

# Nature and electronic structure of Si-H and N-H bonds in $a\text{-SiN}_x\text{:H}$

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X-ray photoelectron spectroscopy was used to investigate the electron structure of Si-H and N-H bonds in hydrogenated amorphous silicon nitride ( $a\text{-SiN}_x\text{:H}$ ). The charge carried by a hydrogen atom in an N-H bond was found to be  $Q^H = -0.35q$ . The density-of-state peaks of the bonding  $\sigma$  orbital of an Si-H defect were found to be located at energies 1.5, 4, and 10 eV above the top of the valence band. Degradation of the memory properties of silicon nitride was investigated: it was explained by a polaron model of breaking of the Si-H and N-H bonds.

Amorphous silicon nitride films are used as insulating layers in MIS transistors, as the storage medium in metal-nitride-oxide-semiconductor (MNOS) memory elements, and as the active medium in solar cells.<sup>1</sup> Such films are synthesized from reagents containing hydrogen ( $\text{SiH}_4$ ,  $\text{SiH}_2\text{C}_2$ , and  $\text{NH}_3$ ), so that a nitride film includes not only Si-N and Si-Si bonds, but also Si-H and N-H bonds. Hydrogen passivates dangling bonds and reduces the density of localized states that act as recombination centers; it also increases the energy of deep centers responsible for the localization of electrons and holes in MNOS structures. Annealing reduces the concentration of Si-H and N-H bonds and the energy of deep centers responsible for the memory effect. Calculations of the electron structure indicate that the level of the bonding  $\sigma$  orbital of an Si-H defect lies in the band gap of  $\text{Si}_3\text{N}_4$ ; Robertson<sup>2</sup> used this to put forward a hypothesis according to which the Si-H defects are responsible for p-type conduction of silicon nitride.

We investigated  $a\text{-SiN}_x\text{:H}$  samples obtained by: a) ammonolysis of monosilane (in a mixture of the  $\text{SiH}_4\text{:NH}_3 = 1:10$  composition) at  $700^\circ\text{C}$  in an atmospheric-pressure reactor (APR); b) ammonolysis of silicon tetrachloride (in a mixture of the  $\text{SiCl}_4\text{:NH}_3 = 1:30$  composition) at  $800^\circ\text{C}$  in a low-pressure reactor (LPR). Vibrational spectra of the films were determined in the range  $2000\text{--}3600\text{ cm}^{-1}$  by the method of infrared spectroscopy of multiple frustrated total internal reflection (MFTIR). Silicon nitride films were deposited on silicon prisms of trapezoidal shape with a tilt angle  $30^\circ$ , which made it possible to observe 55 internal reflections. X-ray photoreflexion spectra were investigated using an HP5250 spectrometer and monochromatized radiation of photon energy 1486.6 eV. The energy calibration of the spectra was carried out on the basis of the 1S line of a hydrocarbon at 285.0 eV.

Figure 1 shows the MFTIR spectra of silicon nitride films  $\sim \text{\AA}$  [sic] thick, synthesized in the APR (a) and LPR (b), respectively. The nitride synthesized in the LPR was characterized by a concentration of the N-H bonds which was comparable with that in the nitride prepared in the APR but the concentration of the Si-H bonds was considerably less. Annealing of the APR nitride for 5 min at  $900^\circ\text{C}$  reduced the concentration of the Si-H bonds by about 30%, but did not alter the concentration of the N-H bonds. Subsequent annealing resulted in an approximately the same reduction in the concentrations of the Si-H and N-H bonds. Table I gives the concentrations of the Si-H and N-H bonds, which were

TABLE I. Concentrations of Si-H and N-H bonds in investigated samples

| Synthesis and treatments           | Concentration of Si-H, $\text{cm}^{-3}$ | Concentration of N-H, $\text{cm}^{-3}$ |
|------------------------------------|---|--|
| APR, original                      | $9.1 \cdot 10^{21}$                     | $6.3 \cdot 10^{21}$                    |
| Anneal. 5 min, $900^\circ\text{C}$ | $9.0 \cdot 10^{21}$                     | $6.2 \cdot 10^{21}$                    |
| Anneal. 2 h, $900^\circ\text{C}$   | $3.5 \cdot 10^{21}$                     | $1.6 \cdot 10^{21}$                    |
| Anneal. 5 min, $900^\circ\text{C}$ | $2.7 \cdot 10^{20}$                     | $2.0 \cdot 10^{20}$                    |
| + 3 h, $1000^\circ\text{C}$        |   |  |
| LPR, original                      | $<2.0 \cdot 10^{20}$                    | $6.3 \cdot 10^{21}$                    |

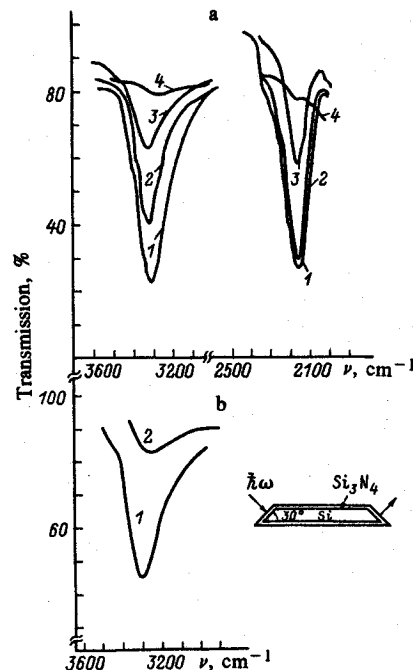
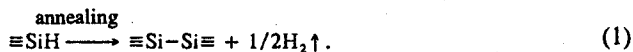


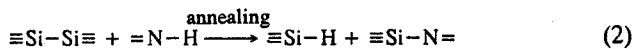
FIG. 1. Transmission spectra of  $a\text{-SiN}_x\text{:H}$  prepared in: a) an atmospheric-pressure reactor (APR); b) a low-pressure reactor (LPR). a: 1) Original sample; 2-4) after annealing for 5 min at  $900^\circ\text{C}$  (2), 2 h at  $900^\circ\text{C}$  (3), 6 h at  $900^\circ\text{C}$  and 3 h at  $1000^\circ\text{C}$  (4). 1) Original sample; 2) after annealing for 2 h at  $1000^\circ\text{C}$ . The inset shows the system used to measure transmission by the method of multiple frustrated total internal reflection (MFTIR).

determined from Fig. 1 assuming that the extinction coefficient was  $10.6 \times 10^{-20}\text{ cm}^{-1}$  for the N-H bond<sup>1</sup> and  $13 \times 10^{-20}\text{ cm}^{-1}$  for the Si-H bond.<sup>3</sup>

It is known that the Si-H binding energy is less than the N-H energy.<sup>1</sup> Consequently, the Si-H bonds dissociate more easily than the N-H bonds. On the other hand, annealing of silicon nitride at 900°C for 5 min reduced the concentration of the N-H bonds, but did not affect the concentration of the Si-H bonds. This paradox can be explained bearing in mind that the Si-H bonds dissociated by heating reform again as a result of structural changes. It is known that two types of paramagnetic centers may exist in silicon nitride: one of these centers is formed by a triply coordinated silicon atom with an unpaired electron:  $N_3Si\cdot$  (Ref. 4) and the other is a doubly coordinated nitrogen atom with an unpaired electron:  $Si_2N\cdot$  (Ref. 5 and 6). We detected experimentally paramagnetic signals and the spectra of these signals are shown in Fig. 1. We found that the concentration of the paramagnetic centers in all the samples was at least one order of magnitude less than the concentrations of the Si-H and N-H defects. This result demonstrated that the formation of the  $\equiv Si\cdot$  and  $\equiv N\cdot$  defects was an intermediate stage; the structural changes should generate paramagnetic defects. An analysis of possible structural changes led to the hypothesis of the following scheme of modification in silicon nitride:



This means that the dissociation of SiH defects gives rise to diamagnetic  $\equiv Si-Si\equiv$  bonds. Then, the  $\equiv Si-Si\equiv$  bonds interact with the N-H bonds in accordance with the scheme



giving rise to the Si-H and Si-N bonds. According to this scheme, in the presence of the Si-Si bonds a hydrogen atom is transferred from one silicon atom to the other, destroying the Si-Si bond and creating an Si-N bond. It follows from Eqs. (1) and (2) that the transfer of hydrogen from nitrogen to silicon occurs in the presence of a constant concentration of the Si-H bonds, as indeed found experimentally (Fig. 1).

According to the proposed scheme of structural transformations, a reduction in the concentrations of the Si-Si and N-H bonds as a result of annealing should be accompanied by an increase in the concentration of the Si-H and Si-N bonds. It was reported in Ref. 4 that the absorption by the N-H bonds decreased as a result of annealing of silicon nitride and this was accompanied by a simultaneous increase in the concentrations of the Si-H and N-H bonds. The covalent Si-Si bond was not detected in the infrared spectra, but a shift of the fundamental absorption edge in the direction of the higher photon energies was reported in Ref. 4 and it indicated a reduction in the concentration of the Si-Si bonds as a result of annealing of silicon nitride.

Figure 2 shows the photoelectron spectra of the 2p level of Si in the original and annealed APR nitride and of the nitride synthesized in the LPR. The width of the 2p level of Si, measured at half-amplitude for the nitride with few Si-H bonds was 1.8 eV, compared with 2.0 eV for the original nitride synthesized in the APR. The broadened spectrum of the sample with a high concentration of the Si-H bonds could be represented by a superposition of two peaks. A peak with the larger amplitude represented the spectrum of samples with low concentrations of the Si-H bonds. The second signal (peak)

was obtained by subtracting, from the spectrum of the original sample, the peak found for the samples with low concentrations of the Si-H bonds.

An analysis of the frequency of the vibrations of the Si-H bonds in silicon nitride on the basis of the concept of an effective electronegativity of the immediate environment led Lucovsky<sup>7</sup> to the conclusion that the Si-H bond was built into a  $SiSiHN_2$  tetrahedron (Fig. 3). The silicon atoms in the  $SiSiN_3$  and  $SiSiHN_2$  tetrahedra should generally have different charges. In this case the signal (Fig. 2) obtained by subtracting the spectra should represent a superposition of two signals corresponding to the  $SiSiN_3$  and  $SiSiHN_2$  tetrahedra.

In estimating the charge on the hydrogen atom in an Si-H bond we must know the charge  $\Delta Q$  transferred to the

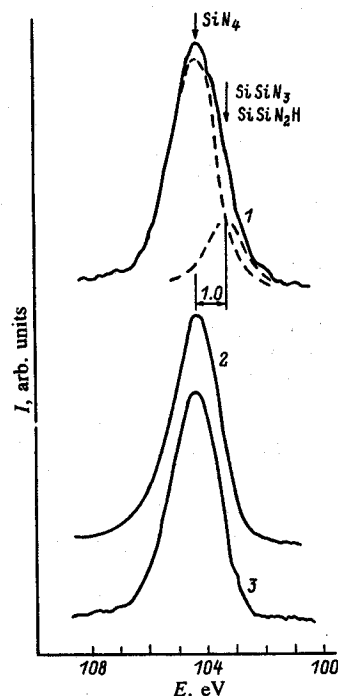


FIG. 2. Photoelectron spectra of the 2p level of Si: 1) original nitride synthesized in the APR; 2) same sample after annealing (corresponds to the spectrum 4 in Fig. 1); 3) nitride synthesized in the LPR.

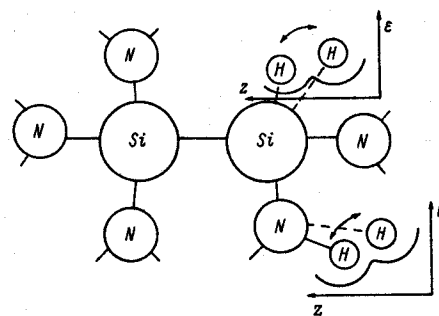


FIG. 3. Structural model of an Si-Si defect coordinated by hydrogen atoms in the first and second coordination spheres. The potential curves illustrate stretching of the Si-H bond due to the capture of a hole (electron) by an Si-Si defect.

Si-H bond. The value of  $\Delta Q$  can be obtained on the basis of Ref. 8, where precision measurements were reported of the energies of the  $2p$  levels of Si in Si,  $\text{Si}_3\text{N}_4$ , and  $\text{SiO}_2$ . The shift of the  $2p$  levels of Si in  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  relative to the position of the same level in pure Si was found to be 2.9 and 4.2 eV, respectively. Experiments on positron annihilation in  $\text{SiO}_2$  (Ref. 9) and calculations of the electron structure<sup>10,11</sup> gave the value of the negative charge carried by an oxygen atom:  $Q^O = 1.0q$ . Consequently, the charge carried by an atom of Si in  $\text{SiO}_2$  is +2.0. If we assume that the chemical shift of the  $2p$  level of Si is proportional to the charge of the Si atom, we find that the charge on the silicon atom in the  $\text{SiN}_4$  tetrahedron is +1.4 $q$  and the charge transferred to the Si-N bond is  $\Delta Q = 0.35q$ . Assuming that the charge carried by an Si atom is determined by the immediate tetrahedral environment and using the coincidence of the chemical shifts of the  $2p$  levels of Si in the  $\text{SiSiNH}_2$  and  $\text{SiSiN}_3$  tetrahedra, we find that the charge carried by an atom of H is  $Q^H = -0.35q$ . The chemical shift of the  $2p$  level of Si in the  $\text{SiSiHN}_2$  tetrahedron, relative to the  $\text{SiN}_4$  tetrahedron, is 1.0 eV (Fig. 2), which is in satisfactory agreement with the value 0.73 eV obtained on the assumption that the charge on the Si atom is proportional to the number of the Si-N bonds.

The proportion of the  $\text{SiSiHN}_2$  tetrahedra deduced from Fig. 2 is about 15% of the total number of the  $\text{SiN}_4$  tetrahedra. The concentration of the Si atoms in  $\text{Si}_3\text{N}_4$  is  $4 \times 10^{22} \text{ cm}^{-3}$ . It therefore follows that the concentration of the Si-H bonds deduced from photoelectron spectrography is  $10^{21} \text{ cm}^{-3}$ .

The photoelectron spectrum of the  $1s$  level of N in the nitride with a high concentration of the N-H bonds was found to be slightly asymmetric and this case due to a high-energy shoulder (Fig. 4). Subtraction from the total spectrum of the symmetric signal corresponding to the  $\text{NSi}_3$  structural unit gave rise to a high-energy peak shifted by 1.8 eV relative to

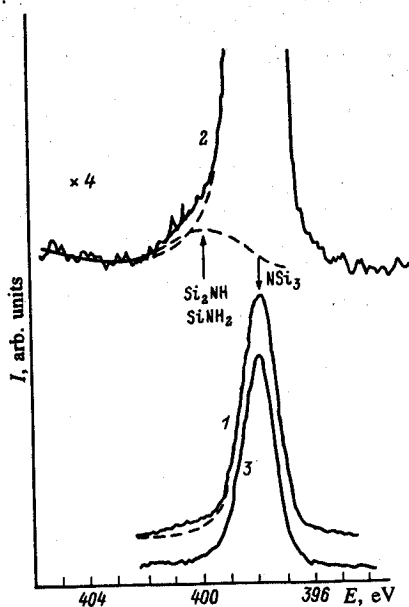


FIG. 4. Photoelectron spectra of the  $1s$  level of N in silicon nitride: 1) original nitride synthesized in the APR; 2) same spectrum obtained using a higher sensitivity; 3) the same sample after annealing (corresponds to the spectrum 4 in Fig. 1).

the main signal. An estimate of the effective charge on the nitrogen atom bound to an atom of hydrogen required the knowledge of solid-state compounds of nitrogen with a known charge, which provided the necessary calibration. The width of the high-energy peak was 2.9 eV at its half-amplitude, which exceeded the width of the main peak (1.5 eV). This result was in qualitative agreement with the hypothesis that the high-energy peak was a superposition of two signals representing the presence of inequivalent nitrogen atoms bound to hydrogen, i.e., the presence of the N-H and N-H<sub>2</sub> bonds.

The relative amplitude of the high-energy peak in Fig. 4 was 5% of the amplitude of the main peak, so that when the concentration of the nitrogen atoms in the nitride was  $5 \times 10^{22} \text{ cm}^{-3}$ , this represented the content of nitrogen bound to hydrogen:  $(2-3) \times 10^{21} \text{ cm}^{-3}$ . Bearing in mind the low precision of this estimate, we concluded that the value obtained was in agreement with the concentration of the N-H bonds ( $6.3 \times 10^{21} \text{ cm}^{-3}$ ) determined by infrared spectroscopy.

An investigation by x-ray emission spectroscopy<sup>12</sup> indicated that the valence band of  $\text{Si}_3\text{N}_4$  was formed from the  $3s$  and  $3p$  orbital of silicon and the  $2p$  orbital of nitrogen. Figure 5 shows the x-ray photoelectron spectra of the valence band of the APR nitride (1), of the same nitride after annealing (2), and of the LPR nitride (3). The spectrum labeled 2 in Fig. 5 represents the spectrum of the valence band of the nitride with low concentrations of the Si-H and N-H bonds. The peak labeled C represents the  $2s$  orbital of nitrogen. According to Ref. 12, the peaks labeled A and B represent the  $3s$  orbital of silicon. The spectrum 3 differs little from the spectrum 2, i.e., the presence of the N-H bonds is not manifested in the photoelectron spectrum of the valence band.

The peak H at 8 eV below  $E_v$  in the spectrum of the APR nitride should be attributed to the  $\sigma$  bonding orbital of the

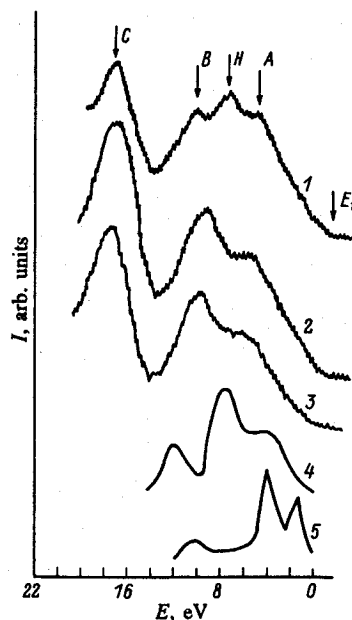


FIG. 5. Photoelectron spectra of the valence band of silicon nitride: 1) original nitride synthesized in the APR; 2) the same sample after annealing; 3) nitride synthesized in the LPR; 4) different spectrum obtained by subtracting the spectrum 2 from 1; 5) partial density of states at an Si-H defect in silicon nitride.<sup>11</sup>

Si-H bond, since it is absent from the spectra 2 and 3. The relative amplitude of peak *A* in the spectrum 1 is considerably higher than the amplitude of the peak *B* in the spectra 2 and 3. Curve 4 in Fig. 5 is the difference found by subtracting spectrum 2 from 1. The different spectrum in the case of the  $\sigma$  bonding orbital of the Si-H bond gives rise to three peaks at energies 5, 8, and 12 eV above the top of the valence band. It was reported in Ref. 10 that a near-stoichiometric nitride had maxima at energies 4 and 8 eV above the top of the valence band. The experiments<sup>10</sup> carried out using synchrotron radiation failed to distinguish the contributions of the N-H and Si-H bonds because at the excitation energies employed the 1s levels of *H* were manifested. The experiments did not predict the calculations according to which the  $\sigma$  orbital of the Si-H bond was located in the band gap.<sup>2</sup> The subsequent calculations predicted three peaks corresponding to the  $\sigma$  orbital in the valence band of silicon nitride (curve 5 in Fig. 5).<sup>13</sup> The calculated peaks of the density of states were shifted toward the top of the valence band compared with the experimental results.

The experiments demonstrated that the flow of the hole current in  $\text{Si}_3\text{N}_4$  increased the conductivity due to a reduction in the energy of hole traps.<sup>1,2</sup> We shall now consider degradation of the memory properties of the nitride using the polaron model. According to this model, the localization of electrons and holes in the nitride occurs at the neutral Si-Si defects.<sup>14,15</sup> The energy binding a carrier to such a defect can be estimated roughly from the expression

$$\Phi_t \approx -\frac{q^2}{4\pi\epsilon_0\epsilon_p R_0}, \quad \epsilon_p^{-1} = \epsilon_\infty^{-1} - \epsilon^{-1}. \quad (3)$$

Here,  $R_0$  is the radius of the defect and  $\epsilon_p$  is the polar permittivity. According to Eq. (1), the energy binding a carrier to a defect may decrease on increase in  $\epsilon_p$ . According to the proposed model, the degradation of the memory properties of silicon nitride is due to a reduction in the energy  $\Phi_t$  of a trap and is due to an increase in  $\epsilon_p$  because of stretching (and finally breaking) of the Si-H bond (Fig. 3). The breaking of the Si-H bonds is accompanied by a reduction in the static permittivity  $\epsilon$  in accordance with the Kramers-Kronig rule

$$\epsilon = \epsilon_\infty + \int_{\omega_1}^{\omega_2} \alpha(\omega) d\omega. \quad (4)$$

Here,  $\alpha(\omega)$  is the absorption coefficient representing in present case the Si-N bonds (with a maximum at 11.5  $\mu\text{m}$ ) and the Si-H bonds (with a maximum at 5.5  $\mu\text{m}$ ). Breaking of the Si-H bonds (with a maximum at 5.5  $\mu\text{m}$ ). Breaking of the Si-H bond reduces the optical absorption in the region of

5.5  $\mu\text{m}$  and, consequently, reduces  $\epsilon$ , i.e., according to Eq. (3), it increases  $\epsilon_p$ . According to the proposed model the effects of low-temperature annealing include restoration of the Si-H bonds, reduction of  $\epsilon_p$ , and a consequent increase in  $\Phi_t$ . According to the proposed model, degradation of the memory properties is associated with stretching (and finally breaking) of the Si-H bonds, as postulated in Ref. 16. Figure 3 shows the structure of a defect which accounts for degradation of  $a\text{-SiN}_x\text{:H}$ . In the proposed model we can expect also degradation because of stretching (breaking) of the N-H bonds. It seems that the contribution of this effect is less since hydrogen in N-H bonds is located in the second coordination sphere of an Si-Si defect.

Our results thus led to a proposed of a model of a structure defect that accounts qualitatively for a reduction in the energy of delocalization of electrons and holes from an Si-Si defect by stretching (and breaking) of the Si-H and N-H bond when the hydrogen atom is located in, respectively, the first and second coordination spheres relative to the silicon atom.

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