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Aluminum Doped Core-shell type ZnO/ZnS Nanowires: Structural and Photoluminescence Studies

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Abstract

In this work, we investigated the effect of Al doping and surface modification on a core–shell type ZnO/ZnS NWs on the structural, electrical and PL properties. Doping and surface modification of the Al:ZnO NWs result in changes in the nature of PL spectra and electronic conductivity. Compared to the bare undoped ZnO NWs, a two times improvement in the electronic conductivity as well as five times enhancement in the UV PL intensity is obtained from the Al(2 at.%):ZnO/ZnS NWs. The UV PL enhancement factor is ~2.8 times higher than the case of undoped NWs coated with ZnS for same time duration. The observed changes are studied in details and origin of the enhancement is discussed.

1. Introduction

Zinc oxide, a versatile material with several important properties, e.g. strong room temperature UV photoluminescence (PL), high transparency in the visible region, piezoelectric, ferromagnetic, and nonlinear optical properties, attracted the attention of the researchers worldwide. These interesting features of ZnO enables to fabricate various nanodevices ranging from field effect transistors to biosensors using various types of ZnO nanostructures [1-3]. Depending upon the growth method, the as–grown ZnO NWs invariably contain several surface defects which have a detrimental effect on the band edge UV emission and related applications. Hence, obtaining highly efficient UV emission from the ZnO nanostructures is one of most important issues for optoelectronic applications. Furthermore, the electronic conductivity of the as–grown ZnO NWs is low for device application. The electrical and optical properties of ZnO can be adjusted desirably not only by impurity doping but also through surface modification [4, 5]. The modification of the surface is considered as one of the advanced techniques to change the properties of ZnO for a better application [6, 7].

In this work, we investigate the combined effects of Al doping and surface modification to prepare a ZnO system with high electronic conductivity as well as strong UV luminescence. The Al doped core–shell type ZnO NWs were prepare by aqueous chemical growth method with Al doping followed by ZnS shell formation. The Al doping and surface modification significantly changed their electrical and PL properties. The observed changes are studied in details and discussed.

2. Experimental

ZnO NWs were grown by aqueous chemical method as described elsewhere [8]. In brief, uniform distribution of ZnO nanocrystal seeds were prepared on Si substrate by spin coating followed by thermal decomposition of zinc acetate. The vertically–aligned ZnO NWs were synthesized by hydrolysis of zinc nitrate in water in presence of hexamethylenetetramine on the above prepared substrate at 95°-C for 24 hour. For Al doping, aluminum nitrate was used as precursor which was mixed properly in the reaction solvent according to the stoichiometric ratio. The substrate was then removed from the solution, rinsed in DI–water and dried in hot air at 100°C for 30 mins. For comparison, undoped ZnO NWs were prepared by the same process without using Al doping precursor.

For the ZnS shell formation, the previously prepared ZnO NWs were dipped into 10 mM aqueous solution of thioacetamide (TAA) at 60°C for 1, 2 and 4 hours and then dried. In this process we prepared core–shell type ZnO/ZnS NWs with varying thickness of ZnS shell layer. The morphology and crystal structure of the above prepared NWs were characterized using field emission SEM, EDX and x-ray diffractometer. The PL spectra of all the samples were recorded with a 325 nm He–Cd laser excitation. For comparative analysis, PL measurements on all the samples were made under identical experimental conditions.

3. Results and discussion

Figure 1(a) shows the SEM morphology image of the 2%(at.) Al doped ZnO (Al(2 at.%):ZnO) NWs grown by aqueous chemical method with the help of ZnO seed layer. As seen from the image, a high density ZnO NWs grew vertically on the Si substrate. The diameters of the NWs are very small, which ranges from 53 to 65 nm and the lengths are about a few microns. The degree of alignment in the as–grown ZnO NWs is strongly controlled by the orientation of the ZnO seed layer. The EDX spectrum (Fig. 1(c)) confirms the presence of Al doping, which shows the presence of 1.46 at % of Al for the 2% doped sample. Undoped ZnO NWs shows similar morphology with diameter ranging from 35–60 nm. Figure 1(b) shows the above Al:ZnO NWs after sulfidization process for 4 h. A clear difference in the

surface morphology of Al:ZnO and Al:ZnO/ZnS NWs can be visualized from the images as the sidewalls of the former are smooth, whereas those of the latter are rough and wrinkled indicating some modification has been occurred due to ZnS layer formation. There is no significant change in the diameter of the Al:ZnO/ZnS NWs indicating that only the surface ZnO layer is converted to ZnS. However, the highest measured diameter is about 75 nm. The larger estimation is due to the formation of very rough sidewall of the NWs. To confirm further, EDX line scan technique is employed across a single core–shell NW, which is shown in Fig. 1(d). It confirms a sharp interface between the Al:ZnO core and ZnS shell. The estimated shell thickness is ~5 nm after 4 h of sulfidization. The x–ray diffraction confirms a highly crystalline structure of all of the NWs with growth orientation along (002) plane of hexagonal structure. The electrical conductivity gradually increases with the increase in the Al concentration in the NWs. The conductivity improved by ~2 times from the Al(2 at.%):ZnO NWs with lowest resistivity ~2×10^{-3} Ω–cm.

The room temperature PL spectra of the undoped, Al:ZnO and Al:ZnO/ZnS NWs are shown in Fig. 2(a–c). The ZnO NWs exhibit near band edge (NBE) UV emission at ~380 nm and a broad visible emission band in the green–yellow region. Gaussian multipeak fitting shows the existence of two emission bands, one at green region (~500 nm) and another at yellow region (580 nm). The observed NBE emission is due to free excitonic recombination while green emission is due to the presence of oxygen vacancy. The yellow emission is commonly observed from the oxide NWs grown by hydrothermal method. It is attributed that, this emission originates from the hydroxyl radicals present on the surface of NWs [9]. During chemical reaction, large amount of hydroxyl radicals formed and easily attached on the surface of the NWs at the oxygen vacancy sites. After the ZnS shell layer formation, no shift in peak positions are observed and yellow emission is completely removed. A new peak is observed in the blue region at 460 nm, which may be originated from complex defect formed by ZnO and ZnS. The observed PL spectra indicate a significant change of the nature of visible emission due to the formation of ZnS layer. The PL intensities gradually increase with the increase in ZnS shell thickness (Fig. 2(d)).

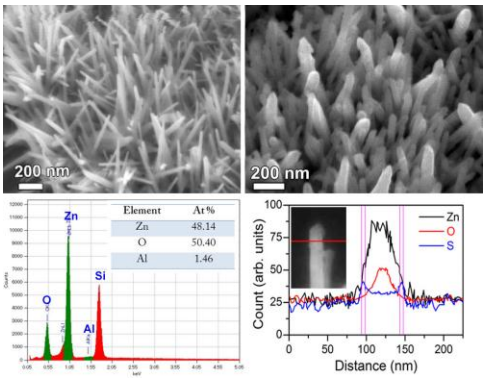

Fig. 1. (Tilted view) SEM images of the chemically grown NWs: (a) Al:ZnO and (b) Al:ZnO/ZnS. (c)EDX spectrum of the Al:ZnO NWs. (d) EDX linescan across a Al:ZnO/ZnS NW.

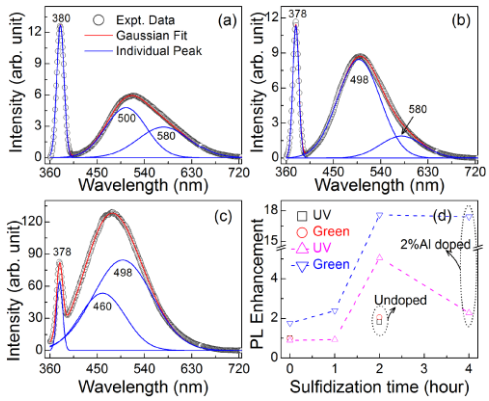

Fig. 2. PL spectra of the: (a) undoped, (b) Al:ZnO, and (c) Al(2 at.%):ZnO/ZnS NWs, respectively. (d) Variations of PL enhancement factors of UV and green emissions of undoped and doped NWs with sulfidization time duration.

Compared to the undoped NWs, ~5 times enhancement in the UV PL intensity is obtained from the Al:ZnO/ZnS NWs. This enhancement factor is ~2.8 times higher than the case of undoped NWs coated with ZnS for equal time duration. When this core–shell structure is excited with 325 nm light, it is expected that both of ZnO (absorption max^{m}. ~367 nm) and ZnS (absorption max^{m}. ~340 nm) get excited and charge transferred occurred from ZnS to ZnO. This process leads to the accumulation of large number of excited charge carriers at the conduction and valance band of ZnO resulting in strong UV PL. At the same time defects in the ZnS (vacancy) influence the nature of the green emission resulting in gradual increment of the green emission.

3. Conclusions

We investigated the effect of Al doping and surface modification on a core–shell type ZnO NWs on the structural, electrical and PL properties. Compared to the bare undoped ZnO NWs, a two times improvement in the electronic conductivity as well as five times enhancement in the UV PL intensity is obtained from the Al(2 at.%):ZnO/ZnS NWs. The UV PL enhancement factor is ~2.8 times higher than the case of undoped NWs coated with ZnS for same time duration. These results indicate that Al doping followed by surface modification on the ZnO NWs is very effective to improve conductivity as well as the UV emission, which is promising for optoelectronic applications.

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