



# Visible photoluminescence of Si clusters embedded in silicon nitride films by plasma-enhanced chemical vapor deposition

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## Abstract

Strong visible photoluminescence (PL) has been observed in the hydrogenated amorphous silicon nitride (a-SiN<sub>x</sub>:H) films prepared by plasma-enhanced chemical vapor deposition (PECVD). With various temperatures annealing, the evolution of the structure and of the PL properties has been studied to explain the PL origin. With the disappearance of PL peak with respect to ≡Si<sup>0</sup> (dangling bonds) at the higher annealing temperature, the intense PL peak shows an obvious blueshift. Accompanying with the blueshift, a new PL peak on the high-energy side, about 640 nm, has been observed in the spectra, and the appearance of the new PL peak has been discussed. In terms of the present results, the intense PL originates from the Si clusters embedded in the silicon nitride.

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## 1. Introduction

The research of silicon-based light-emitting materials is very important because of their low-

cost manufacturing and potential applications in optoelectronic devices based on silicon-integrated circuits. Although bulk silicon has an indirect band gap and low photoluminescence (PL) efficiency, stable efficient light emission can be achieved at room temperature in silicon nanostructures where the selection rules are broken. Since the report of light emission from porous

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silicon by Canham [1], silicon nanostructures have received considerable attentions for their unique characteristics and their potentials in optoelectronic devices applications. PL in the visible range has been studied in many silicon nanostructures in recent years [2–5]. Among them, stable efficient PL is usually achieved for silicon clusters embedded in silicon oxide or silicon nitride which can enable efficient surface passivation. Previously silicon oxide was typically used as a material to embed the Si clusters, while silicon nitride films embedding Si clusters have been little studied. As a matrix, silicon nitride is a better candidate compared with silicon oxide. The band gap of  $\text{Si}_3\text{N}_4$  (5.3 eV) [6] allows the carriers confinement in Si clusters. In particular, the tunneling barrier of silicon nitride (1.5–2.0 eV) is lower than that of silicon oxide (3.1–3.8 eV) [7], which is more advantageous for carrier injection in electroluminescent devices. Up to now, the PL origin of silicon nanostructures is still in debate [2,8,9]. Using silicon nitride in which no oxygen exists as the matrix can help clarify the PL mechanism.

In this paper, silicon nitride film has been used as a matrix to embed Si clusters. We have particularly studied the influence of the annealing on the structure and the photoluminescence properties. The evolution of PL peak intensity and shift with the annealing treatments has been studied to explain the PL origin like previous study [10,11]. In addition, the appearance of a new PL peak at 640 nm after 900 °C annealing has also given supplementary information on the PL origin.

## 2. Experimental

The silicon nitride films studied in this experiment were deposited by plasma-enhanced chemical vapor deposition (PECVD) technique on (100) silicon substrate. The growth temperature and the rf plasma power were 70 °C and 40 W, respectively. The background pressure was  $10^{-2}$  Pa. After the standard RCA clean procedures, the substrate was loaded into the reaction chamber. Before the deposition of silicon nitride, Ar plasma treatment was adopted for 5 min in order to clean the silicon

surface.  $\text{SiH}_4$  and  $\text{NH}_3$  were used as the reactant gas resources to deposit the silicon nitride films. In this experiment, three samples were prepared with different gas flow rate ratios  $R$  [ $\text{NH}_3(\text{sccm})/\text{SiH}_4(\text{sccm})$ ] = 6/10 (I), 6/8 (II), 6/6 (III). The thicknesses of the samples were about 500 nm. After the deposition, pieces of each sample were annealed for 30 min at the temperatures of 300, 500, 700 and 900 °C in  $\text{N}_2$  environment, respectively.

The atomic structure and the composition of the films were followed by infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) experiments. The IR absorption measurements were carried out with a Fourier-transform infrared (FTIR) spectrometer (FTS3000 BIORAD). PL spectra were measured using a micro Raman spectrometer at room temperature, and the 325 nm line of a He–Cd laser was employed as an excitation light source.

## 3. Results and discussion

Fig. 1 shows the typical FTIR spectra for sample I annealed at different temperatures, the

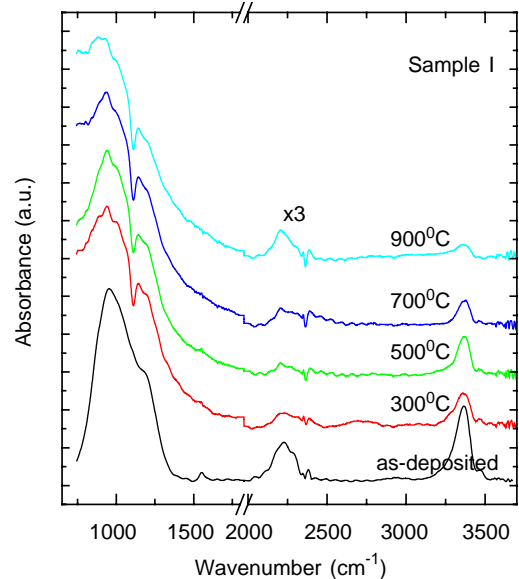


Fig. 1. FTIR spectra of sample I ( $R = 6/10$ ) annealed at different temperatures.

intensity in the figure is magnified three times from 2000 to  $3750\text{ cm}^{-1}$ . As illustrated in Fig. 1, the spectra shows typical absorptions of the bonding groups present in  $\text{SiN}_x\text{:H}$  films, the Si–N, Si–H and N–H vibration modes. The broad absorption band at  $930\text{--}960\text{ cm}^{-1}$  and the shoulder at  $1150\text{ cm}^{-1}$  can be assigned to the Si–N stretching and N–H bending vibration modes. Four other peaks are discernible at 1550, 2220, 3365 and  $3460\text{ cm}^{-1}$ . These absorption peaks correspond to N–H<sub>2</sub> bending, Si–H stretching, N–H stretching and N–H<sub>2</sub> stretching vibration modes, respectively [12,13].

Noticeably, multiple peaks which are assigned to the different bond modes of the Si–N bonds [ $\text{Si}_n\text{N}_{4-n}$  ( $1 \leq n \leq 3$ )] appear in the broad band after annealing because of the combination of the Si atoms and the N atoms. The intensity of the N–H bond absorption peak decreases gradually with the increase of annealing temperature. However, about the change of the Si–H bond absorption peak, there is an interesting trend as shown in the IR spectra. There is a first decrease of the Si–H absorption peak intensity followed by an increase with increasing the annealing temperature. There are many voids in the silicon nitride material where most of the H atoms are located. At  $900\text{ }^\circ\text{C}$  annealing temperature, the Si–H and N–H bonds are broken, and H will start to exhaust from the material. Meanwhile, the Si and N atoms might diffuse a short distance to bond together and form a  $\text{SiN}_x$  network. Because the film is Si-rich silicon nitride, it is reasonable to suggest that there are more Si dangling bonds than N dangling bonds around the void. After all N dangling bonds are bonded, there are still some Si dangling bonds left. The outside network becomes denser and denser, at this time the H atoms dissociated will be captured by the Si dangling bonds around the void and the motion will be recursive. But at lower annealing temperature, Si and N atoms could only bond to the neighboring atoms; thus the network around the void is not dense enough and the motion will hardly be recursive. Therefore, the intensity of the Si–H absorption peak of stretching vibration is decreased. From all the results of IR measurements, the similar change tendency of the Si–N, Si–H, N–H bonds absorption peaks with the

annealing temperature can be also observed in sample II and III.

XPS experiments have been carried out in order to confirm the presence of Si clusters. Fig. 2 shows the Si 2p level XPS spectrum of sample I annealed at  $300\text{ }^\circ\text{C}$ . The chemical composition  $x$  of  $\text{SiN}_x$  is determined from XPS measurement. The  $x$ -value of the sample is 0.31, indicating the sample is highly Si-rich. The spectrum exhibits two clearly separated peaks: one centered at the binding energy of  $102.8\text{ eV}$ , and another small one centered at  $98.1\text{ eV}$ . The large peak at the energy of  $102.8\text{ eV}$  represents the bonded Si. And the small peak at the energy of  $98.1\text{ eV}$  indicates the presence of the zero-valent Si [14]. These results corroborate the presence of two phases: a pure silicon phase and a silicon nitride phase. The existence of the pure silicon phase is a precondition for the formation of the Si clusters. Also, in the following PL study, the shift of the intense visible PL peak with the Si excess and the annealing treatments really confirm that the PL originates from the Si clusters with an enlarged band gap due to quantum confinement effect.

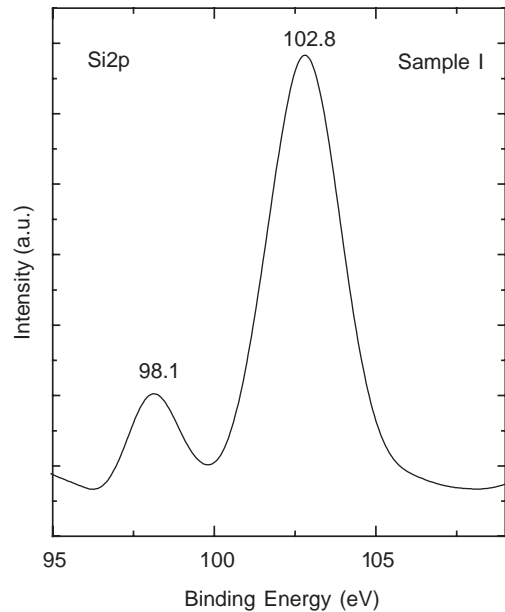


Fig. 2. The XPS spectrum of Si 2p for sample I ( $R = 6/10$ ) annealed at  $300\text{ }^\circ\text{C}$ .

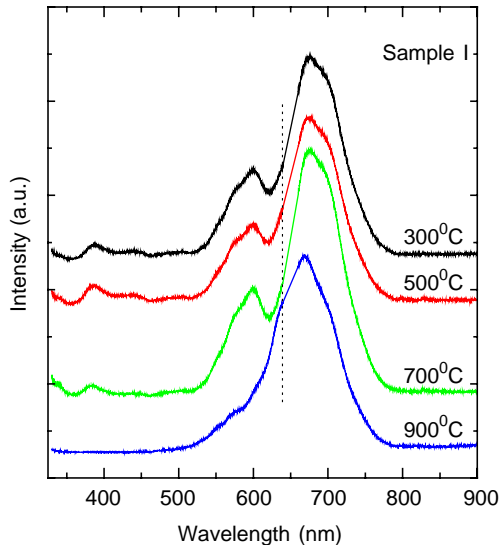


Fig. 3. PL spectra of sample I annealed at different temperatures.

Fig. 3 shows the room-temperature PL spectra of sample I annealed at different temperatures. For the as-deposited samples, PL from the Si clusters has not been observed in the PL spectra. After annealing, an intense PL peak appears in the vicinity of 675 nm, and the FWHM of the peak is about 70 nm. The appearance of the peak is attributed to the improvement of the structure and the diminution of the nonradiative centers. From Fig. 3, the intense PL peak position has no shift approximately in the range 300–700 °C. But when the annealing temperature reaches 900 °C, a shift towards a shorter wavelength can be observed in the spectra. The blueshift of the intense PL peak originates from the formation of the small Si clusters in the films. Because the diffusivity of Si atoms in silicon nitride matrix is rather low [11], the Si atoms might diffuse a short distance to create a majority of small Si clusters. Meanwhile, due to the enlargement of some Si clusters already formed in the film, some Si clusters are large enough to show bulk-like behavior, and the PL from these Si clusters is decreased. Therefore, at 900 °C annealing temperature, we can observe the PL from the new smaller Si clusters formed in the film, rather than from the already existing Si

clusters which are enlarged after 900 °C annealing. However, in the range 300–700 °C, it is estimated that the lower temperature cannot lead to the significant diffusion of the Si atoms in the matrix; therefore, the PL peak does not shift nearly. Two peaks (around 390 and 600 nm) can also be observed in the range 300–700 °C. The two peaks are associated with the electronic transition of  $\equiv\text{Si}^0 \rightarrow E_v$  (valence band) and  $E_c$  (conduction band)  $\rightarrow \equiv\text{Si}^0$ , respectively [15]. But at the annealing temperature of 900 °C, the two peaks disappear completely, which illustrates that the Si dangling bonds in the film are reduced largely. After annealing temperature of 900 °C, a majority of very small Si clusters are formed by the coalescence of the Si dangling bonds in the matrix and some Si dangling bonds are passivated by the H (it has been proved by IR results). So the large decrease of the Si dangling bonds in the film results in the disappearance of the two peaks with respect to the Si dangling bonds.

When the annealing temperature reaches 900 °C, accompanying with the blueshift, an interesting phenomenon that a new PL peak appears at 640 nm can be observed in the PL spectra. Due to the inhomogeneous compositional distribution in silicon nitride films [16], there is a fluctuation about the N/Si ratio  $x$ . After 900 °C temperature annealing, fewer and smaller Si clusters can be created in the higher  $x$ -value regions, while more and larger Si clusters can be created in the lower  $x$ -value regions. And both of the Si clusters formed in the two regions are smaller than the Si clusters that already exist in the film. The intense PL peak and the shoulder at 640 nm are attributed to the small Si clusters formed in the lower and higher  $x$ -value regions, respectively. Obviously, more and larger Si clusters are created in the lower  $x$ -value regions, so the stronger intensity and lower energy PL peak from these Si clusters can be observed. From Fig. 3, the FWHM of the intense PL peak is about 70 nm, which shows the uniformity of the Si clusters size. Therefore, it can be suggested that the dispersed state of Si atoms is also similar in a large range of the film. Thus, it is reasonable that PL from Si clusters of two sizes is prioritized. After 900 °C annealing, a silicon nitride shell, which has higher N/Si ratio compared with existing silicon

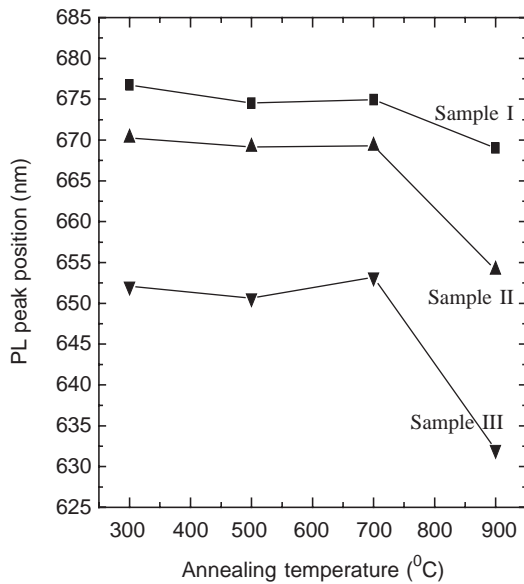


Fig. 4. PL peak position as a function of annealing temperature for three samples [I( $R = 6/10$ ), II( $R = 6/8$ ), III( $R = 6/6$ )].

nitride before 900 °C annealing, is formed around the new small Si clusters [17]. For example, due to the creation of Si clusters, the  $\text{SiN}_x$  film contains Si clusters embedded in a  $\text{SiN}_y$  matrix ( $x < y$ ). As it is known, the increase of N/Si ratio will widen up the energy gap of silicon nitride [18] around Si clusters. Therefore, the improvement of the barrier efficiency has a significant effect on the carriers confinement in the Si clusters. About the origination of the new PL peak, further studies are underway for the detailed information.

Fig. 4 shows the position of the intense PL peak as a function of annealing temperature for three samples. In the range 700–900 °C, the higher the  $R$  [ $\text{NH}_3(\text{sccm})/\text{SiH}_4(\text{sccm})$ ] value, the greater is the blueshift of the PL peak. In the higher  $R$  sample, the density of the dispersed Si atoms in the silicon nitride matrix is lower, so the size of the Si clusters formed after higher temperature annealing is smaller. Therefore, the smaller Si clusters lead to the larger displacement due to quantum confinement effect. From Fig. 4, we can also observe, at the same annealing temperature, the main PL peak position shifts towards the long wavelength with the decrease of  $R$ -value because of the presence of

larger Si clusters in the lower  $R$ -value film. These results show the effect of Si clusters size on the PL peak.

#### 4. Conclusions

In summary, PL property has been studied in silicon nitride films prepared by PECVD. Structural characteristic of the films are showed by IR and XPS spectra. When the annealing temperature reaches 900 °C, the PL peak with respect to the Si dangling bonds disappears, and a significant blueshift of the intense PL peak due to the creation of small Si clusters and appearance of a new PL peak have been observed in the PL spectra. At the same annealing temperature, there is a redshift of the PL peak in the spectra with the Si excess. The clarification of PL origin is very significant for the development of light-emitting devices.

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