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Hydrogen incorporation in silicon (oxy)nitride thin films

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Hydrogen in low-pressure chemical vapor deposited oxynitride films was measured using elastic recoil detection with 2 MeV He ions. A distinction between N- and Si-bonded hydrogen could be made for films deposited from ND_3 instead of NH_3 . The analyses reveal that on an average three times as much hydrogen is incorporated as N—H relative to Si—H, and that a maximum in this ratio is present in oxynitride with a composition around $\text{O}/\text{N} = 0.3$. This optimum coincides with a maximum in total hydrogen content in the film of 3.2 at. %. Hydrogen desorption occurs in a narrow temperature interval around 950 °C and proceeds virtually in an identical way for both binding types.

Hydrogen incorporation in low-pressure chemical vapor deposited (LPCVD) silicon nitride and silicon oxynitride has already been the subject of research.¹⁻³ Both a better understanding of the materials properties and the desire for improved electrical properties are maintaining the interest in this subject. For instance, the concentration of Si—H groups would correlate with the charge stored in the nitride layer,^{1,3} whereas N—H groups might be involved in the oxidation mechanism of (oxy)nitrides.⁴

H profiles and contents in oxynitrides as determined with nuclear reaction analysis (NRA) have been reported in a previous paper.² Total hydrogen concentrations are determined in this way. Si—H and N—H contributions are discernible with infrared spectroscopy (IR), but the limited sensitivity of this technique requires either very thick films, which is no problem in the case of plasma-enhanced CVD (PECVD) material,^{1,5} or a special sample arrangement to allow for multiple internal reflection.^{3,6} Quantitative results from IR studies have, to our knowledge, not been published for LPCVD oxynitrides, but the response to annealing indicated comparable Si—H and N—H bond strengths in Si_3N_4 .^{1,3} A different desorption behavior between N—H and Si—H has been reported for PECVD oxynitride films.⁵

We measured hydrogen in LPCVD (oxy)nitride films using elastic recoil detection (ERD). A 2 MeV He ion beam from a Van de Graaff accelerator is used to generate a recoil spectrum.⁷ The ion beam impinges on the sample surface at an angle of 5° and recoiled particles are detected at a scattering angle of 30°. A 9- μm -thick Mylar foil in front of the silicon surface barrier detector prevents scattered helium or heavier particles from reaching the detector. ERD analyses are carried out in an ultrahigh vacuum scattering chamber in order to reduce any contribution from adsorbed surface species.

LPCVD oxynitride films are usually grown at 820 °C from a mixture of SiH_2Cl_2 , NH_3 , and N_2O , where the $\text{NH}_3/\text{N}_2\text{O}$ ratio governs the film composition.⁸ For this study we used films deposited from SiH_2Cl_2 , ND_3 , and N_2O , under otherwise identical conditions.² Assuming that no H—D isotope exchange occurs during the deposition process, all D will be incorporated as N—D and all H as Si—H. In a reaction-controlled LPCVD process, as in the case of nitride deposition, isotope exchange might occur only as a side reaction of the Si_3N_4 formation; gas phase reactions are

not very likely to proceed. Since deuterium can also be detected in the ERD setup employed, these films would enable us to compare N—H directly with Si—H. As has been argued previously, O—H bonding is absent in LPCVD oxynitrides.²

ERD results were quantified by comparison with a LPCVD Si_3N_4 layer containing 3.5 at. % H, as established with NRA.² The ERD cross section for D was taken 1.1 times that for H, being the result of calibration experiments that will be described separately.⁹ A scattering angle of 30° is sufficiently large to prevent the resonance peak in the ERD cross section of D at 2.13 MeV from affecting the spectra recorded at 2 MeV.¹⁰

Figure 1 shows He ERD spectra of a 37-nm-thick oxynitride film (O/N ratio 0.38), as obtained for the as-deposited sample and after annealing in a vacuum at 850 or 1000 °C. The peak at the higher energies is due to D in the film, while the low-energy peak originates from H. Taking into account the depth resolution of 5–10 nm, the D profile is flat in all cases. In contrast, the H profile displays a surface peak in the as-deposited spectrum. Applying a simulation program, the area of this surface peak was estimated to correspond to 1.25×10^{15} at./ cm^2 , hence a monolayer or less. The remaining part of the H signal corresponds to 1.3×10^{15} at./ cm^2 ,

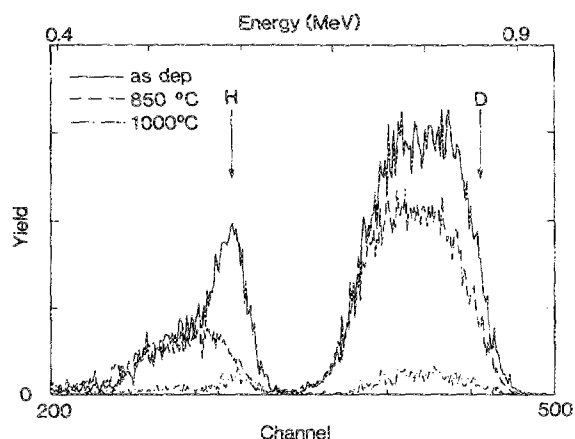


FIG. 1. ERD spectra of 37-nm-thick SiO_xN_y ($x/y = 0.38$) before and after annealing in vacuum at the temperatures indicated. The signal at the higher energies is due to D in the film (from ND_3), the lower energy peak to H (incorporated via SiH_2Cl_2). The arrows identify the surface energy positions of the two isotopes.

and the D peak for the as-deposited sample converts to 6.6×10^{15} at./cm². Since an Auger analysis of this sample indicated that hardly any surface oxidation had occurred, the surface H peak is probably caused by some hydrocarbon contamination. The spectrum of the sample annealed at 850 °C does not show such a surface peak, which indicates that surface contamination did not occur in the ERD vacuum system.

Annealing at 850 °C results in only a limited reduction of the H and D peaks. The spectrum for a 925 °C anneal (not shown in Fig. 1) is very like that of 850 °C. However, annealing at 1000 °C results in a complete desorption of H (the tiny surface peak visible equals 2×10^{14} at./cm² and provides an upper estimate for the surface contamination in the measuring system), and leaves the sample with only 5×10^{14} D at./cm².

ERD measurements were performed on oxynitride samples covering the composition range $0 < O/N < 1.71$. With the areal densities of O, N, and Si determined from Rutherford backscattering spectroscopy (RBS), the measured amounts of H and D were converted into atomic concentrations; see Fig. 2. The data for H are exclusive of any surface peak.

This figure reveals that the H and D incorporations are different: the H content is nearly independent of film composition, whereas the D concentration decreases with increasing O/N ratio. This supports the presumption of no isotope exchange and confirms the expectation that smaller amounts of D will be incorporated when layers with diminishing N contents are grown. However, the D—N relation is not just a simple proportionality: a maximum is observed around O/N = 0.3, which persists after annealing at even 1000 °C.

Annealing affects the D and H contents in a very similar way. This is visualized in Fig. 3, where the D/H ratio for the various oxynitride compositions is plotted after different anneals. The curves indicate that H and D desorb in comparable relative amounts in the temperature range up to 925 °C. At 1000 °C the amounts of H and D are too small to derive reliable D/H ratios, but the data in Fig. 2 give no support for a hypothesis of deviating desorption behavior at this highest temperature. For comparison the N/Si ratio is also plotted in Fig. 3. Apart from the behavior near O/N = 0.3 the general trend obeys $D/H = 3 \times N/Si$, which would imply that

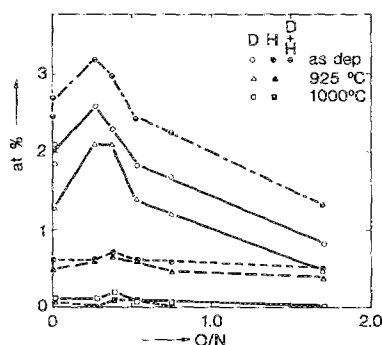


FIG. 2. H and D contents in LPCVD oxynitride films of different composition, as determined for the as-deposited material and after annealing.

in the nondeuterated material roughly three times as much hydrogen is bonded to N as to Si.

The observed similarity between D and H desorption agrees well with the IR results for Si₃N₄ reported by Percy and Stein.¹ Their IR spectra show a N—H/Si—H absorption ratio quite comparable to the D/H ratio of 3 found for Si₃N₄.

The summed H + D content for the various oxynitride films (upper curve in Fig. 2) corresponds very well with the H concentrations measured with NRA in NH₃-grown LPCVD oxynitrides.² This also holds for the values reported for 900 °C anneals. It indicates that NH₃ and ND₃ react similarly and that the kinetic isotope effect is small, as has been concluded before.²

The plots in Figs. 2 and 3 reveal that the maximum in D + H near O/N = 0.3 results primarily from an increased incorporation of D in the film. This points to a reduced decomposition of NH₃ or ND₃ at the growth surface of oxynitride of this composition. This has previously been explained in terms of an increased N—H bond strength, caused by an increased electronegativity of SiN_{4-x}O_x tetrahedra with increasing x.^{2,11} Since the D content declines for O/N ratios in excess of 0.3, the maximum observed cannot be explained on the basis of varying electronegativities alone. We propose that the incorporation of O in the amorphous nitride network adds some flexibility to the growing structure in such a way that a denser material is formed. As this would also apply to adding N to the oxide network, it is feasible that an optimum density would develop at an intermediate composition. At this composition NH or ND groups would be more easily accommodated in the growing layer, so that somewhat less N atoms become completely dehydrogenated.

Indication of an optimum film density is obtained by comparing RBS data for the total number of atoms per cm² with physical layer thicknesses determined from Talystep measurements. The film density in atoms per cm³ follows directly from dividing RBS areal density by film thickness. In Fig. 4 the densities for LPCVD oxynitrides thus determined are plotted relative to the corresponding value for crystalline material; the densities of crystalline oxynitrides are derived by interpolation from the known values of

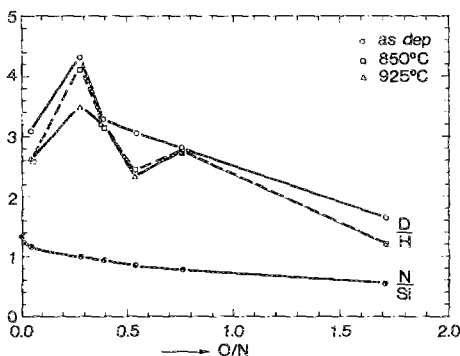


FIG. 3. D/H ratios derived from the data in Fig. 2, indicating the similarity in desorption behavior for both types of hydrogen bonds. The N/Si ratio as obtained from RBS analyses of the various SiO_xN_y films is included for comparison.

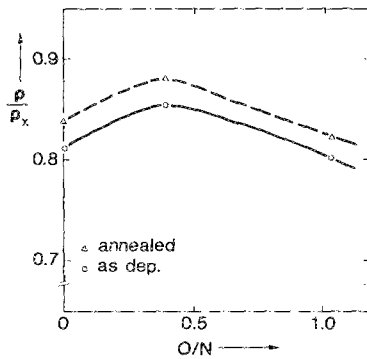


FIG. 4. Atomic density of LPCVD oxynitride layers (ρ) relative to that of crystalline material (ρ_x), determined from RBS and Talystep measurements. The density is found to be increased by a 1 h anneal at 1000 °C in N_2 .

α - Si_3N_4 and quartz. The results in Fig. 4 indeed suggest that material with a higher density is deposited somewhere near a film composition of $O/N = 0.5$. Annealing results in an increase in density of 2–2.5%, which may be related to the corresponding reduction in H content.

The results presented above demonstrate that 2 MeV He ERD analyses may be successfully used to measure H and D

profiles in thin films quantitatively. Most of the hydrogen incorporated during deposition in LPCVD oxynitrides is bonded to N, only about a quarter to Si. For both bonding types existing in this class of material the desorption of hydrogen occurs in a narrow temperature range around 950 °C.

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