

Photoinduced structural change in the defects in a hydrogenated amorphous silicon

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A complex consisting of two, closely spaced, electrically neutral defects of the "broken-bond" type in *a*-Si:H is unstable with respect to the pairing of electrons at one of the defects. As a result of photoexcitation, the complex undergoes a transition to the metastable state with unpaired spins which are localized at different defects.

When an electron subsystem is subjected to a prolonged excitation, for example, when light with a photon energy $\hbar\omega \gtrsim 1.6$ eV is absorbed by an *a*-Si:H system, it exhibits a transition from the ground state *A* to a long-lived metastable state *B* which is characterized by a localized-spin density two- to fourfold higher than the initial density.¹⁻³ An important point here is that the *g*-factor of the photoinduced ESR signal is the same as the *g*-factor of the ESR signal in the state *A*, which in turn is due to the electron spin localized at an isolated, broken, neutral bond T_3^0 . In this letter we propose a microscopic model, in terms of which the phenomenon described above can be explained consistently.

We consider a complex comprised of two isolated broken bonds T_3 with two electrons. In the adiabatic approximation, the Hamiltonian of a system of this sort can be written as

$$H_0 = 2\epsilon_h - \lambda \sum_i u_i (\sum_{\sigma} n_{i\sigma} - 1) + U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} k \sum_i u_i^2, \quad (1)$$

where ϵ_h is the energy of an electron in the state T_3^0 , $n_{i\sigma} = a_{i\sigma}^+ a_{i\sigma}$ is the occupation

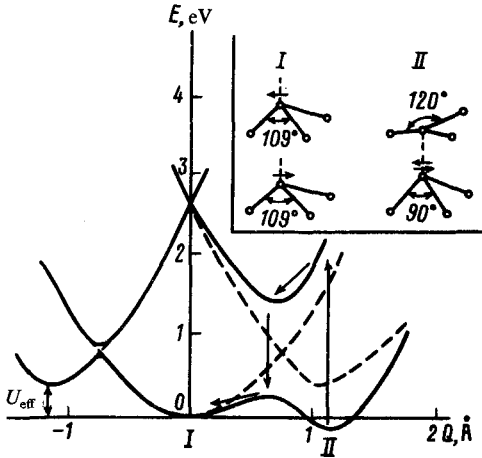


FIG. 1. Adiabatic potentials of two isolated defects of T_3 (dashed curves) and of a complex of two nearby broken bonds (solid curves). The minima are labeled with the designations of the configurations in the inset.

number of the i -th broken bond with spin σ ($i = 1, 2$, and $\sum_{i\sigma} n_{i\sigma} = 2$), U is the Hubbard energy of the repulsion of two electrons by a single center, u_i is the displacement of the i -th atom from the equilibrium position along the direction of the broken bond, and k is the force constant. We assume that at equilibrium the atom at which the broken bond is localized is situated at the center of the tetrahedron. We also assume that this atom can be displaced only along the axis of the tetrahedron, so that the atoms lying at the base are pinned rigidly. In (1) the term linear with respect to the displacement appears due to a change in the hybridization of the broken bond.⁴ As the atom is displaced toward the plane of the base ($u_i < 0$), for example, the initial hybridized sp^3 orbital undergoes a transition to the p_z state. In the case of displacement of the atom in the opposite direction, the hybridized orbital undergoes a transition to the s state. The pairing of two electrons at an isolated center is preferred from the energy standpoint if⁵ $U_{\text{eff}} = U - (\lambda^2/k) < 0$. However, the experimental conditions for $a\text{-Si:H}$ are apparently such that $U_{\text{eff}} \approx 0.4 \text{ eV} > 0$ (see Fig. 1).^{2,6}

As the broken bonds converge, an additional interaction occurs between them,

$$H_{\text{int}} = V \sum_{i \neq j, \sigma} a_{i\sigma}^+ a_{j\sigma} + C \sum_{i \neq j, \sigma, \sigma'} n_{i\sigma} n_{j\sigma'} \quad (2)$$

This interaction is caused respectively by the tunneling of an electron between the states of T_3^0 and by the Coulomb interaction between the electrons that are trapped at the various centers. If the broken bonds are directed in one direction along a single line (see the inset in Fig. 1), the functions V and C depend solely on the difference between the displacements $Q = u_1 - u_2$. Here the term in (1) which is linear with respect to the displacements is $\lambda Q \sum_{\sigma} (n_{2\sigma} - n_{1\sigma})$. In other words, the problem involving $H = H_0 + H_{\text{int}}$ becomes essentially a single-mode problem.

The complete Hamiltonian $H = H_0 + H_{\text{int}}$ can be diagonalized by a method which is described in Ref. 7. As a result, we find the triplet level $E_t = 1/4 kQ^2 + C(Q)$, and the energies of the singlet states are $E_s = E_t + E_1$, where E_1 satisfies the equation

$$E_1^3 + 2\bar{U}E_1^2 - E_1[\bar{U}^2 - \lambda^2 Q^2 - 4V^2(Q)] - 4V^2(Q)\bar{U} = 0, \quad (3)$$

where $\bar{U} = U - C(Q)$. For estimates we set $C \simeq e^2/\kappa(R_0 - Q)$, where κ is the dielectric constant, e is the electronic charge, and $R_0 \gg Q$ is the "seed" distance between the defects. The dependence of the tunneling integral V on the distance $R = R_0 - Q$ between the defects can be approximated by the function

$$V(R) = \begin{cases} V_0, & R < R_1 \\ \beta(R_2 - R), & R_1 < R < R_2 \\ 0, & R > R_2 \end{cases}. \quad (4)$$

We should point out that the scale dimension $(R_2 - R_1)$ of the region of sharpest variation of V is on the order of the localization length a of an electron in the T_3^0 state, and we have $R_1 \gtrsim d$, where d is the distance between the nearest neighbors ($d \simeq a$). From (3) we find that the strongly distorted configuration II, in which the electrons are paired at one of the defects, may become more desirable as a result of convergence of the defects in the region $R_1 < R < R_2$ because of the Coulomb-energy advantage and because of a rather sharp change in $V(Q)$ (see Fig. 1). It is easy to see that this alignment of the defects accounts for the maximum effect.

For $R_0 \simeq R_1$ the conditions under which a pairing of this sort can occur are

$$\begin{aligned} U - C_0 - \frac{\lambda^2}{\mu k} < 0, & \quad \mu = \frac{1}{2} (1 - \alpha + \sqrt{1 - 2\alpha}) \\ \alpha = \frac{8\beta^2}{k(U - C_0)} < \frac{1}{2}, & \quad C_0 \simeq \frac{e^2}{\kappa R_0} \end{aligned} \quad (5)$$

if the functional dependence $C(Q)$ is assumed to be weak. At $\alpha \geq 1/2$ state I, in which the spins are not paired, becomes totally unstable, by analogy with the case in which such an occurrence is accompanied by a Jahn-Teller pseudoeffect. Numerical estimates based on the parameters $U_{\text{eff}} = 0.4$ eV (Refs. 2 and 6), $\lambda = 6.4 \times 10^{-9}$ H, $k = 112$ H/m, $\beta \simeq V_0/a = 1.2 \times 10^{-9}$ H (Ref. 4), and $C_0 = 0.25$ eV show that condition (5) in a -Si:H can be satisfied for a pair of defects with $R_0 \leq (2-3)d$.

As a result of excitation, the system undergoes a transition from the ground state II(A) to the metastable state I(B), in which the weakly paired spins are localized at different defects (Fig. 1). We should point out, however, that for the parameter values given above, the barrier height for a thermally stimulated inverse transition I \rightarrow II is on the order of several tenths of eV. This value is smaller than the experimentally observed activation energy of the reciprocal of the storage time, τ^{-1} , of the state B. The inordinately large values of the time τ are attributable, in our view, to the redistribution of the hydrogen between the Si:H bonds and to the metastable states I that appear as a result of excitation. The isolated T_3^0 states produced in this manner can, according to the current theory,^{2,6} account for the photoinduced change in the optical and dielectric constants of a -Si:H.

A strong IR lattice absorption has been observed in a -Si:H in the frequency range ≤ 500 cm^{-1} . This absorption can be formally described by introducing an effective

ionic charge of the Si-Si bonds, $e_T^* = 0.5 e$.⁸ An ionicity of this level can clearly be linked to the stable II(A) dipole configurations. It would therefore be useful to trace the decrease in the IK activity of *a*-Si:H in the indicated frequency range as a result of transition of the system from state *A* to metastable state *B*.

The presence in *a*-Si:H of two-well potentials, which are associated with complexes of fairly closely separated broken bonds (Fig. 1), makes it possible to explain, in the spirit of the theory developed by Anderson *et al.*,⁹ the functional dependence of the specific heat $c(T)$ at low temperatures, which is nearly a linear dependence and which was observed experimentally by Graebner *et al.*¹⁰

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