Evolution with the annealing treatments of the photoluminescence mechanisms in $a\text{-SiN}_x\text{:H}$ alloys prepared by reactive evaporation

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A wide range of amorphous hydrogenated silicon nitride thin films with an excess of silicon was prepared by evaporation of silicon under a flow of nitrogen and hydrogen ions. A strong visible photoluminescence at room temperature was observed for the as-deposited films as well as for films annealed up to 1100 °C. The chemical composition and the structure of the films were investigated using x-ray photoelectron, thermal desorption, and Raman spectroscopies, infrared absorption measurements, grazing incidence x-ray diffraction experiments, and transmission electron microscopy. Two luminescence mechanisms were identified for the films depending on the annealing temperature. For annealing temperatures below 650 °C, the films are made of amorphous silicon-rich phases mixed with nitrogen-rich phases. These inhomogeneities in the chemical composition, coupled with the evolution of the photoluminescence energies and intensities with the hydrogen content, suggest that the emission is due to the recombination process of the photogenerated carriers within the band-tail states. For temperatures higher than 800 °C, a phase separation occurs and the films could be described as silicon nanoclusters embedded in an insulating amorphous silicon nitride matrix. The clusters are amorphous, and then crystallized when the annealing temperature is high enough. The correlation between the clusters sizes and the photoluminescence results suggests that the emission observed after annealing treatments at temperature higher than 900 °C is due to the quantum confinement of the carriers inside the silicon clusters. By carefully choosing the preparation and the annealing conditions, it is possible to tune the photoluminescence energy in the visible range. © 2007 American Institute of Physics.

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I. INTRODUCTION

During the past decade, observation of efficient photoluminescence (PL) at room temperature in silicon-based films has stimulated considerable research in the development of low-dimensional silicon (Si) materials as promising candidates for optoelectronic applications.

Most of the studies are related to porous silicon^{1,2} (PS) or crystalline silicon nanostructures. Although PS exhibits efficient room temperature PL and electroluminescence (EL) in a wide range of emission wavelengths, aging and operational instabilities of PS devices leave open the question about the most suitable silicon-based material for optoelectronics. Therefore, recent investigations were focused on Si-rich dielectric thin films or Si/SiO₂ multilayers made by techniques compatible with the microelectronic industry, such as sputtering deposition,^{3–5} Si⁺ implantation in SiO₂,^{6,7} laser ablation,^{8,9} reactive evaporation,^{10–12} or chemical vapor deposition.^{13–15} The recent results concerning the optical gain observed in such systems^{16–20} lead us more than ever to think that they are suitable for optoelectronic even as active components.

In these materials, the typical insulating matrix that hosts the Si clusters is, usually, amorphous SiO₂ because of its high gap (≈ 8.2 eV) which enables a good confinement of the carriers in the silicon clusters and its compatibility with the microelectronic industry. However, the use of SiO₂ as an insulator interferes with some issues for EL because of the important field strength needed to inject the electrons (6 MV/cm) and the holes (10 MV/cm) from Si into SiO₂.²¹

To overcome these issues, a silicon nitride matrix Si₃N₄ could be used as an insulator as the field needed to inject electrons and holes is weaker (2–4 MV/cm) than for SiO₂.²² Even if the value of the Si₃N₄ gap is only 5.3 eV, it should be sufficient to confine the carriers into the silicon clusters.

Another major interest for using silicon nitride rather than silicon oxide is the possibility to get efficient emission at shorter wavelength: several groups^{23,24} reported intense luminescence in the blue-green region which is very rare for silicon oxide-based materials. Thus, silicon nitride-based materials have the potential to produce full color emission devices.

The integration of such devices in silicon microphotonics will need efficient optical waveguides with weak optical absorption losses in the visible region. Due to its high refrac-

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tive index and minimum losses, silicon nitride appears as one of the most suitable material for photonic waveguides.^{25,26}

Besides, from a more fundamental point of view, it is of interest to study whether nonoxygen containing materials, such as SiN_x films, have the same PL behavior as PS or Si-rich SiO_x films given that some studies indicate that the light emission could be attributed to oxide-related defects or oxygen centers at the Si/ SiO_2 interface, especially for the optical gain process which is explained through the Si–O bonds.^{16,17} By comparing the luminescence properties from silicon nanostructures embedded in different insulating matrices, the role of the interface states and of the defects could be clarified.

Due to these properties, silicon nitride thin films could be promising materials for future optoelectronic devices. However, detailed investigations of the emission properties must be conducted before considering practical applications. Indeed, the few studies carried out for such structures still make the emission mechanisms unclear. Most of the existing studies are related to $a\text{-SiN}_x\text{:H}$ films with various compositions which have been prepared using chemical vapor deposition (CVD) techniques. Depending on the preparation parameters, the PL is attributed either to radiative recombination between localized band-tail states,^{27–29} or to the quantum confinement of silicon dots in a silicon nitride films.^{30–32}

In this paper, we used an alternative technique, the reactive evaporation in hydrogen-nitrogen gaseous mixture, to prepare $a\text{-SiN}_x\text{:H}$ alloys with a wide range of compositions ($0.1 \leq x \leq 0.63$). In previous papers,^{33,34} our group has prepared amorphous silicon nitride films which exhibit strong PL at room temperature without any annealing treatments but the PL mechanism could not be clearly identified. Here, the complete evolution of the structure and of the PL properties of the $a\text{-SiN}_x\text{:H}$ films prepared by reactive evaporation is studied from the as-deposited to the high temperature (1100 °C) annealed samples

The structural results are obtained from Fourier transform infrared (FTIR) transmission measurements, x-ray photoelectron spectroscopy (XPS), Raman spectroscopy, optical transmission measurements, grazing incidence x-ray diffraction (GIXRD), and transmission electronic microscopy (TEM). PL and optical experiments are interpreted in relation with the composition and the structure of the films.

The results show that, depending on the annealing temperature, two mechanisms are identified as responsible for the emission in the visible range for the $a\text{-SiN}_x\text{:H}$ alloys. At low annealing temperatures, the films structure, the optical measurements, and the evolution of the hydrogen content lead us to think that the carriers are recombining between the band-tail states of the alloys. At temperatures above 900 °C, the structure of the sample is changing and the structural results show that there is a phase separation in Si_3N_4 and Si which lead to the appearance of amorphous or crystallized nanoclusters. The evolution of the PL energies and intensities is consistent with the confinement of the carriers inside the silicon clusters.

II. EXPERIMENTS

The $a\text{-SiN}_x\text{:H}$ thin films were prepared by an ion-beam-assisted evaporation technique with a background pressure equal to 10^{-7} Torr. Silicon was evaporated from an electron beam gun onto (111) silicon and fused silica substrates maintained at 100 °C under the flow of nitrogen and hydrogen ions. An electron cyclotron resonance (ECR) plasma source was used to generate the ion beam.³⁵ Samples of different compositions were prepared by varying the ratio of ultrapure N_2 and ultrapure H_2 in the gaseous mixture. The hydrogen/nitrogen mixtures were prepared before deposition with a nitrogen percentage p . The gaseous flow in the ion source was regulated by maintaining the total pressure in the evaporation chamber at 2×10^{-5} Torr. The silicon deposition rate ($1 \text{ \AA/s}$) was monitored and controlled by a quartz microbalance system. The thickness of the films was 200 nm. 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.

Chemical bonds were studied with (FTIR) spectroscopy. Spectra were obtained with a Fourier transform spectrometer with a resolution of 4 cm^{-1} . The contribution of an uncoated reference silicon substrate was subtracted from the experimental spectra. The number of bonds is determined by integrating the different stretching absorption bands using the formula $A \int (\alpha(\omega)/\omega) d\omega$, where ω , $\alpha(\omega)$, and A are the wave number, the absorption coefficient, and a calibration factor, respectively. A is taken as equal to 6.3×10^{18} , 9.2×10^{19} , and $2.8 \times 10^{20} \text{ cm}^{-2}$ for the Si–N, Si–H, and N–H stretching bands, respectively.³⁶ The bond densities were obtained by dividing the absorbance by the films thickness.

The hydrogen bonding was also studied by thermal desorption spectroscopy (TDS) experiments. The films were inserted into a quartz tube evacuated by an ionic pump and were heated at a constant rate of 10 °C/min to 1100 °C. Hydrogen desorbing from the substrate was detected by a quadrupole mass analyzer.

XPS measurements were performed to measure the x value in the $a\text{-SiN}_x\text{:H}$ alloys and to get information on the chemical configurations of the Si bonds. We used a VG MKII analyzer with basic pressure in the analysis chamber of 5×10^{-9} Torr. The photoelectrons were excited using a monochromatized Mg $K\alpha$ source with energy of 1253.6 eV. The surface sensitivity was estimated to be about 10 monolayers. The accuracy in the binding energy determination was 0.05 eV using an analyzer pass energy of 10 eV. XPS spectra were collected in detail for C 1s, Si 2p, N 1s, and Ar 2p photoelectron peaks. Spectral correction for charging effects was performed by fixing the C 1s energy of the residual carbon atoms contaminating the surface at 285 eV or the Ar 2p energy after bombardment treatments energy at 242 eV. In order to corroborate that the XPS spectra were reflecting the bulk properties, bombardment treatments with a 600 eV Ar^+ and current density of $8 \mu\text{A/cm}^2$ were carried out by sputter erosion. The energy was chosen in order to avoid the preferential sputtering effects which usually appear with high energy ions. No evidence of such preferential sputtering was

observed in the spectra collected after each sputtering treatment. Spectra were not recorded during sputtering since the films can be affected by ion impact or segregation. The intensities were determined from the integrated peak areas assuming the background to be linear. The calculation of element concentrations was made according to the surface approximation technique with the transmission function of the analyzer taken into account.³⁷ To determine the relative sensitivity factors of the Si 2*p* and N 1*s* lines, we used a reference sample of Si₃N₄.

The dimensions and the orientations of the crystallized silicon clusters were determined by GIXRD experiments carried out with Co *Kα* ($\lambda=1.788\,92\,\text{\AA}$) radiation. A germanium crystal with an incidence angle of 1° was used as monochromator. The cluster diameters *D* were calculated using the Scherrer formula $D=K\lambda/\beta \cos \theta$, where *K* is a constant, λ the x-ray wavelength, θ the diffraction angle, and β the integral width of the considered peak. The constant *K* was determined using a polycrystalline silicon sample with grains of known sizes and taken equal to 0.92. The experimental resolution was defined using a crystallized Si powder.

Photoluminescence and Raman measurements were carried out with a multichannel Raman spectrometer equipped with a 300 and 1800 grooves/mm gratings, respectively. The detector was a charge coupled device camera cooled at 140 K. The 488 nm excitation light source was emitted from an argon laser with an incident power of approximately 10 mW/mm². Raman experiments were performed using fused silica substrates instead of silicon. For the PL measurements, the intensity of each spectrum was normalized using the same reference sample.

For the optical characterization, absorption spectra were performed from 190 to 3000 nm with a dispersive spectrometer using fused silica substrates in order to avoid absorption in the near ultraviolet. The thickness of the films used for optical measurements was around 550 nm. The exact procedure used to determine the different optical parameters with the transmittance spectra is described in Ref. 10. The values of the Tauc gap are deduced from the strong absorption region where the absorption coefficient α varies with a power law $\alpha E=B(E-E_g)^2$, where E_g is the optical gap, *B* a constant, and *E* the energy of the photon.³⁸ The medium absorption region, which is mainly due to the static disorder, is characterized by the Urbach energy E_U , namely, the logarithmic slope of the absorption distribution for which $\alpha \sim \exp(E/E_U)$.

III. RESULTS AND DISCUSSION

A. Structural and chemical characterization

1. Film stoichiometries

The nitrogen content *x* of each SiN_{*x*} film was determined by XPS experiments using the intensity ratio of the N 1*s* to Si 2*p* core levels. The evolution of the *x* value with the nitrogen content *p* in the gaseous mixture for the as-deposited films is reported in Table I. The nitrogen content *x* is increasing from 0.1 for *p*=8 % to 0.63 for *p*=60 %. The O 1*s* peak located around 532 eV was not detectable showing that no oxygen contamination occurred in the films. Second-

TABLE I. Values of *x* in the formula SiN_{*x*} as a function of the nitrogen percentage in the gaseous mixture.

Set of samples	% of nitrogen in the gaseous mixture	<i>x</i> in SiN _{<i>x</i>}
A	8%	0.1
B	20%	0.24
C	30%	0.32
D	40%	0.39
E	50%	0.56
F	60%	0.63

ary ion mass spectrometry (SIMS) measurements (not shown here) reveal a good uniformity of the nitrogen and silicon profile.

For each set of samples, the nitrogen content was not modified after the thermal annealing treatments and no oxidation occurred either during exposure to air or annealing treatments. The evolution of the structural results with thermal annealing treatments is very similar for the different sets of samples and therefore, in the following sections, only results from typical samples will be described and presented in the figures. Detail structural studies for the as-deposited samples have already been reported elsewhere^{33,34} so only the main features will be presented.

2. Infrared absorption spectrometry results

Infrared absorption measurements were carried out to obtain information about the presence of hydrogen and the chemical bonds inside the films. Infrared spectra for the samples of set C that were annealed to 1100 °C are presented in Fig. 1. For the as-deposited sample, three major peaks at about 860, 2150, and 3350 cm⁻¹ are observed. These peaks are attributed to the asymmetric Si–N stretching mode, to the Si–H stretching mode, and to the N–H stretch-

FIG. 1. Infrared absorption spectra of films of set C annealed up to 1100 °C. The intensities of the bands located after 2000 cm⁻¹ are multiplied by a factor 2.

FIG. 2. Densities of Si-N and hydrogen bonds as a function of the nitrogen percentage p in the gaseous mixture.

ing mode, respectively.³⁴ The first peak is broad and intense and exhibits shoulders at 630, 1020, and 1150 cm^{-1} which arise from the Si-H wagging vibration, from Si-N bond with an hydrogen atom back bonded to the silicon atom, and from the N-H bending vibration. The lack of a peak at 1545 cm^{-1} indicates the absence of N-H₂ bonds. The characteristic bands of the Si-O-Si symmetric stretching and wagging modes which are usually observed even in samples with few oxygen atoms incorporated into the silicon network^{39,40} were never found in the spectra which confirms that oxygen is not involved in the chemical bonding of the α -SiN_x:H films as already observed with the XPS measurements.

For the as-deposited samples of the different sets, as shown in Fig. 2, with increasing p , the number of Si-N bonds increases while the number of hydrogen bonds (Si-H and N-H bonds) decreases. At the same time, the Si-H and the Si-N stretching bands shift towards higher wave numbers indicating that an increasing number of nitrogen atoms are back bonded to silicon ones.

After annealing treatments, the intensities of the Si-H and of the N-H bands progressively decrease as seen in Fig. 3 which indicates that hydrogen is desorbing from the films. At $T_a=800$ °C, the hydrogen bonds have disappeared for all samples. As for the Si-N band, Fig. 4 shows that, before $T_a=650$ °C, the position of the Si-N peak remains the same and above this temperature there is a noticeable shift toward higher wave numbers. This shift indicates that the number of nitrogen atoms bonded to a silicon one is increasing, for example, a N₂Si-SiN bond is replaced by a N₃-SiN one. There is enrichment of nitrogen atoms in the silicon nitride phase approximating it to Si₃N₄ as T_a increases. At the same

FIG. 3. Evolution of the hydrogen bond density of each set of sample with the annealing temperature T_a .

FIG. 4. Evolution of the position of the Si-N stretching band with the annealing temperature T_a .

time the film stoichiometries remain the same with T_a , the only possibility to explain the shift is that the enrichment of the silicon nitride phase in nitrogen after $T_a=650$ °C is occurring with an appearance of a pure silicon phase (not detectable in infrared absorption measurements). The substoichiometric nitride phases in the as-deposited films change toward a biphasic Si/Si₃N₄ mixture. This phase separation process has already been evidenced in SiO_x films and was also attributed to a shift of the Si-O stretching band toward higher wave numbers.^{10,41}

3. Thermal desorption measurements

To confirm the FTIR measurements and to have information about the possible presence of nonbonded hydrogen atoms inside the films (which cannot be detected in FTIR), TDS was performed. The spectra of a Si:H reference sample and of α -SiN_x:H films are represented in Fig. 5. For the Si:H sample, the hydrogen is effusing from the film between 350 and 500 °C with a maximum at 400 °C. This band has already been identified as arising from the rupture of the Si-H bond followed by the formation of H₂ molecules.⁴² For the α -SiN_x:H samples, two bands are visible: a small one around 200 °C and the most important one with a maximum between 400 and 520 °C. The small peak between 100 and 300 °C is produced from the effusion of nonbonded hydrogen atom adsorbed on the surface or by hydrogen molecules which need less energy to effuse from the films. As the nitrogen content in the films increases, the intensity of the main peak decreases and its position shifts towards the high temperatures. The decrease in the peak intensity is in agreement with the reduction in the quantity of hydrogen incorporated in the films when p increases. The shift of the effusion

FIG. 5. Effusion spectra of the H₂ species of a pure hydrogenated silicon film Si:H compared with different SiN_x:H films.

FIG. 6. Si 2p XPS spectra of the as-deposited sample and the one annealed at $T_a=950$ °C for set F. The small spectra in dashed and dotted lines correspond to a -Si and a -Si₃N₄ reference samples.

spectra and the increase of their width are explained by the fact that hydrogen effuses from N–H bonds and from different Si_{3–n}N_n–Si–H ($n=1, 2, 3$) groups which have desorption energies higher than the one of the Si_{3–n}–Si–H configuration present in the a -Si:H film. There is an increase in the Si–H bond energy when nitrogen atoms are back bonded to the silicon atom. As the number of nitrogen atoms linked to silicon increases, it becomes more difficult to break the Si–H bonds. This reaction has already been observed in a -SiO_x:H samples.⁴³ The TDS results confirm the FTIR spectrometry experiments: before 350 °C, only the adsorbed hydrogen desorbs from the films and the number of hydrogen bonds detected in FTIR experiments remains equivalent. After 350 °C, the thermal energy is used to break the bonding hydrogen (Si–H or N–H). For all the sets of samples, the two experiments clearly show that after 800 °C, there is no more hydrogen in the films.

4. X-ray photoelectron spectroscopy

The evolutions of the Si–N stretching band position in FTIR experiments suggest that a phase separation is appearing after 650 °C. Nevertheless, the FTIR measurements are not adequate to precisely explore the chemical configuration of the bonds between silicon and nitrogen and to detect the presence of a pure silicon phase. Therefore, x-ray photoelectron spectroscopy measurements were performed. The Si 2p core-level binding energy spectra for the as-deposited sample of set F and the one annealed at 950 °C are shown in Fig. 6. The two small spectra on the top correspond, for the left one, to the spectrum of a reference a -Si:H sample deposited with the same technique and, for the right one, to a Si₃N₄ reference sample. The vertical lines are used as guide lines to identify the presence of a pure Si phase or a pure Si₃N₄ phase.

The Si 2p core-level spectra of SiN_x films are generally interpreted in terms of different chemically shifted components which correspond to the possible Si–Si_{4–n}–N_n ($n=0, 1, 2, 3$, or 4) bonding configurations. In fact, as nitrogen is

added to the network, the homopolar Si–Si bonds are replaced by heteropolar Si–N bonds and the charge transfer from the Si atom to the more electronegative N atoms leaves a positive charge on the Si which results in a shift toward higher energies. Thus, the Si 2p line could be described as a superposition of five peaks corresponding to Si atoms bonded to 0, 1, 2, 3, or 4 atoms of nitrogen. In a study by Kärcher *et al.*,⁴⁴ the Si⁰ component corresponding to a pure a -Si film is around 99.6 eV while the Si⁴⁺ component corresponding to a pure Si₃N₄ film is around 102.6 eV. Each component is separated by an energy estimated between 0.62 and 0.78 eV depending on the stoichiometry value. As the electronegativity of a hydrogen atom is close to that of a silicon atom, the replacement of a Si atom by a hydrogen atom in a Si–Si bond would slightly affect the binding energy.

For the as-deposited sample of set F, the spectrum is composed of a main peak located around 101.8 eV and a shoulder at lower energy. Concerning the chemical structure of silicon nitride films, two models are commonly proposed. One is the random bonding model,⁴⁵ (RBM) and the other is the random mixture model (RMM).⁴⁶ The RBM considers the a -SiN_x network as a statistical distribution of the Si–Si_{4–n}N_n ($n=0, 1, 2, 3$, or 4) components. In this model, the Si 2p spectrum is made of a unique broad peak whose position is gradually shifting toward high energy when the nitrogen content is increasing. The film is composed of the five possible nitride phases. With the RMM, the spectra is an overlapping of the only two peaks corresponding to the pure silicon phase and the pure Si₃N₄ phase with an intensity ratio which is a monotonic function of the nitrogen content. The RMM is ruled by the chemistry and only the more stable phases Si and Si₃N₄ are formed while the RBM is purely statistical and depends only on the relative concentrations of nitrogen and silicon atoms. In our case, neither the RMM nor the RBM models can adequately describe the structure of our films as the spectra are not composed of two clearly separated peaks or of one unique peak. The shape of the spectra suggests that the as-deposited films are mixtures of silicon subnitrides forming silicon-rich and nitrogen-rich domains. The spectra of all the as-deposited samples for all sets have been reported elsewhere³⁴ and are in agreement with the proposed description. When x is increased, the nitrogen-rich phase becomes more important than the silicon-rich phase. This model assumes local spatial fluctuations of the chemical composition of our films.

With the annealing treatments, no noticeable changes are identified in the spectra before T_a reaches 800 °C. At 950 °C, major changes are visible: two peaks are now clearly identified and separated. By looking at the guide lines, the low energy peak can be identified as a characteristic of a pure silicon phase. At the same time, the high energy peak shifts to 102.4 eV which is close to the position of the Si₃N₄ reference. The peaks of intermediate energies which correspond to subnitride species are progressively disappearing. This behavior clearly indicates a phase separation occurring after 800 °C. The evolution with T_a of the ratios of the Si⁰ peak area to the total Si 2p line area for all sample sets is reported in Fig. 7. For higher T_a , the area of the Si⁰ component corresponding to the pure Si phase is increasing for all

FIG. 7. Evolution of the fraction of the pure silicon phase with the annealing temperature.

the sample sets while the high energy peak shifts to the exact position of Si_3N_4 . The phase separation temperature identified in XPS matches well with the one at which the position of the Si–N stretching absorption band is shifting in the infrared absorption spectra. This phase separation process occurs at $T_a = 800^\circ\text{C}$ for the sets A, B, and C or 950°C for the others. The difference for the phase separation temperature is explained by the fact that as x increases the number of nitrogen atoms increases as well and it becomes more difficult for the atoms to diffuse in the network and to initiate the phase separation.

5. Raman and x-ray diffraction measurements

Raman spectroscopy is an efficient method to determine the presence of pure silicon in its crystalline or amorphous form. The spectra of the as-deposited film, the one annealed at 950°C , and the one annealed at 1100°C of set E are shown in Fig. 8. The spectrum of the as-deposited film shows peaks at 150 and 480 cm^{-1} which indicate the presence of amorphous silicon. At $T_a = 950^\circ\text{C}$, the intensities of the peaks increase, which confirms the phase separation, and a small thin feature around 500 cm^{-1} appears. Such a thin peak is characteristic of the formation of small silicon nanocrystals. As T_a increases the amorphous characteristic peak disappears and the small peak increases and shifts simultaneously toward the position of the pure crystalline silicon

FIG. 8. Raman spectra of set E samples, as deposited and annealed at $T_a = 950$ and 1100°C . The substrates are fused silica wafers.

FIG. 9. Evolution of the x-ray diffraction pattern of samples of set E annealed at different temperatures T_a .

peak located at 520 cm^{-1} . This indicates an increase of the number of nanocrystals and of their mean sizes.^{47,48}

The sizes of these crystals can be obtained by x-ray diffraction experiments (Fig. 9). For annealing temperatures lower than 900°C , it was verified that all the films were amorphous. For the film of set E annealed at 950°C , the spectrum shows a first peak around 33° and two peaks not well defined between 50° and 70° . The first peak corresponds to the (111) peak of crystalline silicon and the second large one corresponds to the (220) (located at 55°) and the (311) (located at 66°) peaks of silicon. Those large peaks indicate the beginning of the nucleation of silicon grains partly amorphous and partly crystallized as already seen with the Raman measurements. For higher annealing temperatures, the peaks are more intense and the peaks at (220) and (311) become well separated, indicating a better crystallization of the clusters. At 1100°C , small peaks located at 82° and 91° characteristics of the (400) and (331) orientations of silicon are visible. At the same time, peaks are becoming thinner because of the growth of the grain sizes. The application of the Scherrer formula using the integral breadth of the (111) peak enables us to calculate the diameters of the clusters. The (111) peak has the advantage to be more intense and well defined compared to the (220) and the (311) diffraction peaks and also minimizes the broadening due to a possible strain.⁴⁹ For set E, the estimated sizes are, respectively, 2.3, 2.8, 3.5, and 5.0 nm for $T_a = 950, 1000, 1050$, and 1100°C . For all the annealing treatments, the position of the (111) peak remains unchanged which indicates a small uniform strain in the Si clusters. Moreover, we can assume that the broadening of the diffraction peak in our samples is entirely due to a size effect and neglect the nonuniform strain effect which is the other source of peak broadening. Indeed, if the broadening due to the strain was important, its effect would be more visible for higher diffraction angles.⁴⁹ In our samples, the evolution of the broadening with the annealing treatments is the same for the (111), the (220), and the (311) peaks which indicates a weak strain in Si crystallites. The absence of an important strain effect on the diffraction spectra of Si nanocrystallites has already been observed by Comedi *et al.*⁵⁰ Thus, the estimated cluster mean sizes determined by the diffraction experiments could be considered as reliable. Moreover, the mean sizes match well with the ones determined by TEM measurements.

FIG. 10. (a) Dark field transmission micrograph of set C sample annealed at 980 °C and (b) bright field transmission micrograph of set C sample annealed at 1070 °C.

For sample sets B, C, D, E and F, the crystallization begins at 950 °C and the mean sizes of the silicon clusters at 1100 °C are all around 6 nm with an important size and shape dispersions. Only set A, which is very poor in nitrogen, begins to crystallize just after 800 °C and has grains of 8 nm average diameter at 1100 °C. The high annealing crystallization temperature could be explained by the fact that the introduction of nitrogen atom induces strain on the silicon network which slows down the crystallization process. The diffusion process of the atoms is also slowed down and the growth of the grains is not as fast in films rich in nitrogen as they are in poorly nitrogenated films.

6. Transmission electron microscopy

To have a direct view of the silicon crystallites, TEM measurements were performed. Figure 10(a) shows a dark field image of a sample from set C annealed at 980 °C and Fig. 10(b) shows the bright field micrograph of the film from the same set annealed at 1070 °C. At 980 °C, small crystal-

FIG. 11. PL spectra of set E samples annealed at different temperatures T_a .

lites are clearly visible, which confirms the beginning of the crystallization process around 950 °C and, at 1070 °C, the average size of the silicon crystallites is increasing up to 6 nm as seen in the x-ray diffraction patterns.

7. Summary of the structural evolutions

The evaporation technique of silicon under a flow of hydrogen and nitrogen ions enables us to obtain α -SiN_x:H films with x between 0.1 and 0.63. Such films have a different structure than films elaborated by CVD related techniques. Indeed, α -SiN_x:H films grown by CVD are prepared using either a SiH₄/N₂ or a SiH₄/NH₃ gaseous mixture. The use of N₂ leads to poorly hydrogenated films close to Si₃N₄ films while the use of NH₃ enables us to have a more important range of compositions (from $x=0$ to $x=1.5$). In those last films, due to the use of NH₃, the percentage of hydrogen is increasing at the same time as the percentage of nitrogen and thus, the films are highly hydrogenated. In our case, the percentage of incorporated hydrogen decreases when the nitrogen content increases which leads to a structure different from the usual α -SiN_x:H films.

The as-deposited samples are a mixture of a hydrogenated silicon-rich phase and a hydrogenated nitride-rich phase. With increasing p , there is nitrogen enrichment for the two phases. With the annealing treatments, two main structural changes occur depending on the annealing temperature T_a . With the increase of T_a up to 800 °C, the hydrogen progressively effuses from the samples. At 800 °C, no more hydrogen can be detected inside the films. Once the hydrogen has effused from the film, atoms of nitrogen and silicon begin to diffuse in the films and a phase separation in a pure silicon phase and a nitrogen-rich phase occurs. At around 900 °C, films are composed of silicon clusters embedded in an insulating silicon nitride matrix which becomes closer to Si₃N₄ as T_a increases. The clusters are first amorphous up to $T_a=950$ °C then crystallized for higher temperatures and the nanocrystallite sizes are around 6 nm at 1100 °C.

B. Photoluminescence

1. Photoluminescence results

Photoluminescence experiments were performed for all samples deposited on silicon substrates. The PL evolution with T_a of the films of set E is shown in Fig. 11. This evolution is similar for all the other sets. Two different tempera-

FIG. 12. Recapitulative graph of the PL wavelength for the films of the different sets annealed at the temperature T_a . The signs $\times$ correspond to set A, $\blacksquare$ to set B, $\bullet$ to set C, $\blacktriangle$ to set D, $\blacktriangledown$ to set E, and $\blacklozenge$ to set F.

ture domains could be identified. The as-deposited sample exhibits a broad PL band center around 700 nm. For $T_a = 350$ °C, the PL shifts towards higher wavelengths and its intensity remains similar. At $T_a = 500$ °C, the intensity decreases and the PL becomes very weak. At $T_a = 650$ °C and $T_a = 800$ °C, the PL has disappeared, and at $T_a = 950$ °C the PL reappears at lower wavelengths (around 620 nm). With increasing temperatures up to 1100 °C, the PL intensity increases and its wavelength shifts towards higher wavelengths.

The temperature at which the PL evolution changes (disappearance for $T_a > 650$ °C and reappearance for $T_a > 900$ °C) is the same as the one at which important structural changes are observed. This fact suggests that there is a close correlation between the structural evolution and the PL behavior. The disappearance of the PL is probably linked to effusion of the hydrogen and the reappearance of the PL occurs at the same time as the phase separation process. Figure 12 recapitulates the energies of the PL peaks vs T_a for the different sets of films. Two domains are clearly visible: for $T_a < 650$ °C, the emission occurs at wavelengths higher than 700 nm, and for $T_a > 900$ °C, the PL wavelengths are smaller than 700 nm. This difference in the PL energy domains coupled to the correlation with the structural results suggests the existence of two different PL mechanisms for zones 1 and 2.

2. Photoluminescence mechanisms

The evolution of the PL can be discussed considering two models: the model of the quantum confinement of the carriers inside silicon nanoclusters or the model of the band-tail states. This last model is the one usually used to describe the PL in amorphous silicon alloys such as $a\text{-SiN}_x\text{:H}$,^{27,29,51} $a\text{-SiC}_x\text{:H}$,^{52,53} or even $a\text{-Si:H}$.^{54,55} In this model, the carriers are radiatively recombining within the localized states at the band tails of the alloy gap. As the nitrogen content increases, the band gap energy also increases, which leads to a blueshift of the PL energy. For this mechanism, the emission usually occurs at wavelengths higher than 680 nm. To verify whether this mechanism is involved in the PL for $T_a < 650$ °C (zone 1) optical measurements were performed for the as-deposited samples and compared with the PL results. The values of the Tauc gaps deduced by using the procedure described in Ref. 10 are reported in Table II for the as-deposited sample of

TABLE II. Gap and Urbach energy values of the as-deposited samples of the different sets.

Set of samples	Tauc gap (eV)	Urbach energy (meV)
A	1.96	50
B	1.99	70
C	2.05	95
D	2.16	120
E	2.16	150
F	1.85	220

each set. The PL energies and intensities of the same sample are shown in Fig. 13. The gap is increasing with the content in nitrogen from 1.96 eV for $p = 8\%$ to 2.16 eV for $p = 50\%$. The increase of the optical gap with the nitrogen content is an expected result which was shown theoretically.⁵⁶ Our gap values are very similar to those obtained by Guraya *et al.*⁵⁷ on sputtered samples but lower than the theoretical predictions. Those low gap values could be due to the inhomogeneous structure of our films composed of a mixture of a silicon-rich phase and a nitrogen-rich phase. For $p = 60\%$, the decreasing of the gap could be due to the important diminution of the hydrogen concentration, which leads to the breaking of Si-H and N-H bonds and, thus, to the reappearance of localized states within the gap.⁵⁸ The presence of nonradiative states explains the observed PL intensity decrease. The increase of the gap with p is well correlated to the blueshift of the PL signal as expected for the band-tail mechanism. In addition to the gap increase, nitrogen alloying induces structural disorder resulting in an increase in the width of the localized states which consequently broadens the PL band. This structural disorder is measured by the Urbach energy values derived from the transmission spectra. Figure 14 shows the full width at half maximum of the PL band and the Urbach energies for the as-deposited samples. The two values have the same evolutions with p which confirms that, for these samples, the bandwidth of the PL depends on the width of the localized states. The comparison between optical and PL results leads to think that the band-tail PL mechanism is involved in the emission of the as-deposited samples, as it was proposed for other $a\text{-SiN}_x\text{:H}$ alloys.^{27,29}

The $a\text{-SiN}_x\text{:H}$ films, for which the PL is usually explained using a band-tail PL mechanism, have a different structure than ours. Indeed, those films are described using the random bonding model from the structural point of view,

FIG. 13. PL energies and intensities of the as-deposited films as a function of the nitrogen percentage p in the gaseous mixture.

FIG. 14. Urbach energies and PL bandwidth of the as-deposited samples for the different p values.

which implies a homogeneous film while, for our films, we have seen that they are composed of a mixture of silicon-rich phase and nitrogen-rich phase. This structure implies gap fluctuations inside the films with a silicon-rich phase having a gap lower than the gap of the nitrogen-rich phase. Thus, the carriers would be spatially confined in those low gap domains and would recombine through the band-tail states of the silicon-rich phase (Fig. 15). The evolution of the PL intensity with p could then be interpreted in terms of nonradiative defects, such as in a -Si:H.⁵⁹ With increasing p , the silicon-rich domains are better confined inside nitrogen-rich domains, which increase the efficiency of the recombination and therefore the PL intensity, by lowering the influence of defects. For $p=60\%$, the number of Si-H bonds is decreasing drastically and a large amount of dangling bonds are no longer passivated, which explains the decrease of the PL intensity. This is in agreement with the fact that, for p values of 80% or 100% (i.e., for samples with almost no hydrogen), no PL is observed for the as-deposited samples. Therefore, the PL observed for the as-deposited samples can be attributed to recombinations of the carriers between the band-tail states of silicon-rich domains confined inside nitrogen-rich domains. The role of hydrogen is of prime importance because it enables to passivate the dangling bonds and to limit the nonradiative recombinations.

The evolution of the PL with the thermal treatments matches well with the structural changes and the proposed PL mechanism. The PL intensity reaches a maximum value for $T_a=500^\circ\text{C}$ and disappears for $T_a=650^\circ\text{C}$. This behavior is shown in Fig. 16 in which the PL intensities for T_a up to 650°C are reported for all the sets. The first increase is

FIG. 15. Scheme of the mechanism proposed to explain the PL for the a -Si $_x$ N $_y$:H films annealed at temperatures lower than 650°C .

FIG. 16. Evolution of the PL intensities with the annealing temperature T_a up to 650°C , for the different sets of samples.

due to an improvement of the structure with thermal annealing treatments which probably eliminates some nonradiative defects. Beyond 350°C , the hydrogen bonds begin to break which gives rise to the appearance of dangling bonds in the structure. These dangling bonds act as nonradiative defects explaining the decrease of the PL intensity. Beyond 650°C , hydrogen has completely effused from the sample and the increasing number of nonradiative recombination centers explains the disappearance of the PL.

In summary, in zone 1 of Fig. 12, the PL evolution is explained by a carrier recombination mechanism within the band-tail states of the silicon-rich phase confined by the nitrogen-rich phase. For temperatures higher than 650°C , the PL disappears and reappears for temperatures higher than 900°C at lower wavelengths. This evolution suggests that a different mechanism is responsible for the reappearance of the PL. This PL band is systematically correlated to the phase separation process leading to the creation of pure silicon aggregates embedded in a matrix close to Si $_3$ N $_4$. Depending on the annealing temperature, those grains are amorphous and then crystalline as seen in the TEM micrographs. These results are in good agreement with the quantum confinement of carriers inside the clusters. The domain of energy in which the PL is reappearing matched well with the theoretical predictions for small silicon clusters. Another argument in favor of the quantum confinement is the evolution of the PL wavelength when T_a is increasing. Indeed, the spectra are shifting toward higher wavelengths when T_a is increasing. Considering the quantum confinement mechanism, this redshift should be related to an increase of the grain sizes, which is effectively the case as shown by the x-ray diffraction experiments. The large PL bandwidth is due to the fact that the sizes of the silicon crystallites could not be controlled in these thin films, which leads to a large distribution of sizes at high annealing temperatures, as seen in the TEM micrograph. The increase of the PL intensity with annealing temperatures is due to the increasing number of silicon grains and to the fact that the insulating matrix is getting closer to Si $_3$ N $_4$, which improves the confinement. In zone 2 of Fig. 12, we could notice that for some samples (sets D and F), between 950 and 1050°C , the PL energy is blueshifted instead of the expected redshift. This behavior is directly correlated to the change from the amorphous to the crystalline state of the silicon nanoclusters. A detailed study of the transition between the amorphous and the crystallized states and their effects on the PL energy and intensity has been

reported elsewhere⁶⁰ and confirms that the quantum confinement mechanism is strongly involved in the PL for the samples of zone 2.

IV. CONCLUSIONS

Hydrogenated amorphous silicon nitride alloys α -SiN_x:H have been prepared by reactive evaporation of silicon under a plasma obtained from a hydrogen-nitrogen gaseous mixture containing a nitrogen percentage p . As p increases from 8% to 60%, the nitrogen content x increases from 0.1 to 0.63. For the as-deposited samples, PL is observed in the visible range at room temperature. This PL is due to recombination of the carriers in the band-tail states. With annealing treatments, the PL intensity firstly increases for $T_a=350$ °C and then disappears at $T_a=650$ °C. The increase can be correlated to an improvement of the structure during the first annealing steps and the decrease of the PL is due to the breaking of the hydrogen bonds and the effusion of hydrogen which creates nonradiative centers. For $T_a=950$ °C, a PL band is appearing and is due to a phase separation phenomenon in the films, which begins at $T_a=800$ °C. This phase separation leads to the creation of silicon clusters embedded in an insulating matrix close to Si₃N₄. The crystallization of the silicon clusters is observed around 1000 °C and accompanied by a growth of their sizes up to 6 nm. The redshift observed for the PL wavelength as the cluster sizes are increasing is in agreement with a mechanism of quantum confinement of the carriers inside the silicon nanograins.

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