Localized surface plasmon resonance enhanced photoluminescence from SiNₓ with different N/Si ratios

Feng Wang,¹² Minghua Wang,¹ Dongsheng Li,¹,²,* and Deren Yang¹

¹State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China
²Cyrus Tang Center for Sensor Materials and Applications, Zhejiang University, Hangzhou 310027, China
*mselds@zju.edu.cn

Abstract: Silver (Ag) nanostructures with different sizes and densities were deposited onto the luminescence matrixes to improve the photoluminescence (PL) intensity of silicon nitride (SiNₓ) films via localized surface plasmon resonance (LSPR) coupling. The shape of PL spectra from the SiNₓ matrices is mainly determined by their stoichiometric ratio. Moreover, both the surface coverage and the size of Ag nanostructures should be considered for the improvement of PL intensity. The optimal PL intensity of SiNₓ films might be achieved by the addition of Ag nanostructures with proper surface coverage and size due to the enhanced photo-excitation by LSPR. The dipolar resonance absorption of Ag nanostructures has an insignificant contribution on this improvement.

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OCIS codes: (240.6680) Surface plasmons; (310.6860) Thin films, optical properties; (350.4600) Optical engineering; (300.6280) Spectroscopy, fluorescence and luminescence.

References and links


#175844 - $15.00 USD  Received 10 Sep 2012; revised 20 Sep 2012; accepted 20 Sep 2012; published 24 Sep 2012 (C) 2012 OSA 1 October 2012 / Vol. 2, No. 10 / OPTICAL MATERIALS EXPRESS 1437


1. Introduction

As an alternative material of silicon-based light sources, silicon nitride (SiNx) has received enormous amount of attentions due to its comparability with current metal-oxide semiconductor (CMOS) procedure as well as its promising luminescence efficiency in comparison to other silicon-based emitters [1–3]. During the past decades, there were lots of researches on the characterization of its energy-band structure and its luminescence properties [4–9]. As have been investigated, the barrier height for the carrier injection of SiNx matrix is extremely lower than that of silicon oxide (SiOx) which is the commonly used material for silicon-based light sources [5,10,11]. This lower barrier height is extremely valuable for the fabrication of light sources with low working voltage and promising efficiency due to its preferable carrier injection. Despite that the photoluminescence (PL) as well as the electroluminescence (EL) of SiNx matrices have been achieved in recent year [4,5], the luminescence efficiency of SiNx films is still too low to meet the demands of silicon-based light sources [3,5,12,13]. This poor efficiency is partially originated from the strong nonradiative recombination due to their disorder structure [5]. Besides, the low carrier injection efficiency resulted from the unbalanced injection barriers for electrons and holes also has a contribution to this inefficient luminescence [11,14].

Due to the inherent problems mentioned above in SiNx matrix, various methods on the improvement of its luminescence efficiency have been proposed in recent years [15–17]. For the weakening of the nonradiative recombination and enhancing the EL intensity of SiNx-based light-emitting devices (LEDs), the ammonia gas (NH3) plasma pretreatment was employed to improve the SiNx/Si interfacial state or passivate the nonradiative defects [16]. In addition, the EL from SiNx fabricated by ion implantation of silicon into Si3N4 films can be improved by high temperature post-thermal annealing, from which the implantation damages can be recovered [7,18]. For the improvement of carrier injection, Kim et al. employed the n-type SiC layer to balance the electron and hole injections and obtained 2.8 times enhancement of light output power [19]. Furthermore, Ni/Au contact placed on SiNx layers can also be applied for improving the carrier injection [15]. Among all the methods employed to improve the luminescence efficiency, the application of localized surface plasmon resonance (LSPR) has attracted extensive attention recently, which cannot only increase the radiative recombination rate by introducing an additional recombination path via Purcell effect [3,20–22], but also improve the carrier injection by the enhancement of the local electrical fields surrounding metal nanostructures [3,23].

LSPR refers to the collective oscillation of confined conduction electrons within metal nanostructures excited by the incident electromagnetic fields [3]. The excitation of LSPR by an electric field or light occurs when the energy of the confined collective oscillation of electrons in metal is similar with that of the incident electromagnetic field, by which the intense dipolar resonance absorption band appears and the local electromagnetic fields are enhanced significantly [24,25]. Abundant works on LSPR improved emission from GaN matrix have been made, which was the widely-used state-of-the-art high efficiency light sources emitted at the similar wavelength with that of SiNx films [26–29]. By inserting silver (Ag) nanoparticles underneath the InGaN/GaN quantum wells active layer, Kwon et al. achieved a 2 times increase of PL intensity and a 32.3% enhancement of optical output power, both of which were originated from the increased spontaneous recombination rate through LSPR coupling [28].
Despite of lots of excellent work on LSPR enhanced emission from GaN-based materials, there are still few researches on the improvement of the luminescence from SiN\textsubscript{x} matrix via this LSPR coupling [30]. Furthermore, there is a lack of work on the enhancement of PL intensity by the modulation of LSPR as well as the influence of LSPR on the intensity and peak position of PL from SiN\textsubscript{x} with different N/Si ratios, from which the optimal LSPR enhanced SiN\textsubscript{x}-based LED with promising EL efficiency can be fabricated.

During the last decades, various approaches on the fabrication of metal nanostructures on semiconductor templates have been proposed [31–36]. By employing the silica/polystyrene (PS) colloidal arrays, Ee et al. achieved the controlled depositions of highly-ordered close-packed two-dimensional (2D) micro/nano-particles arrays in the device configurations [31–33]. Moreover, the highly-ordered and ultra-high density metal nanostructures could be fabricated by using diblock-copolymer lithography templates [35,36]. In this paper, we fabricated the Ag nanostructures by a simple CMOS compatible technique, where the size and density were controlled by the original thickness of Ag layer and the post-thermal annealing procedure. The effects of Ag nanostructures with different sizes and densities on the improvement of PL intensity from SiN\textsubscript{x} matrixes were demonstrated. Furthermore, we investigated the influence of Ag nanostructures with different LSPRs on the PL from SiN\textsubscript{x} matrixes of various N/Si ratios. Both the size and the surface coverage of metal nanostructures were considered to the improvement of the luminescence efficiency from active matrixes.

2. Experimental

SiN\textsubscript{x} films with different stoichiometric ratios were deposited onto the quartz substrates by plasma-enhanced chemical vapor deposition (PECVD) technique, where NH\textsubscript{3} and nitrogen-diluted 10% silane (SiH\textsubscript{4}) were used as the reactant gas sources. The stoichiometric ratios of SiN\textsubscript{x} films were modulated by the flow rate ratios of NH\textsubscript{3} and SiH\textsubscript{4} (N/Si ratio). Three samples with the N/Si ratios of 3/8, 2, and 6 were fabricated, which were labeled as N3/8, N2, and N6, respectively. After the deposition of SiN\textsubscript{x} films, a silver layer was sputtered onto them by magnetron sputtering technique and the nanostructural Ag was obtained, as shown in Figs. 1(a) and 1(c). Two thicknesses measured by a film thickness monitor, 6 nm and 12 nm, were chosen for the investigation here, and we labeled them as Ag6 and Ag12, respectively. After that, a post-thermal annealing (TA) process in Ar atmosphere at 400 °C for 30 min to form Ag nanostructures with larger sizes and lower density was carried out. To differentiate the samples with TA process from the ones without this process, we labeled the former ones as Ag\_TA and the later ones as Ag\_no TA. SiN\textsubscript{x} films without the addition of Ag nanostructures were also fabricated for comparison.

The scanning electron microscopy (SEM) was used to characterize the size and morphology of Ag nanostructures. The PL signals of samples were excited by a 325 nm He-Cd laser and recorded by an Acton SpectraPro-2500i monochromater coupled to a photomultiplier tube (PMT). The extinction spectra were measured by a HITACHI U-4100 spectrophotometer.

3. Results and discussion

Figure 1 represents the SEM images of Ag nanostructures with different sizes and dispositions (the data can be found in Fig. 2). No distinct difference of Ag nanostructure morphology is observed for SiN\textsubscript{x} film substrates with different N/Si ratios. For the samples without the post-thermal annealing, the surface coverage (\(\eta\)) of Ag nanostructures is rather higher and the shape of them is very irregular. The average sizes of Ag6 and Ag12 are 25.7 ± 5.5 nm and 44.8 ± 9.3 nm, respectively. And the \(\eta\)s of Ag6 and Ag12 are ~65% and ~70%, respectively. Since the SiN\textsubscript{x} films deposited by PECVD technique were very flat with the root-mean-square roughness smaller than 2 nm [3], the roughness measured from the Ag layer deposited onto the active matrix (without TA process) should be mainly originated from the roughness of the metal layer. After the process of TA, the shape of these Ag nanostructures becomes more and more regular (circle). Meanwhile, the \(\eta\) of Ag nanostructures decreases significantly (from >65% to
with the increase of their sizes due to the Ostwald ripening process. The average sizes of Ag6_TA and Ag12_TA are 45.0 ± 10.6 nm and 77.9 ± 25.7 nm, respectively. Moreover, two sizes of Ag nanostructures can be distinguished obviously, which are more distinct for the samples with the post-thermal annealing, as shown in Figs. 1(b) and 1(d). Consequently, we fit the size distributions of Ag nanostructures by Gauss fittings with two central peaks, as shown in Fig. 2. Obviously, good fittings can be obtained for all the samples. This distribution of two sizes may result from the incomplete Ostwald ripening process that Ag nanostructures with smaller sizes can’t be incorporated into larger sized ones completely. Interestingly, the average size of Ag nanostructures for Ag6_TA is comparable with that for Ag12_no TA, where the influence of η on the PL of SiNₓ films can be investigated.

Fig. 1. SEM images of (a) Ag6 without post-thermal annealing (Ag6_no TA), (b) Ag6 with post-thermal annealing (Ag6_TA), (c) Ag12 without post-thermal annealing (Ag12_no TA), and (d) Ag12 with post-thermal annealing (Ag12_TA).
Fig. 2. Size distributions of (a) Ag6 without post-thermal annealing (Ag6_no TA), (b) Ag6 with post-thermal annealing (Ag6_TA), (c) Ag12 without post-thermal annealing (Ag12_no TA), and (d) Ag12 with post-thermal annealing (Ag12_TA). Their Gauss fittings (red lines) are also provided.

Fig. 3. Extinction spectra of the SiN$_x$ films with different N/Si ratios (N3/8, N2, and N6). Inset is their optical bandgap fittings via the Tauc model, black square for N3/8, red circle for N2, and blue triangle for N6.

Figure 3 shows the extinction spectra of SiN$_x$ films with different N/Si ratios. As can be observed, the absorption edge of the SiN$_x$ films is blue shifted with the increase of N/Si ratio. Usually, the optical bandgap ($E_{opt}$) of SiN$_x$ films can be obtained by the fitting of its extinction
spectra via the Tauc model [2,37]. This Tauc model is given as \( a h\nu = A(h\nu - E_{\text{opt}})^n \), where \( a \), \( h\nu \), \( A \), and \( n \) stand for the absorption coefficient, energy of absorption photons, fitting constant, and the exponential factor determined by the type of luminescence matrix (\( n = 2 \) for our SiN\(_x\) matrix here and \( n = 1/2 \) for direct bandgap materials). Consequently, we can extract the values \( E_{\text{opt}} \) from the intercept of the linear fittings of \((ah\nu)^{1/2}\) vs. \( h\nu \), as shown in the inset of Fig. 3. As can be observed, this \( E_{\text{opt}} \) increases distinctly with the N/Si ratio from \(~4.8\) eV for N6 to \(~2.6\) eV for N3/8, which indicates that the composition of our SiN\(_x\) films evolves from silicon-rich to nearly stoichiometric ratio.

**Fig. 4.** Normalized extinction spectra of Ag nanostructures on (a) N3/8, (b) N2, and (c) N6, black circle for Ag6 without post-thermal annealing (Ag6_no TA), red triangle for Ag6 with post-thermal annealing (Ag6_TA), green diamond for Ag12 without post-thermal annealing (Ag12_no TA), and blue star for Ag12 with post-thermal annealing (Ag12_TA). The PL spectra of (a) N3/8, (b) N2, and (c) N6 without the addition of Ag nanostructures are also provided at the right side (black lines).

PL spectra of these SiN\(_x\) films with different N/Si ratios are measured, as shown in Fig. 4 (right). The peak of PL from the SiN\(_x\) films gradually blue-shifts from \(~630\) nm to \(~450\) nm with the increase of N/Si ratio. All these PL peaks are originated from the radiative recombination.
between the band tails in SiN films [2]. The difference between the central peaks of PL may result from the different state densities of band tails for different N/Si ratios [2,3,38]. Deeper band tail, mainly the N dangling bands (= N⁻), contributes to the larger value of $E_{\text{opt}}$ as well as the shorter PL wavelength of SiN matrixes. Good consistence is obtained between the $E_{\text{opt}}$ and the PL wavelength, as shown in Fig. 4 (right) and in the inset of Fig. 3. This deeper band tail is originated from the more N excess environment induced by larger N/Si ratio. Consequently, the blue-shift of PL wavelength with the increase of N/Si ratio may result from its deeper band tail, which is originated from its less silicon excess environment.

Figure 4 (left) represents the normalized extinction spectra of Ag nanostructures onto the SiN films with different N/Si ratios. Two LSPR peaks can be resolved in the extinction spectra which may result from the two resonance modes of Ag nanoparticles, the longitudinal resonance mode (longer wavelength from ~650 nm to ~700 nm) and the transverse resonance one (shorter wavelength from ~450 nm to ~520 nm). The generation of two extinction peaks from these two resonance modes can be explained by collective nanoparticle plasmon resonances which are originated from the electromagnetic coupling between neighboring nanoparticles [39,40]. Under the polarized incident light, neighboring nanoparticles with surface charges of same (opposite) signs will repel (attract) each other and increase (decrease) the energy required for driving an oscillation resonance, from which the wavelength of dipolar resonance peak is shorter (longer) relatively. This interparticle coupling is much more distinct for Ag nanostructures with smaller space by comparing the extinction spectra of Ag6_TA with that of Ag12_no TA, as shown in Fig. 4 (left), which is also consistent with the finite integration simulation results by Sweatlock et al. [40]. Furthermore, the transverse resonance component is dominant in the electric field of surface plasmon polaritons (SPPs) with small wavenumbers and low frequencies, while the longitudinal resonance mode is comparable with the transverse one only when the wavenumbers are very large [41]. Consequently, the longitudinal resonance mode cannot be excited efficiently in the Ag nanostructures (Ag_TA) with small $\eta$ as well as large interparticle distance. Meanwhile, the longitudinal resonance component of Ag nanostructures is not as distinct as the transverse resonance one due to its lower excitation efficiency at the detection wavelength we employed, as shown in Fig. 4 (left).

The main LSPR peak originated from the transverse resonance mode is red shifted with the increasing size of Ag nanostructures with similar values of $\eta$, see the comparison of Ag6_TA (red triangles) and Ag12_TA (blue stars) or Ag6_no TA (black circles) and Ag12_no TA (green diamonds) shown in Fig. 4 (left). Moreover, the $\eta$ of Ag nanostructures has an important influence on the LSPR peak and its width. For the Ag nanostructures with similar average size, the wavelength of dipolar resonance peak of Ag nanostructures with smaller $\eta$ is much shorter than that of Ag nanostructures with larger $\eta$, see the comparison of Ag6_TA and Ag12_no TA shown in Fig. 4 (left). Meanwhile, the width of the main LSPR peak is decreased significantly after the post TA process for Ag nanostructures, which might be also originated from the reduced $\eta$ as the samples of Ag6_TA and Ag12_no TA have the similar average size. Interestingly, the absorption of SiN, matrixes also has an important influence on the shape of extinction spectra. The shape of extinction spectra for Ag nanostructures onto N3/8, as shown in Fig. 4(a), is different from that for Ag nanostructures onto N2 or N6, as shown in Fig. 4(b) or Fig. 4(c), extremely for the short wavelength. There is a distinct increase of absorption for Ag nanostructures onto N3/8 at lower than ~450 nm which is originated from the band edge absorption of SiN, films, as shown in Fig. 3.

As shown in Fig. 4(a), the PL peak of N3/8 is far from the main dipolar resonance peak of Ag nanostructures. However, this resonance peak is very close to the PL peak of the sample N2 or N6, as shown in Fig. 4(b) or Fig. 4(c). Differently, the wavelength of PL peak for N2 is a little longer than that of dipolar resonance peak for Ag nanostructures, which is opposite from the situation of N6. Consequently, the improvement of PL from SiN, matrixes by LSPR may be more distinct for N2 and N6 than that for N3/8 due to their preferable consistence between the LSPR peak and PL peak. For the investigation of the LSPR effect of Ag nanostructures on the
PL of SiN$_x$ films, PL spectra of SiN$_x$ films with different N/Si ratios with and without the addition of Ag nanostructures with different dispositions were measured.

As shown in Fig. 5, there is little effect of the LSPR of Ag nanostructures on the overall shape of PL spectra of SiN$_x$ films. However, the intensity of PL from SiN$_x$ matrixes is affected significantly by the addition of Ag nanostructures. On the whole, PL intensity is improved by the addition of Ag nanostructures with post-thermal annealing, which have a lower $\eta$. But for the samples with the addition of Ag$_6$ no TA and Ag$_{12}$ no TA, the PL intensity is decreased significantly, which may result from the poor light extraction due to the larger $\eta$ of Ag nanostructures. Interestingly, the optimal PL intensity of SiN$_x$ films is achieved by the addition of Ag$_{12}$ TA for all the samples investigated here, even though the $\eta$ of Ag$_6$ TA is the same as that of Ag$_{12}$ TA (the data can be found in Fig. 2). It may result from their different effects of LSPR on the enhancement of absorption and scattering for different sizes of Ag nanostructures [24]. Absorption is dominant for the nanoparticles smaller than 50 nm (Ag$_6$ TA), while for the
large sized particles (~100 nm), scattering is more significant and more relevant to the applications of solar cells and optoelectronics [3,42]. It is worth noting that too large sized particles would introduce the multipole oscillation modes, from which the scattering efficiency of the metal particles would be decreased [42,43].

Consequently, both the size and the surface coverage of metal nanostructures should be considered to improve the emission from luminescence materials via the coupling between the localized surface plasmons and excitons in active matrix. Absorption induced by the LSPR dominates for the small sized Ag nanostructures (<50 nm) [41], from which a part of light would be absorbed by the metal nanostructures. With the increasing size of Ag nanostructures (<100 nm), the scattering efficiency as well as the PL intensity would be increased. It explains the reason of better PL performance for Ag12_TA than that for Ag6_TA, even though the LSPR peak of Ag6_TA is narrower and closer to the PL peak of SiNx matrix (N6) than that of Ag12_TA, as shown in Figs. 4(c) and 5(c). On the other hand, for particles with η too small, the coupling between metal nanostructures becomes very weak, from which the scattering efficiency would be decreased significantly. While for nanostructures with too large η, light generated from SiNx matrixes would be confined inside and only little amount of it can be extracted to the outer space. By combining these two effects, we obtained the optimal PL intensity of SiNx matrixes with different N/Si ratios by the addition of Ag12_TA in our experimental, as shown in Fig. 5.

![Enhancement factor of PL](image)

**Fig. 6.** Enhancement factor of PL by dividing the PL intensity of SiNx with Ag12_TA by that of SiNx without Ag nanostructures. Inset is the integrated enhancement factor of PL intensity.

For the comparison of these optimal PL from SiNx films with different N/Si ratios by the addition of Ag12_TA, we plot the PL enhancement factor by dividing the PL intensity of SiNx films without the addition of Ag nanostructures by that of SiNx films with Ag12_TA, as shown in Fig. 6. There is a large difference on the spectra shape of PL enhancement factor between the SiNx films with different N/Si ratios. Two distinct enhancement peaks can be observed for the samples of N3/8 and N6, while there is only one wide peak for the sample of N2. Nevertheless, the overall effect of Ag nanostructures on the enhancement of PL from the SiNx films with different N/Si ratios is similar, where the maximal enhancement factor is ~2.5-3.0. By integrating the PL enhancement factor of the SiNx films with different N/Si ratios, we compare the overall PL enhancement effect of Ag nanostructures more directly, as shown in the inset of
Fig. 6. This integrated value is decreased with the increase of N/Si ratio, where the sample of N3/8 has a little better enhancement result among them. Nevertheless, the same order of magnitude of this integrated enhancement factor is obtained for all the samples, which indicates that the overall enhancement effect of Ag12_TA for SiN_x films with different N/Si ratios is similar. This result is inconsistency with the speculation from the comparison of the dipolar resonance peak and the PL one, as shown in Fig. 3, which has been mention above. This inconsistency may indicate that the role of the dipole resonance absorption from Ag nanostructures on the improvement of luminescence intensity is very weak. The enhanced photo-excitation by LSPR may have a main contribution to the improved luminescence intensity, which is consistence with our early works [30].

Fig. 7. PL spectra of the SiN_x films with different N/Si ratios with and without the addition of Ag nanostructures, (a) Ag6 without post-thermal annealing (Ag6_no TA), (b) Ag6 with post-thermal annealing (Ag6_TA), (c) Ag12 without post-thermal annealing (Ag12_no TA), and (d) Ag12 with post-thermal annealing (Ag12_TA).

The influence of Ag nanostructures on PL from the SiN_x films with different N/Si ratios is also provided, as shown in Fig. 7. The sample of N6 has the weakest intensity of PL among all the SiN_x films investigated here no matter the addition of Ag nanostructures, which may result from its extremely poor absorption of excited light from He-Cd laser, as shown in Fig. 3. Besides, the deterioration of PL intensity by the addition of Ag nanostructures with high $\eta$ is much more distinct for the sample N3/8 than that for N6, as shown in Figs. 7(a) and 7(c). However, the improvement of PL intensity by the addition of Ag nanostructures with low $\eta$ is similar for N3/8 and N6, as shown in Figs. 7(b) and 7(d). Consequently, further optimization of the LSPR enhanced emission from SiN_x films can be achieved by the modulation of the composition of SiN_x films (N/Si ratio) as well as the size, area density, and shape of metal nanostructures. This optimization would be especially valuable for the fabrication of LSPR enhanced SiN_x-based LEDs with promising EL efficiency.

4. Conclusion

In conclusion, we demonstrate the improvement of PL intensity from SiN_x films with different N/Si ratios via the modulation of LSPR. This modulation of LSPR is achieved by modulating the sizes and densities of Ag nanostructures via the control of sputtering time and post-thermal
annealing process. On the whole, there is little effect of the dipolar resonance absorption of Ag nanostructures on the shape of PL spectra, which is mainly determined by the N/Si ratio of SiNx films. However, the PL intensity varies much by the addition of Ag nanostructures with different sizes and densities. The PL is very weak for SiNx films with larger N/Si ratio, which is originated from its poor absorption of excited He-Cd laser at 325 nm. The PL intensity is degenerated by the addition of Ag nanostructures with high surface coverage, which may result from its poor extraction of light due to the strong backscattering of Ag. While for the nanostructures with low surface coverage, the PL intensity of SiNx matrix is improved via the LSPR coupling. Our work may provide an alternative approach for the fabrication of silicon- or SiNx-based light source with high efficiency. Optimal LSPR enhanced SiNx luminescence (PL and EL) may be achieved by the addition of Ag nanostructures with proper designed size and surface coverage. Further optimization of luminescence efficiency from SiNx matrixes may be achieved by the modulation of the shape of Ag nanostructures.

Acknowledgments

We acknowledge the National Natural Science Foundation of China (No. 61176117), the 863 Program (Grant No. 2011AA050517), and the Innovation Team Project of Zhejiang Province (No. 2009R5005).