Wigner crystallization of electrons and holes in amorphous silicon nitride. Antiferromagnetic ordering of localized electrons and holes as a result of a resonance exchange interaction

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(Submitted 9 September 1996)
Pis'ma Zh. Éksp. Teor. Fiz. **64**, No. 7, 489–494 (10 October 1996)

The predicted quantitative relation between the density and trapping cross section of traps in Si_3N_4 and the Coulomb repulsion radius in the Wigner crystallization of carriers in localized states is observed experimentally. The absence of ESR for localized electrons and holes in Si_3N_4 is interpreted on the basis of a model of a resonance exchange interaction of electrons on account of tunneling via localized states.
 [S0021-3640(96)00819-5]

PACS numbers: 61.43.Dq, 71.23.Cq, 76.50.+g

The possibility of the formation of a quasiperiodic lattice on account of the Coulomb repulsion of the electrons localized in an insulator with a high trap density was analyzed in Ref. 1. A new exchange interaction mechanism, due to resonance tunneling of electrons along unfilled localized states, was also proposed there. Such an interaction can result in antiferromagnetic pairing of localized electrons, as a result of which the total spin of the system will equal zero. Our objective in the present work is to study experimentally the occurrence of localization of electrons and holes in amorphous silicon nitride (Si_3N_4) and to analyze the possibility of Wigner crystallization and a resonance exchange interaction.

Amorphous Si_3N_4 is a typical insulator with a high density of localized states (traps) for electrons and holes. A silicon atom in Si_3N_4 is coordinated by four nitrogen atoms; a nitrogen atom is bound with three silicon atoms.[2] The synthesis conditions for the nitride are such that excess superstoichiometric silicon is always present in it. Silicon in the form of Si–Si bonds replaces nitrogen atoms in the tetrahedron $SiN_\nu Si_{4-\nu}$ ($\nu=0, 1, 2, 3$).[3] In reality, the chemical formula for silicon nitride has the form $SiN_{x<4/3}$. In what follows, for simplicity, we shall denote the nonstoichiometric, silicon-enriched silicon nitride as Si_3N_4. The Si_3N_4 layers were synthesized by pyrolysis of a mixture of SiH_2Cl_2 and NH_3 at 850 °C and a mixture of $SiCl_4$ and NH_3 at 750 °C. MNOS (metal–nitride–oxide–semiconductor) structures with a thin (20 Å) oxide were investigated.[3]

1. WIGNER CRYSTALLIZATION

The density of filled traps n_t^e and n_t^h for electrons and holes, respectively, and the electron and hole trapping cross sections σ_t^e and σ_t^h, respectively, were determined from the kinetics of the pulsed polarization of MNOS structures by the method developed in Ref. 4. The accuracy of the method employed is low, $\simeq 100\%$.[4]

The following data were obtained for both technologies: $n_t^e = n_t^h = (5 \pm 3) \cdot 10^{18}$ cm^{-3}; $\sigma_t^e = \sigma_t^h = (6 \pm 4) \cdot 10^{-13}$ cm^2. For both technologies the relation

$$n_t^{-1/3}/2 = (\sigma/\pi)^{1/2}, \tag{1}$$

is satisfied, to within the limits of error, for electrons and holes localized in Si_3N_4. According to Ref. 1, relation (1) holds in an insulator with a high trap density under conditions when on account of the Coulomb repulsion of localized carriers the filled-trap density n_t is low compared with the density N of existing traps ($n_t \ll N$).

The average distance a between the electron- and hole-filled traps is the same and equals $a^e = a^h = N^{-1/3} = 60 \pm {}^{20}_{10}$ Å. The average trapping radius for electron and hole traps is the same and equals $R^e = R^h = (\sigma/\pi)^{1/2} = 45 \pm {}^{15}_{20}$ Å. We note that in the experiment the quantities L and R are determined independently.

According to the model proposed in Ref. 1, the distance $2R_q$ between two electrons localized in traps is determined by equating the Coulomb repulsion energy and the characteristic phonon energy E_{ph}

$$e^2/4\pi\varepsilon_p\varepsilon_0 R_q = E_{\text{ph}}. \tag{2}$$

Substituting in Eq. (2) the value[2] $E_{ph} \simeq kT$ for $\varepsilon_p = 10$ in Si_3N_4, we obtain $R_q \simeq 55$ Å. Here $\varepsilon_p^{-1} = \varepsilon_\infty^{-1} - \varepsilon^{-1}$ is the polaron dielectric constant. The relation (2) does not contain a parameter which depends on the sign of the carriers. Therefore the quantity R_q is the same for electrons and holes. Within the limits of error, the quantity R_q equals the average trapping radius and half the average distance between the electron- and hole-filled traps:

$$(n_t^e)^{-1/3}/2 = (\sigma^e/\pi)^{1/2} = R_q^e, \tag{3}$$

$$(n_t^h)^{-1/3}/2 = (\sigma^h/\pi)^{1/2} = R_q^h. \tag{4}$$

Relations (3) and (4) are a quantitative criterion[1] for the formation of a quasiperiodic lattice under conditions of carrier trapping in an insulator with a high trap density $N \gg n_t$.

In Ref. 5, the relation (1) for electrons was obtained in more accurate experiments on the polarization kinetics of Si_3N_4-based MIS structures with electron injection from the top electrode. In the present study samples we investigated in which Si_3N_4 was subjected to different actions, so that the filled trap density n_t in the sample varied. A decrease of n_t^e was accompanied by a decrease of σ_t^e, so that the relation (1) was satisfied for all n_t^e (Ref. 5). These experiments rule out the conjecture that traps with density $N = (2R_q)^{-3}$ are present in Si_3N_4.

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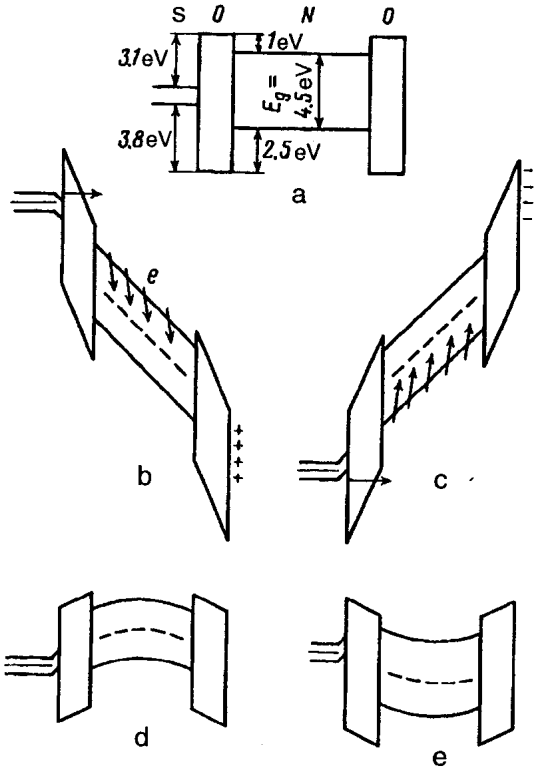

FIG. 1. Energy diagram of SONO (silicon–oxide–nitride–oxide) structures: a) Flat-band regime; b) polarization in a corona discharge, electron injection from Si; c) structure with localized electrons; d) polarization, hole injection from Si; e) structure with localized holes.

Thus, in Si_3N_4 the filled-trap density and the trapping cross section are determined by the characteristic Coulomb repulsion radius. This fact attests to the formation of a quasiperiodic, three-dimensional lattice of localized electrons and holes in Si_3N_4.

2. ANTIFERROMAGNETIC ORDERING

In Refs. 6 and 7 a polaron model of electron trapping on diamagnetic defects $\equiv$Si–Si$\equiv$ in Si_3N_4 was proposed. A dash indicates a chemical bond involving two electrons. The presence of Si–Si defects in the Si_3N_4 studied was detected in direct Raman scattering experiments.[a)] A line with frequency 475 cm^{-1}, corresponding to the TO vibrational mode of the Si–Si bond, and a line with frequency 296 cm^{-1}, corresponding to the LO mode, were recorded.[8] MINDO/3 quantum-mechanical modeling of a Si–Si defect in Si_3N_4 showed that, just as in SiO_2, a defect can trap electrons and holes. Trapping of an electron or hole on a Si–Si defect should lead to the formation of electron spin resonance (ESR) of the active center.

Special silicon—oxide (200 Å)—nitride (2100 Å)—oxide (500 Å) structures (SONO) were fabricated to investigate ESR in Si_3N_4 (Fig. 1). Polarization of the SONO

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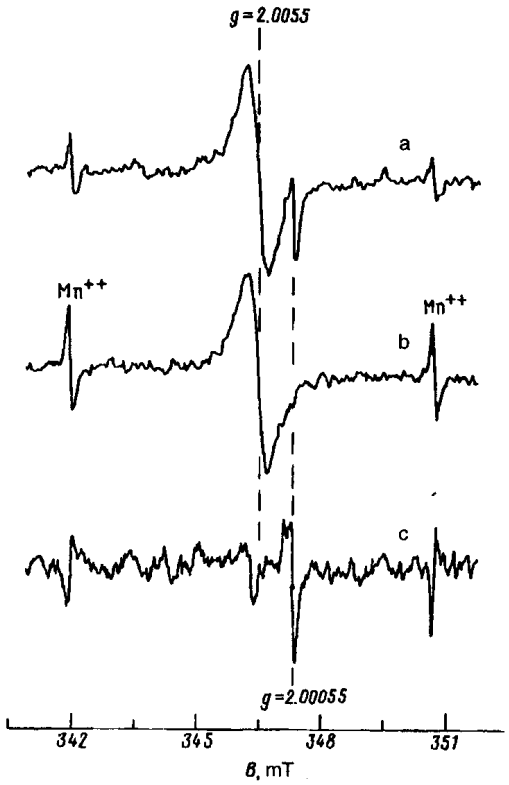

FIG. 2. ESR spectra of SONO structures: a) With localized holes; b) initial unpolarized structure; c) difference spectrum obtained by subtracting the spectra a and b.

structures was accomplished with the aid of a corona discharge plasma. A high electric field was produced in the insulator by means of charged ions which were deposited on the surface from the plasma (see Fig. 1). Electron and hole injection from the silicon was accomplished by a tunneling mechanism. Since the trap density in SiO_2 is low, most of the injected carriers were trapped in the Si_3N_4. After polarization, the surface density of the charge accumulated in the Si_3N_4 was determined by means of $C-V$ measurements. Then the silicon wafer was cut into 4×7 mm rectangles and ground so that the thickness decreased from 400 μm to 10–15 μm. The samples were assembled into a stack ($\simeq 100$ samples) and ESR measurements were performed. This made it possible to increase by two orders of magnitude the number of spins localized in the Si_3N_4 in the resonator of the spectrometer as compared with measurements performed on only one sample, as is usually the case.

The ESR spectra of SONO structures with $6 \cdot 10^{14}$ localized holes are displayed in Fig. 2. Two signals are observed (Fig. 2a). The wide signal with $g=2.0055$ (half-width $\Delta G=5$ G) is observed in amorphous silicon and on the surface of crystalline silicon. It is due to triply coordinated silicon atoms with an unpaired electron, Si_3Si. This ESR signal is associated with defects which are formed when the silicon is ground; it is present in the unpolarized sample (Fig. 2b). The narrow signal ($\Delta G=1.4$ G) with $g=2.00055$ (Fig. 2c)

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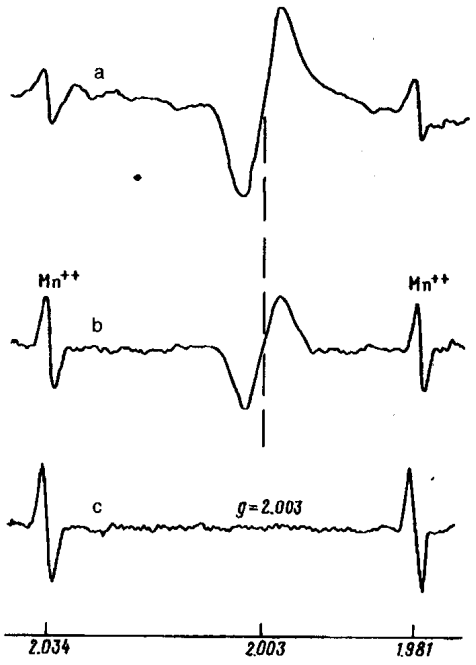

FIG. 3. ESR spectra: a) Silicon-enriched nitride $SiN_{1,2}$; b) stoichiometric Si_3N_4 after UV irradiation for 2 h with an unfiltered radiation from a 400 W hydrogen lamp; c) Si_3N_4 before UV irradiation.

is due to the well-studied[9] E' center in SiO_2. An E' center arises when a hole is trapped on a $\equiv Si-Si\equiv$ defect in SiO_2 near the $Si-SiO_3$ boundary.[10] When a hole is trapped on a $\equiv Si-Si\equiv$ bond in Si_3N_4, an ESR signal can be expected from triply coordinated silicon atoms N_3Si with an unpaired electron. Such a signal with $g \simeq 2.003$ is observed in silicon-enriched nitride $SiN_{x\simeq 1}$ (Fig. 3a) and after Si_3N_4 is irradiated with photons with $\hbar\omega > E_g$ (Fig. 3b).

In summary, in the experimental samples holes are trapped on the Si–Si defects in SiO_2. Hole trapping is accompanied by the formation of paramagnetic defects O_3Si. Hole trapping in Si_3N_4 is not accompanied by the appearance of an ESR signal. Similar experiments were performed with electrons localized in Si_3N_4, and no ESR signal was recorded in that case, either.

The absence of an ESR signal in Si_3N_4 with localized electrons and holes can be explained by assuming that pairing of localized spins, such that the sum of the spins equals zero, occurs. In Ref. 11 the absence of ESR in Si_3N_4 is explained on the basis of the assumption that the pairing in Si_3N_4 is due to trapping of a pair of electrons and holes on triply coordinated silicon atoms.

Let us analyze the possibility of pairing of spins not on one trap, as was done in Ref. 11, but rather on neighboring filled traps on account of a resonance exchange interaction.[1] The potential energy diagram for pairs of nearest electrons, localized in the Si_3N_4 in a plane parallel to the silicon–insulator boundary, is displayed in Fig. 4. The repulsive

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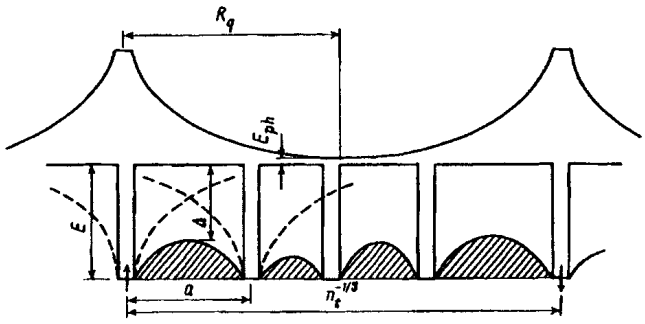

FIG. 4. Potential energy diagram illustrating spin pairing in Si_3N_4 on account of an exchange interaction with tunneling via unfilled states.

Coulomb potential describes the interaction of the localized electrons with a third, test electron. The attractive potential describes the polaron interaction of a localized electron with a polar lattice (as the Si_3N_4 lattice is):

$$V(z) = -e^2/8\pi\varepsilon_p\varepsilon_0 z. \tag{5}$$

The overlapping of the Coulomb polaron potentials of two neighboring traps results in a lowering of the barrier separating the traps (Fig. 4). For the two nearest traps the potential has the form

$$V(z) = -\frac{e^2}{4\pi\varepsilon_p\varepsilon_0}\left(\frac{1}{z} + \frac{1}{N^{-1/3} - z}\right). \tag{6}$$

We note that the lowering of the barrier between traps in SiN_x on account of the overlapping of the potentials as described by Eq. (6) was observed experimentally in Ref. 12. The density of Si–Si defects was estimated to be $\simeq 10^{21}$ cm^{-3}. Antiferromagnetic pairing of electrons on two neighboring traps will occur if the exchange interaction energy E_{ex} exceeds the Zeeman splitting $g\mu H$ (μ is the Bohr magneton and H is the intensity of the magnetic field). For clarity, we shall use the WKB approximation to estimate the magnitude of the magnetic interaction.

The probability of electron tunneling between two neighboring traps in the case when the potential of only the nearest traps is taken into account is (Fig. 4)

$$P = \exp\left(-\frac{2}{\hbar}\int_{z_1}^{z_2}\sqrt{2m\left(E - \frac{e^2}{4\pi\varepsilon_p\varepsilon_0}\left(\frac{1}{z} + \frac{1}{N^{-1/3} - z}\right)\right)}\,dz\right), \tag{7}$$

where z_1 and z_2 are the turning points. The quantity P is an exponential function of the density N and energy E of the traps. To obtain a rough estimate, we replace in Eq. (7) the potential which separates the traps by a square-well potential. For this, we set in Eq. (7) $z = N^{-1/3}/2$, $z_1 = 0$, and $z_2 = -N^{-1/3}$. According to data from different experiments, the energy of the traps in Si_3N_4 lies in the range 1.3–2.0 eV,[13,14] and the effective mass is $m^* \simeq 0.4m_e$.[15] Setting $N = 10^{21}$ cm^{-3} and $E = 2.0$ eV, we obtain the strongly underestimated value $P \simeq 3 \cdot 10^{-4}$. The underestimation is due to the replacement of the potential

by a square-well potential. The exchange interaction energy is $E_{ex}=e^2P/4\pi\varepsilon_p\varepsilon_0N^{-1/3}\simeq 5\cdot 10^{-5}$ eV. This is close to the Zeeman splitting in Si_3N_4: $g\mu H\simeq 6\cdot 10^{-5}$ eV ($g=2.003$, $H=10^4$ G).

In summary, the resonance exchange interaction mechanism explains the absence of ESR in Si_3N_4 with localized electrons and holes. Observation of ESR under conditions of a low density of localized carriers, such that the exchange interaction is weak, would be a direct, unequivocal proof of the exchange interaction mechanism in Si_3N_4.

We thank T. I. Nedosekin and A. G. Klimenko for preparing the samples for ESR.

[a] We thank A. I. Talochkin for providing the results of the Raman scattering investigations prior to publication.

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Translated by M. E. Alferieff