Novel photoluminescence properties of $InAlO_3(ZnO)_m$ superlattice nanowires*

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One-dimension $InAlO_3(ZnO)_m$ superlattice nanowires were successfully synthesized via chemical vapor deposition. Transmission electron microscopy measurements reveal that the nanowires have a periodic layered structure along the ⟨0001⟩ direction. The photoluminescence properties of $InAlO_3(ZnO)_m$ superlattice nanowires are studied for the first time. The near-band-edge emissions exhibit an obvious red shift due to the formation of the localized tail states. The two peaks centered at 3.348 eV and 3.299 eV indicate a lever phenomenon at the low-temperature region. A new luminescence mechanism is proposed, combined with the special energy band structure of $InAlO_3(ZnO)_m$.

Keywords: $InAlO_3(ZnO)_m$, superlattice nanowires, photoluminescence, energy band structure

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1. Introduction

Transparent oxide semiconductors (TOSs) have attracted much attention due to their potential application in fabricating electronic and optoelectronic devices.[1−4] In particular, ZnO-based TOSs, such as $InMO_3(ZnO)_m$ (M = In, Ga, Fe, Al) superlattice nanostructures, have attracted considerable interest. The band gap of such superlattice nanostructures is larger than 3 eV,[5] which is suitable for short-wavelength lasers. Many groups have paid attention to the synthesis of superlattice nanostructures, which could greatly increase the versatility and power of the material for nanoscale electronic and nanoscale photonic applications. Studies on $In_2O_3(ZnO)_m$ superlattice nanowires (NWs),[6] indium–zinc–oxide superlattice nanobelts,[7] and homologous compound $InGaO_3(ZnO)_m$[8] have gained significant progresses. Recently, one-dimension $InAlO_3(ZnO)_m$ (IAZO) NWs have been successfully synthesized.[9] However, discussion on the optical properties of IAZO is rare up to now. In this paper the photoluminescence (PL) properties of IAZO superlattice NWs are investigated for the first time. We measured the PL of IAZO superlattice NWs grown via the chemical vapor deposition route in the temperature range from 14 K to 250 K. A new luminescence mechanism is proposed, combined with the special energy band structure of IAZO.

2. Experiment method

IAZO superlattice NWs were grown via chemical vapor deposition. Firstly, Au thin films were sputtered on Si substrates. The mixture of ZnO, In and Al powders was placed in an alumina boat, and the Si substrates were placed at the downstream of the mixture. Then, the boat was put into an alumina tube, which was inserted into a furnace. The mixture was kept at the center of the furnace. The furnace was heated to 1000 °C in 40 min and kept there for 2 min under a N_2 flow of rate 200 sccm. The pressure was kept at 500 Pa, and the furnace was sequentially heated to 1300 °C in 20 min, held there for 20 min. The furnace was naturally cooled to room temperature. The synthesized products were characterized by using scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM PHILIPS Tecnai 20) equipped with an energy dispersive X-ray (EDX) spectrometer. PL spectra were measured using the 325-nm line of a He–Cd laser as the excitation source.

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3. Results and discussion

A typical SEM image of the samples is shown in Fig. 1. High-density NWs are clearly seen on the substrate in the image. The length of the NWs is about ten μm and the diameter is estimated to be several tens of nanometers.

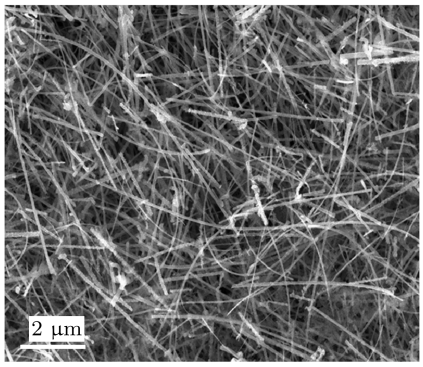
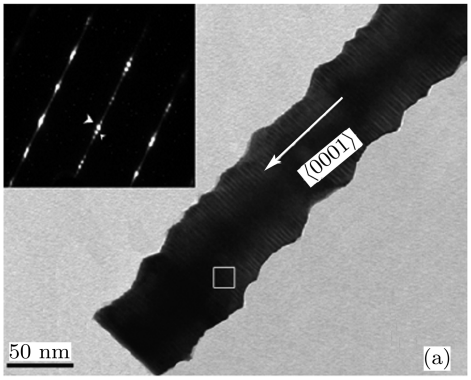


Fig. 1. SEM image of $InAlO_3(ZnO)_m$ superlattice nanowires.

In order to clearly observe their surface morphology, the low-magnification TEM image of the NWs was taken along the $\langle 10\bar{1}0\rangle$ zone axis, and is shown in Fig. 2(a). The image shows that the NW has a periodic layered structure along the growth direction. The formation of the periodic nanostructure may originate from the relaxation of lattice strain inside NWs.[10] The superlattice, in which the dark contrast corresponds to the InO_2^- layers and the bright contrast corresponds to the $AlO(ZnO)_m^+$ blocks, is typical for an IAZO system.[9] The inset of Fig. 2(a) is the selected area electron diffraction (SAED) pattern of the NW, which shows a series of satellite diffraction spots (as marked by small arrow) between the two adjacent main diffraction spots (as marked by big arrow). The low-magnification TEM result and the SAED pattern both indicate that the NWs have a superlattice structure. The EDX spectrum (shown in Fig. 2(b)) taken from the labeled region in Fig. 2(a) confirms that these NWs are indeed composed of In, Al, Zn and O with an atomic ratio of 2.5 : 0.8 : 39.0 : 57.7. The Cu signal comes from the TEM grid.

In order to investigate the PL properties of the superlattice NWs, the PL spectra were measured as a function of temperature. Figure 3 shows a typical low-temperature PL spectrum, which consists of a broad and weak visible emission band and multi-ultraviolet (UV) emission peaks. According to the ZnO PL mechanism, the visible emission band could be associated with oxygen defects. The prominent UV emission peaks center at 3.228 eV, 3.299 eV (denoted by I_1), and 3.348 eV (denoted by I_2). The peak centered at 3.228 eV is the longitudinal optical (LO) phonon replica of the peak centered at 3.299 eV and is denoted by I_1-LO. As the energy difference between the two peaks is 71 meV, which is approximately equal to the LO phonon energy of 72 meV in ZnO.



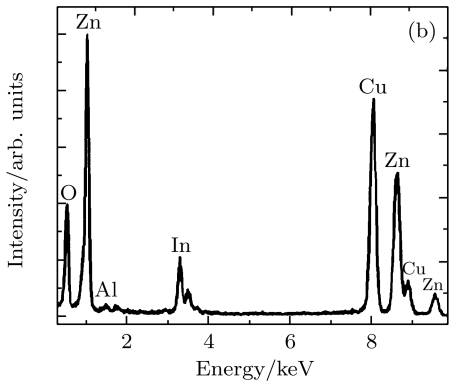


Fig. 2. (a) The low-magnification TEM image of a $InAlO_3(ZnO)_m$ nanowire. The inset is the selected area's electron diffraction pattern. (b) EDX spectrum.

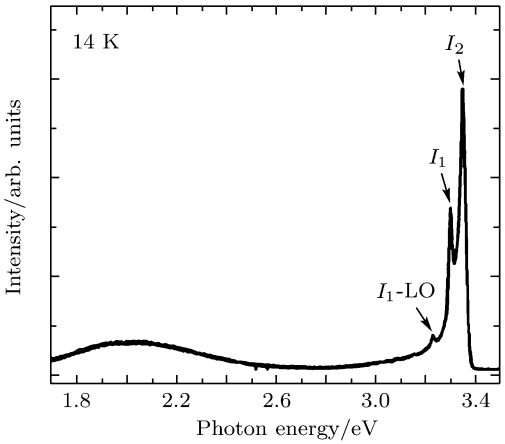


Fig. 3. The low-temperature PL spectrum of $InAlO_3(ZnO)_m$ superlattice nanowires at 14 K.

Naghavi *et al.*[11] studied the optical characters of In_2O_3–ZnO thin films and concluded that the optical band gap (E_g) can be estimated by the atomic ratio of Zn to Zn + In. When $0.82 \leq Zn/(Zn+In) \leq 1$,

$E_g \approx 3.37$ eV, the crystal has a wurtzite structure. In our experiment, the atomic ratio Zn / (Zn + In + Al) is ~ 0.92. So we deduce that $E_g \geq 3.37$ eV for the IAZO superlattice NWs. In the present experiment, the highest energy peak I_2, which is the near-band edge (NBE) emission of IAZO superlattice NWs, shows an obvious red shift (≥ 22 meV) at 14 K compared to 3.37 eV. The red shift is caused by the formation of localized band tail states (see text below). Figure 4(a) presents the UV PL spectra from 14 K to 250 K for the IAZO superlattice NWs. All the peaks show a red shift with increasing temperature due to the shrinkage of the band gap. In order to study the luminescence properties of I_1 and I_2, the temperature dependence of the peak energy is shown in Fig. 4(b). The solid squares and the solid circles denote the experimental data. The solid curves are obtained by fitting the experimental data with the Varshni's formula:

$$E(T) = E(0) - \frac{\alpha T^2}{\beta + T}, \tag{1}$$

where T is temperature, $E(0)$ is the energy at $T = 0$ K, α is a temperature coefficient and β is a constant. The best fit of peak I_1 gives $\alpha = 7.1 \times 10^{-4}$ eV$\cdot$K^{-1} and $\beta = 938$ K. That of peak I_2 gives $\alpha = 7.1 \times 10^{-4}$ eV$\cdot$K^{-1} and $\beta = 876$ K. These features indicate that the NBE emissions, I_1 and I_2, have the same photoluminescence nature. From 14 K to 60 K, the peak I_2 dominates the UV spectrum. With temperature increasing to 80 K, the peak I_1 begins to dominate, while the peak I_2 simultaneously reduces. This so-called lever phenomenon may result from the special IAZO superlattice band structure.

In order to explain the above observations, we propose an energy band model of IAZO based on the model suggested by Zhang *et al.*[5] Nomura *et al.* proposed that a random distribution of Ga^{3+} and Zn^{2+} ions in the $GaO^+(ZnO)_5$ slab of $InGaO_3(ZnO)_5$ thin films would modulate the electronic structure around the conduction band edge and lead to a statistical distribution of localized potential tail states just below the conduction band edge.[12] In a similar way, the random distribution of Al^{3+} and Zn^{2+} ions in the (Al/Zn–O) blocks of IAZO could lead to the statistical potential tail states, forming different well depths and potential barriers. Combined our PL data with the known band structure,[12] the band structure is considered to be composed of two kinds of potential wells and a barrier, as shown in Fig. 5. One represents the deeper wells and the other represents the shallower wells. Based on the energy band model, a new luminescence mechanism is proposed. The large thermionic electron emission might happen with the increase of the temperature. These thermionic electrons are scattered and then hop into the deeper wells. There would be more electrons in the deeper wells to take part in radiative recombination, which results in the enhancement of I_1 and the reduction of I_2.

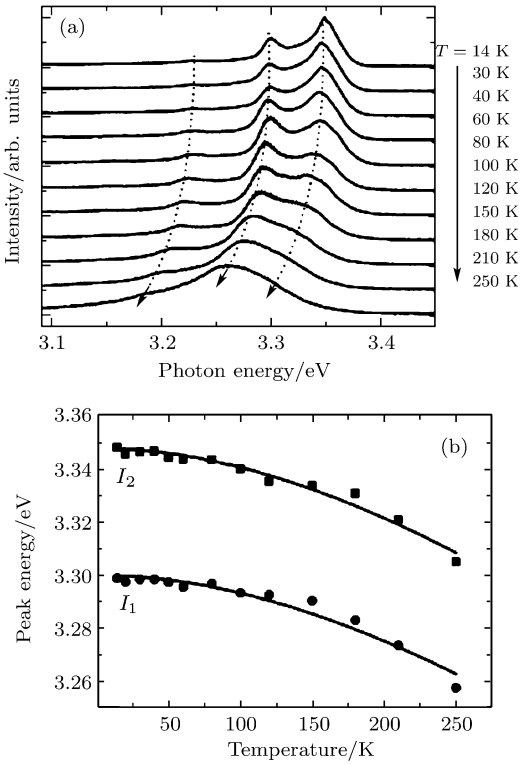


Fig. 4. (a) PL spectra as a function of temperature for $InAlO_3(ZnO)_m$ superlattice nanowires in the UV range. (b) The peak energies (solid circles and solid squares) of I_1 and I_2 at different temperatures. The solid lines denote the fitting results using Vashni's formula.

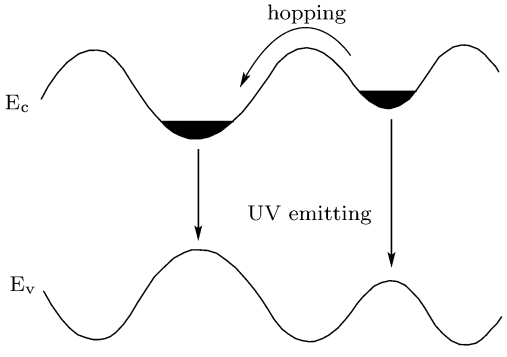


Fig. 5. A model of energy band for $InAlO_3(ZnO)_m$.

4. Conclusion

In conclusion, TEM results and the SAED patterns confirm that one-dimension $InAlO_3(ZnO)_m$ superlattice NWs are successfully synthesized. The

near-band edge emissions from the $InAlO_3(ZnO)_m$ superlattice NWs exhibit an obvious red shift due to the localized potential tail states. The lever phenomenon for I_1 and I_2 at the low-temperature region is attributed to thermionic electrons hopping into the deeper wells with the increasing temperature.

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