Effect of pressure and Al doping on structural and optical properties of ZnO nanowires synthesized by chemical vapor deposition

Antaryami Mohanta^a, Jay G. Simmons Jr.^b, Henry O. Everitt^c, Gang Shen^d,
Seongsin Margaret Kim^d, Patrick Kung^{d,*}

^a Oak Ridge Institute for Science and Education, Research Participation Program, U.S. Army Aviation and Missile Research Development and Engineering Center (AMRDEC), Redstone Arsenal, AL 35898, USA

^b Department of Chemistry, Duke University, Durham, NC 27708, USA

^c U.S. Army Aviation and Missile Research Development and Engineering Center (AMRDEC), Redstone Arsenal, AL 35898, USA

^d Department of Electrical and Computer Engineering, The University of Alabama, Tuscaloosa, AL 35487, USA

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ABSTRACT

The effect of Al doping concentration and oxygen ambient pressure on the structural and optical properties of chemical vapor deposition-grown, Al-doped ZnO nanowires is studied. As Al doping increases, the strength of the broad visible emission band decreases and the UV emission increases, but the growth rate depends on the oxygen pressure in a complex manner. Together, these behaviors suggest that Al doping is effective in reducing the number of oxygen vacancies responsible for visible emission, especially at low oxygen ambient pressure. The intensities and quantum efficiencies of these emission mechanisms are discussed in terms of the effect growth and doping conditions have on the underlying excitonic decay mechanisms.

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1. Introduction

Zinc oxide (ZnO) is a II–VI semiconductor whose wide band gap (~ 3.37 eV) and high exciton binding energy (~ 60 meV) make it compelling for ultraviolet optoelectronic device applications [1]. ZnO becomes even more compelling when doped with Al – thereby increasing its intrinsic n-type conductivity – as an alternative to the popular transparent conductor indium tin oxide [2,3]. In addition, growth and characterization of ZnO-based nanostructures have been actively investigated, and several one dimensional (1D) nanoscale devices have been demonstrated [4–8]. In both cases, the most popular means to synthesize these ZnO nanostructures is chemical vapor deposition (CVD) [7,8].

Photoluminescence (PL) spectroscopy may be used to characterize the electronic structure and carrier dynamics of the different forms of ZnO. In addition to UV emission from excitonic recombination near the band edge, a broad visible wavelength (“green”) emission band near 2.4 eV is often observed [3–13]. This green emission band, which is generally associated with oxygen vacancy defect levels and can be stronger than band edge emission in ZnO

nanostructures [4–6,14], is mediated by energy transfer from bound excitons [15]. The strength of the green emission band in ZnO has also been reported to be significantly affected by Al doping [2,3,16–20]. By increasing the Al concentration in Al:ZnO nanofibers, Liu et al. [19] have observed a decrease in the green emission intensity but no change in the UV emission intensity. In studies of Al-doped ZnO films, Sharma et al. [20] found a decrease in green emission compared to the band edge emission, plus a reduction in the grain size that caused nonradiative recombination to increase as the surface to volume ratio increased. By contrast, Shalish et al. have shown that increasing the surface to volume ratio in ZnO nanowires causes green emission to increase and UV emission to decrease [6]. Clearly, the complex dependence of UV and visible emission intensities on Al doping and ZnO nanostructuring is still not well understood, exacerbated by the fact that Al doping can directly affect the optical properties as an n-type dopant and indirectly through the improved binding of oxygen. The latter affects the growth rate and surface-to-volume ratio of the resulting ZnO nanostructure, as well as the intensity of the green emission associated with the number of oxygen vacancies.

Here we report a comparative investigation of the structural and optical properties of undoped ZnO and Al-doped ZnO nanowires grown at different pressures by CVD with different Al concentrations.

* Corresponding author. Tel.: +1 205 348 1764.

E-mail address: patkung@eng.ua.edu (P. Kung).

We observe that UV emission increases and the green emission decreases with increasing Al concentration. This effect is shown to be more pronounced in Al:ZnO nanowires grown at lower oxygen pressure, suggesting more effective Al doping and fewer oxygen vacancies at lower pressure. By exploring the effect of Al doping and oxygen pressure on UV and green emission intensity and quantum efficiency, we explore how the underlying excitonic decay relaxation channels are affected by growth conditions [21].

2. Experimental

The undoped and Al-doped ZnO nanowires were grown by CVD in a horizontal quartz tube furnace following carbothermal reduction process. Samples were grown at two different pressures, 100 and 280 Torr, under a constant 29 sccm flow of an argon carrier gas plus a 1 sccm flow of an oxygen:argon mixture (20% O₂:80% Ar). The source precursor used for undoped ZnO nanowires was a 1.5 g mixture of ZnO and graphite powders with a 1:2 M ratio, and to this mixture were added various amounts of Al powder for the Al:ZnO nanowires. The source material was kept in a quartz boat at the center of a 900 °C furnace for 30 min. Metal catalysts were not used to synthesize the nanowires in order to avoid introducing unintentional metal impurities and degrading device performance. Instead, a ZnO seed layer on c-plane sapphire substrate was deposited prior to loading into the furnace. The procedure of depositing the ZnO seed layer consists of wetting the c-plane sapphire substrate with droplets of 0.005 M zinc acetate dihydrate in alcohol, drying and then oxidizing in air [22]. The nanowire samples grown at high pressure (280 Torr) are denoted by H_u and $H_{0.87}$, while those grown at low pressure (100 Torr) are denoted by L_u , $L_{1.2}$ and $L_{1.8}$. The undoped samples “u” are compared to samples with average Al concentrations of 0.87 at%, 1.2 at% and 1.8 at% as measured by energy-dispersive x-ray spectroscopy (EDS). Salient information about these samples is summarized in Table 1.

Table 1
Structural and optical data for the Al:ZnO nanowires.

Growth pressure (Torr)	Sample name	Al content in source mixture (g)	Nanowire Al concentration (at%)	Nanowire diameter (nm)	Nanowire length (μm)	I_g/I_{uv}
280	H_u	0	0	123 ± 15	9 ± 0.1	77
	$H_{0.87}$	0.5	0.87	181 ± 15	7.9 ± 0.1	24
100	L_u	0	0	87 ± 15	13.8 ± 0.1	53
	$L_{1.2}$	0.5	1.2	67 ± 15	7.1 ± 0.1	2.6
	$L_{1.8}$	1	1.8	41 ± 15	3 ± 0.1	0.74

The nanowires were also characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), photoluminescence (PL), and external photoluminescence quantum efficiency (η) measurements. SEM imaging was carried out using a field emission microscope (JEOL7000F). X-Ray diffraction patterns were measured using a Panalytical X'Pert PRO diffraction system. PL measurements were carried out using a xenon arc lamp excitation source followed by a monochromator tuned to transmit radiation at 350 nm. Following a second grating spectrometer, a liquid nitrogen cooled charge coupled device (CCD) detected the PL. Quantum efficiency measurements were performed under similar conditions using a 10 cm diameter integrating sphere and a method reported elsewhere [23].

3. Results and discussion

SEM images of the five nanowire samples are shown in Fig. 1, and cross-sectional SEM images are shown in the left top corner of each image. The average diameters and lengths of the nanowires are estimated from the images shown in Fig. 1 and listed in the Table 1. Sample H_u contains a bimodal distribution of both thin and thick nanowires, but the average diameter is larger than the L_u nanowires. The length of the sample H_u nanowires is smaller than that of the L_u nanowires. The nanowires grown at lower pressure shrink in diameter as more Al source material is added, but the nanowires grown at higher pressure increase in diameter when Al source material is added. By contrast, the lengths decrease as the Al content increases at a rate that depends on both Al content and growth pressure: the rate is higher for the low pressure L_x nanowires than the high pressure H_x nanowires.

To understand this, consider first the growth mechanism of the undoped nanowires based on a carbothermal reaction at the source (900 °C):

Fig. 1. SEM images of the undoped and Al-doped ZnO nanowire samples. The insets show the corresponding cross-sectional SEM images.

The Zn vapors generated in both reactions oxidize and condense on the ZnO seed layer, catalyzing the growth of the ZnO nanowires. Since metal catalysts are not used, the growth process follows a vapor–solid growth mechanism instead of the conventional vapor–liquid–solid mechanism [7]. In the high growth temperature (900 °C), oxygen poor, low pressure environment, more of the Zn vapors remain unoxidized. As oxygen partial pressure increases, the Zn vapor can more efficiently oxidize to form ZnO [24]. However, the nanowires L_u grown at lower pressure are longer (13.8 μm) than the nanowires H_u grown at higher pressure (9.0 μm). This can be understood by considering the evaporation rate of the source precursor, which is proportional to $(P_v - P)$ according to Langmuir evaporation equation [25], where P_v is the vapor pressure and P is the ambient pressure. Therefore, more source precursor vapor is generated at lower pressure due to higher rate of evaporation, producing taller nanowires. The desorption and re-evaporation rate of Zn vapor is also higher due to low partial pressure of oxygen, thereby limiting the growth in lateral direction at lower chamber pressure and explaining why the average diameter is smaller in L_u than in H_u nanowires. This lower partial pressure of oxygen suggests that the L_u nanowires will have many more oxygen vacancies than the H_u nanowires. The greater length and smaller diameter of the L_u nanowires are another consequences of this growth condition.

The room temperature PL spectra of the undoped ZnO nanowire samples confirm these observations. Fig. 2a reveals the PL spectra contain two emission bands, an UV emission band dominated by excitonic recombination and LO phonon replicas [26], and a green emission band associated with oxygen vacancies [4,11–13]. The decay process of photogenerated excitons follows three primary mechanisms: radiative recombination to emit an UV photon, nonradiative decay (primarily at or near the surface traps), and energy transfer from the band edge to the defect states that activate the green emission [14,15,21]. The quantum efficiency for a given channel x (η_x) is related to the corresponding decay rate k_x ($x = uv, g$):

$$\eta_x = \frac{k_x}{k_{uv} + k_{nr} + k_g} \quad (3)$$

It should be noted that k_g is not the decay rate of the green emission but the rate at which photoexcited excitons activate the green emission. In other words, k_g increases as the number of oxygen vacancies increases.

The quantum efficiency of these samples is very low ($\eta_g < 2\%$, $\eta_{uv} < 0.1\%$), indicating that $k_{nr} \gg k_{uv}$, k_g , a consequence of surface recombination in nanowires with a high surface-to-volume ratio [6,14,21]. The green emission band dominates the UV emission band in both undoped ZnO nanowire samples, suggesting a large number of oxygen vacancies in both samples (i.e. $k_g \gg k_{uv}$). The fact that the L_u nanowires exhibit more green emission than the H_u nanowires confirms the larger number of oxygen vacancies in L_u .

Since the L_u nanowires have smaller diameters, the associated increase in green emission may be ascribed to changes in the near-surface trap density caused by the increased surface-to-volume ratio [6]. The integrated intensity of the UV (I_{uv}) and green (I_g) emission bands for L_u and H_u nanowires were estimated by fitting Gaussian lineshapes. Following the formalism developed in Ref. [6], the relative intensity of these bands

$$\frac{I_g}{I_{uv}} = C \frac{2rt - t^2}{(r - t)^2} \quad (4)$$

depends on nanowire radius r and surface recombination layer thickness t . Fitting the data for the L_u and H_u nanowires gives $C = 2$ and $t = 52$ nm. The coefficient C is greater than one because the

Fig. 2. (a) Room temperature PL spectra of undoped and Al-doped ZnO nanowires excited at 350 nm by a xenon lamp followed by a monochromator. (b) The variation of the integrated UV emission band intensity with Al concentration. (c) The variation of the integrated green emission band intensity and η_g with Al concentration.

green emission efficiency is greater than the UV emission efficiency. For t to be comparable to the radii of the nanowires suggests that oxygen vacancies responsible for green emission are distributed throughout. Unfortunately, Eq. (4) does not fully describe the behavior in the $r \approx t$ regime because it does not predict that the narrower L_u nanowires will generate more UV emission than the larger H_u nanowires. This shortcoming may be partially attributed to the fact that the H_u nanowires were grown under different conditions that produced a broader, bi-modal distribution of diameters. Although η_{uv} was too small to be measured in either undoped sample, it is evident that the low pressure growth environment favors the creation of oxygen vacancies (increasing k_g) and a reduction in the nonradiative decay rate k_{nr} .

When the source precursor includes Al (ZnO:C + Al), both Al and Zn vapors oxidize as they propagate to the seed layer upon which Al-doped ZnO nanowires grow. The boiling point of Al (2467 °C) is much higher than for Zn (907 °C). Consequently, for a given pressure and temperature, the vapor pressure of Al is lower than that of Zn, ensuring a lower concentration of Al_2O_3 than ZnO at the substrate. XRD spectra (not shown) confirm that a separate

phase of Al_2O_3 is not observed in the Al:ZnO nanowires, so Al incorporates as point substitutions and perhaps defect complexes. Since Al is trivalent and Zn is divalent, Al can bond to more O atoms than Zn, and the Al^{3+} ions that occupy Zn^{2+} sites are positively charged ($\text{Al}_{\text{Zn}}^\bullet$ in the Kroger–Vink notation). The commensurate increase in Al:ZnO electron concentration has been reported previously [2,27,28].

The relationship between nanowire length, nanowire diameter, and Al concentration derives from the standard Gibbs free energy for the formation of the associated oxide, which is more negative for Al_2O_3 ($\Delta G = -1582.3$ kJ/mol) than for ZnO ($\Delta G = -320.5$ kJ/mol), and the associated bonding energy, which is larger for Al–O (511 ± 3 kJ/mol) than for Zn–O (159 ± 4 kJ/mol) [3]. As a result, Al more readily oxidizes, affecting the relative ability of Al and Zn to incorporate into the growing Al:ZnO lattice, especially in an oxygen-poor atmosphere.

These effects may be seen by comparing the volumes of the nanowires grown at low and high pressures. The concentration of Al is higher in $L_{1.2}$ nanowires of length $7.1 \mu\text{m}$ than the $H_{0.87}$ nanowires of length $7.9 \mu\text{m}$ for the same 0.5 g of Al precursor. However, the $H_{0.87}$ nanowires have much larger diameters and volumes and contain almost six times as much Al as the $L_{1.2}$ nanowires. Nanowires grown at low pressure (L_x) generally become thinner and shorter as Al percentage x increases for several reasons: Al precursor evaporates at a slower rate than Zn, adding Al to the source reduces the fraction of Zn in the source, and Al vapor oxidizes more rapidly than the Zn vapor. Consequently, the oxidation of Zn vapor is limited, and Zn re-evaporation is enhanced by the low oxygen partial pressure.

By contrast, the H_x nanowires are larger in diameter because the higher oxygen partial pressure allows more of the Zn vapors to oxidize and fewer of the Zn atoms to re-evaporate. In addition, during the growth of the $H_{0.87}$ nanowires, the fraction of Zn able to evaporate from the source is less than for the H_u nanowires due to the addition of Al into the source. As a result, less Zn vapor reaches the substrate than in the case of the H_u nanowires. As such, most of the Zn vapor is able to oxidize and the potential for re-evaporation of Zn is reduced compared to the H_u nanowires. For these reasons, $H_{0.87}$ growth produced no thin nanowires – unlike the bimodal distribution of H_u nanowire diameters – and the thicker nanowires had a much narrower size distribution. This means that the average diameter of $H_{0.87}$ nanowires was larger than that of H_u . Likewise, the increased oxidation of Zn and Al vapors explains why $H_{0.87}$ nanowires have more total Al but lower Al percentage than in $L_{1.2}$ for the same precursor concentration [24].

Most importantly, as the Al concentration increases, these arguments predict that the number of oxygen vacancies will decrease. Given that nanowire length, diameter, and green emission for undoped ZnO are related to the number of oxygen vacancies, the length, diameter, and green emission of Al:ZnO nanowires will similarly depend on the number of oxygen vacancies, determined by the relative abundance of Al (i.e. doping concentration) and O (i.e. pressure) during growth.

Again, the PL spectra confirm these expectations. Fig. 2b and c plot I_{uv} and I_g as a function of Al concentration. Note the decrease in I_g with increasing Al concentration for samples grown at both pressures, confirming a recent report by Liu et al. on Al:ZnO nanofibers [19]. Clearly the addition of Al reduces the number of oxygen vacancies as it slows the longitudinal growth rate of the nanowires. Notice as well that I_g and nanowire lengths are more sensitive to Al concentration for the lower pressure samples than for the higher pressure samples. Table 1 indicates that the decrease in growth rate is $\sim 1/30 \mu\text{m}/\text{min}/x$ for the H_x nanowire lengths and $\sim 6/30 \mu\text{m}/\text{min}/x$ for the L_x nanowire lengths, again correlated with the number of oxygen vacancies. Recall that nanowire diameter is determined by Zn desorption and re-

evaporation. At the same time, oxygen vacancies are mostly derived from breaking the weaker Zn–O bonds. Although the diameter of the L_x nanowires decreases with increasing Al concentration, the number of oxygen vacancies and green emission also decreases because the Al–O bond is stronger, which efficiently binds oxygen atoms to the lattice. For the same reason, even though the average H_x nanowire diameter increases with increasing Al concentration, the number of oxygen vacancies and green emission still decreases, albeit at a slower rate indicating less effective Al doping in H_x nanowires than in L_x nanowires.

The way η_g and I_g depend on Al concentration is similar (Fig. 2c). To understand this, we must first consider the UV emission. In contrast with the green emission, the UV emission intensity I_{uv} increases with increasing Al concentration. This is a natural consequence of the decreasing number of oxygen vacancies, causing k_g to decrease and η_{uv} to increase with increasing Al doping. The question is whether there is a simultaneous change in k_{nr} ; in other words, does Al doping change the number of nonradiative recombination sites too? If the increase in I_{uv} matches the decrease in I_g , then total emission and k_{nr} remains a constant, and all that is changing is the size of k_g (i.e. the number of oxygen vacancies). This is precisely what happens from L_u to $L_{1.2}$. However, from $L_{1.2}$ to $L_{1.8}$, the UV emission strength more than doubles while the integrated green emission intensity and η_g drop by less than 35%. Similar behavior is observed from H_u to $H_{0.87}$.

Together, these observations indicate that as more Al is incorporated during L_x and H_x nanowire growth, k_{nr} decreases faster than k_g , suggesting that nonradiative recombination is reduced even more than green emission with increasing Al doping. Note that this contradicts the predictions of Eq. (4) that I_g should increase and I_{uv} decrease as nanowire diameter decreases. Since Al prevents the formation of oxygen vacancies, the contradiction must be ascribed to the role played by Al in decreasing k_g and especially k_{nr} . It is unclear whether Al prevents the formation of nonradiative recombination centers or whether the increasing number of Al-contributed electrons in this n-type material may mitigate nonradiative recombination. Further study is required to understand in detail.

4. Conclusions

In conclusion, we have studied the effect of growth pressure on structural and optical properties of Al:ZnO nanowires. We have observed that the Al doping is more effective during low pressure growth to reduce the number of oxygen vacancies and the associated green emission intensity. As the concentration of Al dopants increases, the UV emission increases at a rate faster than the green emission decreases, indicating that Al additionally reduces the rate of nonradiative recombination, perhaps by increasing the number of electrons and/or by decreasing the number of nonradiative traps.

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