Role of oxygen on the dangling bond configuration of low oxygen content SiN_x:H films deposited at room temperature

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SiN_x:H films with a wide composition range and, some of them, with low oxygen content are deposited at room temperature. The defects observed in the films are attributed to Si-dangling bonds, with a structure depending on film composition. For the N-rich films they are of the form $\cdot Si\equiv(N_3)$, whereas for the films with similar [N]/[Si] ratio but containing oxygen, the predominant defect is proposed to be $\cdot Si\equiv(Si_2O)$, despite of the high N content and the low O content of these films. The spin density of the films has been related to the bonds that hydrogen establishes (either Si–H or N–H), with the maximum value corresponding to the minimum hydrogen content. Both maximum and minimum values, respectively, are obtained at the silicon percolation limit of the Si–Si bonds into the SiN_x:H network, $x\sim1.10$. © *1995 American Institute of Physics.*

Deposition of oxynitride films has been encouraged in the last years in order to combine the suitable electronic characteristics that both, silicon nitride and silicon oxide present. Although they are well known the different paramagnetic properties of Si_3N_4 and SiO_2,[1,2] the influence that N and O atoms have on the dangling bond structure when both are introduced into the amorphous-silicon matrix is not clarified yet. To this aim, this letter presents novel results about the electron paramagnetic resonance (EPR) and the optical properties of nearly stoichiometric and N-rich SiN_x:H films with low oxygen content, which can contribute to a better knowledge of the dangling bond structure of oxynitride films. Differences are found with the results obtained for Si-rich SiN_x:H films without oxygen content also presented in this work. Furthermore, to date, little relation has been found between the paramagnetic behavior and the hydrogen content of the films,[3] and this letter presents results that could contribute to the understanding of the N–H bond role in the N-rich SiN_x:H films.

The samples are deposited at room temperature by the electron cyclotron resonance (ECR) plasma deposition method. Details of the deposition process can be found elsewhere.[4,5] Films with different [N]/[Si] ratios and, some of them, with low oxygen content are analyzed. As we have already reported,[5] sputtering of the quartz liner inserted into the plasma source by the energetic nitrogen ions at microwave powers higher than 150 W and N_2/SiH_4 ratios higher than[6] results in oxygen incorporation into the SiN_x:H films. This incorporation is unintentional but reproducible, as the conditions of the sputtering of the liner are determined by the microwave power and N_2/SiH_4 ratio used. The [N]/[Si] ratio, given by x, and the oxygen content are measured by Auger electron spectroscopy (AES). For those oxygen-containing films, the oxygen content ranges from 3 to 7 at. %, depending on the deposition conditions. Films deposited on silicon substrates are used to measure the EPR and the infrared (IR) spectra. The EPR measurements are performed using a Bruker ESP 300E *X*-band spectrometer at 0.5 mW microwave power, which is low enough to avoid saturation of the signal. UV irradiation of samples is carried out using a Xe lamp and an Oriel filter transmitting from 280 to 370 nm. The IR spectra are collected in a FTIR spectrometer in the midinfrared region. Si–H and N–H bond density, as well as hydrogen content are calculated from the IR spectra.[6] Transmittance and reflectance in the 200–2500 nm range are used to calculate the absorption coefficient of films deposited on quartz substrates.

Figure 1 shows the Urbach tail parameter (E_0), as a function of the [N]/[Si] ratio in the films. Increasing values of E_0 indicate increasing disorder in the films, as E_0 is related to the slope of the valence band tail. The plot indicates that the nitrogen incorporation increases the disorder in the films until the silicon percolation limit into the SiN_x:H network is reached ($x\sim1.10$).[7] The most interesting feature in Fig. 1 is the values of E_0 obtained for oxygen-containing films, lower than those obtained for oxygen-free SiN_x:H

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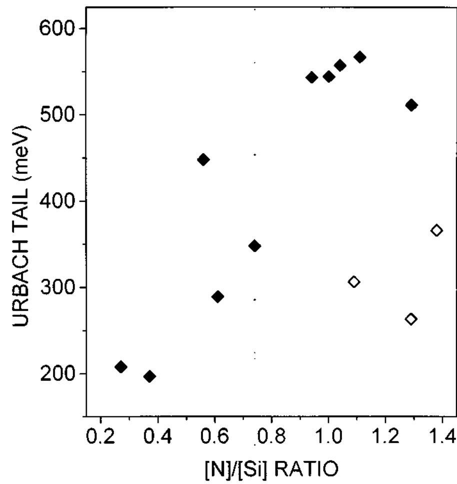

FIG. 1. Urbach tail parameter as a function of the [N]/[Si] ratio in the films. Open symbols indicate oxygen containing films.

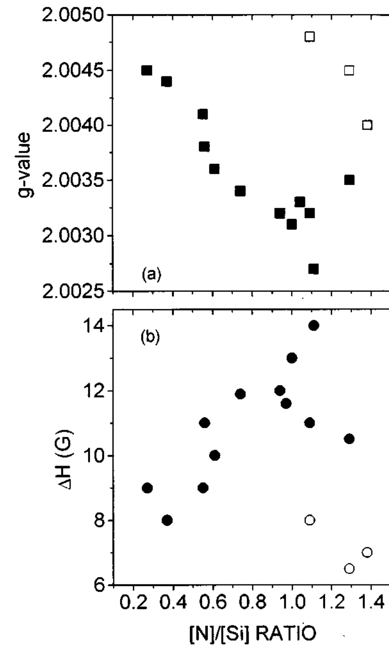

FIG. 2. (a) g value and (b) linewidth ΔH vs the [N]/[Si] ratio in the films. In all cases, open symbols indicate oxygen-containing films.

films with similar [N]/[Si] ratio. These values indicate that, even for low oxygen content in the films, an increasing order is observed as oxygen is incorporated into the nitride network.

The EPR spectra of SiN_x:H films have been measured at room temperature. In all cases, a single isotropic line has been detected, with g value ranging from 2.0050 to 2.0026 and linewidth ΔH (peak-to-peak of the first derivative curve) from 6.5 to 14 G depending on the [N]/[Si] ratio and on the oxygen content. The values of g and ΔH versus the [N]/[Si] ratio are plotted in Figs. 2(a) and 2(b), respectively. The dependence of g and ΔH with the[N]/[Si] ratio indicates that the measured line is a composition of several lines corresponding to Si-dangling bond defects of type $\cdot Si{\equiv}Si_{3-y}N_y$,[3] the relative proportion of each in the sample depends on x. The results for nearly stoichiometric samples ($g\approx 2.0030$, $\Delta H\approx 13$ G) indicate that the most abundant defect is $\cdot Si{\equiv}N_3$ ($y=3$), which is known as the K center,[3] whereas for Si-rich samples ($x\approx 0.27$) the values ($g\approx 2.0045$, $\Delta H=8$ G) indicate that most dangling bonds are of the form $\cdot Si{\equiv}Si_3$. The larger linewidth of the K center is due to hyperfine (HF) interaction of the unpaired electron with the nuclear spin ($I=1$) of the three nearest-neighbor N nuclei.[3]

On the other hand, a striking change appears in the values of g and ΔH for films containing oxygen with regard to oxygen-free films with similar x. As can be observed in Figs. 2(a) and 2(b), the values of g ($\approx$2.0045) and ΔH ($\sim$7 G), fall out of the general trend. That means that oxygen favors a different predominant defect, despite its low concentration (3–7 at. %), and it seems reasonable that this defect should be associated to oxygen. Among the various possibilities, the single line structure of the spectrum and its g value precludes assignation of the defect to oxygen-hole centers or peroxy radicals, as observed in a-SiO_2.[8] Thus, these defects should correspond again to dangling bonds and should be associated to Si, because a N-dangling bond would produce a triplet structure in the line due to the HF interaction,[3] which has not been observed. Moreover, the small ΔH value of the line cannot be accounted for if any of the three backbonds is saturated by N atoms,[3] i.e., the center should be of the form $\cdot Si{\equiv}(Si_{3-z}O_z)$. Further, as the oxygen content is low, it seems plausible that no more than one O atom exists in the center. In agreement with this, the measured g values fall between those for centers $\cdot Si{\equiv}(Si_2O)$ (2.0038) and $\cdot Si{\equiv}Si_3$ (2.0055) in a-SiO_x.[9] Therefore, we propose that both centers are present in those films containing oxygen with [N]/[Si] ratios higher than 1.00–1.10 here analyzed, in spite of the low oxygen content. Furthermore, as it will be shown, UV illumination experiments indicate that the most abundant defect is the $\cdot Si{\equiv}(Si_2O)$.

Figure 3(a) displays an estimation of the absolute number of spin density versus the [N]/[Si] ratio before and after UV illumination. The spin density is calculated by comparing the integrated area under the EPR absorption curve to that from a weak pitch standard sample. No significative changes of g value and linewidth are observed for any sample after UV illumination. However, UV light produces an increase of the spin density for all oxygen-free samples, larger in the films with x in the 0.79–1.00 range. Saturation is observed after 120 min of UV illumination. The increase of the density of paramagnetic Si dangling bonds observed after UV illumination is due to charge redistribution within existing defects.[7] Thus, the spin density measured after illumination should be a better estimate of the total defect center density in the samples, as before UV illumination not all the defects are paramagnetic active. The gradual increase of the spin density with the [N]/[Si] ratio until $x=0.97$, and the sudden decrease observed for larger x values, agrees with the trend already obtained for other plasma deposited SiN_x:H films.[10] The result at $x=1.00$, which falls out of the general trend, should be due to problems in the measurement in the

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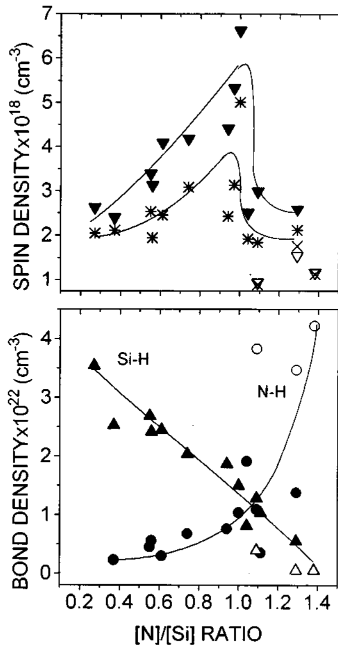

FIG. 3. (a) Spin density before and after illumination, as a function of the [N/]/[Si] ratio in the films: for films with (*) and without oxygen (×) before illumination; for films with (▼) and without oxygen (▽) after illumination. (b) Si–H (up triangles) and N–H (circles) bond density as a function of the [N]/[Si] ratio in the films. Open symbols indicate oxygen-containing films. In both figures, the lines drawn are guides for the eyes.

0.97–1.09 composition range, related to the striking changes around $x=1.00-1.09$.[7,10,11]

A different behavior is observed for the films containing oxygen, as no changes in the EPR signal after UV illumination are detected within experimental error. This result seems to indicate that the Si-dangling bonds for these films have a positive correlation energy U, in contrast to the negative U attributed to the K center,[3] present in the free-oxygen films of similar [N]/[Si] ratio. The result also suggests that the most abundant center in these samples is the $\cdot Si\equiv(Si_2O)$, if one assumes that it is less UV sensitive than the $\cdot Si\equiv Si_3$ is. Moreover, the total defect center density for films containing oxygen is lower than that for oxygen-free films, which indicates that oxygen effectively reduces the total precursor density in nearly stoichiometric SiN_x:H films, even for the low oxygen content in the films were analyzed

Figure 3(b) presents the Si–H and N–H bond density as a function of the [N]/[Si] ratio. The minimum hydrogen content in the film, calculated from the sum of these densities, is obtained for films with x at 1.00–1.09 about, values near the percolation limit of the Si–Si bonds into the SiN_x:H network, $x=1.10$. This fact results from the decreasing Si–H bond density, that reaches its minimum value and almost disappears at $x=1.00-1.09$, and from the appearance at the same x value of N–H bonds, which density further increases with x. As compared with Fig. 3(a), we find that the total spin density measured after UV illumination reaches the maximum value at the [N]/[Si] ratio that corresponds to the minimum hydrogen content, increasing (or decreasing) when the hydrogen content decreases (or increases). Moreover, we observe this maximum value is located at the [N]/[Si] ratio for which the N–H bonds appear in the films. If we observe now Fig. 1, we can see a similar critical behavior at $x=1.00-1.09$, [N]/[Si] ratio at which E_0 reaches the maximum value. All these facts seem to indicate that, as proposed by Robertson,[7] the silicon percolation limit of the Si–Si bonds into the SiN_x:H network ($x\sim1.10$) is the critical value that separates the different behavior between Si-rich and N-rich films, and not the stoichiometric $x=1.33$ value.

For $x>1.10$, the weak Si–Si bonds, broken by the N incorporation into the network, have been proposed to be the precursors of the Si-dangling bonds.[7,10] Moreover, these bonds form the band edges that give rise to the Urbach absorption edge. The breakdown of these weak bonds explains the increase observed until the $x=1.10$ value of both, E_0 and spin density.[10] The formation of Si dangling bonds for N-rich films ($x>1.10$) has not been fully modeled yet. Robertson has proposed[7] that Si–H bonds could be the precursors of these dangling bonds. For similar types of films, Hasegawa *et al.*[10] have attributed them to the increase of the optical band gap of the film, promoted by the incorporation of N–H bonds instead of that of solely N bonds to reduce the stress. The results here presented seem to agree with the proposition of these authors, as no Si–H bonds are observed for $x>1.10$, further supported by the correlation found between the increase of the N–H bond density and the decrease of the Si-dangling bond density.

Two major conclusions can be obtained from the results presented. (1) A strong influence of low oxygen concentrations on the properties of SiN_x:H films has been observed. The oxygen changes the structure of the predominant Si-dangling bonds and increases the order of the network. (2) A correlation between the increase of the N–H bond density and the decrease of the spin density for N-rich films has been found. Small oxygen concentrations in SiN_x:H films as those analyzed in this work can be employed as a method to modelate the structure of the defect centers, and can be useful to control the electrical behavior of the films used as gate dielectric in different semiconductor devices.

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