducible and reliable p-type ZnO is still hard to obtained yet, mainly due to the selfcompensating effects from donor defects like oxygen vacancies or zinc interstitials. The most promising p-type dopant has proven to be N, since the ionic size of N is almost the same with that of O.[7] Besides, the crystal quality of doped ZnO is another problem, which will affect the performance of device.

Resent years, some novel methods attracted researcher's attention. In Jong Hyun Lee's report, they use AlN codoped ZnO film, and obtain the excellent p-type behavior ZnO film. The experiment results proved p-type AlN:ZnO films have a

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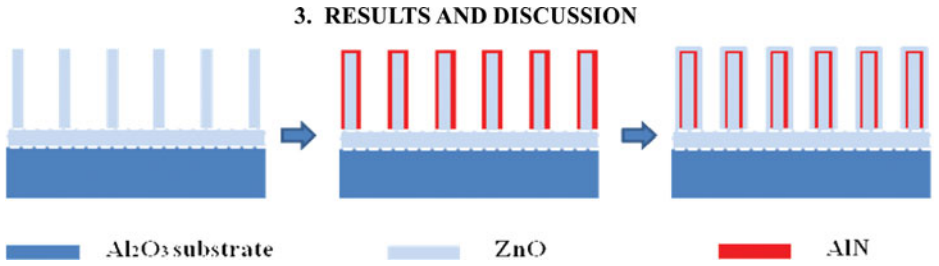

Figure 1. Schematic diagram of the formation process of core-shell ZnO/AlN/ZnO core-shell NWs.

polycrystalline phase, and make a hexagonal columnlike ZnO thin film at high temperture, resulting from incorporation of Al and N into the ZnO film.[8–10] This method will be very helpful for ZnO homojunction fabrication.

In this work, with unique advantages such as high specific surface area and high electronic transport property, core/shell nanowires of ZnO/AlN and ZnO/AlN/ZnO were grown by hydrothermal and atom layer deposition (ALD), the morphologies and structural properties were investigated. In addition, the optical property was discussed indetail.

2. Experiments

In this study, ZnO/AlN/ZnO core-shell nanowire arrays (NWs) are fabricated and its unique properties will be discussed. The process of the growth condition as followed.

Firstly, ZnO NWs have been formed on ZnO film-coated Al_2O_3 substrates by a hydrothermal growth method.[11] 0.01 mol/L zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and 0.01 mol/L hexamethylenetetramine (HMT) were dissolved in 100 ml deionized water and then mixed solution were transferred to a Teflon-lined stainless autoclave. The coated Al_2O_3 substrate was put into the solution. The autoclave was conducted in an electric oven at 90°C for 24 h. After the reaction, the autoclave was taken out of the oven and cooled to room temperature. Later the sample was washed thoroughly with by deionized water and dried at 60°C for 1h.

Secondly, AlN and ZnO thin films were deposited by using LabNano^{TM} 9100 atomic layer deposition (ALD) system from Ensure Nanotech (Beijing). For AlN growth, trimethylaluminium (TMA) and NH3 were used as precursor source and high purity nitrogen (N_2) was used as the purging gas. The growth temperature was 300°C and the growth cycles were 200. The thickness of AlN thin film was about 10 nm. For ZnO growth, Diethylzinc (DEZn) and water were used as precursors, and the growth temperature was 170°C,and the growth cycles were 216. The thickness of ZnO thin film was about 10 nm. Finally, the as-grown samples were annealed at 800°C for 30 min in air. Figure 1 shows the schematic diagram of the formation process of core-shell ZnO/AlN/ZnO core-shell NWs.

All samples were investigated by scanning electron microscopy (SEM, JEOL-6010LA). The crystal structure of the ZnO NWs and ZnO/AlN/ZnO core-shell NWs

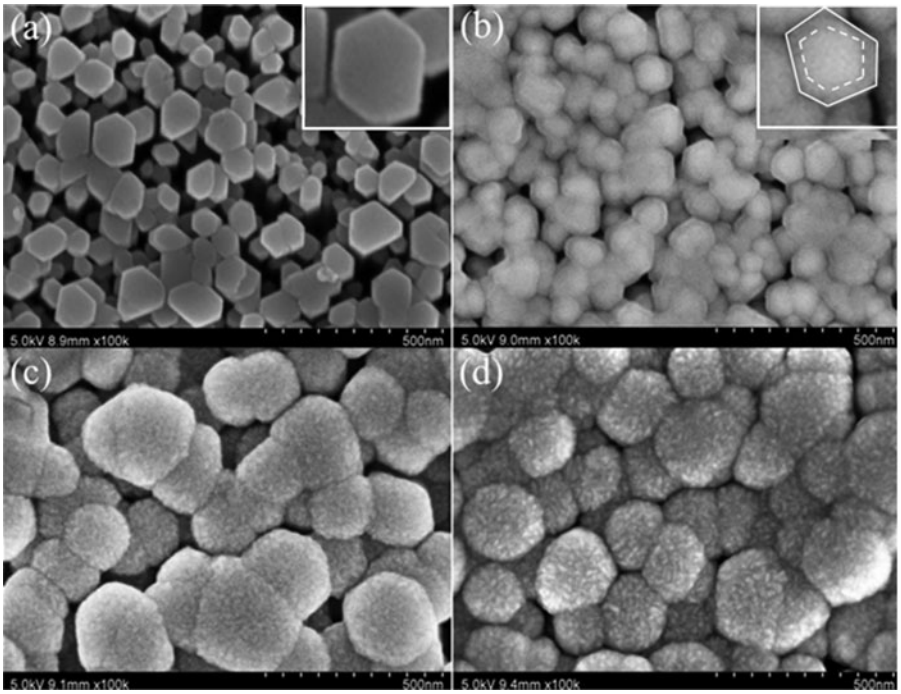

Figure 2. The SEM images of the different stage of the experiment (a) ZnO NWs (b) ZnO NWs after coating AlN thin film (c) ZnO /AlN NWs after coating ZnO thin film (d) ZnO/AlN/ZnO NWs after annealing at 800°C.

were characterized by X-ray Diffraction (Bruker AXS D8 DAVINCI) with Cu-Ka radiation ($\lambda = 1.5406$ Å). And the photoluminescence (PL) measurements were performed using a He-Cd laser line of 325 nm as the excitation source.

3. Results and discussion

The SEM images of ZnO NWs are shown in Figure 2. It can be observed that the ZnO NWs are hexagonal structure and have the smooth surfaces with the diameter about 150nm, as shown in Figure 2 (a). The density of the ZnO NWs are increased and the hexagonal structures connected together after AlN film coating (Figure 1 (b)), and core-shell structure appeared clearly. In Figure 2 (c) the connection phenomenon is more obvious, and the surface of ZnO/AlN/ZnO NWs became rough. Furthermore, particulate matter formed on the surface after annealing at 800°C (as shown in Figure 2(d)). From the SEM results, after AlN film coating, the ZnO NWs can still keep the hexagonal structure, however, for multi-core/shell sample and annealed sample, the morphologies of ZnO changed a lot.

Figure 3 shows the XRD patterns of the samples. All the curves in Figure 2 are normalized to the Al_2O_3 substrate peak value, respectively. The distinct diffraction peaks positioned at 31.8° and 34.5° are assigned to (002) orientation planes of ZnO with hexagonal wurtzite structure. [12] After coating, the peaks gradually shift toward the high-angle side compared to that of ZnO NWs, indicating extensive residual strain along the c axis, and thus tensile biaxial strain within the growth

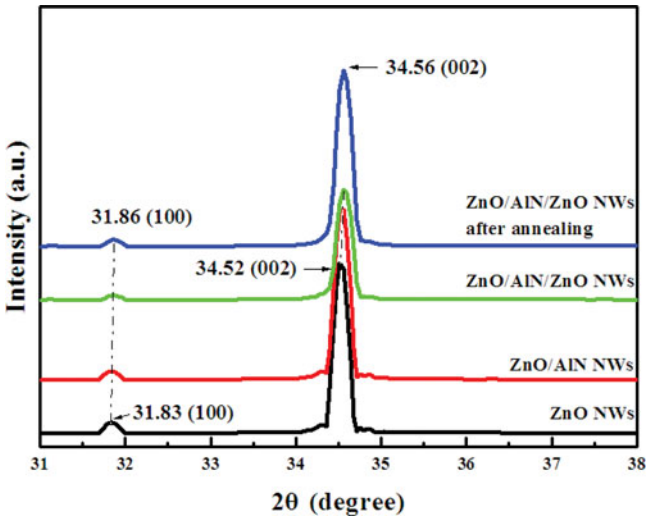

Figure 3. XRD pattern of the ZnO NWs, ZnO/AlN NWs, ZnO/AlN/ZnO core-shell NWs, respectively.

plane. [13] The shift trend is similar to the Jong Hyun Lee's report. However, in our work, the shift appeared at the process of the deposition. Significant deterioration in crystallinity was observed in coating samples. This phenomenon could be ascribed to the damage during the coating process and the poor crystal quality of the AlN and ZnO thin film. These results indicate that Zn atoms might occupy Al sites, resulting in the AlN bondings, which have a hexagonal structure similar to ZnO film. [8]

It is important to understand the optical performances of ZnO/AlN/ZnO core-shell NWs thoroughly, and low temperature PL spectroscopy is a powerful tool for characterizing acceptor/donor impurities.

Figure 4 (a) shows the low temperature photoluminescence spectrum of the ZnO NWs (at 93.25K). The curve exhibit a main peaks at 3.365 eV, which is

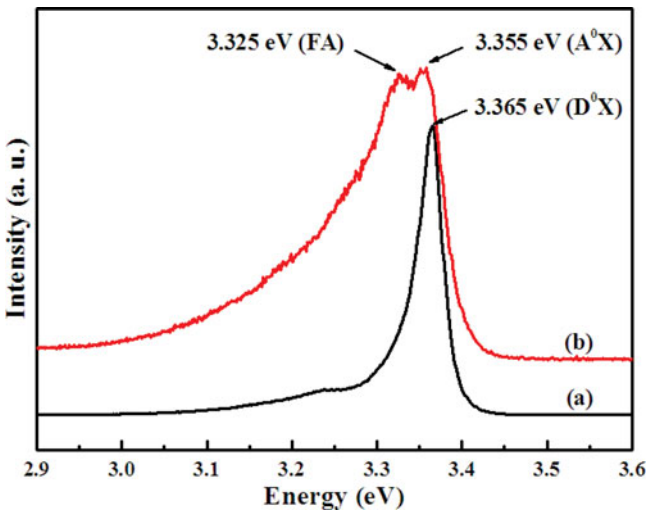

Figure 4. Low temperature photoluminescence spectra of (a) ZnO NWs, (b) after annealing ZnO/AlN/ZnO core-shell NWs at 93.25K.

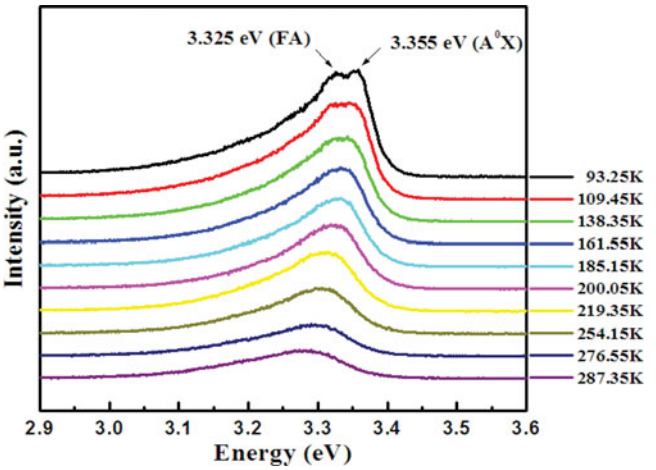

Figure 5. Temperature-dependent PL spectra of after annealing ZnO/AlN/ZnO core-shell NWs sample.

assigned to the radiative recombination of neutral donor-bound exciton (D^0X).[5] In Figure 4(b), after annealing ZnO/AlN/ZnO core-shell NWs sample, the low temperature PL spectrum shows the emission peak at 3.355 eV and 3.325 eV. The peak at 3.355 eV comes from the neutral acceptor-bound exciton (A^0X) emission.[11] The emission at 3.325 eV is considered as the recombination of free electron to the acceptor transition (FA). Based on the previous reports of doped ZnO nanowires, [14, 15] we know the broadening peak edge between 3.14 eV and 3.25 eV could be related to the acceptors in ZnO.

To further understand the origination of the emissions, the temperature-dependent PL spectra of the after annealed ZnO/AlN/ZnO core-shell NWs sample were measured. As shown in Figure 5, with the temperature increasing, FA transition energy indicated a continuous red-shift. FA is usually observed at p-type doped ZnO sample. [16] According to the Eq. 1, we can fit the FA binding energy peak. [17]

$$E_{FA}(T) = E_g(T) - E_A + K_B T/2 \tag{1}$$

Eg (T) and EFA are the temperature-dependent band gap energy and free electron to acceptor energy, respectively. EA is the binding energy that related to the acceptor. K_B is Boltzmann's constant, and T is temperature. $E_g(T)$ is a function of temperature, which is fitted with the Eq. 2. [17]

$$E_g(T) = E_g(0) - \alpha T^2/(T + \beta) \tag{2}$$

Eg (0) is the band gap energy when T is equal to 0 K. The acceptor binding energy of E_A is about 120 meV. In Figure 6, the FA emission sampling points of annealed sample is coincides with theoretical fitting peak curve approximately.

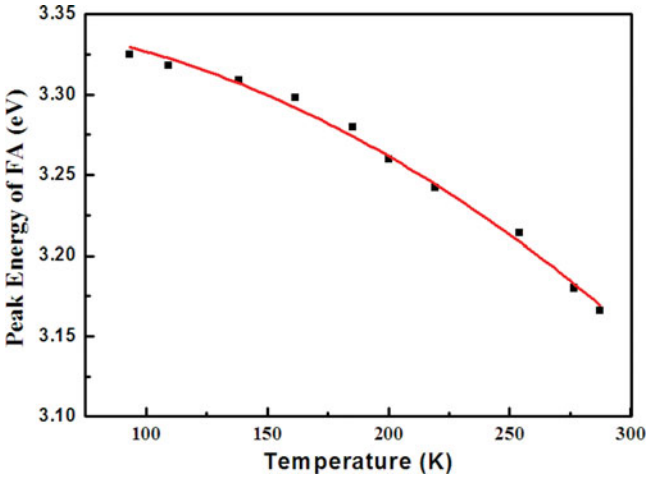

Figure 6. The illustration is FA emission peak curve fitting with temperature.

4. Conclusions

In conclusion, a wide band gap AlN doped p-type ZnO/AlN/ZnO core-shell NWs have been fabricated by using hydrothermal growth method and ALD system. From the SEM and XRD results, we describe the process of the formation of ZnO/AlN/ZnO core-shell NWs. The SEM results indicate the connection phenomenon of the ZnO NWs after deposition AlN and ZnO thin film and particulate matter formed after annealing. The XRD patterns show the AlN doped during the deposition process, and the crystal quality become better after annealing. The PL spectra show a peak at 3.355 eV comes from the neutral acceptor bound exciton (A0X), and the peak locate at 3.325 eV could be ascribe to the recombination of free electron to the acceptor transition (FA), and the result is agreement with the calculation from the formula.

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