Photoluminescence properties of un-doped and Mn-doped ZnO nanostructures

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ABSTRACT

We presented combinations of vapor phase transport (VPT) of mixture of methanol and acetone and thermal evaporation of brass (CuZn) which contain \textit{in-situ} three stages in obtaining un-doped and Mn-doped zinc oxide (ZnO) nanostructures (NSs). The structure and morphology were characterized by energy dispersive X-ray analysis (EDAX), field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD). The role of Ar as feed gas and interaction between methanol and brass have been predicted based on work reported elsewhere. Photoluminescence (PL) properties of un-doped and Mn-doped ZnO showed significant changes in the optical properties providing evidence for several types of defects such as zinc interstitials ($\text{Zn}_{\text{i}}$), oxygen interstitials ($\text{O}_{\text{i}}$), zinc vacancy ($\text{V}_{\text{Zn}}$), singly charged zinc vacancy ($\text{V}_{\text{Zn}}^{-}$), oxygen vacancy ($\text{V}_{\text{O}}$), singly charged oxygen vacancy ($\text{V}_{\text{O}}^{+}$) and oxygen antisite defects ($\text{O}_{\text{Zn}}$) in the grown NS. The Mn-doped ZnO NSs have exhibited shifted PL peaks compared to the un-doped ZnO.

Keywords: Zinc Oxide, Manganese, Nanowire, Photoluminescence, Thermal Evaporation, Doping.

1. INTRODUCTION

The native doping of zinc oxide (ZnO) which is a $n$-type semiconductor has embarked several favorable properties, including good transparency, high electron mobility 2000 cm\textsuperscript{2}/(Vs) at 80 K,\textsuperscript{(1)} wide band gap 3.37 eV and strong room temperature luminescence.\textsuperscript{(2)} In addition to these properties, ZnO emits different color lights and all constituents of white light due to large number of extrinsic and intrinsic deep-level impurities and clusters.\textsuperscript{(3–5)} These properties have created applications for various fields; transparent electrodes in liquid crystal displays (LCD), energy saving and heat protecting windows as well as in the field of electronics as thin film transistors and light emitting diodes (LED). Thus, many investigations and researches based on growth techniques have been employed and reported elsewhere. In late 90’s methanol was used as a source of oxygen and most of the studies have been reported at low temperatures on selected transition metals surfaces. Rufael et al. have reported that methanol undergoes thermal dissociation on iron, Fe (110) surface to form adsorbed methoxy (CH$_3$O-) species and hydrogen at 100 K.\textsuperscript{(6)} Levis et al. also have reported about thermal decomposition of methanol but on palladium, Pd (110) surface, methanol decomposed into CH$_3$O and H$_2$O at 125 K.\textsuperscript{(7)} Both Rufael and Levis have described that the CH$_3$O species undergoes dehydrogenation to form CO and H$_2$ which later leads to formation of ZnO NSs. Harikumar et al. have used X-ray photoelectron spectroscopy (XPS) and vibrational electron energy loss spectroscopy (VEELS) to trace the C–O bond scission of ethanol that happens at a relatively low temperature on polycrystalline Zn surface that giving rise to hydrocarbon species and oxygen.\textsuperscript{(8)} Meanwhile, the co-adsorption of methanol and C–O bond scission has...
been noted at lower temperatures on both polycrystalline and single crystal surface of Zn.

In this work we report a study to grow ZnO NSs, involving three stages. This technique consumes deposition period and is feasible in growing ZnO at suitable temperature on silicon substrate. This involves the combination of VPT of methanol and thermal evaporation of CuZn to obtain large area of deposition with reduced time of reaction. Methanol was used as a source of oxygen whilst brass (CuZn) alloy as source of Zn and as the catalyst in obtaining doped and un-doped ZnO NSs. The first and second stages depicted a method of obtaining polycrystalline Zn surface and the third stage is to produce an un-doped and doped ZnO NSs. The grown ZnO NSs were optimized using field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and photoluminescence (PL).

2. EXPERIMENTAL PROCEDURE

A smoothly finished Si (001) wafer was used as a substrate for the growth of ZnO NSs. They were cut into about 2 by 2 cm and cleaned ultrasonically about 30 minutes in hydrofluoric (HF) acid to remove the presence of oxide layer and then in acetone solution to remove any impurities on the surface. Then they were rinsed in deionised (DI) water to remove the existing acetone solution on the Si. The procedures to obtain ZnO NSs were divided into two stages.

2.1. Obtaining Zn Layer in Ar Disallowed Environment

One-sided hollow CuZn alloy as illustrated in Figure 1 was used. The CuZn alloy rod of $1.3 \pm 0.1$ cm diameter and $1.3 \pm 0.1$ cm in height was grooved 1 cm diameter hollow in the middle of the brass. The hollow portion of the CuZn was placed on the smoothly finished Si surface and two thermocouples were mounted onto Si substrate and CuZn alloy to detect and monitor the surface temperatures of Si and brass simultaneously. The temperature of Si substrate was maintained at around 800 °C while the temperature of CuZn was under controlled for a deposition period of 30 min. Here Ar was flowed at 100 sccm but disallowed into the hollow portion of the CuZn whereby Ar disallowed environment was created in the one-sided hollow CuZn.

2.2. Obtaining Polycrystalline Zn layer in Ar Allowed Environment

Here two-sided hollow CuZn alloy rod was used to allow Ar pass through at flowrate of 100 sccm. In order to obtain this, a minor change on the one-sided hollow CuZn alloy rod was worked up. A small hole about 0.5 cm in size was drilled on the other side of the similar CuZn as used earlier.

2.3. Obtaining Un-Doped and Doped ZnO NSs on Polycrystalline Zn Layer

To obtain an un-doped ZnO NSs, Ar was flowed at 100 sccm through a mixture of methanol (50 g) and acetone (4 g) solution. Use of methanol alone as feedstock led to oxidation of the hot wire which has resulted gradual reduction on the diameter of hotwire and contamination on the Si substrate. Thus, Tzeng has suggested that acetone to be mixed with methanol solution to prevent the deterioration of tungsten wire as it was heated at high temperatures(9) about 1800 °C at 0.5 ±0.1 cm above the two sided hollow CuZn alloy rod. To obtain the doped ZnO NSs, manganese oxide salt was diluted in the methanol solution mixed with acetone. The role of Ar and brass were determined by comparing procedure 2.1 and 2.2. Meanwhile the role of methanol was perceived by comparing procedure 2.2 and 2.3. The samples, Zn films, un-doped and doped ZnO NSs were characterized using the EDAX, FESEM Leica S440, XRD using Cu $K_{a}$, 1.54 Å radiations and PL characterization. The PL study was carried out using Renishaw inVia Raman microscope at room temperature using a 325 nm helium–cadmium (He–Cd) laser light which passes through three visible lens sets and a diffraction grating of 1200 lines/mm.

3. RESULTS AND DISCUSSION

3.1. EDAX Analysis

The formation of Zn film and ZnO NSs were confirmed with EDAX analysis. Figures 2(a) and (b) are the respective spectrum obtained for Ar disallowed (one-sided hollow CuZn) and Ar allowed (two-sided hollow CuZn) environment at 100 sccm. The respective spectra show formation of 100% of Zn nanoparticles on the Si substrate. Spectrum 2c (Ar allowed through mixture of methanol and acetone) also confirms the presence of Zn with an additional of oxygen and carbon atoms. This proves the growth of ZnO NSs on the Si substrate. This is due to the carbon
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3.2. FESEM Analysis

The surface morphology of grown film on Si substrate via one and two-sided hollow CuZn alloys are significantly compared to distinguish the role of Ar and CuZn in this study. Figure 3 shows typical FESEM images of Zn film. 3(a) and (b) are the FESEM images of Zn film for Ar disallowed (one-sided hollow CuZn) and Ar allowed (two-sided hollow CuZn) environment at 100 sccm. The image 3(a) is observed to be the Zn film with larger boundary in size compared to 3(b). A comparative study between 3(a) and (b) depicts that Ar played an important role in the formation of Zn film. Image 3(c) reveals growth like wire on the Si substrate that was placed under two-sided hollow CuZn alloy. Here Ar was allowed at 100 sccm through mixture of methanol and acetone solution. Images 3(b) and (c) reveals the role of methanol solution in producing ZnO nanowires (NWs). Image 3(d) is the Mn-doped ZnO which exhibits significant changes in morphology compared to the undoped ZnO. The magnified version reveals hexagonal structure of ZnO and NWs.

3.3. XRD Analysis

3.3.1. Role of Ar: Comparison Between Zn and ZnO

Figure 4 shows the XRD spectra of prepared Zn films of different grain size and ZnO NWs designated as sample 4(a)–(c). The XRD patterns 4(a) and (b) which were grown under one and two-sided hollow CuZn alloy rod respectively indicate nanosized Zn particles were distributed on Si substrate with polycrystalline hexagonal structure. Spectrum 4(a) shows strong (002) preferred orientation in c-axis with calculated average grain size of 147 nm. A very close observation of (101) in sample 4(a) between 2θ range of 43°–43.6° shows split up with an average grain size of 105 and 119 nm. Whereas growth orientation in (100), (110), (004) and (202) are not observable in the spectrum 4(a). However XRD Spectrum 4(b) that corresponds to Zn film deposited under two-sided hollow CuZn alloy rod shows polycrystalline nature of Zn film with reflection of planes (002), (100), (101), (102), (103), (110), (004), (112), (200), (201), (104) and (202). But suppressed growth in (002) orientation is noticeably corresponding to the low intensity. Enhanced (101) preferred orientation with calculated average grain size of 43 nm and growth in (004) and (202) directions are only observable in sample 4(b) compared to sample 4(a). An additional of Ar flow through mixture of methanol and acetone solution to Si substrate placed under two-sided hollow CuZn alloy significantly changed the XRD profile from Zn film to ZnO NWs as in 4(c). Spectrum 4(c) exhibits most likely the ZnO NWs grown in (002) direction along the c-axis.

3.3.2. Comparison of Un-Doped and Mn-Doped ZnO NSs

Figure 5 shows XRD spectrum of (a) un-doped and (b) Mn-doped ZnO NSs obtained via two-sided hollow CuZn alloy rod. Spectrum (b) shows significant changes in the crystallographic structure compared to the un-doped ZnO. Spectrum (a) is indexed with a JCP2.2CA: 00-036-1451 that corresponds to the hexagonal wurtzite crystal structure of ZnO. On the other hand additional peaks and broaden peaks in spectrum (b) are related to the un-limitation of this technique in detecting the intrinsic defect due to Mn doping into the lattice of ZnO. The observed peaks in the Mn-doped ZnO can be indexed to wurtzite ZnO and tetragonal ZnMnO₂ (JCP2.2CA:01-071-2499) diffraction peaks which were identified as (200), (103), (211), (202), (004), (220), (213), (305), (105), (312), (303), (321), (224), (215), (305), (332), (422), (404) and (325) as shown in Figure 5. Other two peaks (#020) and (#211) were related to orthorhombic MnO₂ (JCP2.2CA:01-072-1983). The ZnO diffraction peaks in spectrum (b) not shifted as reported by Jinxia Duan et al.\cite{10,11} however, they were broadened may be...
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Fig. 3. FESEM images of Zn film (a) prepared in Ar disallowed environment, (b) Ar allowed environment (c) undoped ZnO NWs and (d) Mn-doped ZnO NWs prepared in Ar allowed environment through mixture of methanol and acetone solution.

due to decrease in the crystallite size. The calculated average crystallite size was 20 and 67.5 nm for the Mn-doped and un-doped ZnO. This shows proof of incorporation of Mn ion inside the ZnO crystal lattice.

Nevertheless, the lattice parameter $a$ of Mn-doped ZnO (2.8606 Å) is lower than the un-doped ZnO which is 3.2511 Å but the lattice parameter $c$ of Mn-doped ZnO is 5.2096 Å is slightly higher than 5.2085 Å of un-doped ZnO. The decrement in lattice parameter $a$ and

Fig. 4. XRD spectra of deposited Zn film on Si under (a) one-sided hollow CuZn alloy rod, (b) two-sided hollow CuZn alloy as function of Ar flowrate 100 sccm and (c) ZnO NWs as function of Ar flowrate 100 sccm through mixture of methanol and acetone via two-sided hollow CuZn alloy.

Fig. 5. XRD spectra of (a) un-doped ZnO NSs and (b) Mn-doped ZnO NSs.
3.4. Photoluminescence Analysis

Figure 6 shows the PL spectrum of un-doped (a) and Mn-doped (b) ZnO NSs measured at room temperature. The comparative study of the spectrum exhibits the ultraviolet (UV) emission peak, green luminescence (GL) broadband and red luminescence (RL) band peaks shifted to the right in the Mn-doped ZnO compared to the un-doped ZnO NSs. Spectrum 6(a) shows a weak UV peak at 381 nm (3.25 eV) while the Mn-doped ZnO shows a shifted UV peak to 417 nm (2.97 eV). This may be due to sp-d spin exchange interaction between the band electrons and localized d electron of Mn ions substituting in cations sites.\(^{(16, 17)}\)

The UV emission near the band edge transition of un-doped ZnO is to be related to the recombination of free excitons through an exciton–exciton collision process.\(^{(18, 19)}\) The un-doped ZnO NSs also exhibits a broad band from 800–1300 nm that is more dominant than of the 420–750 nm. The band from 420–750 nm in the un-doped ZnO is subjected to the GL band, which is due to the radial recombination of a photo-generated hole with the electron of singly ionized charged particles in the \(V_o\).\(^{(20, 21)}\)

On the other hand the broad GL band is shifted to the yellow luminescence (YL) with extremely very low intensity in the Mn-doped ZnO NSs. Suppression in the intensity as in Mn-doped ZnO NSs has been reported earlier.\(^{(22, 23)}\) This indicates presence of low oxygen defects due to the trapped of Mn particles into the \(V_o\) of ZnO NSs which suppresses the formation of \(V_o\) during the growth of Mn-doped ZnO NSs.\(^{(24)}\) Furthermore, the reduced intensity can be related to lattice and surface defects, which produces various non-radiative centers between the bandgap of Mn-doped ZnO.\(^{(25)}\)

This further proposes that the potential of our method, combination of the solvothermal of MnO salt in the mixture of methanol and acetone, and thermal evaporation of Zn from CuZn have produced a low concentration of oxygen defects and high optical quality of Mn-doped ZnO nanostructures.\(^{(26, 27)}\) In addition, a broad peak is observable from 775–945 nm in the Mn-doped ZnO NSs which corresponds to the infrared luminescence at 826 nm. Whereas in the un-doped ZnO a near infrared peak at 762 nm is observable. The dominant broad peak in the undoped ZnO that relates to the far infrared region is likely not observable in the Mn-doped ZnO due to very low oxygen defects which resulted from the Mn interstitials in the lattice of ZnO.

A closer look and analysis using the Gaussian curve fit to the UV emission peak, GL broadband and red band peaks of un-doped and Mn-doped ZnO shown in Figure 7 was noticed and summarized in Table I. The un-doped ZnO NSs shows three peaks that attributes to UV emission band ~376 nm (3.29 eV), 381 nm (3.25 eV) and 387 nm (3.20 eV) nm with high intensity centered at 381 nm. This attributed to 1-longitudinal optical (LO) phonon replicas of neutral donors (D\(^+\)X) or ionized donors (D\(^+\)X).\(^{(28)}\) The Mn-doped ZnO exhibits six peaks 395 nm (3.14 eV), 409 nm (3.03 eV), 417 nm (2.97 eV), 425 nm (2.92 eV), 427 nm (2.90 eV), 444 nm (2.79 eV) and 460 nm (2.69 eV) that attribute to the violet emission region. The high intensity of violet emission region of Mn-doped ZnO is noticeable at 417 nm (2.97 eV) and could be ascribed due to the transition occurring from Zn\(_i\) to the valence band.\(^{(29)}\) The un-doped ZnO also exhibits broad peak of visible PL emission ranged from 400–750 nm. At this broad range seven peaks were indentified at 459, 490, 518, 538, 548, 585 and 655 nm with the respective energy of 2.70, 2.53, 2.39, 2.30, 2.26, 2.12 and 1.89 eV. The high intensity centered at 548 nm (2.26 eV) that corresponds to the GL band near to the yellow region. This visible PL emission in the un-doped ZnO NSs can be...
attributed to different intrinsic defects such as $\text{Zn}_i$, $\text{O}_i$, $V_{\text{Zn}}$, $V_{\text{O}}$, $V_{\text{Zn}}^-$, $V_{\text{O}}^+$, $O_{\text{Zn}}$. Nevertheless, defects due to carbon incorporation in the un-doped ZnO NSs are also responsible as reported earlier by Chrissanthopoulos et al. This corresponds to the EDAX spectrum 2(c) which has exhibited C peak in un-doped ZnO. On the other hand the Mn-doped ZnO exhibited high intensity of peak centred at 594 nm (2.09 eV) that relates to the YL near to the orange region. Additional of six shifted peaks were identified in the Mn-doped ZnO using the Gaussian curve fit at 488, 549, 571, 620, 653, 692 nm. The shifts from the UV emission band to the violet region and from GL band

![Fig. 7. The Gaussian curve is fitted at UV emission band and GL band for (a) and (c) of un-doped and (b) and (d) of Mn-doped ZnO nanostructures.](image)

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to yellow luminescence clearly reveals Mn-doping in the ZnO NSs.

4. CONCLUSION

The combination of VPT mixture of methanol and acetone and thermal evaporation of CuZn has been successfully employed to produce undoped and Mn-doped ZnO NSs. This three stage in situ technique has significantly changed the grain sized Zn film 147 nm to nano sized Zn film 43 nm in the Ar environment whereas a crystalline size reduction of about 70% is obtained. XRD spectra 4(a) and (b) further confirmed that Ar has a role in enhancing the growth of Zn particles in planes (100), (110), (200) and (202) that corresponds to the standard JCP2.2CA:00-012-1238 of Zn. Introduction of methanol has promoted O and C incorporation in the Zn film which is evident from the EDX and PL spectrum. Significant changes in the optical properties of undoped and Mn-doped ZnO showed evidence for several types of defects such as Zn, O, VZn, VZn, V o, V o and O Zn in the grown NSs. The Mn-doped ZnO NSs have exhibited shifted PL peaks compared to the un-doped ZnO. The UV and GL band of undoped at 381 and 417 nm respectively have been shifted to 548 and 594 nm in the Mn-doped ZnO NSs.

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