Multiphonon capture and radiative transitions in *a*-Si_3N_4

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The most important unsolved problem in the physics of amorphous silicon nitride (a-$SiN_{x\leq 4/3}$) is the nature of deep centers responsible for the memory effect, i.e., for the ability to localize injected electrons and holes for an extremely long time ($\tau \sim 10$ years at 300 K). It has been suggested[1] that the memory effect and radiative transitions in a-Si_3N_4 are due to Si–Si defects. Our purpose was to refine and confirm experimentally this hypothesis. With this in mind we introduced Si–Si defects, representing silicon in excess of the stoichiometric ratio, during synthesis of the nitride.

Excess silicon shifted the fundamental absorption edge of a-SiN_x toward lower energies.[2] Photoelectron spectroscopy experiments established[3] that excess silicon shifted upward the valence band of a-SiN_x in the direction of the band gap. The authors of Refs. 4 and 5 demonstrated that an increase in excess silicon in a-SiN_x caused a low-energy shift of the $L_{2,3}$ x-ray absorption edge of Si. On the basis of these experiments, a model of a low-energy shift of the absorption edge of SiN_x was proposed independently in Refs. 3 and 4.

According to this model, a reduction in x is accompanied by an increase in the Si–Si bonds in $SiN_\nu Si_{4-\nu}$ tetrahedra, where $\nu = 0, 1, 2, 3, 4$.

The splitting of the bonding σ orbitals (representing a symmetric combination of the sp^3 ψ functions of Si) and of the antibonding σ^* orbitals (antisymmetric combination of the ψ functions) occurs because of lifting of the degeneracy so that delocalized electron states become split off from the band edges of Si_3N_4 (Fig. 1a). According to this model of the σ and σ^* orbitals, the levels of isolated Si–Si defects coincide with the band edges E_V and E_C of Si_3N_4 (Fig. 1a). Calculations of the electron structure of Si–Si defects in Si_3N_4 (Ref. 6) and of the $SiSi_4$ tetrahedron immersed in the Si_3N_4 matrix[7] are in agreement with this hypothesis (within the limits of the calculation error).

The localization of electrons (holes) in the postulated polaron model can be represented as the

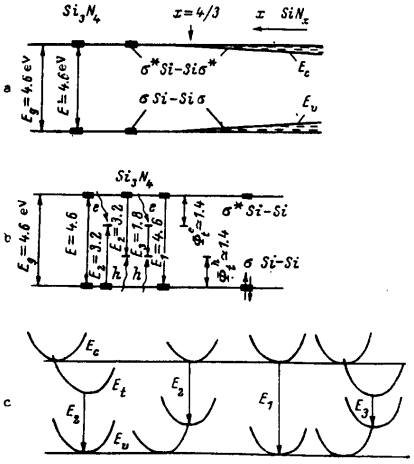

FIG. 1. Model of the low-energy shift of the absorption edge of a-SiN_x (a), electron transitions in the polaron model (b), and postulated configuration diagram illustrating multiphonon and optical transitions of electrons and holes (c). The dashed lines in Fig. 1a represent delocalized states of the Si–Si bonds responsible for the red shift of the absorption edge.

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capture by the σ^* (or σ) orbital and a subsequent multiphonon transition to a state with a negative energy Φ_t (see the configuration diagram of electron transitions in Fig. 1c). The large electron- and hole-capture cross sections $\sigma_t^e \approx \sigma_t^h \approx 5\cdot10^{-13}$ cm^2 found experimentally[2] are due to the fact that the wave functions of the σ and σ^* orbitals are strongly delocalized. When an electron (hole) is captured, a neutral Si–Si defect becomes charged. The Coulomb interaction of a localized electron (hole) with a free hole (electron) accounts for the giant recombination cross section $\sigma_R \approx 3\cdot10^{-13}$ cm^2 predicted by the polaron model and observed experimentally.[8]

The polaron model assumes three recombination channels: dissociation of a pair with an energy E_1 at a defect; recombination of localized electrons with free holes and of localized holes with free electrons (transition E_2), and annihilation of an electron–hole pair with an energy E_3 (Fig. 1b). The quantum efficiency of the photoluminescence of Si_3N_4 is low, so that we carried out experiments designed to detect the predicted optical transitions on excitation with an electron beam (E = 3 keV, I = 30 μA). In these experiments we found that all three transitions predicted by the model appeared against the background of a wide spectrum: the energies of these transitions were E_1 = 4.6 eV, E_2 = 3.2 eV, and E_3 = 1.8 eV (Fig. 2). It should be pointed out that a peak with the energy 1.9 eV was observed in the electroluminescence spectra.[9] Photoexcitation of Si_3N_4 by a waveguide method using an argon laser also revealed a peak of 1.8 eV energy (Ref. 10). The spectra of electron energy losses in a-Si_3N_4 indicated additionally the occurrence of transitions with energies 4.6 and 3.2 eV (Ref. 11).

The thermal energy of delocalization, determined as for the investigated sample of Si_3N_4, was $\Phi_t^e = \Phi_t^h = 1.50 \pm 0.06$ eV. Therefore, we observed experimentally the relationships that follow from the polaron model: $E_1 = E_g$, $E_1 = E_2 + \Phi_t$, $E_3 = E_1 - 2\Phi_t$. The rise of the intensity of the E_2 line on increase in the excess silicon content allowed us to attribute this line to Si–Si defects.

The polaron shift Φ_t due to the capture by a defect of radius R_0 can be estimated roughly from the Mott expression $\Phi_t \approx -q^2/\varepsilon_p R_0$, where $\varepsilon_p = \varepsilon_\infty - \varepsilon$. In the case of Si_3N_4, we have $\varepsilon_\infty = 4$ and $\varepsilon = 7$. The value $\Phi_t \approx 1.5$ eV corresponds to a reasonable radius $R_0 \approx 10^{-8}$ cm.

The anomalously small width of the E_2 line ($\Delta \approx kT$) indicates that the disorder-induced scatter of the energies of the localized states participating in this transition does not exceed kT (the disorder is not only due to the absence of the long-range order but also due to lack of order in the immediate environment). In view of the low intensity of this line, it is not likely that the small width of the line is due to stimulated transitions.

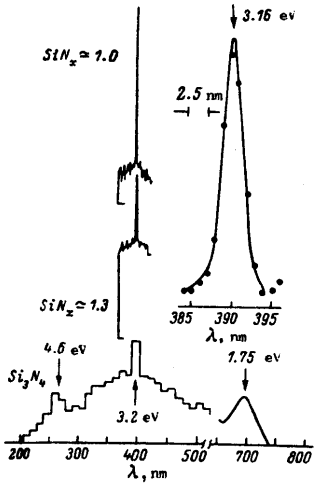

FIG. 2. Luminescence spectra of Si_3N_4 and SiN_x. The high-energy region was determined in the photon-counting regime using an FÉU-39A photoamplifier and the spectrum was not normalized to allow for the instrumental function. The inset shows a line with energy 3.16 eV.

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