Surface plasmon enhanced photoluminescence in amorphous silicon carbide films by adjusting Ag island film sizes*

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Ag island films with different sizes are deposited on hydrogenated amorphous silicon carbide (α-SiC:H) films, and the influences of Ag island films on the optical properties of the α-SiC:H films are investigated. Atomic force microscope images show that Ag nanoislands are formed after Ag coating, and the size of the Ag islands increases with increasing Ag deposition time. The extinction spectra indicate that two resonance absorption peaks which correspond to out-of-plane and in-plane surface plasmon modes of the Ag island films are obtained, and the resonance peak shifts toward longer wavelength with increasing Ag island size. The photoluminescence (PL) enhancement or quenching depends on the size of Ag islands, and PL enhancement by 1.6 times on the main PL band is obtained when the sputtering time is 10 min. Analyses show that the influence of surface plasmons on the PL of α-SiC:H is determined by the competition between the scattering and absorption of Ag islands, and PL enhancement is obtained when scattering is the main interaction between the Ag islands and incident light.

Keywords: amorphous silicon carbide, surface plasmons, photoluminescence enhancement

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1. Introduction

Hydrogenated amorphous silicon carbide (α-SiC:H) is a bandgap-adjustable semiconductor material. It has great potential for optical emission adjustable LEDs, microelectronic devices, and solar cell manufacturing.[1–4] Various technologies have been used to fabricate α-SiC:H materials, such as hot filament chemical vapor deposition, pulsed laser deposition, magnetron sputtering, plasma enhanced chemical vapour deposition, and the optical emission from near-infrared to visible.[5] However, the low quantum efficiency of α-SiC:H films caused by the indirect bandgap characteristic blocks its application, and improving the optical emission property has become a very important project in α-SiC:H material research. The surface plasmon investigation has attracted great attention due to the nanotechnology improvement, and researchers have focused on the coupling of plasmons to optical emitters, nanoscale optical antennas, plasmonic lasers, optical trapping in a solar cell, and so on.[6–8]

The surface plasmon resonance energy can be adjusted by changing the size, shape and environment of the metal nanoparticles. PL enhancement for optical emitters at different wavelengths has been achieved by designing suitable metal structures. Okamoto *et al.*[9] reported that the optical emission quantum efficiency of InGaN quantum well could be enhanced by nano Ag film. Liu *et al.*[10] achieved PL enhancements of bandgap emission by 12 times in ZnO film. Biteen *et al.*[11] obtained 4 times optical emission and 58% quantum efficiency enhancement of nanocrystalline Si by Au nanoparticles. The above results provide a possibility of improving the PL intensity of α-SiC:H films by metal nanoparticles.

In this work, the influence of Ag island films on the α-SiC:H films has been investigated, and 1.6 times PL enhancement is obtained on the main PL band of α-SiC:H film. AFM, extinction, PL, and PLE spectra are used to investigate the PL enhancement mechanism, and the results indicate that there are two resonance absorption bands which correspond to the out-of-plane and in-plane surface plasmon modes, respectively. Both the excitation and emission fields contribute to PL enhancement, and PL enhancement occurs when the scattering effect becomes the main interaction between metal nanoparticles and incident light. The maximum enhancement appears at the longer wavelength of the resonant peak.

2. Experimental details

The α-SiC:H films were deposited on fused silica by using plasma enhanced chemical vapor deposition technique. The CH_4, SiH_4, and H_2 flow rates were kept at 1.2, 0.6, and 60 sccm. The working pressure, the deposition temperature, and the power of plasma were kept at 1 Pa, 300 °C, and 300 W, respectively. The films were deposited for 60 min. Then, Ag island films were deposited by pulsed laser ablation technique on half of the deposited films. The SiC film without Ag coating is defined as S_0. The Ag island films, which are deposited

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for 5, 10, and 15 min, were defined as S_1, S_2, and S_3, respectively.

The infrared absorption was deduced from the transmittance measurements in a Fourier transform infrared spectrophotometer (FTIR, Bio-Rad 60 V). The atomic force microscope (AFM) (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) was employed to observe the morphology of the Ag island films. The transmission spectra of the samples were measured by a Zolix UV–VIS spectrometer. The PL and PL excitation spectra were detected by an FLS920 fluorescence spectrometer, and the exciting light was from a 450-W Xe lamp. The PL and PL excitation were from the substrate side of the samples.

3. Results and discussion

The FTIR spectrum of α-SiC:H films is shown in Fig. 1. As can be seen, three absorption regions located at around 780, 2100, and 2900 cm^{-1} are obtained, which correspond to the stretching vibration modes of Si–C, Si–H_n, and C–H_n bonds, respectively. The Si–C absorption peak located at 780 cm^{-1} suggests that the films mainly consist of amorphous SiC.[12]

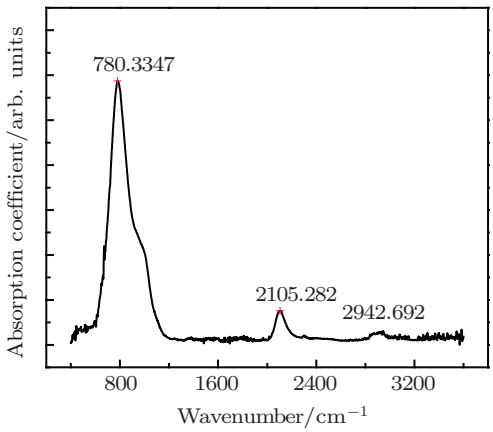


Fig. 1. FTIR spectrum of α-SiC:H films.

Figure 2 shows the AFM images of Ag island films deposited for different times, and the scanning area is 2 μm×2 μm. It is shown that no continuous films are formed after Ag coating, and the Ag films consist of spherical Ag island particles, which are named Ag island films. The size of the Ag nanoparticles becomes larger and larger with increasing deposition time, and the surface roughness increases too. The size and the distance of the Ag islands are random, and localized surface plasmon mode forms at the interface.

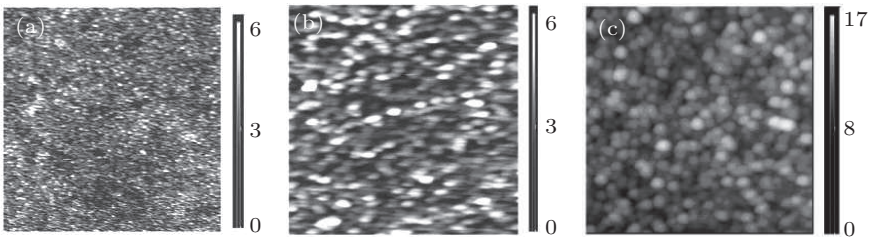


Fig. 2. Typical AFM images of the Ag island films with a deposition time of (a) 5, (b) 10, and (c) 15 min.

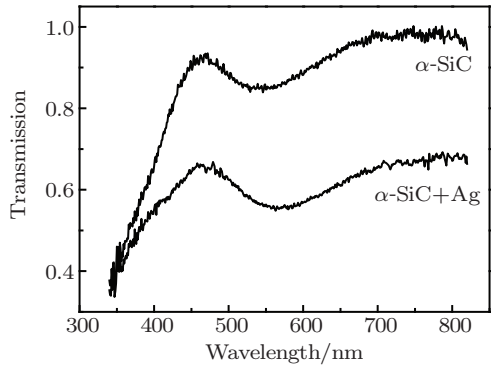


Fig. 3. Transmission spectra for S_2 and the reference sample.

Figure 3 shows the transmission spectra of S_2 and the reference sample. Interference effect is observed for all the samples due to the thick α-SiC:H films, and the transmission for Ag island films is difficult to observe. However, the absorption of the samples with Ag films coating becomes stronger, which is caused by the resonance absorption of localized surface plasmons generated by Ag island films. The extinction of the Ag island films can be expressed as[13]

$$E_{\mathrm{Ag}} = \log(1/(T_{\mathrm{n\#}}T_0)),$$

where $T_{\mathrm{n\#}}$ is the transmission of S_{n}, and T_0 represents the transmission of the reference samples. Figure 4 shows the extinction spectra of the Ag island films with different sizes. All island films exhibit two extinction peaks, which correspond to two different localized surface plasmon resonant modes, and the low-energy band comes from the dipole oscillation parallel to the substrate plane (in-plane mode), and the high-energy band is due to the oscillation of the normal mode (out-of-plane mode).[14,15] The resonant frequency of the localized surface plasmon can be influenced by the shape, size, and its surroundings.[16] The main parameter effecting the optical extinction in our samples is the size of Ag island films. Both the

absorption and scattering contribute to the optical extinction of the metallic nanoparticles. Both the wavelength and width of localized surface plasmon resonances change with the size of nanoparticles. As can be seen from Fig. 4, both surface plasmon oscillation modes shift towards longer wavelength with increasing size of nanoparticles.

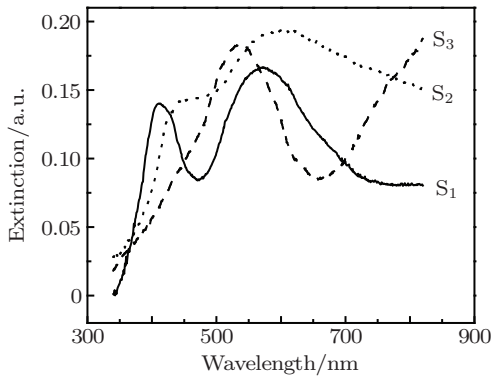


Fig. 4. Extinction spectra of the Ag island films deposited for different times.

Figure 5 shows the PL spectra of the samples with different Ag island films sizes. As can be seen, the optical emission properties of α-SiC:H films can be greatly influenced by the Ag island films. PL quenching occurs in S_1, while the PL intensity of S_2 and S_3 are enhanced, and the PL enhancement band changes with the Ag particles increasing. In order to investigate the influence of the Ag island film on PL intensity and position of α-SiC:H films, PL enhancement factor (F_p) is defined as $F_p = S_n/S_{ref}$, where S_n and S_{ref} mean the PL intensity. The variation of F_p with deposition time is shown in Fig. 6. It can be seen that PL quenching occurs for S_1in all the scanned PL wavelength, 1.6 times PL enhancement on the main PL band is obtained for S_2, and the F_p shifts towards longer wavelength with further increasing nanoparticles. Interestingly, the largest PL enhancement occurs at the longer wavelength corresponding to the resonant peak of the surface plasmons.

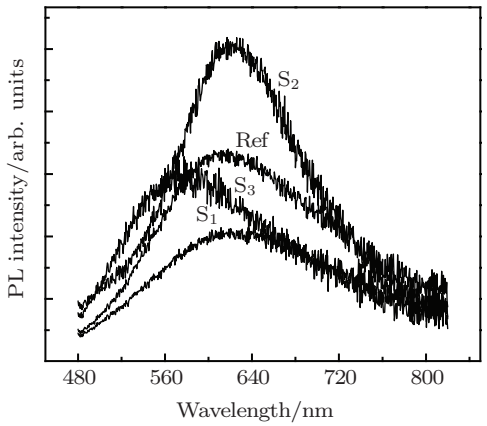


Fig. 5. The PL spectra of the samples with different Ag island film deposition times.

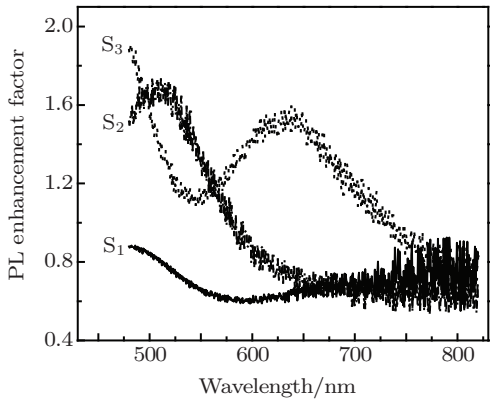


Fig. 6. The PL enhancement factor of the samples with different Ag island film deposition times.

The extinction of Ag nanoparticles is the sum of scattering and absorption, in which scattering leads to PL enhancement, while absorption causes ohmic loss leading to PL quenching. When the surface plasmon resonance coupling generated scattering dominates over the absorption process, the surface Plasmon energy can be recovered to free space to enhance the light emission intensity. Otherwise, the PL intensity will be quenched.[17] For small particles in the quasistatic limit, the scattering and absorption cross sections are given by[18]

$$C_{abs} = \frac{2\pi}{\lambda}\mathrm{Im}\left[\frac{2\pi}{\lambda}\right], \quad C_{sca} = \frac{1}{6\pi}\left(\frac{2\pi}{\lambda}\right)^4 |\alpha|^2,$$

where α is the polarizability of the particles, given by $\alpha = 3V\varepsilon - 1/(\varepsilon+2)$ in a vacuum, with V being the volume of the particle, and ε the permittivity of Ag. The scattering efficiency Q_{sca} is given by $Q_{sca} = C_{sca}/(C_{sca}+C_{abs})$. Scattering and absorption depend on the size of the particles. Metallic particles in S_1 are much smaller than the wavelength of light, and the particles tend to absorb more. Absorption dissipates heat, and PL quenching occurs. The size of the particles in S_2 is increased, scattering effect dominates absorption, so PL enhancement is obtained. However, increasing the particle size further leads to enhanced retardation effects and higher-order multi-pole excitation modes, which reduces the efficiency of the scattering process.[19] The scattering efficiency changes with wavelength, and the maximal optical absorption is achieved at the resonant frequency, so the largest PL enhancement occurs at the longer wavelength for all the samples. In addition, it should be noted that both the in-plane and out-of-plane surface plasmon modes can enhance the PL intensity. However, the PL enhancement near the in-plane mode is more important for α-SiC:H application.

Figure 7 shows the PL excitation spectra for S_2 and reference sample. As can be seen, the PL excitation intensity is enhanced after Ag island film coating. The ratio of the PL excitation spectra intensity of the films with and without Ag coating is used as the PL excitation enhancement factor (F_{pe}),

and the inset shows the F_{pe} changing with excitation wavelength for S_2. The F_{pe} increases first and then decreases, and the largest enhancement is located at about 420 nm. The extinction spectra have shown that the out-of-plane mode surface plasmon resonance wavelength for S_2 is at about 420 nm, so the excitation field can also be enhanced by the surface plasmons.

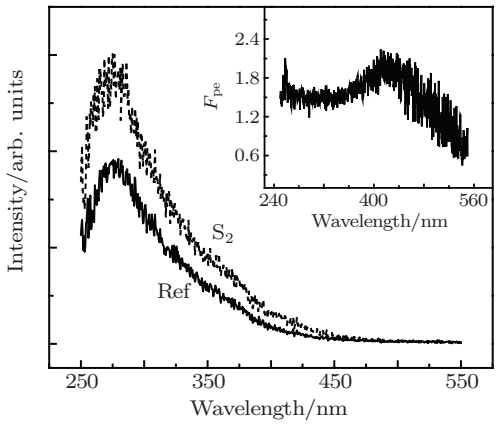


Fig. 7. The PL excitation spectra for S_2 and the reference sample. The inset shows the PL excitation enhancement factor.

The surface plasmon resonant frequencies include in-plane and out-of-plane modes in our samples. According to Sun *et al.*,[20] both the excitation and emission field enhancements contribute to the PL enhancement. At the excitation stage, the excitation F_p is proportional to $(\omega_0/\omega_{ex})^2$, where ω_0 and ω_{ex} represent the surface plasmons resonant wavelength and optical excitation wavelength, respectively. At the emission stage, two PL enhancement bands corresponding to the two surface plasmon modes are found. The in-plane-mode resonant band of the surface plasmons is further away from the excitation wavelength than that of the out-of-plane mode, so the maximal PL enhancement is obtained at the vicinity of the high-energy resonance band. However, the main PL band of α-SiC:H film is located at the vicinity of the in-plane resonance band. It is a process of compromise between the PL initial intensity and PL enhancement in practical application, and the maximal PL intensity at the proper wavelength should be obtained. Proper metal structure will be designed to achieve the largest PL enhancement at the main optical emission band of α-SiC:H film in further work.

4. Conclusion

The Ag island films with different sizes are deposited on α-SiC:H films, and the effects of localized surface plasmons on the PL characteristics of α-SiC:H are investigated. The PL intensity changing from quenching to enhancement is found by varying the size of the Ag nanoparticles, and the maximal PL enhancement by a factor of 1.6 is achieved at the main PL band of α-SiC:H film. The PL enhancement or quenching is caused by the competition between Ag particle scattering and absorption, and PL excitation spectra confirm that both optical excitation and emission fields contribute to the PL enhancement.

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