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## Visible photoluminescence in amorphous $\text{SiN}_x$ thin films prepared by reactive evaporation

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Photoluminescence in the visible domain can be observed in amorphous silicon nitride ( $a\text{-SiN}_x$ ) alloys prepared by evaporation of silicon under a flow of nitrogen ions. A strong improvement of the photoluminescence intensity was obtained with annealing treatments in the range 500–1150 °C. Structural investigations were performed by infrared and Raman spectrometry experiments. The optical gap was obtained from transmission measurements in the ultraviolet, visible, and near infrared range. The evolutions of the structure and the optical properties with annealing treatments are correlated to the evolution of the photoluminescence. © 2000 American Institute of Physics. [S0003-6951(00)03748-7]

Since the observation of a strong visible photoluminescence (PL) in porous silicon at room temperature, there was significant activity to obtain new silicon-based light-emitting materials, specially by techniques compatible with the microelectronics industry technology. PL in the visible range has been studied in structures such as  $\text{Si}^+$  implanted  $\text{SiO}_2$  films,<sup>1</sup>  $\text{Si/SiO}_2$  multilayers,<sup>2</sup> or in Si-rich  $\text{SiO}_2$  films grown by sputtering, chemical vapor deposition, or evaporation.<sup>3</sup> Several explanations were proposed to explain the PL, like silicon-based chemical compounds as siloxene or polysilane, interfaces states, defects states, or carrier confinement. Although the latter seems to be more credible, the detailed origin of the PL is still a matter of debate. Therefore the study of new silicon-based systems in which no hydrogen and no oxygen is implicated could give new information on the PL origin. In particular  $\text{SiN}_x$  alloys are good candidates to investigate the PL in a silicon-based compound mostly because  $\text{Si}_3\text{N}_4$  with a gap equal to 5.3 eV could allow the confinement of silicon clusters. Moreover, very few PL studies have been performed with  $\text{SiN}_x$  films,<sup>4,5</sup> although the barriers at the  $\text{Si/Si}_3\text{N}_4$  for electrons and holes are smaller than at the  $\text{Si/SiO}_2$  interface, which provides better conditions for carrier injection in electroluminescent devices.

In this letter, we show that it is possible to observe very intense PL in the visible range in  $a\text{-SiN}_x$  thin films prepared by an ion-beam-assisted evaporation technique and we study the evolution of the structure and of the photoluminescence properties with the annealing treatments. Silicon was evaporated under a continuous flow of nitrogen ions with a deposition rate equal to 1 Å/s. Silicon and nitrogen ions were provided by an electron beam gun and an electron cyclotron resonance microwave plasma source, respectively. The nitrogen flow was regulated by maintaining the total pressure in the evaporation chamber at  $2 \times 10^{-5}$  Torr. The films were deposited on silicon and fused silica substrates maintained at 100 °C. Their thickness was 2000 Å. After deposition, each film was annealed in a quartz tube with a pressure equal to

$10^{-8}$  Torr and with a heating rate equal to 10 °C/min. The samples were cooled down immediately after the annealing temperature  $T_a$  was reached.

The optical transmission measurements were performed in the range 190–3300 nm by a Varian Cary 5 ultraviolet-visible-near infrared (UV-VIS-NIR) spectrophotometer. The evolution of the atomic structure was followed by infrared (IR) and Raman spectrometry experiments. The IR transmission measurements were carried out with a Nicolet 460 Fourier transform spectrometer with a resolution of 4  $\text{cm}^{-1}$ . PL and Raman measurements were carried out with a multichannel Jobin Yvon T64000 Raman spectrometer equipped with a 300 and 1800 grooves  $\text{mm}^{-1}$  grating, respectively. The detector was a charge coupled device camera cooled at 140 K. The 488 nm excitation light source was emitted from a Spectra Physics argon laser and the incident power of around 10  $\text{mW/mm}^2$  was chosen so as not to induce any crystallization of the analyzed samples.

The values of the optical gap  $E_G$ , derived from the Tauc relation, versus the annealing temperatures are represented in Fig. 1. As a consequence of optical interference fringes, the curve are not perfect lines. The induced error values for  $E_G$  are estimated by taking into account this effect and are always below 0.05 eV. For the as-deposited film,  $E_G$  is equal to 1.4 eV. The gap increases when  $T_a$  is less than 800 °C and is equal to 2.1 eV for  $T_a = 800$  °C and it decreases for higher annealing temperatures. This evolution will be discussed with the following results.

Figure 2 shows the Fourier transform infrared spectra of the films versus  $T_a$ . The spectrum shows a very intense band at around 840  $\text{cm}^{-1}$ , characteristic of the asymmetric stretching vibration of the Si–N bonds.<sup>6–8</sup> The IR spectra are not modified for  $T_a$  less or equal to 500 °C. In the range 500–950 °C, the intensity of the peak increases. For higher annealing temperatures, the peak is displaced toward the higher wave numbers.

Figure 3 shows the PL spectra of the films as-deposited and after different annealing temperatures. For  $T_a$  less than or equal to 500 °C, there is practically no PL. In the range 500–950 °C, the PL appears and increases with a maximum

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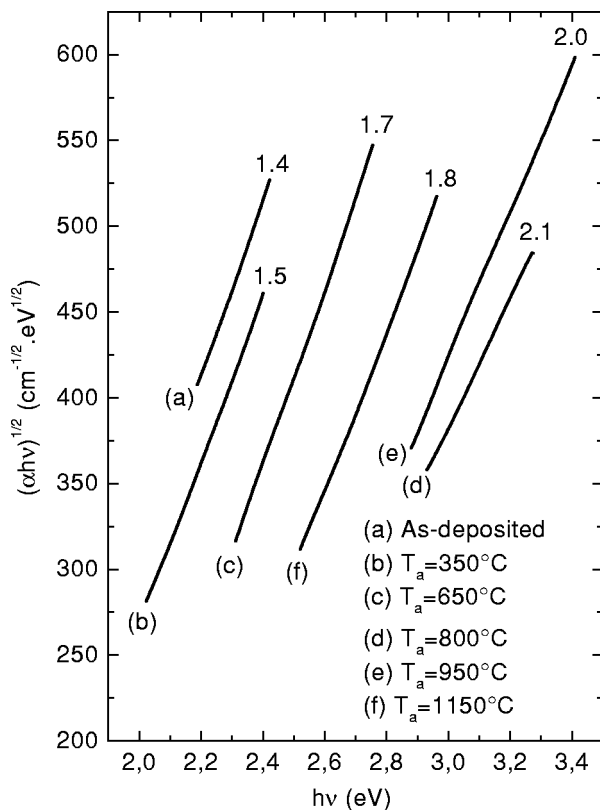


FIG. 1. Absorption coefficient of  $\text{SiN}_x$  samples plotted in the form suggested by Tauc.  $T_a$  is the annealing temperature and the numbers indicate the optical gap in eV.

at 720 nm. For higher temperatures  $T_a$ , the PL increases again with a slight displacement of the maximum toward the lower wavelengths.

The Raman effect is an efficient way to determine the presence of pure silicon in its crystalline or amorphous form. Bulk crystalline silicon exhibits a very thin band with a Raman shift at  $520\text{ cm}^{-1}$ . In amorphous silicon, the selection rules are broken and Raman spectrum is characterized by the density of phonon states, which presents two broad bands at  $150$  and at  $480\text{ cm}^{-1}$ . As the crystalline silicon substrate do not allow us to observe the crystallized silicon phase, experiments were also performed on fused silica substrates. In this case, the crystallization can be observed, but the presence of a silicon amorphous phase cannot be clearly determined be-

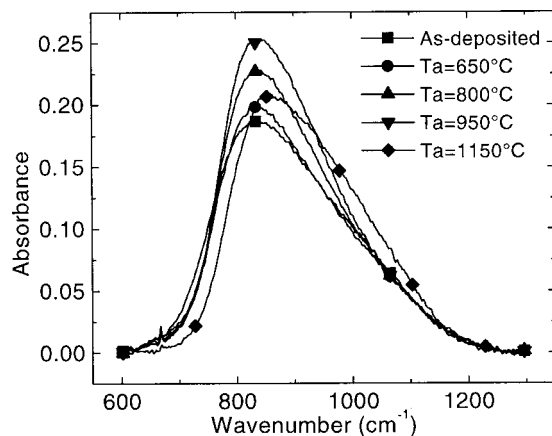


FIG. 2. IR absorption spectra of  $\text{SiN}_x$  samples annealed at different temperatures  $T_a$ .

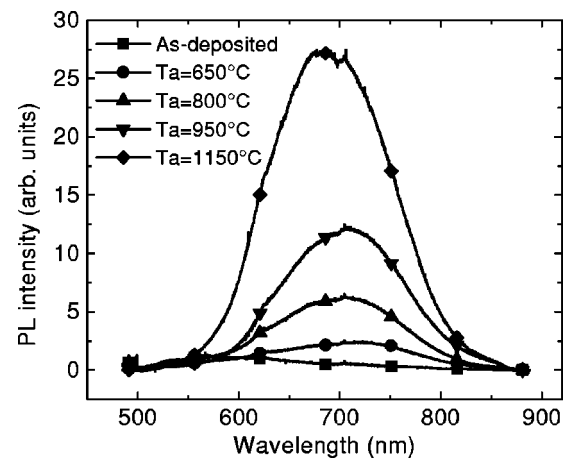


FIG. 3. PL spectra of  $\text{SiN}_x$  samples annealed at different temperatures  $T_a$ .

cause of the broad bands of the  $\text{SiO}_2$  substrate. Figure 4 shows Raman shifts versus  $T_a$  of films deposited on silicon and fused silica substrates. For  $T_a$  less than  $950^\circ\text{C}$ , the Raman spectra are identical to the spectra of the as-deposited films. They show that the layers contain an amorphous phase of pure silicon. For higher annealing temperatures, the amorphous peaks disappear and give a shoulder of the crystalline peak at  $504\text{ cm}^{-1}$ , which corresponds to the formation of silicon nanocrystals.<sup>9,10</sup> This evolution is clearly visible with the films deposited on fused silica substrates. The narrow band at  $300\text{ cm}^{-1}$  is due to the longitudinal acoustic mode of the crystalline silicon substrate, clearly visible for the films

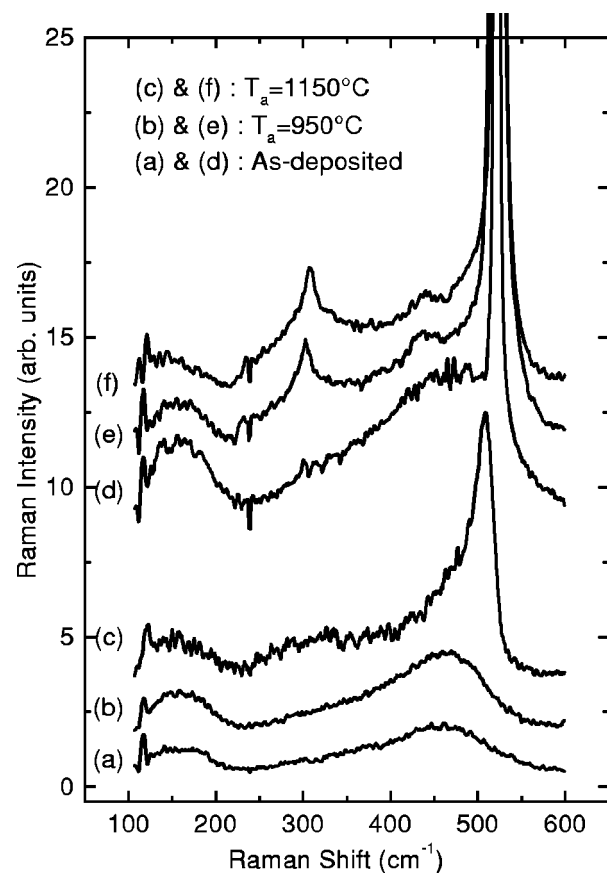


FIG. 4. Raman spectra of  $\text{SiN}_x$  samples deposited on fused silica (a), (b), and (c) and crystalline silicon (d), (e), and (f) substrates vs the annealing temperature  $T_a$ .

annealed at temperatures greater than 500 °C. Indeed for these films, the absorption coefficient is smaller than for the as-deposited films and the Raman contribution of the substrate is greater.

From these different experimental results, several stages in the evolution of the structure and of the optical properties can be defined. The as-deposited film is amorphous, as seen by transmission electron microscopy. IR and Raman spectra show the presence of Si–N bonds and of pure silicon domains, respectively. These results suggest that the film contains amorphous silicon clusters in a SiN<sub>x</sub> matrix. The optical gap is low, which could be due to the existence of a lot of electronic defects. For  $T_a$  less than 500 °C, the atomic structure is not modified but there is suppression of some deep electronic defects since the optical gap increases from 1.4 eV for the as-deposited sample to 1.7 eV for  $T_a$  equal to 500 °C. The second stage corresponds to the range 500–950 °C. During the thermal treatments, new Si–N bonds are created as shown by the increase of the intensity of the IR band at 840 cm<sup>-1</sup>. It can be deduced from this behavior that the as-deposited material presents a great number of silicon and nitrogen dangling bonds which disappear during annealing treatments with the formation of Si–N bonds. This evolution is confirmed by the increase of the optical gap. The improvement of the structure is sufficient to observe the increase of the PL with a maximum at 720 nm. The appearance of the PL is attributed to the diminution of the nonradiative defects. For  $T_a$  greater than 950 °C, the Raman spectra show the apparition of nanocrystals which originate from the crystallization of the amorphous regions or from the creation of new silicon crystals due to diffusion of the silicon atoms in the SiN matrix. The resulting increase of the nitrogen content in the matrix can be correlated to the displacement of the IR absorption peak toward the higher wavelengths. The PL intensity grows up, which can be explained by the increase in the number of silicon clusters. The creation of these nanocrystals could explain the decrease of the optical gap with the annealing temperature, which was already observed with SiO<sub>x</sub> samples.<sup>11</sup> Indeed, it can be shown that the absorption of the film is dominated by the phase which has the lower optical gap and that the value of  $E_G$  should decrease because of the low optical gap of amorphous silicon.

The PL peak is very similar to the peak observed in Si-rich silicon oxide films,<sup>3,11</sup> which was interpreted by the

presence of nanometric amorphous silicon regions in the SiO<sub>x</sub> matrix. However the evolution of the PL in SiN<sub>x</sub> is different from that observed in SiO<sub>x</sub> films. In these latter films, the PL presents a maximum at 650 °C and the maximum shifts toward the lower energy, which was explained by the growth and the coalescence of the silicon nanoclusters in the SiO<sub>x</sub> matrix. In the SiN<sub>x</sub> samples, no PL energy shift is observed until 950 °C. The atomic structure is modified only after 500 °C and the increase of the PL intensity with annealing treatments is presumably related to the diminution of the nonradiative defects. The network is more rigid and it can be assumed that the coalescence due to the long-range diffusion is absent. For annealing temperature greater than 950 °C, the short-range diffusion should only permit the creation of nanocrystals. Therefore the apparition of a majority of very small clusters could explain both the strong improvement of the PL intensity and the small blueshift of the PL energy.

In conclusion, visible PL can be observed in SiN<sub>x</sub> films prepared by evaporation of silicon under a flow of nitrogen ions. The PL intensity increases with annealing temperatures until 1150 °C. The evolution of the infrared absorption and Raman spectrometries correlated to UV-VIS-NIR absorption and PL experiments suggest that the PL originates in the presence of silicon clusters in the SiN<sub>x</sub> matrix.

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