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On the Nature of Deep Centres Responsible for the Memory Effect and Luminescence of a-SiN_x with $x \leqq 4/3$

By

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A model of deep centres according to which the capture of electrons and holes in a-Si_3N_4 is realized on the point defect Si-Si has been proposed by the authors of /1/. The present note deals with experimental results on the cathodo- and photoluminescence of silicon nitride, in which the ≡ Si-Si ≡ bonds were introduced into silicon nitride during the process of synthesis.

The nitride samples, enriched with silicon, were obtained in a low pressure reactor from a mixture of SiH_4 and NH_3 at 1100 K. The modification of composition was ensured by changing the SiH_4/NH_3 ratio over the range from 0.01 to 1. The composition of samples was determined by X-ray photoelectronic spectroscopy normalizing the line intensities of Si2p and N1s levels on the familiar cross-sections of photoionization.

A narrow intensive peak (the width at half-height is 0.06 eV) with energy 3.16 eV (Fig. 1) has been observed in the cathodoluminescence spectra (CL). This peak shows up on the background of a wide spectrum in the range 2 to 5 eV, just as it was observed in a-Si_3N_4 /1/. The amplitude of the peak at 3.16 eV increases with the increase of the excess Si concentration. This allows to conclude that the peak is connected with ≡ Si-Si≡ defects. In the range 2 to 3 eV the photoluminescence spectra (PL) (at the excitation energy $\hbar\omega_E = 3.8$ eV) have no sharp structure, they do not precisely coincide with the CL spectra (Fig. 1). Analogous PL spectra were observed under laser excitation in Si_3N_4 /2/. The PL excitation spectra (at the photoluminescence energy $\hbar\omega_L =$ $= 2.25$ eV) look like a wide maximum. The maximum correlates with the red shift of the absorption edge in a-SiN_x (Fig. 2).

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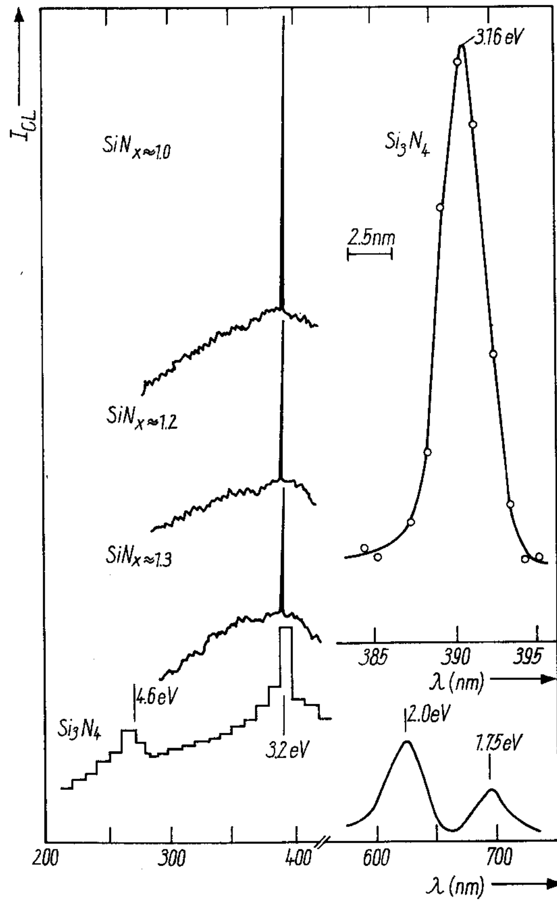

Fig. 1. Cathodoluminescence spectra of Si_3N_4 in the accumulation regime and of SiN_x of varying composition. Excitation energy and current are 3 keV and 20 μA, respectively

The enrichment of SiN_x with silicon is accompanied by low energy displacement of the $SiL_{2,3}$ absorption edge /3, 4/. The results prove that in SiN_x, where $x \leq 4/3$, the antibonding σ^*-orbitals of the ≡ Si-Si ≡ bond are situated near the conduction band. The low energy displacement of the top of the valence band E_v, which we observed in the XPS spectra, shows that the bonding σ-orbitals of the ≡Si-Si≡ bond are situated near the top of the SiN_x valence band. We suppose that the signal at E_2 = 4.6 eV, observed in the CL spectra (Fig. 1) gives the energy gap between the above mentioned σ- and σ^*-states of the

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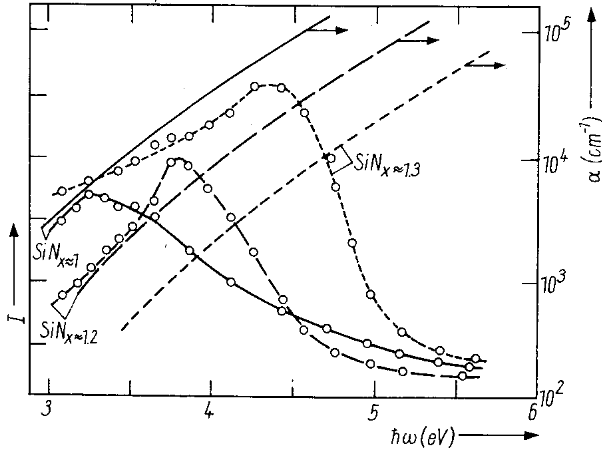

Fig. 2. Photoluminescence excitation spectra (for $\hbar\omega_L$ = 2.25 eV) and absorption spectra

≡Si-Si≡ bond. Such a supposition explains the excitation peak in Si_3N_4 with energy 4.6 eV /5/ and the red shift of the a-SiN_x absorption edge /6/. Calculations of the electronic structure of the ≡Si-Si≡ defect in Si_3N_4 prove the energy gap between σ-and σ*-orbitals to be 5 /7/ and 8 eV /8/.

In accordance with the proposed model the localization of electrons and holes in Si_3N_4 is realized at the expense of the energy gain appearing at lattice polarization. According to Mott and Davis /9/ when capturing a neutral centre, the electron creates a potential well with energy $V_p = -q^2/\varkappa_p R_o$, where R_o is the radius of the defect and $\varkappa_p^{-1} = \varkappa_\infty^{-1} - \varkappa^{-1}$ is the polaron dielectric permittivity. In Si_3N_4 $\varkappa_\infty = n^2 = 4$, $\varkappa = 6.5$, consequently, $\varkappa_p = 10$. The radius of the defect, $R_o = 10^{-8}$ cm, corresponds to the typical energy localization $E_t^{e,h}$ = = 1.5 eV observed in the experiment.

According to the proposed model the electron capture is realized on the antibonding σ*-orbital, the hole capture on the bonding σ-orbital. The energy of the electron and hole localization is determined only by the effective radius of the defect R_o and the dielectric permittivity $\varkappa_p$. In such a way, the accepted model suggests equal localization energies for electrons and holes. Investigations of the charge transfer in the MNOS structures show that the localization energies of electrons and holes in Si_3N_4 are really equal ($E_t^e = E_t^h$) .

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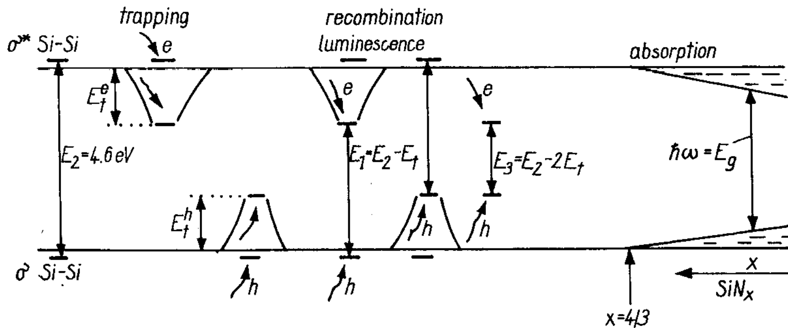

Fig. 3. A model of electron states in a-$SiN_{x \leq 4/3}$

The big capture cross-sections $\sigma_t^{e,h} = 5x10^{-13}$ cm^2, observed in Si_3N_4, we refer to the Coulomb interaction appearing in the lattice polarization. The Coulomb interaction explains as well the decrease of the energy delocalization in strong field (Frenkel effect). By the Coulomb interactions the proposed model explains the big cross-sections of the electron and hole recombination observed in the experiment $\sigma_R = 10^{-13}$ cm^2 /10/ and $5x10^{-14}$ cm^2 /11/. The model of VAP defects /12/ explains the big cross-sections σ_t^e, σ_t^h, but does not explain the big recombination cross-sections σ_R.

In our model the luminescence with energy $E_1 = E_2 - E_t = 3.15$ eV corresponds to the recombination of localized holes with free electrons and localized electrons with free holes (Fig. 3). The absence of peak splitting confirms the equality of localization energies $E_t^e = E_t^h$. In our model the excitation with energy 3.2 eV observed in /5/ corresponds to the excitation of the ≡Si-Si≡ defect.

We interpret the wide spectrum of the cathodo- and photoluminescence as luminescence on the ≡ Si-Si≡ defect, the levels of which are displaced by the presence of hydrogen and by the inhomogeneity of the nitride structure. The ≡Si-H and ≡N-H bonds according to the last theoretical calculations do not give localized states in the forbidden band of Si_3N_4 /8/. We suppose that due to the energy of the ≡ Si-H and ≡N-H bond hydrogen leads to a decrease of the effective dielectric permittivity of the nearest environment of the ≡Si-Si≡ defect. According to the above presented formula this corresponds to an increase of the bond energy of electrons and holes.

The correlation of the maximum in the photoluminescence excitation spectrum with the optical absorption edge of SiN_x (Fig. 2), which is determined by the σ- and σ^*-orbitals of the ≡Si-Si≡ bonds speaks in favour of the proposed model. In accordance with the proposed ideas the luminescence with energy $E_2 - (E_t^h + E_t^e)$ can be expected in SiN_x. At $E_2 = 4.6$ eV and E_t^e, $E_t^h = 1.3$ to 1.5 eV the energy of the expected transition must be in the range 1.6 to 2.0 eV. In the CL and PL spectra a band at 1.8 eV has been observed. Its excitation spectrum has characteristic peculiarities at 3.2 and 4.6 eV ($\hbar\omega_E \approx E_g$). A luminescence peak with energy 1.8 to 1.9 eV has been observed in the electroluminescence spectra of Si_3N_4 by the authors of /13, 14/. We believe that this peak is determined by the E_3 luminescence on the ≡Si-Si≡ defect (Fig. 3).

The suggested model explains the basic experimental facts connected with the memory effect in Si_3N_4:

1. Large cross-sections of electron and hole capture, the presence of the Frenkel effect;
2. two-band conductivity of Si_3N_4 /15, 16/;
3. equal concentration of traps for electrons and holes ($N_t^e = N_t^h$), the neutrality of Si_3N_4;
4. big recombination cross-sections of electrons and holes /10, 11/;
5. diamagnetic properties in a non-polarized state /1/;
6. increase of the localization energy with increase of the content of hydrogen in silicon nitride /17/;
7. red shift of the absorption edge in SiN_x /6/;
8. decrease of the activation energy of conductivity at enrichment by excess silicon /18/.

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