Photoluminescence properties and chemical bond variations of SiN$_x$:H films with silicon quantum dots[*]

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Hydrogenated silicon nitride (SiN$_x$:H) thin films are deposited on p-type silicon substrates by plasma enhanced chemical vapor deposition (PECVD) using a gas mixture of ammonia and silane at 230 °C. The chemical compositions and optical properties of these films, which are dealt at different annealing temperatures, are investigated by Fourier transform infrared (FTIR) absorption spectroscopy and photoluminescence (PL) spectroscopy, respectively. It is shown that the FTIR presents an asymmetric Si-N stretching mode, whose magnitude is enhanced and position is shifted towards higher frequencies gradually with the increase of the annealing temperature. Meanwhile, it is found that the PL peak shows red shift with its magnitude decreasing, and disappears at 1100 °C. The FTIR and PL spectra characteristics suggest that the light emission is attributed to the quantum confinement effect of the carriers inside silicon quantum dots embedded in SiN$_x$: H thin films.

During the past decade, a great deal of interest has been paid to the photoluminescence (PL) from hydrogenated silicon nitride (SiN$_x$:H) thin films with silicon quantum dots[1-4]. Moreover, due to its quantum confinement effect, the new silicon materials with tailored band gap by assembling silicon quantum dots within silicon nitride matrix can be exploited in the solar cells. Up to now, the exact PL mechanisms of silicon quantum dots embedded in silicon nitride matrix still remain controversial[5]. Therefore, detailed studies of PL properties of SiN$_x$:H thin films must be done before considering their practical applications. Depending on the preparation parameters, the PL is attributed either to radiative recombination between localized band-tail states[6], or to the defect centers[7], or to the quantum confinement effect of silicon quantum dots in silicon nitride films[8]. Some groups[9,10] have also suggested that the PL properties of silicon quantum dots are closely related to the surface chemical environment. Consequently, making any step toward an insight into the understanding of PL mechanisms is valuable. In this paper, in order to better understand PL mechanism from silicon quantum dots embedded in silicon nitride matrix, SiN$_x$:H thin films are fabricated by plasma enhanced chemical vapor deposition (PECVD) method at low temperature. The PL properties and chemical bonds of the films with different annealing temperatures are systematically studied by PL and Fourier transform infrared (FTIR) spectra, respectively.

A conventional 13.56 MHz parallel plate radio frequency PECVD system was employed to prepare SiN$_x$: H thin films on p-type (100) silicon substrates. Hydrogen-diluted 10% SiH$_4$ and NH$_3$ with the purity above 99.999% were used as reactant gases, and the flow rates of SiH$_4$ and NH$_3$ were maintained at about 80 cm^3/min and 30 cm^3/min, respectively. The plasma power, substrate temperature and total pressure were fixed at around 40 W, 230 ^{o}C and 0.75 Torr, respectively. After deposition, the silicon wafers were cut into several smaller parts for annealing treatments from 500 ^{o}C to 1100 ^{o}C. Each smaller sample was annealed in a quartz tube furnace with a flowing environment of nitrogen (purity 99.999%) for 30 min. The bonding configurations of the samples were analyzed by means of a VERTEX 70 FTIR spectrometer with a resolution of 4 cm^{-1}. Room temperature PL measurements were carried out using an FP-6500 fluorescence spectrometer. A 75 W Xe lamp was used as the excitation source, and the excitation wavelength was fixed at 325 nm. In the process of PL measurements, a transmission filter of L38 was used to eliminate the influence of the strong overtone bands centered at 650 nm on the PL signal of every sample.

Infrared absorption measurements were performed on samples with different annealing temperatures in order to investigate the bonding configurations and compositions

of the SiN$_x$:H films. Fig.1 shows the FTIR spectra of the as-deposited sample and the samples annealed at different temperatures. From Fig.1, the typical vibration modes related to different bonds in PECVD SiN$_x$: H films can be clearly identified. The absorption bands at about 465 cm^{-1}, 830 cm^{-1}, 1170 cm^{-1}, 2160 cm^{-1} and 3355 cm^{-1} can be assigned to the Si-N symmetric stretching, Si-N asymmetric stretching, N-H bending, Si-H stretching and N-H stretching modes, respectively[11]. Fig.2 depicts the FTIR absorption peak intensities of Si-N asymmetric stretching, Si-H stretching and N-H stretching modes as a function of the annealing temperature. When the annealing temperature is increased, the Si-N peak is increased, and the Si-H and N-H peaks are diminished, because the increased temperature promotes the release of hydrogen atoms from N-H and Si-H bonds. Fig.3 shows the position of the Si-N asymmetric stretching modes shifts toward higher wave number with annealing temperature up to 1100 °C. The shift indicates that the number of nitrogen atoms bonded to a silicon atom is increased, for example, an N$_2$Si-SiN bond is replaced by an N$_3$-SiN one. There are many nitrogen atoms in the silicon nitride phase approximating to Si$_3$N$_4$ as annealing temperature increases[6]. The blue shift of Si-N peak and the increase of intensity both indicate that the number of nitrogen atoms bonded to one silicon atom is larger at higher annealing temperature[5]. While the N/Si ratio remains unchanged for the samples with the same substrate temperature, the change of the Si-N peak is expected to be accompanied by the increase of pure silicon phase[5], and the pure silicon phase may be silicon quantum dots. The existence of silicon quantum dots in the SiN$_x$:H films can be demonstrated by the combination of FTIR measurements and the following PL analyses of the samples.

Fig.2 FTIR absorption peak intensities of samples as a function of the annealing temperature

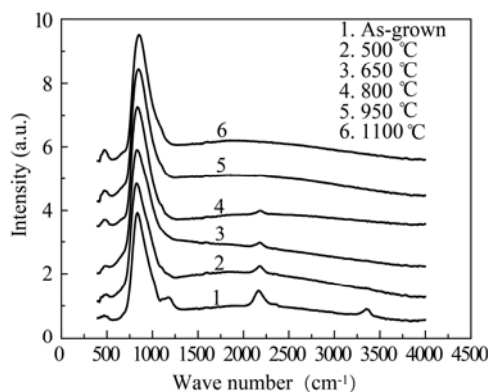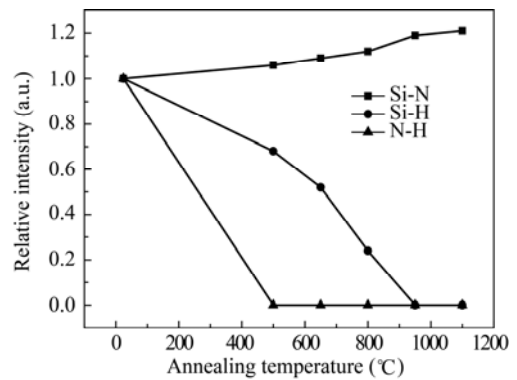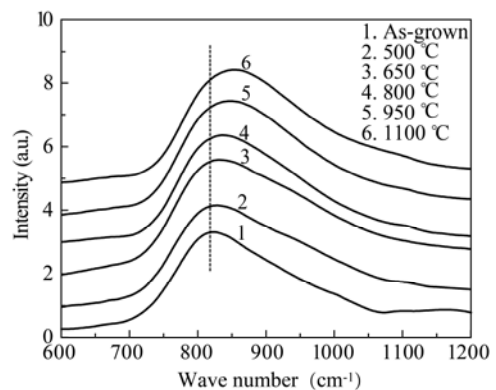**Fig.3 The shift of the Si-N asymmetric peak with the increase of annealing temperature**

Fig.1 FTIR spectra of the as-grown sample and samples annealed at different temperatures

Fig.4 shows the PL spectra of the samples annealed at different temperatures. The as-grown film produces the strongest PL signal. The PL peak exhibits a continuous red shift from 560.9 nm in the as-deposited film to 646.9 nm in the sample with annealing temperature of 950 °C, accompanied with an obvious decrease of the luminescence intensity, and the PL peak of the film disappears as

the annealing temperature increases to 1100 °C. Generally, the peak position of defect-related PL depends only on the defect energy level. It is almost fixed for a given defect, and can not be easily controlled[12]. Therefore, the PL spectra can't be attributed to related radiative defects in the SiN$_x$: H films. The evolution of the PL spectra also can be discussed considering two models: the model of the quantum confinement of the carriers inside silicon quantum dots or the model of the band-tail states. For the first model, many researchers[6,12] have found that the luminescence peak position of silicon quantum dots can be tuned by controlling the size of silicon quantum dots. The last model is the one usually used to describe the PL in amorphous silicon alloys, such as a-SiN$_x$:H, a-SiC$_x$:H or even a-Si:H[6]. In this model, the luminescence is ascribed to radiative recombination of carriers which are thermalized in the conduction and valence band tails, and the PL peak shifts following the enlargement of the band gap when the concentration of alloying N atoms is raised. Such an interpretation has also been applied[13] to non-homogeneous films composed of a mixture of silicon-rich phase with lower gap and nitrogen-rich phase with higher gap. The emission peak positions of PL are in range of 560.9–646.9 nm as shown in Fig.4. The results are in better agreement with the PL peak in shorter wavelengths (450–650 nm) of silicon quantum dots in SiN$_x$:H film[14-16]. However, for the model of the band-tail states, the emission usu-

ally occurs at wavelengths higher than 680 nm[6]. Therefore, the possibility of PL from radiative recombination between localized band-tail states also can be excluded.
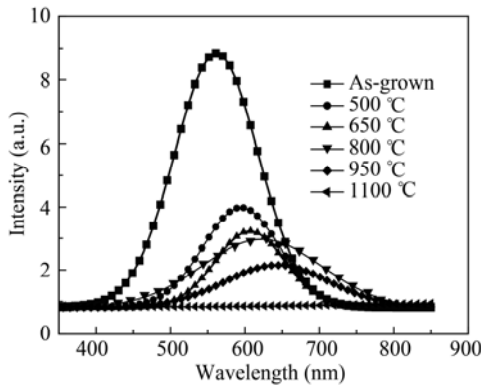

Fig.4 PL spectra at room temperature of the as-grown sample and the samples annealed at different temperatures

The red shift of PL peak with the increase of annealing temperature is mainly due to the increase of the size of silicon quantum dots. With the increase of annealing temperature, annealing treatments help to create new silicon quantum dots and increase the size of already existing silicon quantum dots. However, when annealing temperature increases, the coalescence, overgrowth and expansion of silicon quantum dots reduce the dot density, but still increase the dot size[5]. Therefore, the PL spectra for the samples exhibit a clear and continuous red shift in peak position, and the PL peak intensity continues to drop with the increase of annealing temperature. In fact, the decrease of the PL intensity can be explained by not only the decrease of silicon quantum dot density, but also the loss of the hydrogen, which makes the nonradiative defects not well passivated. Such an interpretation can be confirmed by the decrease of intensity of the Si-H and N-H bonds as shown in Fig.2. Moreover, since the larger silicon quantum dot has a larger surface area, the nonradiative defects tend to exit on the surface of the larger silicon quantum dots[17], and the electron-hole radiative recombination rate caused by the quantum confinement effect may decrease for larger silicon quantum dots[18]. The two factors also can lead to the decrease of the PL peak intensity. After the annealing at 1100 °C, the PL peak almost disappears as shown in Fig.4. It is maybe due to the rest of silicon quantum dots in the sample are very few and the passivation caused by the loss of the hydrogen atoms is poor. Therefore, based on the above discussion and the variations in PL peak position and intensity with the increase of annealing temperature, it is reasonable to believe that the quantum confinement effect of silicon quantum dot may be the main origin for the PL of the samples.

The evolutions of PL spectra at room temperature and the chemical bonds of SiN$_x$:H thin films are investigated. Based on the PL results combined with the analyses of the bonding configurations, the PL emission is attributed to the quantum confinement effect of silicon quantum dots embedded in SiN$_x$:H thin films. The continuous red shift in PL peak position with the increase of annealing temperature is mainly due to the increase of the size of silicon quantum dots. The decrease of PL intensity can be attributed to the reduction of density of silicon quantum dots, the increase of the nonradiative defects, and the poor passivation due to the loss of the hydrogen atoms.

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