

Photoluminescence of Ag-doped ZnSe nanowires synthesized by metalorganic chemical vapor deposition

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Photoluminescence of Ag-doped ZnSe nanowires synthesized by metalorganic chemical vapor deposition is investigated in the temperature range from 10 to 300 K. Ag impurities were introduced into the ZnSe nanowires during the growing process. Some dominating Ag-related centers are found. Especially, the strong zero-phonon bound exciton luminescence with energy near 2.747 eV is attributed to a neutral Ag_{Zn} acceptor complex. This is because the emission peak at the same energy is observed only in the photoluminescence spectrum of the Ag-doped bulk ZnSe. A new luminescence peak at 2.842 eV is attributed to the recombination of excitons bound to ionized acceptors (I_2^h) in the hexagonal phase of ZnSe nanowires. The physical origins of the emissions are briefly discussed. © 2005 American Institute of Physics. [DOI: 10.1063/1.1931828]

The wide-band-gap semiconductor ZnSe has attracted much attention due to its potential applications in UV light-emitting devices. Studies on epilayers,¹ two-dimensional structures, like quantum wells,² and zero-dimensional quantum dots³ have seen some significant progresses. Recently, one-dimensional (1D) nanometer-sized semiconductor structures in the forms of nanowires and nanoribbons have also been successfully synthesized.^{4–6} However, studies on photoluminescence (PL) of 1D structure have been rather scarce up to now, although luminescence properties are very important for their future applications. As dimensions get smaller, surface states and internal defects become more detrimental to the radiative recombination processes of carriers. Experimentally, it becomes more difficult to observe the near-band-edge (NBE) PL from the 1D nanomaterials.^{5,6} We present in this letter the PL of Ag-doped ZnSe nanowires, grown via the metalorganic chemical vapor deposition (MOCVD) route, in the temperature range from 10 to 300 K. Emission peaks related to Ag impurities are found in the PL spectra, and a new emission peak at an energy 2.842 eV, higher than the band gap of zincblende structured ZnSe, is found at 10 K. The physical origins of PL emission peaks are discussed with reference to their temperature dependence, and the dynamic processes that give rise to this dependence are also investigated.

The Ag-doped ZnSe nanowire samples studied in this work were grown using the MOCVD system on Si (100) substrates. Colloidal Ag nanoparticles (average diameter, ~10 nm) were dispersed on Si substrates as catalysts. Details of the growth and surface morphology of the ZnSe nanowires can be found elsewhere.⁴ Ag impurities were introduced into the ZnSe nanowires during growing. The PL measurements were performed using the 325 nm line of a He–Cd laser as the excitation source.

Figure 1 shows a typical PL spectrum of the ZnSe nanowires at 10 K. The spectrum is clearly dominated by six emission peaks centered at 2.842, 2.779, 2.747, 2.712, 2.60, and 2.273 eV. It is noted that there are some shoulders ac-

companying the peaks. The inset of Fig. 1 shows an enlarged view of the NBE PL spectrum. The peak at 2.779 eV is associated with recombination of excitons bound to substitutional acceptor (Ag_{Zn}) complex (I_1^{Ag}).⁷ From its peak position, the binding energy ($E_{\text{ex}}=18$ meV) of the free exciton (FX),⁸ and the accepted band gap energy of 2.820 eV (E_g) at 10 K,⁸ an estimation of the activation energy of (Ag_{Zn}) acceptor complex gives the value of $E_A(\text{Ag}_{\text{Zn}})\approx 0.23$ eV, according to an empirical ratio $E_A=10E_B$,⁹ where $E_B\approx E_x - I_1^{\text{Ag}}$ is the binding energy of acceptor-bound exciton, E_x (2.802 eV) is the radiation energy of FX. Reference 7 reported $E_A(\text{Ag}_{\text{Zn}})$ to be 0.24 eV. The 2.747 eV peak ($I_1^{*\text{Ag}}$) is identified as exciton bound to $\text{Ag}_i\text{Ag}_{\text{Zn}}$ acceptor complex.^{7,10–12} Holtz *et al.*¹⁰ observed an analogous PL band at 2.747 eV in bulk ZnSe:Ag, and Tournie *et al.*¹² suggested that the emission peaks at 2.747 and 2.712 eV are observed only in ZnSe:Ag, but not in pure ZnSe. The emission intensity centered at 2.712 eV ($I_1^{**\text{Ag}}$) is significantly higher than that of $I_1^{*\text{Ag}}$ band (2.747 eV). Thus we think that the $I_1^{**\text{Ag}}$ peak probably is not the phonon replica of the 2.747 eV peak, although the energy separation between them is near the LO-phonon energy ($\hbar\omega_{\text{LO}}=31.8$ meV), while it might result from the Ag impurity associates. An analogous peak (2.710 eV) was reported by Ivanova *et al.* in the ZnSe:Ag.¹¹

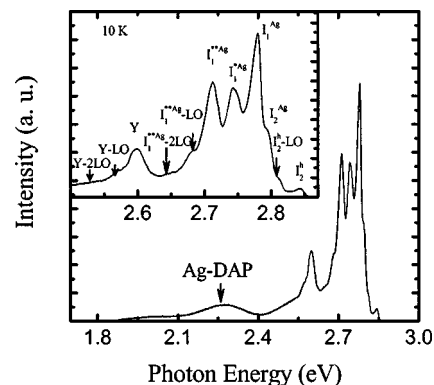


FIG. 1. Photoluminescence spectrum of a MOCVD-grown Ag-doped ZnSe nanowires at 10 K. (Inset) Enlarged view of the near-band-edge emission peaks.

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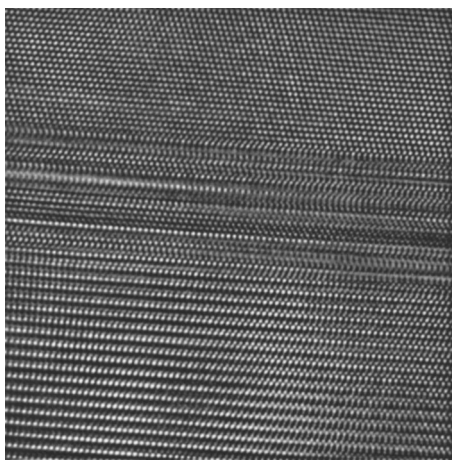


FIG. 2. High-resolution transmission electronic microscopy image of ZnSe nanoribbons synthesized by MOCVD.

The donor-acceptor pair (DAP)¹⁰ is responsible for the luminescence band at 2.27 eV, although this value is 0.04 eV higher than that in Ref. 10, due to an overlap of DAP luminescence from both cubic and hexagonal structured ZnSe (see the text). The shoulders centered at 2.682 and 2.652 eV could be the phonon replica of the 2.712 eV peak, as the energy separation between these peaks is identical to the LO phonon energy. The PL band centered at 2.60 eV originates from the Y-line luminescence.¹³ These shoulders centered at ~ 2.568 and 2.537 eV are the phonon replicas of this peak. The shoulder at 2.796 eV is associated with the recombination of excitons bound to interstitial donor $\text{Ag}_i(I_2^{\text{Ag}})$,^{7,10} which falls in the region of I_2 line in pure ZnSe. It is unlikely that the 2.842 eV peak originates from contamination-related recombinations in cubic ZnSe, because 2.842 eV is far higher than bulk cubic band-gap energy. In addition, this higher energy peak could not be a result of the quantum confinement effect in nanowires, since their average diameter is about ~ 80 nm. In our judgment, this emission is due to recombination of exciton bounds to ionized acceptors in the hexagonal-structured ZnSe (I_2^h),¹⁴ because there are some nanoribbons that co-exist with the nanowires in the synthesized product. The high-resolution transmission electron microscopy result, shown in Fig. 2, proves that both cubic and hexagonal phases coexist in the nanoribbons. The emission peak (I_2^h -LO) at 2.810 eV is assigned to the phonon replica of I_2^h , because its energy is lowered by ~ 32 meV.

Figure 3 shows the typical PL spectra of the nanowires at selected temperatures. Although the overall intensity of the

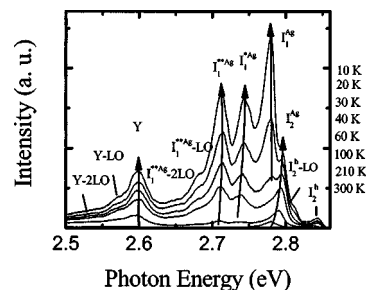


FIG. 3. PL spectra of ZnSe:Ag nanowires at different temperatures.

peaks decreases with increasing temperature, the intensity ratio of I_2^{Ag} to I_1^{Ag} quickly increases. I_2^{Ag} peak becomes stronger than the I_1^{Ag} peak at 30 K. Finally I_1^{Ag} peak disappears at about 60 K. However, the I_2^{Ag} peak can still be clearly observed at room temperature. The dependences of the peak energies of I_1^{Ag} , I_2^{Ag} , and I_2^h on temperature are shown in Fig. 4. The solid circles denote the experimental data for the I_2^{Ag} (Ag_iX) peak. The solid curve is obtained by fitting the Varshni's formula to the experimental data:¹⁵

$$E(T) = E(0) - \frac{aT^2}{b + T}, \quad (1)$$

where $E(0)$ is an exciton energy at $T=0$ K, a and b are constants, and T is temperature. The best fit gives a and b of 7.3×10^{-4} eV K⁻¹ and 303 ± 9 K, respectively. These values are in agreement with that of Ref. 16. Above 240 K, I_2^{Ag} peak energy deviates from the solid line, which should be attributed to thermal activation from an Ag_iX exciton to a FX and an Ag_i^+ ionic center. The dotted curve in Fig. 4 represents a fit by setting $E(0)=2.802$ eV to FX peak energy using the previous values of a and b . We note that the dotted curve is in rough agreement with the experimental data of I_2^{Ag} in the higher temperature range. Wang and Yoon also obtained a similar result in Ga-doped ZnSe,¹⁷ indicating that finally, the I_2^{Ag} peak will be replaced with the FX transition peak at higher temperature. Further, the evidences that support the peak at 2.842 eV is from the recombination of the excitons in the hexagonal phase are the almost linear dependence of the peak intensity, but not the energy, on the incident power (not shown) and the best fit to the experimental data gives a and b of 9.4×10^{-4} eV K⁻¹ and 317 K.

Figure 5 shows the temperature dependence of the integrated PL intensity of the Ag_iX peak (I_2^{Ag}). A three-step quenching process is employed to fit our experimental data

$$I = \frac{I_0}{1 + C_1 \exp(-E_a^1/k_B T) + C_2 \exp(-E_a^2/k_B T) + C_3 \exp(-E_a^3/k_B T)}, \quad (2)$$

where I_0 , C_1 , C_2 , and C_3 are constants, and E_a^1 , E_a^2 , and E_a^3 are activation energies, and k_B is the Boltzmann's constant. This formula describes the dissociation processes of bound excitons. The solid line is the best fit to the experimental data. It yields activation energies 6, 28, and 136 meV, correspond-

ingly. The dotted line is the best fit to the experimental data below 150 K, when only two nonradiative mechanisms are considered, i.e., by setting C_3 to zero in Eq. (2). The deviation of this model from the experimental data at moderately low to room temperature could be attributed to the need of

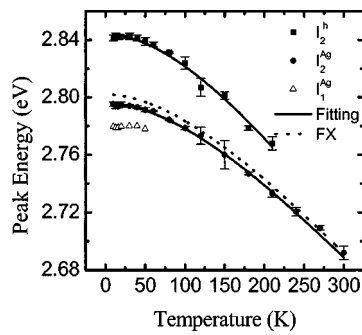


FIG. 4. The temperature dependence of the PL peak positions of the I_1^{Ag} , I_2^{Ag} , and I_2^{h} emissions. The solid curves are the best fits to the experimental data of the I_2^{Ag} and I_2^{h} energy, using Eq. (1). The dotted curve represents the fit by setting $E(0)=2.802$ eV to free-exciton peak energy, and using the same values of a and b as in the solid curve.

another nonradiative mechanism with an activation energy of $E_a^3=136$ meV. These fitting results confirm that the quenching of I_2^{Ag} peak involves three nonradiative processes. The first quenching process is suggested as the dissociation of Ag_i donor-bound excitons, the second is associated with the thermal ionization of Ag_i donors into FXs and Ag_i^+ ions. This is because $E_B(\text{Ag}_i\text{X})=E_x-I_2^{\text{Ag}}=6$ meV, $E_D(\text{Ag}_i)\approx 5E_B=30$ meV,¹¹ where $E_B(\text{Ag}_i\text{X})$ and $E_D(\text{Ag}_i)$ denote the binding energies of Ag_iX bound-exciton and the ionization energy of Ag_i donor, respectively. The real origin of the third quenching process is not clear at this moment. We suspect that as the temperature increases further, the neutral residual acceptor atoms (A^0) are thermally ionized into A^- ionic centers. The Ag_iX bound-excitons might be scattered by A^- ionic centers, forming a third quenching mechanism.¹⁷ We have also studied the excitation power dependence of the intensities of the peaks. A linear dependence were observed for the peaks, in particular for the I_2^{h} and I_2^{Ag} peaks (data not shown), within the varied power range (0.4–10 mW, focused to a circular spot of about 20 μm radius).

In conclusion, photoluminescence of Ag-doped ZnSe nanowires grown by MOCVD was investigated at temperatures range from 10 K to room temperature. The emission peak (I_2^{Ag}) at 2.796 eV is attributed to originate from the recombinations of the interstitial Ag bound excitons. The thermal quenching of I_2^{Ag} involves three dissociation processes. A new emission peak at 2.842 eV is identified as the recombination of the excitons bound to ionized acceptors (I_2^{h}) in the hexagonal phase of ZnSe nanoribbons.

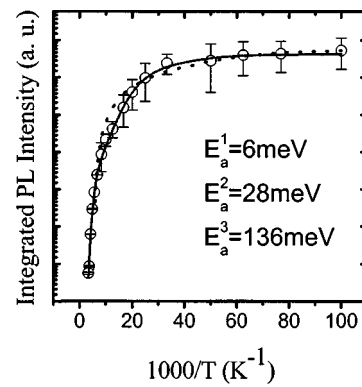


FIG. 5. The temperature dependence of the integrated PL intensity of the Ag_iX emission peak (I_2^{Ag}). The solid line denotes the best fit to the experimental data (\circ), using Eq. (2) and the dotted line represents the best fit to the data below 150 K, by setting C_3 to zero in Eq. (2).

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