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Temperature dependence of surface plasmon mediated near band-edge emission from Ag/ZnO nanorods

Y P Liu¹, Y Guo^{1,4}, J Q Li¹, M Trunk², A Yu Kuznetsov², J B Xu³,
Z X Mei¹ and X L Du^{1,4}

¹ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

² Department of Physics, University of Oslo, PO Box 1048 Blindern, NO-0316 Oslo, Norway

³ Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong

E-mail: yangguo@aphy.iphy.ac.cn and xldu@aphy.iphy.ac.cn

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Abstract

Surface plasmon (SP) mediated near band-edge emission in Ag/ZnO nanorods has been systematically studied by using a temperature-dependent photoluminescence spectra technique. It was found that the mediation mainly concerns SP couplings with two emissions, one from neutral donor-bound exciton D^0X recombination and another from the radiative transition of free electron to neutral acceptor (e, A^0). The first coupling process is demonstrated to prevail in the temperature range from 300 to 150 K, while the second is dominant below 150 K. The competition mechanism and the role of exciton and carrier delocalizations in the coupling processes have been explored in the unique Ag/ZnO nanostructures.

Keywords: ZnO nanorods, MBE, surface plasmon, photoluminescence

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, surface plasmon (SP) induced light emission enhancement in wide bandgap materials, such as ZnO and GaN, has been attracting more and more attention [1–6]. The amplification of near band-edge emission (NBE) both in InGaN quantum wells and in ZnO film has been simply achieved by using a silver cap layer [1, 2]. This emission enhancement phenomenon originates from the high spontaneous recombination possibilities of SP modes coupled with radiative dipoles on the metal/semiconductor interface, which mainly depend on the SP density of states (DOS) and numbers of delocalized exciton or carrier pairs in the semiconductor [5, 6]. The energy transfer between SP and photonic modes readily occurs, if phase matching conditions are well satisfied on the boundary. Thus the SP effect is an effective method to enhance light emissions and improve the quantum efficiency of optoelectronic semiconductor devices.

The SP effect becomes more obvious in metal/dielectric nanostructures due to the large surface-to-volume ratio and the high spatial confinement of SPs [7–12]. It is well known that the localized SP plays an important role in surface-enhanced Raman spectroscopy and nanophotonic devices [8, 9]. Very recently, Bergman and Stockman proposed a new concept of quantum SP amplification by stimulated emission of radiation (SPASER), where a coherent high-intensity field can be generated in a spatial size much smaller than the wavelength [10, 11]. This idea has triggered extensive and exciting studies aiming for a new nanolaser based entirely on surface plasmons. In 2009, Noginov *et al* demonstrated the stimulated emission of SPs in a luminous mode with a 531 nm wavelength by using a hybrid Au nanoparticle encapsulated in silica spheres with a diameter of 44 nm [12]. A following work pushed the SPASER nanolaser towards a shorter wavelength (489 nm); this was composed of a hybrid CdSe semiconductor nanowire separated from a flat Ag substrate by a 5 nm thin dielectric MgF₂ layer [13]. To explore a novel SPASER with

⁴ Authors to whom any correspondence should be addressed.

much shorter wavelength and higher performance, ZnO is a promising candidate considering its direct wide bandgap of 3.37 eV (370 nm) and high exciton binding energy of 60 meV at room temperature. Although in the past few years a lot of results have been demonstrated concerning both the fabrication of various ZnO nanostructures and the investigation of their properties, to our knowledge there are very few studies on the SP effect on mediating the emission behaviour of metal-capped ZnO nanostructures [14, 15], not to mention the mediation on the near band-edge emission (NBE). It would be a fundamental but important topic in exploring the possible applications of ZnO nanostructures in a new SPASER.

In this contribution, we report the temperature dependence of surface plasmon mediated NBE from Ag-capped ZnO nanorods grown by using a catalyst-driven molecular beam epitaxy (MBE) method, keeping thin film samples as a reference. It is found that there are two temperature-dependent SP coupling processes with neutral donor-bound excitons and radiative dipoles of free electron to neutral acceptor in Ag-capped ZnO nanorods, respectively. We demonstrate that the factor of exciton and carrier delocalization in ZnO nanorods plays a key role in determining the competition between two different SP coupling processes.

2. Experimental details

The catalyst-driven MBE growth of ZnO nanorods was performed in a radio-frequency plasma assisted MBE chamber which was used for the growth of single crystal ZnO films in our previous studies [16]. Briefly, after deposition of a catalyst seed layer of 20 nm thin Ag film on Si(111) substrate at room temperature, site-selective nucleation and growth of ZnO are achieved on Ag/Si substrate at a temperature of 450 °C. Two samples are used in the present studies. One is a sample of ZnO nanorods/Si substrate where the oxidation source is high purity oxygen gas while the other is a reference sample of ZnO film/Si substrate and the oxidation source is high purity oxygen radicals produced by an rf-plasma generator (SVTA). Except for the oxidation source other growth conditions were kept the same for both samples. After growth, the morphology of these samples was characterized by a field emission scanning electron microscopy (FE-SEM). Temperature-dependent photoluminescence (PL) measurements were performed using a continuous wave He-Cd laser with 325 nm wavelength as the excitation source.

3. Results and discussion

In order to prepare Ag/ZnO nanorod/Si heterostructure for the studies of SP effect, an Ag catalyst seed layer was *in situ* deposited on Si(111) substrate in an MBE chamber. Figure 1(a) shows the morphology of the Ag layer containing Ag nanoparticles with an average size of ~20 nm. Our previous studies have demonstrated that the size and density of Ag particles can be delicately controlled by the growth temperature and deposition time [17]. Here, we find that the Ag particle size plays a key role in determining the size of the consequent ZnO nanorod grown by the Ag catalyst-driven

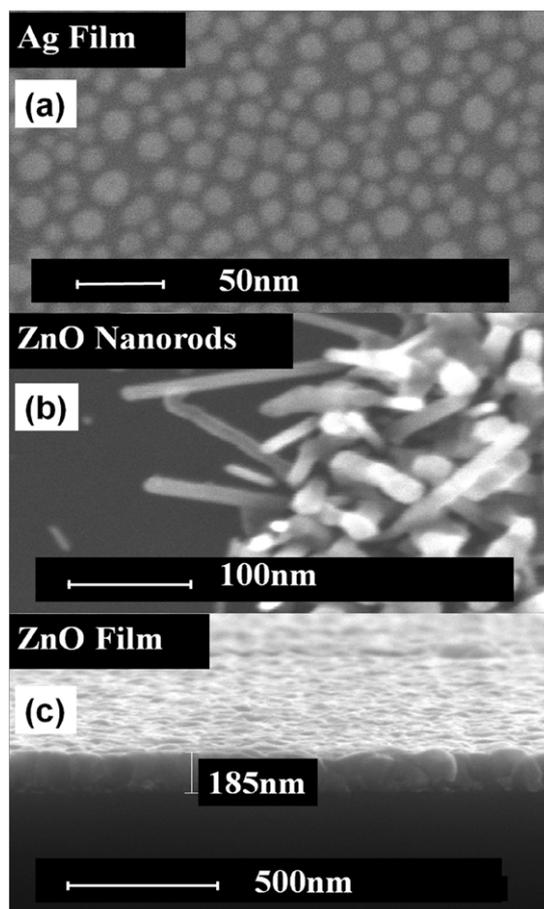


Figure 1. FE-SEM images of (a) the catalyst seed layer of 20 nm thin Ag film, (b) ZnO nanorods and (c) ZnO film.

method. It is well known that at the initial growth stage AgO_x will be formed firstly because of the oxidation of Ag particle by oxygen molecules, and then the arriving Zn atoms will diffuse into the AgO_x and react with it to form ZnO. Finally, the ZnO nanorod was formed with the Ag particle coating on the top, which was clearly evidenced by using transmission electron microscopy characterizations [18]. Figure 1(b) is an FE-SEM image of the Ag/ZnO nanorod sample, illustrating ZnO nanorods with an average diameter of ~15 nm and length of 180 nm. In contrast, ZnO film, not ZnO nanorods, is obtained if a radical oxygen source is adopted, because the growth of ZnO film can be easily achieved without Ag catalysis (figure 1(c)). In that case, the Zn is oxidized directly by the active oxygen atoms instead of robbing oxygen from AgO_x ; hence AgO_x is buried under the continuous ZnO film. This film sample has a thickness of ~185 nm, and a different structure of ZnO/ AgO_x /Si from that of the ZnO nanorods sample with the structure of Ag/ZnO/Si.

It should be noted that a ZnO nanorod sample without the presence of the metallic structure would make the comparison of emission spectra and the influence of surface plasmon more convincing. However, it is very difficult to grow ZnO nanorods on Si(111) without an Ag catalyst by the MBE technique, because the adsorption of Zn atoms on a Si(111) surface at

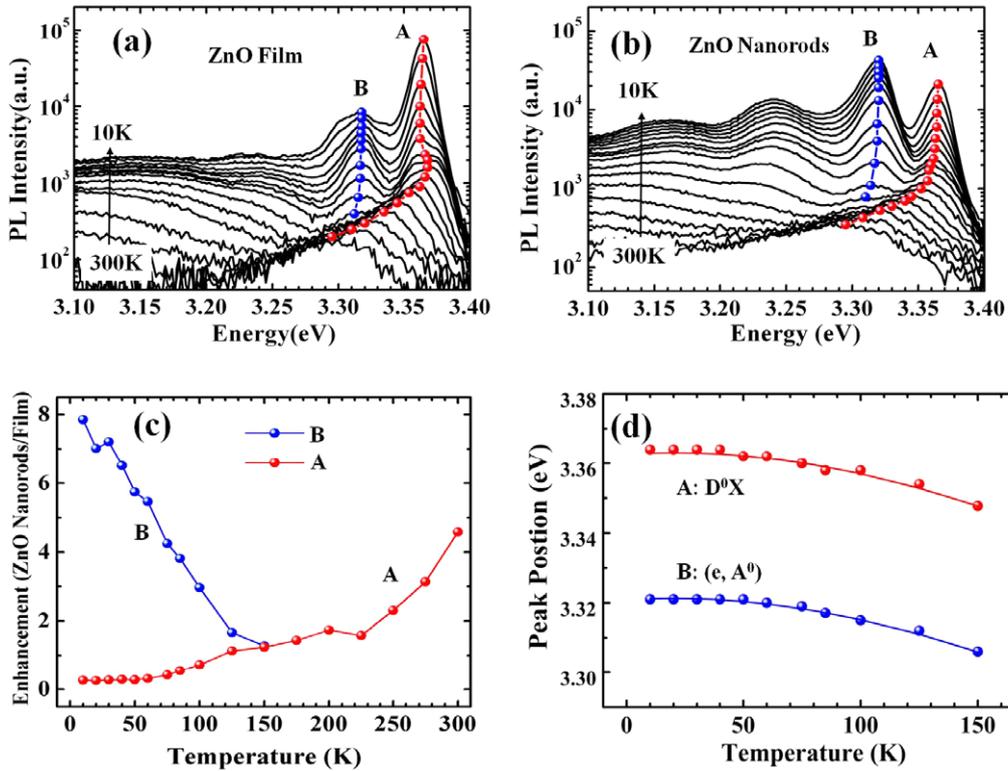


Figure 2. Temperature-dependent PL spectra of (a) ZnO film and (b) ZnO nanorods from 300 to 10 K. The peaks of NBE are labelled as A (red balls) and B (blue balls). (c) Temperature dependence of the enhancement factor of the integrated PL intensities of NBE from ZnO nanorods over that from ZnO film. (d) Experimental and fitting curves of the PL peak positions of the A line and the B line as a function of temperature.

the growth temperature is too low to nucleate, which is the key factor for ZnO nanorod growth [19]. If we synthesis the nanorods by using other methods instead of MBE, some unknown impurities will be introduced. In that case, the impurities will definitely have an influence on the PL spectra, which makes the comparative study more complicated. To exclude this unwanted influence, both ZnO nanorods and ZnO film samples were grown in UHV environment with high purity sources.

Figures 2(a) and (b) illustrate the temperature-dependent PL spectra of the ZnO film and ZnO nanorod samples. They exhibit a similar NBE spectrum structure which mainly consists of an A line (3.365 eV at 10 K) and a B line (3.321 eV at 10 K). The SP effect on the NBE in ZnO nanorods can be clearly observed from the enhancement factor of the integrated PL intensities of the NBE from ZnO nanorods in comparison with that from ZnO film, as shown in figure 2(c). It is obvious that the NBE of ZnO nanorods contributed from the A line shows an about five-fold emission enhancement at 300 K, taking ZnO film as a reference. With the temperature decreasing, the enhancement factor of the A line monotonically decreases, which is similar to the result observed in Ag/InGa_N quantum wells with a low internal quantum efficiency by Lu *et al* [6]. This kind of temperature-dependent behaviour was attributed to the localization process of carriers with decreased temperature, resulting in a decrease of available carriers to couple with the SP. Moreover, it is interesting to find that

the enhancement factor of the B line showed a completely reverse trend compared with the A line. With temperature decreased from 150 to 10 K the enhancement factor of the B line increased rapidly from 1.2 to 8.0, while this value for the A line continued decreasing from 1.2 to 0.3, which is lower than unity. This means that there is a competition between the A line and the B line in ZnO nanorods within the low temperature range.

The temperature-dependent peak position shifts of both the A line and the B line in ZnO nanorods are further analysed, mainly focusing on the temperature range from 10 to 150 K. It is obvious that both the A line and the B line showed blue shifts with temperature decreasing (figure 2(d)). The A line is attributed to the emission of the neutral donor-bound exciton D^0X , and it can be well fitted using the following expressions [20]:

$$E(A) = E_G(T) - E_{FB} - E_{LOC} \quad (1)$$

$$E_G(T) = E(0) - \alpha T^2 / (T + \beta) \quad (2)$$

where $E_{FB} = 60$ meV is the binding energy of the free exciton of ZnO, E_{LOC} the localization energy between the D^0X state and the free exciton (FX) state, and equation (2) is the Varshni formula in which the constants $E(0) = 3.44$ eV for the band gap energy of ZnO at $T = 0$ K, $\alpha = 1.0 \times 10^{-3}$ eV K⁻¹ and $\beta = 925$ K are taken from [22]. As a result $E_{LOC} = 12$ meV is determined. On the other hand, the B line showed a different

temperature-dependent behaviour which was well fitted using the equation for the radiative transition from free electron to neutral acceptor state (e, A^0) [21, 22]:

$$E(B) = E_G(T) - E_A + k_B T/2 \quad (3)$$

where k_B is the Boltzmann constant and E_A the binding energy of the acceptor involved. $E_A = 117$ meV is determined in our fitting, as Thomas obtained in [21]. Therefore the B line of NBE in our sample is also attributed to the emission from the radiative transition (e, A^0).

The SP energy of the Ag/ZnO interface can be quantitatively calculated by using the following dispersion relation:

$$\hbar K_{SP} = (\hbar\omega/c)(\epsilon_{Ag}\epsilon_{ZnO}/\epsilon_{Ag} + \epsilon_{ZnO})^{1/2} \quad (4)$$

where K_{SP} is the wavevector of the SP, ϵ_{Ag} and ϵ_{ZnO} are the dielectric functions of Ag and ZnO, respectively, and $\hbar\omega/c$ is the incident energy. The SP energy of the Ag/ZnO interface is determined as 2.93 eV according to the equation. This value is very close to the UV band emission of ZnO, which makes the resonant coupling between Ag SP and UV emission of ZnO much easier. A similar phenomenon of UV emission enhancement in Au coated ZnO nanorods has been reported by Lin *et al* [14]. They suggested that the UV emission was enhanced by the SP effect, not by quantum confinement effects. Moreover, it is reasonable to observe the quantum confinement in ZnO when the size of the structure is smaller than 2 nm (which is comparable to the Bohr radius of ZnO), such as ZnO nanoparticles or nanocrystals [23].

To clearly explain the SP effect on modulating NBE in ZnO nanorods, a schematic diagram of ZnO energy band structure and SP coupling processes is drawn in figure 3. The energy levels of the D^0X state and A^0 state were determined using our calculated values $E_{LOC} = 12$ meV and $E_A = 117$ meV. In the PL measurements, after an excitation of electron-hole pairs by an external optical field, there are two kinds of radiation occurring in our ZnO samples, i.e. D^0X exciton recombination and the radiative transition (e, A^0), labelled by the red and blue arrows in figure 3, respectively. In the high temperature range from 300 to 150 K, the D^0X exciton is delocalized to form a free exciton, which can be coupled with the SP in Ag, thus resulting in an enhancement of NBE contributed from the A line in ZnO nanorods. The monotonically decreasing tendency of the enhancement factor of the A line with temperature is caused by the localization process of excitons. The localization energy E_{LOC} of D^0X is about 12 meV, which corresponds to the thermal activation temperature of around 150 K. Below this temperature D^0X became fully localized at potential minima, thus SP coupling with these excitons was basically blocked. On the other hand, below 150 K the radiative dipole (e, A^0) becomes predominantly coupled with the SP in ZnO nanorods due to the absence of localization limitations for free electrons. Due to the high spontaneous recombination probabilities of the SP, the emission from the radiative transition (e, A^0) becomes obviously enhanced, and the emission from localized D^0X exciton recombination in ZnO nanorods is further suppressed

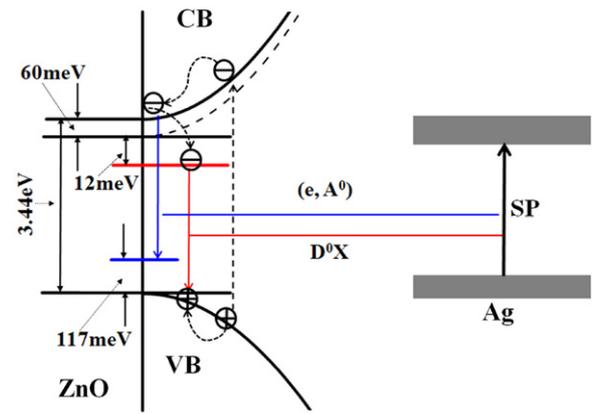


Figure 3. Schematic diagram of ZnO energy band structure and coupling processes of the SP in Ag with D^0X excitons and radiative dipoles in ZnO.

to be slower than that in ZnO film below 125 K. Moreover, the increase in the enhancement factor of the B line with decreased temperature could be well understood considering the increased plasmonic DOS at low temperature, as indicated in Ag/ZnO film by Li and Ong [24].

4. Conclusions

In summary, we have investigated the modulation of the SP effect on the NBE behaviour of Ag-capped ZnO nanorods by using a temperature-dependent PL technique. Our results indicate that the SP coupling process with the exciton D^0X prevails in the temperature range from 300 to 150 K, but the coupling effect monotonically lowers with decreased temperature due to the localization process of excitons. On the other hand, the SP coupling process with the radiative dipole (e, A^0) becomes dominant below 150 K and the coupling efficiency monotonically increases with further lowering of the temperature because of the increase of the plasmonic DOS. Carriers and exciton delocalization in ZnO nanorods play a key role in determining the competition between the two SP coupling processes. Our findings may promote the optimization of metal-ZnO nanostructures and accelerate the development in the new design of ZnO-based nanolasers.

Acknowledgments

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