



Influence of rapid thermal annealing processes on the properties of $\text{SiN}_x\text{:H}$ films deposited by the electron cyclotron resonance method

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Abstract

We have analyzed the effects of rapid thermal annealing on the composition and on the bonding and optical properties of amorphous hydrogenated silicon nitride ($\text{a-SiN}_x\text{:H}$) thin films deposited at room temperature by the electron cyclotron resonance plasma method. Films with three different as-grown compositions have been studied, namely $x = 0.97$, 1.43 and 1.55. Annealing effects were related to film composition. In films with the presence of both Si–H and N–H bonds (as-grown compositions $x = 0.97$ and 1.43), we found that a reorganization of bonds takes place at temperatures $\leq 500^\circ\text{C}$, where the well-known cross linking reaction $\text{Si-Si} + \text{N-H} \rightarrow \text{Si-H} + \text{Si-N}$ occurs without detectable release of hydrogen. In the same range of temperatures, an increase of the band gap was observed and attributed to Si–Si bond substitution for Si–H, but no changes in composition were detected. At higher temperatures ($T \geq 600^\circ\text{C}$), the optical gap decreases and both Si–H and N–H bonds are lost along with a release of hydrogen and nitrogen. For the films with an as-grown composition $x = 1.55$, we observe that the release of hydrogen only occurs at temperatures above 900°C , but it is not accompanied by any loss of nitrogen. An increase of the optical gap until the release of hydrogen begins and a decrease thereafter is observed. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Rapid thermal annealing process; $\text{SiN}_x\text{:H}$ films; Electron cyclotron resonance method

1. Introduction

The fabrication of metal-insulator-semiconductor (MIS) devices with III–V semiconductors is a complex matter due to severe problems at the insulator/semiconductor interface where the presence of a high density of interface states produces the Fermi level pinning [1] and prevents the modulation of the channel conductivity. Additionally, due to

the thermal instability of III–V semiconductors, the deposition of the dielectric has to be done at a relatively low temperature. This is the reason which has motivated intensive research on amorphous hydrogenated silicon nitride deposited by plasma techniques at low temperature [2]. $\text{SiN}_x\text{:H}$ is already widely used as a passivation layer in integrated circuit manufacturing and as a gate dielectric in thin film transistors for flat panel displays.

The electron cyclotron resonance (ECR) plasma technique meets the requirement of low temperature

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processing. With this technique, the hydrogen content in the films can be kept in the range of 10 to 20 at.%. Deposition parameters may be chosen to obtain a wide range of optical and bonding properties, which are excellent in films with a nitrogen to silicon ratio near the stoichiometric one ($x = 1.33$).

The optimization of $\text{SiN}_x\text{:H}$ films using rapid thermal annealing (RTA) processes has been reported recently [3,4]. Until now, those studies have mainly considered the effects of RTA on bonding properties of the films and the analysis is usually made on films with compositions around $x = 1.33$. The effects of RTA on other key parameters of the films such as the optical gap and the composition is scarcely analyzed.

The aim of this paper is to study RTA effects on the composition and on the optical and bonding properties of $\text{SiN}_x\text{:H}$ films deposited by ECR. We use films of three different compositions: (i) $\text{SiN}_{0.97}\text{:H}$, where both Si–H and N–H bonds are present and Si–H bonds are predominant, (ii) $\text{SiN}_{1.43}\text{:H}$, which has more N–H bonds than Si–H bonds, and (iii) $\text{SiN}_{1.55}\text{:H}$, where hydrogen is only bonded to nitrogen.

2. Experimental procedure

The films were made using an ECR-CVD reactor (Astex AX4500). Precursor gases were N_2 and SiH_4 . The nitrogen to silane gas flow ratio, R , was varied to obtain the three compositions we have analyzed: $R = 1$ for films with $x = 0.97 \pm 0.03$, $R = 1.6$ for films with $x = 1.43 \pm 0.02$ and $R = 7.5$ to obtain $x = 1.55 \pm 0.04$.

The substrates used for IR absorption and composition measurements were high resistivity (111) n-type silicon polished on both sides. The wafer was cut in square pieces (3 cm \times 3 cm) in which lines were drawn with a diamond needle to allow for easy post-deposition cut in nine 1 cm \times 1 cm substrates; in this way, the samples annealed at different temperatures were in fact part of the same film for each composition. To determine the optical gap, we used UV–VIS–NIR spectroscopy to films grown on silica substrates in the same deposition conditions.

The cleaning of the substrates was done using standard chemical procedures starting with dips in

acetone and methanol which were followed by drying with nitrogen. This step was common to silicon and silica substrates. Then silicon was successively subjected to the following cleaning steps: $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ (1:2:5) for 5 min, deionized H_2O , $\text{HF}:\text{H}_2\text{O}$ (1:10) for 1 min and deionized H_2O . Finally, the substrates were blown dry again with nitrogen.

Rapid thermal annealing of the samples was performed in an argon atmosphere at temperatures ranging from 300°C to 1050°C during 30 s. The heating ramp was linear and had a duration ranging from 7 s for the 300°C anneal to 14 s for the anneal at 1050°C.

The three following measurements were done.

(i) Optical: we have measured the transmission and reflection spectra in the range 2500–200 nm with a spectrophotometer (Perkin Elmer Lambda 9). From these data, we calculated the refractive index and the optical absorption coefficient using the procedure of reference [5]. The method of calculation requires an initial estimation of the sample thickness so that a computer program can use it to calculate the refractive index and absorption coefficient vs. wavelength from the expressions that relate the optical properties and thickness of both the film and the substrate with the transmissivity through the multilayer and the reflectivity for the upper surface. Then, the thickness parameter is varied until the solutions for the refractive index vs. λ provide the best fit to a Cauchy dispersion law. The values of the absorption coefficient vs. $h\nu$ (h is Planck's constant and ν is the photon frequency) are then fitted to the well-known Tauc law [2,6] and the optical gap is obtained from this fit together with its error bar.

(ii) Bonding: IR absorption spectra were measured with an FTIR spectrophotometer (Nicolet 5PC). We used the method of Lanford and Rand [7] to obtain the Si–H and N–H bond densities from the relevant absorption band areas. The density of bonded hydrogen is the sum of both densities. Additionally, molecular hydrogen may exist in the film [8] but H–H bonds cannot be considered to be part of the network and this hydrogen was not detected by IR spectroscopy. The main source of error in the determination of bond densities is introduced by the film thickness, which is measured with a profilometer (accuracy $\pm 5\%$) (Dektak). The errors in the determi-

nation of the IR band intensities are considered to be negligible in comparison with those of the profilometer.

(iii) Composition: it was analyzed by backscattering (RBS) and energy dispersive X-rays (EDX). RBS spectra were measured with 1.4 MeV He^+ ions and then fitted by the iterative computer program 'RUBSODY'. The given error limits refer only to the statistical error which results from a sequence of eight simulation fits. The EDX analysis was performed with a beam voltage of 5 kV and by comparing with a Si_3N_4 standard sample. The EDX spectra were evaluated by using the so-called Proza method [9], including a correction with respect to the limited film thickness. In EDX, the statistical error for the concentration determination was $\pm 0.3\%$. A systematic deviation between the N/Si ratios x determined by both methods, which has been discussed in Ref. [10], was found. In this study, therefore, we use for x the average of the RBS and the EDX data.

3. Results

In Fig. 1, we present the Si–H and N–H bond concentration vs. annealing temperature for the samples with the as-grown compositions $x = 0.97 \pm 0.03$ ($R = 1$) and $x = 1.55 \pm 0.04$ ($R = 7.5$). In the film

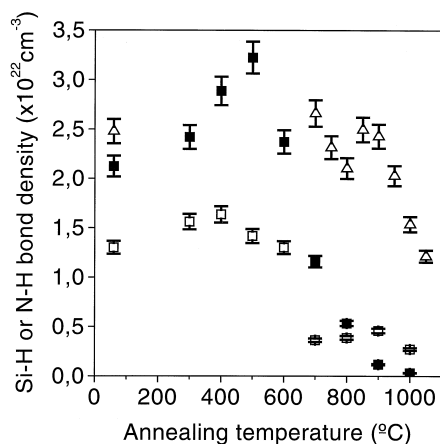


Fig. 1. Density of bonded hydrogen vs. annealing temperature for films with two different as-grown compositions. The films with $x = 0.97 \pm 0.03$ have both Si–H (■) and N–H (□) bonds, while films with $x = 1.55 \pm 0.04$ only show the presence of N–H bonds (△).

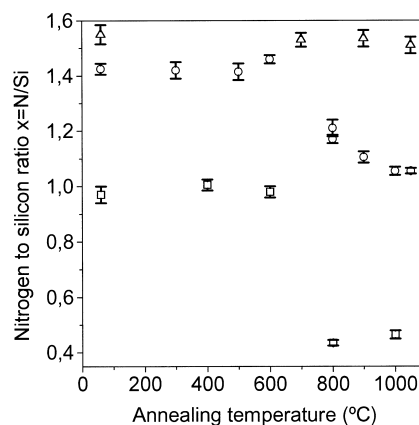


Fig. 2. The average ratio of N and Si atoms derived from RBS and EDX measurements for the three types of films employed in this study vs. annealing temperature. The as-grown composition of the three types of films are: $x = 0.97 \pm 0.03$ (□), $x = 1.43 \pm 0.02$ (○) and $x = 1.55 \pm 0.04$ (△).

with $x = 0.97 \pm 0.03$, there is an increase in the density of Si–H bonds with increasing annealing temperatures to 500°C. In the same range of temperatures, the density of N–H bonds shows a minor increase and starts to decrease at 400°C. At temperatures higher than 600°C, both Si–H and N–H bond densities decrease and so does their sum, which is the total bonded hydrogen density $[H]$. This quantity follows the exponential law $[H_0] - [H] = \text{Ce}^{(-E_a/KT)}$, where $[H_0]$ is the bonded hydrogen density before the net loss of hydrogen begins [3]. We find that the activation energy of this process is $E_a = (0.12 \pm 0.02)$ eV.

The results for the sample with $x = 1.43 \pm 0.02$ are similar to those of the film with $x = 0.97 \pm 0.03$, except that N–H bonds predominate over Si–H bonds, but these data are not included in the figure for the sake of clarity. The activation energy for hydrogen release is $E_a = (0.77 \pm 0.04)$ eV, which is larger than in the previous case because N–H bonds are harder to break than Si–H bonds, as we will discuss in Section 4.

Regarding the films with $x = 1.55 \pm 0.04$, we observe N–H bonds but no Si–H bonds. The density of N–H bonds starts to decrease at temperatures greater than 900°C, which is higher than that of the films with both Si–H and N–H bonds. The activation energy for the loss of hydrogen is in this case $E_a = (1.52 \pm 0.20)$ eV.

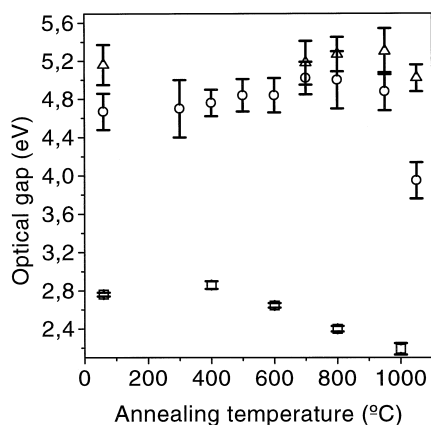


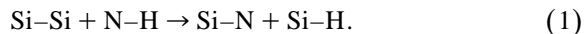
Fig. 3. Optical Tauc gap as a function of annealing temperature for films with as-grown compositions of $x = 0.97 \pm 0.03$ (□), $x = 1.43 \pm 0.02$ (○) and $x = 1.55 \pm 0.04$ (△).

Fig. 2 shows the average N/Si ratio from RBS and EDX data. The film with $x = 1.55 \pm 0.04$ does not change composition within errors of measurement with annealing. Quite different is the behavior of the films where Si–H bonds are present, i.e., for $x \leq 1.43$. These films lose nitrogen for annealing temperatures above 600°C.

In Fig. 3, we present the optical gap E_g vs. annealing temperature for the three types of films. Note that E_g increases slightly upon annealing up to the temperature at which the loss of hydrogen begins and decreases at the temperatures where hydrogen is being released.

4. Discussion

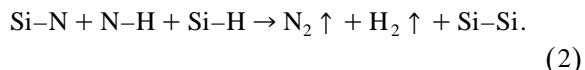
Let us first consider the case of the films with both Si–H and N–H bonds ($x \leq 1.43$). For temperatures below 600°C, the increase of the Si–H and N–H bond densities (Fig. 1) together with the fact that there is no change in composition (N/Si ratio) at those temperatures (Fig. 2) must be explained by the well-known [8] network bond reaction involving nearest-neighbor Si and N atoms:



This reaction is based on the tendency of chemical ordering, whereby Si–N and Si–H bonds are favored at the expense of Si–Si and N–H bonds. Si–Si

bonds have been proposed to be potentially harmful defects in the a-SiN_x:H films currently used in device applications. Therefore, the formation of Si–H bonds prevents the formation of silicon dangling bonds which otherwise would be easily formed by breaking Si–Si bonds [11]. The calculations find that replacing Si–Si bonds by Si–H bonds decreases E_v and increases E_g because Si–H σ states lie deeper than Si–Si σ states, thereby decreasing E_v , while Si–H σ^* states lie at a similar energy as Si–Si σ^* states so that E_c is little changed [12]. The trend observed in Fig. 3 for the optical gap is in accordance with this model.

For temperatures above 600°C, the decrease in the number of both Si–H and N–H bonds (Fig. 1), the decrease in the optical gap (Fig. 3) and the decrease in the nitrogen to silicon ratio (Fig. 2) are explained tentatively by the following bond reaction:

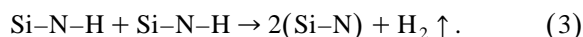


Now we have the formation of Si–Si bonds and the breaking of Si–H bonds, a fact that explains the narrowing of the optical gap according to the aforementioned argument. This reaction is a collective process of the whole network and it is only possible because of the cooperation of the Si–H and N–H bonds. Indeed, an additional hint to this cooperative phenomenon is given by the fact that the N–H bond dissociation energy of ~ 4.7 eV and the Si–H bond dissociation energy of ~ 3.5 eV are each for itself much higher than the activation energy for H-atom release ($E_a = 0.12 \pm 0.02$ eV) that we presented in Section 3.

Let us now turn to the films with an as-grown composition of $x = 1.55 \pm 0.04$. The IR spectra of these films show the presence of N–H bonds but they do not show any Si–H bonds. At temperatures below 900°C, no changes occur in the composition nor in the hydrogen content. The weak bond-dangling bond conversion model was proposed by Stutzmann [13] in a-Si:H and has been used to explain several results in a-Si:H [14] as well as in amorphous silicon alloys such as silicon nitride [11,15]. This model proposed that weak-bond states towards the end of the valence-band tail would convert into dangling bond states near midgap due to bond break-

ing. Anyway, this process does not explain the increase in the optical gap because tail states only contribute to the Urbach tail of the optical absorption constant, which is at energies below E_g .

Above 900°C, we observe a loss of N–H bonds (Fig. 1) and a decrease of the optical gap (Fig. 3), but there is no change of composition. According to Robertson [12], this must be explained by the fact that in a-SiN_x:H, the introduction of =NH groups rather than N–N bonding increase the gap by raising E_c . E_v is not decreased as the valence-band maximum is still formed by N $p\pi$ states. The increase of E_c appears to be due to an admixture of N–H states, which have a greater gap. Thus, it appears that while Si₃N₄ has a conduction-band edge of small effective mass, which remains relatively unaffected by topological disorder, it is increased by a large proportion of =NH groups. This would explain the reduction in the optical gap when they are lost. The release process involves in this case pairs of nearest-neighbour SiN–H groups. The overall reaction for release from these groups can be exothermic if molecular species are formed and/or Si–N bond reconstruction occur. The reaction equation that applies in this case is given by [3]:



Using nominal bond energies values, this overall reaction is exothermic, indicating that the activation energy of the H-release process may be associated with the reaction barrier.

5. Conclusions

We have found that rapid thermal annealing has different effects on the bonding and optical properties and on the composition of a-SiN_x:H thin films. These depend strongly on the as-grown composition and, to be more specific, on the relative contribution of Si–H and N–H bonds to the network.

Films with as-grown compositions $x \leq 1.43$ show the presence of both Si–H and N–H bonds. At annealing temperatures below 600°C, these films

undergo an interchange bond reaction where N–H bonds are replaced by Si–H ones. As a consequence, the band gap increases from (2.76 ± 0.02) eV to (2.86 ± 0.04) eV in the films with $x = 0.97$ and from (4.67 ± 0.19) eV to (5.02 ± 0.17) eV in the films with $x = 1.43$. At annealing temperatures above 600°C, these films lose both hydrogen and nitrogen through a collective process that involves all bonds present in the network.

By contrast, in films with $x = 1.55$, hydrogen is fixed predominantly in N–H bonds, while Si–H bonds do not play any essential role. To promote hydrogen release in these films, temperatures in excess of 900°C are found to be necessary. Under that temperature, the only relevant outcome is the breaking of Si–Si weak bonds. This is in accordance with the fact that no significant change in the nitrogen content is observed at any annealing temperature.

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