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Mechanism of the enhancement and quenching of ZnO photoluminescence by ZnO-Ag coupling

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Abstract – New nanostructural composites consisting of Ag nanoparticles (NPs)-SiO₂-ZnO films were fabricated by depositing ZnO films on silica substrates which had already been implanted by Ag ions at different energies and fluences. The photoluminescence (PL) emission of ZnO films from these nanostructural composites can be enhanced or quenched comparing to that of a ZnO film directly deposited on bare silica substrate. The enhancement of the band gap emission is ascribed to the local field enhancement induced by the resonant coupling between the excitons of ZnO and the surface plasmons (SPs) of Ag NPs, while the quenching is due to the electron transfer from ZnO to Ag NPs. Our results can be used to clarify the ambiguity in controlling the light emission enhancement and quenching of a semiconductor coupled with the SPs of metal NPs, which is very important for the design and applications of semiconductor and metal coupling to highly efficient optoelectronic devices, biosensor, etc.

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Introduction. – Surface plasmon (SP), excited at the interface of metal nanostructure and dielectric, has attracted great scientific interest due to its wide applications, including plasmon lasers [1], as well as enhancing the light absorption [2] and Raman scattering intensity [3] of materials near its surface. Recently, SP-mediated emission has also become a popular research topic because of the dramatic improvement of luminescence intensity and efficiency of light-emitting materials and devices [4–18]. Okamoto et al. reported a giant PL enhancement of InGaN/GaN quantum well by capping of Ag layer and claimed the importance of SPs-mediated emission in improving the efficiency of light-emitting diodes (LEDs) [4,5]. The idea was also applied to enhance the light emission of semiconductors in many semiconductor-metal nanostructures coupling systems such as Si-Au [6], CdSe-Au [7–9], and ZnO-Ag (Au, Al and Pt) [10–18], where the semiconductor and metal materials were chosen to engineer the matching between the emission energy of the semiconductor and the SP energy of the metal.

In fact, either PL quenching or enhancement were often observed in semiconductor-metal nanostructures coupling systems [7–9,19–21]. However, the mechanisms of PL enhancement or quenching are not clear and still under hot debate due to the complicated coupling process between excitons and SPs. Understanding the coupling process and the mechanism are extremely important for the application of SP. The PL enhancement or quenching sensitively depend on many factors, such as the matching between emission energy and SP energy, the geometry of the metal, as well as the separation distance between semiconductor and metal. In general, the emission energy of the semiconductor that matches quite closely with the SP energy of the metal can induce a larger enhancement due to a strong resonant coupling effect [4,14]. Besides, both the roughness of the metal films and the size of the metal NPs were also observed to affect the competition between the PL enhancement and quenching [15,22–24]. PL enhancement usually occurs on rough metal surfaces or metal NPs with larger size, while PL quenching occurs
on flat metal surfaces or smaller metal NPs. In addition, the separation distance between semiconductor and metal was found to play a very important role in determining the competition between the PL enhancement and quenching [7,9,13]. For shorter distance, the quenching by metal dominates the emission property of the semiconductor. At longer distance, as the SP is an evanescent wave that exponentially decays with distance from the metal surface, the enhancement decreases progressively with the increase of separation distance. The optimal distance of about 10 nm for PL enhancement has been reported by some groups [7,9]. There are mainly three mechanisms that account for the PL enhancement and quenching: 1) the radiating plasmon model proposed by Lakowicz that surface plasmon resonance (SPR) scattering of metal may enhance the emission while SPR absorption quenches the emission [22], 2) the local field enhancement leads to an increased excitation rate and radiative recombination rate (PL enhancement) whereas nonradiative energy transfer from semiconductors to metal nanostructures leads to PL quenching [7,13,23,24], and 3) the PL can be enhanced due to the electrons transfer from metal NPs to semiconductors, conversely, the electrons transfer from semiconductors to metal NPs results in PL quenching [8–12,19].

Although the mechanisms for the PL enhancement or quenching are complicated, in order to control and tailor the SP of metal NPs for its application in optoelectronic devices, it is desirable to establish the underlying coupling mechanism between semiconductor and metal. In this letter, we design a unique approach to investigate the coupling mechanism between excitons and SPs by depositing ZnO films on Ag NP embedded silica substrates. The enhancement and quenching of the band gap emission of ZnO are reached by controlling ion implantation parameters. An underlying interaction process between exciton and SP is proposed to elaborate the PL enhancement and quenching: 1) the radiating plasmon model proposed by Lakowicz claims that surface plasmon resonance (SPR) scattering of metal may enhance the emission while SPR absorption quenches the emission [22], 2) the local field enhancement leads to an increased excitation rate and radiative recombination rate (PL enhancement) whereas nonradiative energy transfer from semiconductors to metal nanostructures leads to PL quenching [7,13,23,24], and 3) the PL can be enhanced due to the electrons transfer from metal NPs to semiconductors, conversely, the electrons transfer from semiconductors to metal NPs results in PL quenching [8–12,19].

Results and discussion. – Figure 1 shows the room temperature PL spectra of the S1-4 and the reference sample. Sharp emissions in the UV range (≈380 nm) and broad emission bands in the visible region (≈580 nm) are observed. It is well known that the UV emission belongs to the band gap emission, while the visible emission is due to the defect emission arises from the recombination of holes with electrons trapped at the oxygen vacancies in ZnO [25]. The corresponding enhancement factors of band gap emission after normalization (the ratios of the PL peak intensity of S1-4 (I) to that of the reference sample (I0)) are illustrated in the inset of fig. 1. It could be seen that the band gap emission is enhanced (S1-3) or quenched (S4) comparing to the reference sample. The largest enhancement factor of 2.7 is obtained in the S1. Moreover, slight red shifts from 376 to 380 nm for the band gap emission peaks are observed in both the enhancement and quenching cases. Such red shifts of the band gap emission peaks of ZnO have also been reported [14,17]. For the defect emissions, however, the PL intensities are always enhanced. Thus, it appears that the embedded Ag NPs has great influence on the band gap and the defect emissions of the top ZnO films.

To study the physical origin of the observed PL enhancement and quenching effects, we performed the optical absorption spectra of the Ag+ as-implanted and reference samples before (S1′–S4′) and after (S1–4) deposition of ZnO films. In fig. 2(a), the obvious absorption peaks around 405 nm can be attributed to the surface plasmon resonance (SPR) absorption of the Ag NPs formed in the implanted samples [26]. While the extra absorption peaks around 365 nm, which belong to the intrinsic exciton absorption of ZnO films [27], are observed once the ZnO films are deposited (fig. 2(b)). The position of the ZnO exciton peak (λexciton) is close to the SPR wavelength (λSPR) of the Ag NPs, which makes resonant coupling of the excitons to the SPs possible. Further carefully comparing the absorption spectra in fig. 2(a) to those in 2(b), it can be found that, on the one hand, the SPR positions of Ag NPs in the S1-3 samples have no obvious shift except a blue shift from 415 to 405 nm in the S4. On the other hand, the absorption intensities of the ZnO exciton peaks in all the S1-4 are

Experimental details. – High-purity silica (SiO2) slides were used as the substrates for the fabrication of Ag NPs-SiO2-ZnO film nanostructural composites. In the first step, four samples were prepared by Ag+ ion implantation at room temperature into silica slides. Silica slide 1 (S1′) and 2 (S2′) were implanted by Ag ions at 30 keV to fluences of 3 × 1016 and 5 × 1016 ions/cm2. Silica slide 3 (S3′) and 4 (S4′) were implanted by 5 × 1016 and 1 × 1017 Ag+ ions/cm2 at 60 keV. Subsequently, the 60 nm thickness of ZnO films were deposited onto the surface of the as-implanted silica substrates using the RF magnetron sputtering system [16]. Here, we name the ZnO-covered S1′-4′ as S1-4. A reference sample with the deposition of ZnO film on bare silica substrate under the same condition was also prepared.

The PL spectra were excited at room temperature by the 325 nm line of a He-Cd laser. The optical absorption spectra were measured using a UV-vis-NIR dual-beam spectrophotometer (Varian Cary5000) with wavelengths varying from 800 to 200 nm. Microstructural characterization of the samples was performed by a JEOL 2010 (HT) transmission electron microscope operating at 200 kV. The surface morphologies of the Ag-implanted silica substrates were characterized by atomic force microscope (AFM, Shimadzu, SPM-9500J3).
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Fig. 1: Room temperature PL spectra of the S1-4 and reference samples. The inset is the enhancement factor of the band gap emission after normalization with the reference sample.

Fig. 2: The optical absorption spectra of the Ag+ as-implanted and reference samples before ((a), S1′-4′) and after ((b), S1-4) deposition of ZnO films.

enhanced comparing to that of the reference sample. These spectra provide an important clue for the understanding of the coupling process between excitons and SPs.

In order to investigate the relationship between the Ag NPs size and distribution in silica and the PL enhancement factor of the top ZnO films, the microstructural characterization of the samples (S1-4) was performed by TEM, as shown in fig. 3. The TEM image of the S1 shows that the Ag NPs distributed at a narrow distance from the near surface to about 40 nm in depth. In this case, the PL enhancement factor reaches the maximum.

Fig. 3: Cross-sectional TEM images of the S1 (a), S2 (b), S3 (c), S4 (d).

Comparing to the size and distribution of Ag NPs in the S1 and S3, by increasing the energy of implanted Ag+ from 30 to 60 keV, the size of Ag NPs in the S3 is smaller and the distribution is little bit deeper into the substrate than that in the S1. It means that the coupling strength between the ZnO and Ag NPs is weaker than that in the S1, and thus the enhancement factor is decreased. However, when the ion implantation fluence increases to \(1 \times 10^{17}\) ions/cm\(^2\) (S4), Ag NPs located at the surface are seen to be directly in contact with the ZnO film due to the surface sputtering effect during the process of Ag ions implantation \[28\]. The surface sputtering effect becomes serious for the low-energy ion implantation at high fluence and the sputtered thickness is proportional to the fluence \[28\]. Therefore, the surface silica may be sputtered during the implantation process, and the exposed Ag NPs will be directly in contact with the deposited ZnO film.

To verify the above-mentioned mechanism of the surface sputtering effect, the surface morphologies of the Ag+ as-implanted samples (S1′-4′) were observed by AFM. It can be seen from figs. 4(a) and (c) that the surface of the S1′ and S3′ are flat, meaning that all Ag NPs are embedded in silica, and thus the ZnO films are separated from the Ag NPs by a layer of SiO\(_2\). However, some Ag NPs appear on the SiO\(_2\) surface with the increase of implantation fluence (S2′). Especially in the S4′, due to the serious surface sputtering effect, many Ag NPs appear on the surface of S4′, which leads to direct contact and the electrons transfer between ZnO film and Ag NPs.

There are four physical processes that account for the PL enhancement and quenching. Firstly, the PL enhancement can be caused by the local field enhancement due to the coupling between excitons of semiconductor and SPs of metal NPs. There are two enhancement mechanisms. One is to enhance the incident excitation field, and the other is to enhance the radiative recombination rate. In the optical excitation process, the resonant oscillation of the electrons in metal NPs creates a local field close to the particle surface, which may couple into the incident field to enhance the optical energy density of the incident
source near the semiconductor and the optical absorption rate of the semiconductor [29]. As a consequence, more excitons or electron-hole pairs can be excited by the enhanced incident field. In the light emission process, the radiative decay rate can be increased since the excitons are easier to recombine under intense field, which provides another opportunity to enhance the light emission [5]. Secondly, the local field excitation by SP can produce more excitons and result in PL enhancement. When the SP energy of metal NPs is larger than the emission energy of the semiconductor, the SP can be used as a source to excite the semiconductor. This process has been observed by Kulakovich et al. and Chen et al. in the CdSe-Au coupling system in which an increased excitation of CdSe quantum dots by SP waves of Au NPs resulted in PL enhancement [7–9]. Therefore, through the resonant excitation by the SP waves of metal NPs, the PL emission intensity of the semiconductor can be enhanced. However, this process is not allowed when the SP energy is smaller than that of the light emission. Thirdly, an efficient energy transfer may occur between the semiconductor and metal NPs due to exciton-SP quadrupole interaction [18]. When the energy of excitons is larger than the SP energy, the energy transfer from excitons to SPs occurs, this can result in a red shift of the emission peak. Conversely, a blue shift of the emission peak is observed due to the energy transfer from SPs to excitons. Lastly, the electron transfer between semiconductors and metal NPs usually takes place when they are directly in contact with each other. Depending on the band structures of semiconductor and metal, as well as the emission energy states, the electrons can transfer from semiconductor (metal) to metal (semiconductor). When the electrons transfer from metal NPs to semiconductors, the light emission can be enhanced. Meanwhile, the SP absorption peak of metal NPs will undergo a red shift for the decreasing of the electron density in the metal. Conversely, the PL quenching happens and the SP absorption peak of the metal suffers a blue shift when electron transfer from semiconductor to metal occurs. Therefore, in order to implement a practical PL enhancement relying upon the SP coupling technique, the interaction processes underlying in the PL enhancement and quenching should be understood clearly.

Consistent with the above exciton-SP interaction processes, a brief diagram for the PL enhancement and quenching in our experiment is plotted in fig. 5. In drawing the band alignment, the conduction band of ZnO is located at $-4.19 \text{ eV}$ vs. absolute vacuum scale (AVS), and the Fermi level of silver is at $-4.26 \text{ eV}$ vs. AVS [30,31]. As shown in fig. 5(a), an enhanced local field occurs due to the resonant coupling between excitons of the ZnO films and SPs of Ag NP, as proposed in earlier reports [14–17]. In our case, the SP energy of Ag NPs was detected at around 405 nm as shown in fig. 3, which is very close to the band gap emission of ZnO at around 380 nm. Such energy matching is seen to provide a great possibility of resonant coupling between the Ag NPs and ZnO films. On the one hand, the local field enhancement due to SPs of Ag NPs can enhance the incident excitation field and increase the radiative recombination rate, which results in the enhancement of the band gap emission. Meanwhile, the local field enhancement can also enhance the optical absorption intensity. The enhanced optical absorption intensities of the ZnO exciton peak in all
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the $S1-4$ are observed, as shown in fig. 2. On the other hand, excitons are generated in ZnO by He-Cd laser and the exciton energy can transfer to the SP when the band gap energy is comparable to the SP energy and the exciton-SP interaction occurs. The fact that the band gap emission peaks in all the $S1-4$ suffer red shifts from 376 to 380 nm is just a result of nonradiative energy transfer from excitons to SPs. In addition, some red shifts of the band gap emission peaks can be used to exclude the possibility of a PL enhancement due to the reflection of Ag. If the PL enhancement is due to the reflection of metal “mirror”, the band gap emissions should not shift their positions according to the results reported by Lu et al. [17].

For our samples, the obtained penetration depth at 405 nm is 52.7 nm. The reduction of intensity in the penetration depth at 405 nm is just a result of nonradiative energy transfer from excitons to SPs. In addition, some red shifts of the band gap emission peaks can be used to exclude the possibility of a PL enhancement due to the reflection of Ag. If the PL enhancement is due to the reflection of metal “mirror”, the band gap emissions should not shift their positions according to the results reported by Lu et al. [17].

The local field excitation, however, since the SP energy of Ag NPs is smaller than the exciton energy of the ZnO film, the SP waves cannot excite the excitons in ZnO, thus the local field excitation by SP waves is not allowed. Therefore, combining the PL spectra with the TEM images, we can conclude that the largest enhancement factor of band gap emission observed in the $S1$ is not due to the local field excitation but to the local field enhancement. Besides, the enhancement factor of the $S3$ is smaller than that of the $S1$. The enhancement reduction for $S3$ is comprehensible if the dependence of the evanescent field on the separation distance (thickness of SiO$_2$) between ZnO film and Ag NPs is considered. The SP fringing field penetration depth $Z$ can be calculated as

$$Z = (\lambda/2\pi)[(\varepsilon_{SiO_2} - \varepsilon_{Ag})/\varepsilon_{SiO_2}]^{1/2},$$

where $\varepsilon_{SiO_2}$ and $\varepsilon_{Ag}$ are the real parts of the dielectric constants of SiO$_2$ and Ag, respectively [32]. For our samples, the obtained penetration depth at 405 nm is 52.7 nm. The reduction of intensity in the $S3$ therefore is attributed to the weakening of the evanescent field of SP because of a deeper distribution of Ag NPs. For the defect emission at 580 nm, although the energy does not match well with the SP of Ag NPs, the off-resonance enhancement by local field enhancement is still possible, which leads to a moderate PL enhancement. The local field excitation induced by SP waves may also enhance the defect emission because the SP energy of Ag NPs is larger than the energy of defect emission.

However, the local field enhancement mechanism cannot be used to explain the PL behaviors of the $S2$ and $S4$. From the AFM images shown in figs. 4(b) and 4(d), it can be seen that Ag NPs appear on the SiO$_2$ surface, which results in the electrons transfer between ZnO and Ag NPs after deposition of ZnO films on Ag NPs. According to the band structures of ZnO and Ag presented in fig. 5(b), the initial Fermi level of the ZnO film is lower than that of Ag NPs. When directly in contact with each other, electrons will transfer between the Ag NPs and ZnO, and then produce a band bending. The electrons in the Ag NPs can be excited by the incident field to an excited state which is higher than the conduction band edge of ZnO. Although the excited electrons in Ag NPs can transfer to the conduction band of ZnO, these electrons in the conduction band will be easily transferred back to the Fermi level of Ag NPs because the conduction band of ZnO is higher than the Fermi level of Ag. Therefore, the band gap emission will be quenched. In the case of the $S2$, some Ag NPs appear on the SiO$_2$ surface and electrons transfer from the ZnO film to Ag NPs also occurs. As a result of the competition between the local field enhancement and electron-transfer-induced quenching, the intensity of the band gap emission does not change significantly. While in the $S4$, the electrons-transfer-induced quenching becomes overwhelming. The electrons transfer process can be verified by comparing the optical absorption spectra of the $S4$ before and after the deposition of the ZnO films, as shown in fig. 3(a) and (b). The absorption peak of Ag NPs in the $S4$ suffers a blue shift from 415 to 405 nm after the deposition of the ZnO film. The position of plasmon absorption of Ag NPs is represented by the following equation:

$$\lambda_p = [4\pi^2 m_{eff} S_0^2 / N c^2]^{1/2},$$

where $m_{eff}$ and $N$ are the effective mass of the free electron and the electron density of the metal, respectively. For spheric Ag NPs with size smaller than 20 nm, the position of the plasmon absorption is related to the electron density of the metal. In the $S4$, the blue shift of the plasmon absorption peak of Ag NPs suggests that the electron density of Ag NPs is increased. The increase of the electron density of Ag NPs is due to the electron transfer from the ZnO film to Ag NPs when they are in contact. For the defect emission, since the Fermi level of Ag NPs is higher than the defect level located at ZnO films, it is therefore possible that the electrons can transfer from the Fermi level of Ag NPs to the defect level of ZnO films. Thus the defect emission is still enhanced even when the ZnO films are seriously in contact with the Ag NPs. The behavior of the defect emission in our experiment is not consistent with the results reported by Li et al. and Lin et al. in the ZnO-Au and ZnO-Pt coupling systems, where the defect emissions were greatly quenched [10,11]. The phenomena can be interpreted by considering the band structures of semiconductor and metal as well as the defect states level. In the ZnO-Au and ZnO-Pt coupling systems, since the work function of Au or Pt is larger than that of Ag, the Fermi level of Au or Pt is lower than the defect states level, the electrons located at the defect states can easily transfer to the Fermi level of the Au or Pt NPs. As a result, the defect emission is effectively suppressed.

Retrospecting the three above-mentioned mechanisms for the PL enhancement and quenching, the PL quenching in our experiment cannot be explained by the radiating plasmon model. According to the radiating model, the relative contribution of SP absorption and scattering of metal NPs (depending on their size) will cause PL quenching and enhancement [22]. For smaller metal NPs, absorption dominates over the scattering process. Therefore, the size of metal NPs should be large enough to suppress quenching (for example, >20 nm for Ag) [33]. In our case, however, the size of Ag NPs in all the samples is smaller than 20 nm. If the radiating plasmon model is applied into the $S1$ and $S4$, the PL quenching should be
observed in the S1 and the PL intensity of the S1 should be smaller than that of the S4. Thus the PL enhancement observed in the S1 due to the SP scattering of Ag NPs can be excluded. For the nonradiative energy transfer model, the nonradiative energy transfer from semiconductor to metal may be responsible for the PL quenching, this is very efficient when the distance between semiconductor and metal is shorter than 10 nm and can completely compensate the PL enhancement induced by the local field. Although the nonradiative energy transfer cannot be ruled out in our results, we still consider that the electrons transfer is mainly responsible for the PL quenching. The band alignment satisfies the condition that the electrons transfer from ZnO to Ag NPs when the ZnO film is in close contact with Ag NPs, and the blue shift of about 10 nm of the optical absorption peak of Ag NPs is a result of the electrons transfer. Thus, it is fair to conclude that the PL enhancement is due to the local field enhancement induced by resonant coupling between excitons and SPs, while the PL quenching is caused by the electrons transfer from the ZnO film to Ag NPs.

Conclusion. – In summary, we prepared Ag NPs-SiO$_2$-ZnO film nanostructural composites by depositing ZnO films on silica substrates which had already been implanted by Ag ions. The band gap emission of ZnO can be enhanced or quenched under different implantation parameters. The underlying mechanism can be explained by the competition between the local field enhancement induced by resonant coupling between excitons of ZnO and SPs of Ag NPs, and the electrons transfer from the ZnO film to the Fermi level of Ag NPs. Our results clarify the ambiguity in controlling the emission enhancement of a semiconductor coupled with SPs of metal NPs, and will be very important for the future design of optoelectronic devices with improved luminescence efficiency by SP.

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