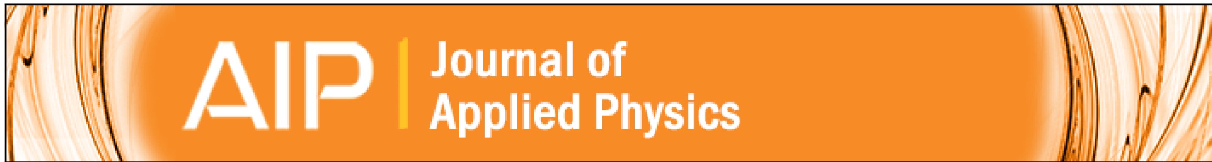

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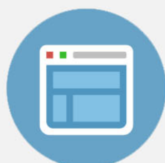
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Defect structure of SiN_x:H films and its evolution with annealing temperature

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The structure of defects of SiN_x:H films is investigated by electron-spin resonance. It is found that a relaxation process takes place at annealing temperatures below 600 °C for those compositions in which the nitrogen-to-silicon ratio is above the percolation threshold of the Si–Si bonds in the nitride lattice. The nature of this process is discussed and attributed to a thermally activated charge transfer between metastable defects. No such relaxation occurs in the films with a composition below the percolation threshold, possibly due to a positive correlation energy and a structural lack of flexibility. For higher annealing temperatures, an increase of the defect density is observed and associated with the thermal release of hydrogen. © *2000 American Institute of Physics.*
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Amorphous hydrogenated silicon nitride (SiN_x:H) has important applications in several microelectronics devices such as thin-film transistors,[1] solar cells,[2] and memory devices.[3] The structure of defects of this material has been a subject of intense research due to the importance of charge trapping phenomena in determining the electrical properties of the dielectric.[4] Two types of defects may appear in the covalent network of the SiN_x:H film: the Si dangling bond and the N dangling bond. Both centers can be detected by electron-spin resonance (ESR) spectroscopy under suitable conditions. The paramagnetically active Si center, also known as the *K* center, appears in the ESR spectrum as a resonance at a value of the spectroscopic splitting factor of $g=2.0028$ for the material in thin-film form, and $g=2.0018$ in powders, although both values increase when the nitrogen-to-silicon ratio (x) deviates both to silicon-rich ($g=2.005$) and nitrogen-rich ($g=2.004$) compositions.[5,6] The detection of the N dangling bond requires first the saturation of the signal of the *K* center by means of a high microwave power, because its characteristic three-line spectrum at a g value of 2.0052 appears superimposed to the Si signal, and the number of N centers is much smaller.[7] The N dangling bond tends to be in a diamagnetic state occupied by two electrons, due to its energy position in the proximity of the valence band. For this reason, ultraviolet (UV) illumination is often needed to make this center magnetically active, and in some cases thermal annealing has to be applied in order to favor the release of the hydrogen that passivates the dangling bonds.

In this communication, we analyze the influence of the temperature of rapid thermal annealing (RTA) on the defect structure of SiN_x:H films deposited by an electron cyclotron resonance plasma process. The reactor was an Astex 4500 machine operating at a microwave power of 100 W and a pressure of 0.67 mTorr. The properties of the films are mainly fixed by the gas flow ratio R (nitrogen to silane) used in the growth process. R values of 1, 1.6, and 7.5 resulted in as-grown nitrogen-to-silicon ratios (x) of 0.97 (silicon rich), 1.43 (near-stoichiometric), and 1.55 (nitrogen rich), respectively, as determined by combined Rutherford backscattering spectrometry and energy-dispersive x-ray analysis.[8] The substrates were high-resistivity (111) silicon wafers which were cut in $1\times0.2\ cm^2$ pieces after deposition. For each measurement a stack of five of those pieces was used to enhance the level of the detected signal. The thickness of the as-grown film was 640 nm for the nitrogen-rich samples, 480 nm for the near-stoichiometric samples, and 200 nm for the silicon-rich samples. Increasing the silicon proportion in the film results in a higher stress that leads to loss of adherence and film peeling at high thickness values. This factor limits the higher thickness that can be grown at each composition. The substrate holder was not intentionally heated during deposition, but the films were subjected to RTA postdeposition treatments at temperatures between 300 and 1050 °C, in order to study the evolution of the defect structure as a function of temperature and find possible relations with the amount and distribution of the hydrogen content.[8]

The ESR study was performed with a Bruker 300E spectrometer operating in the X band at a microwave power of 0.5 mW. Some ESR measurements were carried out on samples previously illuminated with UV light. To this purpose, a Xe lamp and a filter transmitting in the 280–370 nm range were employed. In all cases the signal associated with the Si dangling bond could be identified and the density of magnetically active spins was quantified by comparison with the signal of a calibrated weak pitch standard.[9,10]

The evolution of bonded hydrogen with annealing temperature was determined from the infrared (IR) absorption bands of the Si–H and N–H bonds, using the calibration factor and oscillator strength ratio calculated by Lanford and

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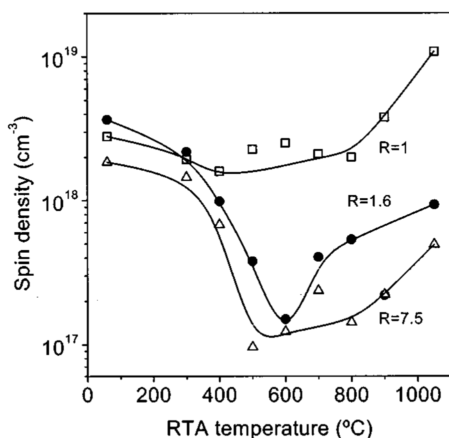

FIG. 1. Density of paramagnetic silicon dangling bonds as a function of annealing temperature. The gas flow ratio (R) that characterizes each type of film appears indicated in the figure.

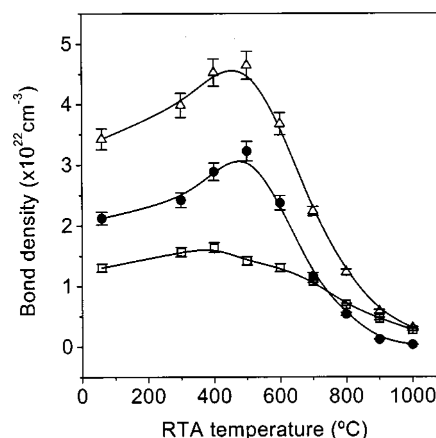

FIG. 2. Density of Si–H (●) and N–H (□) bonds, and total content of bonded hydrogen (△), vs annealing temperature for the samples deposited with $R=1$. There is an increase in the amount of bonded hydrogen at moderate annealing temperatures.

Rand.[11] The IR spectra were recorded with a Nicolet 5PC Fourier transform spectrometer on samples deposited under the same experimental conditions as those for the ESR measurements.[8,9]

In order to test the detection of the N center, the ESR spectrum of a film deposited with the higher nitrogen-to-silane ratio ($R=7.5$) and annealed at 1050 °C was measured before and after 90 min of UV illumination, first with a microwave power of 0.5 mW, which is low enough to prevent the saturation of the K absorption,[10] and then at a microwave power 20 times larger, which causes the saturation of this signal. It was observed that the UV illumination produces an increase of the signal associated with the K center, which is then saturated by the higher power level without the appearance of a recognizable three-line pattern. Therefore, no evidence for the nitrogen dangling bond could be established in these films.

Figure 1 shows the density of detected unpaired spins associated with the K center for the three types of films analyzed. The trends with annealing temperature indicate a significant reduction of the density of paramagnetic dangling bonds up to 600 °C and an increase at higher temperatures, except for the films with the lower nitrogen content, in which the initial decrease is much less significant.

The decrease of the density of magnetically active spins can be due to three possible causes: (i) a real disappearance of the defects as a consequence of a reconstruction of the network, (ii) a passivation by hydrogen atoms, and (iii) a charge transfer that renders the defects diamagnetic. Figures 2 and 3 show the thermal evolution of the bonded hydrogen content for the three types of films, obtained from the IR measurements. In the silicon-rich and near-stoichiometric samples there is an increase of the Si–H bond density up to 500 and 700 °C, respectively. Although these graphs may seem to support the hypothesis of a passivation of silicon dangling-bond centers by the formation of Si–H bonds, it should be noted that a similar increase of Si–H bonds is detected for the samples with $R=1$ and $R=1.6$, but the defect density does not show a comparable decrease for the sample with $R=1$. This different behavior could be related to the change in N–H-to-Si–H bond density, as N content increases. In Refs. 8 and 12 it was shown that the changes of Si–H and N–H bond density at moderate temperatures (lower than 500 °C for the silicon-rich films and 700 °C for the near stoichiometric) are due to the breaking of weak Si–Si bonds accompanied by a reaction of incorporation of hydrogen trapped in microvoids of the structure, taking place simultaneously with a transfer of hydrogen from N–H to Si–H bonds according to a reaction of chemical ordering.[8,12] In the silicon-rich composition, the lower proportion of N–H bonds limits the extent to which this hydrogen transfer reaction can take place, and therefore, can explain the less significant passivation of dangling bonds. Nevertheless, it is important to note that Si–H bonds are not observed in the $R=7.5$ films (Fig. 3).[8] For this reason, and due to the parallelism between the $R=1.6$ and $R=7.5$ samples with regard to the trend of the ESR signal (Fig. 1), we propose that the observed decrease is a consequence of charge transfer be-

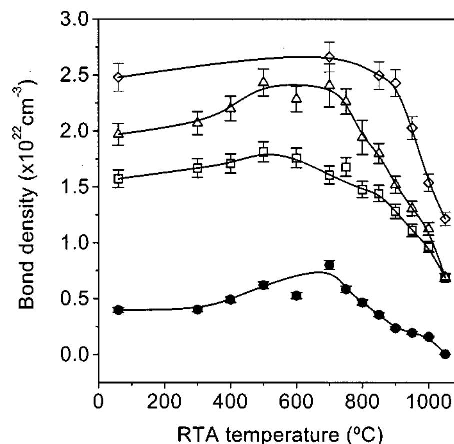

FIG. 3. Density of bonded hydrogen for the films characterized by a gas flow ratio parameter of $R=1.6$ and $R=7.5$. In the $R=1.6$ case, Si–H groups are represented as (●), N–H as (□), and the total amount is denoted by (△). For the $R=7.5$ films, no Si–H bonds are detected in the infrared spectra at any annealing temperature, and the density of N–H bonds is represented as (◇).

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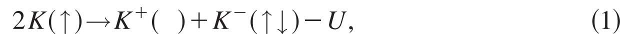
tween paramagnetic defects. This charge transfer would be in agreement with the negative correlation energy that it is known to be a characteristic of these centers.[13,14] The consequence of the negative correlation energy model is that the intermediate charge state $K^0(\uparrow)$ has more energy (is less stable) than the lower $K^+(\ )$ and higher $K^-(\uparrow\downarrow)$ charge states. The net process could then be written as



$$2K(\uparrow)\rightarrow K^+(\ )+K^-(\uparrow\downarrow)-U, \quad (1)$$

where U is the correlation energy.

The as-grown composition of the films with $R=1$ is below the percolation threshold ($x=1.1$) of Si–Si bonds in the lattice of the nitride, which means that there are continuous chains of Si–Si bonds spanning throughout the whole dielectric, resulting in a rigid and strained structure. This may be one of the reasons why those films do not experience the structural relaxation that takes place at moderate annealing temperatures for the other two types of films, whose as-grown composition is above the percolation limit. Results of measurements of the optical properties and the interface density of states as a function of annealing temperature seem to support this explanation.[9,12] Additionally, the narrowing of the optical gap that occurs with the increase of the Si proportion in the film is likely to modify the energy position of the defect centers, reducing the difference among them and possibly even making the correlation energy positive.[13] In that case, the process described by Eq. (1) would no longer be an energetically favored reaction.

In Ref. 9 the increase of the spin density above 600 °C was related to a decrease of the resistivity and the dielectric strength and an increase of the density of states at the interface, for the particular case of the nitrogen-rich samples. These processes could not be explained by the results of the IR spectra because the nitrogen-rich films did not show any detectable absorption associated with Si–H bonds. The release of nonbonded hydrogen trapped in microvoids could be responsible for the deterioration of the electrical properties because of the subsequent increase of the surface-to-volume ratio of the film. Without nonbonded hydrogen in the film available to passivate broken Si bonds, the weak-bond dangling-bond conversion[15] will generate unpaired spins, and an increase of the ESR signal is expected, as observed experimentally. Further studies in progress at this moment suggest that this same model explains the increase of the spin density at high temperatures for the near-stoichiometric and silicon-rich compositions, whose electrical characteristics experience a deterioration in coincidence with the increase of the ESR signal.

In summary, we conclude that rapid thermal annealing induces a thermally activated charge transfer between paramagnetic defects in hydrogenated silicon nitride for temperatures up to 600 °C when the composition is above the percolation threshold. This is observed as a considerable decrease of the density of paramagnetic silicon dangling-bond defects detected by ESR. In the samples in which Si–H bonds can be detected, this process takes place simultaneously with chemical reactions of hydrogen-bond formation, although it seems that both processes must be analyzed separately due to the different orders of magnitude of the involved amounts. The exception are the films in which percolation of Si–Si bonds occurs in the lattice. In that case, the network is too rigid and does not permit defect relaxation. For higher annealing temperatures the dielectric experiences loss of hydrogen and an increase of the density of ESR active centers.

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