Direct Measurement of Electron Emission from Defect States at Silicon Grain Boundaries

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(Received 26 June 1979)

The first direct measurements of charge emission from silicon grain-boundary defect states have been made by monitoring the recovery of the nonequilibrium grain-boundary barrier capacitance. The density of grain-boundary states obtained in this fashion is in excellent agreement with the values found from deconvoluting room-temperature *I-V* data. These data are shown to suggest strongly that the double-depletion-layer/thermal-emission model gives a good description of silicon grain boundaries.

According to the double-depletion-layer model of the electronic structure of semiconductor grain boundaries, impurity levels or disorder-induced electronic states within the band gap can cause majority-carrier trapping in the boundary plane with the consequent buildup of depletion regions on both sides of this plane.[1-3] For wide depletion layers thermionic emission of majority carriers over the resultant potential barrier is expected to be the dominant conduction mechanism.[1,2] However, substantial amounts of a second phase (such as SiO_2 in Si grain boundaries) or large perturbations of the band gap caused by local distortions at the boundary plane could introduce important additional barriers to current flow.[4,5] Such barriers would be expected to cause grain-boundary transport properties to differ considerably from simple double-depletion-layer/thermionic-emission model predictions. There are several sources for such discrepancies: The barrier height would be different from that expected from the amount of trapped charge alone, tunneling through the extra barrier might be important, and the change of barrier height with applied voltage will be slower than that predicted for simple double depletion layers. The applicability of thermionic emission to silicon grain-boundary transport is addressed experimentally in this paper.

The present work provides the first direct measure of electron emission rates from grain-boundary defect states. Comparison of these data with a determination of the grain-boundary density of states, $N_T(E)$, from dc transport measurements shows excellent agreement and gives the first strong evidence for the double-depletion-layer/thermionic-emission model for Si grain boundaries. In addition, these measurements provide a new and different approach to investigations of the electronic character of the grain-boundary defect states.

The single silicon grain boundaries measured in the present studies were isolated by optical and electrical examination from device-grade, float-zone, bulk polycrystalline silicon originally purchased from Monsanto Corporation. Neutron transmutation doping[6] at levels of (1.4 and 10)$\times 10^{21}$ phosphorus/m^3 was followed by a 750-°C vacuum anneal for 40 min to remove the radiation-induced damage.[7] After a ~40-μm Sirtl etch to eliminate saw damage, samples were provided with four Ti-Au sputtered contacts and glued to sapphire plates with G.E. 7031 varnish for insertion into a cryogenic Dewar. Four-terminal capacitance and conductance measurements were made in the 3–20-kHz range using driven shield cables (to minimize amplifier input capacitance), operational amplifier input buffers, and a PAR 5204 dual-phase lockin amplifier. Although all data presented here were obtained on samples with $N_d = 10^{22}$ m^{-3}, similar results were observed in the lower doped silicon.

The amount of charge in the grain boundary was measured capacitatively. Within the framework of the double-depletion-layer model the total excess number of charges per unit area in the grain-boundary barrier, Q, and the barrier height, φ_B, can be shown to be related to the zero-bias capacitance per unit area, C_0, in the following fashion[1]:

$$Q = \epsilon\epsilon_0 N_d / C_0 \text{ (mks units)} \tag{1}$$

and

$$\varphi_B = \epsilon\epsilon_0 N_d e / 8C_0^2. \tag{2}$$

Initial measurements revealed that the capacitance observed below $T = 190$ K displayed several unusual features. These were marked changes of C_0 upon exposure to room light, considerable nonreproducibility, with occasional low C_0 readings suggesting barriers as high as 2.5 eV, and noticeable drift of measured C_0 values above 175 K. This behavior suggested that at low temperatures, charge in *excess of thermal-equilibrium values* could be occupying grain-boundary traps resulting in large, nonequilibrium barrier heights shown in Fig. 1(a).

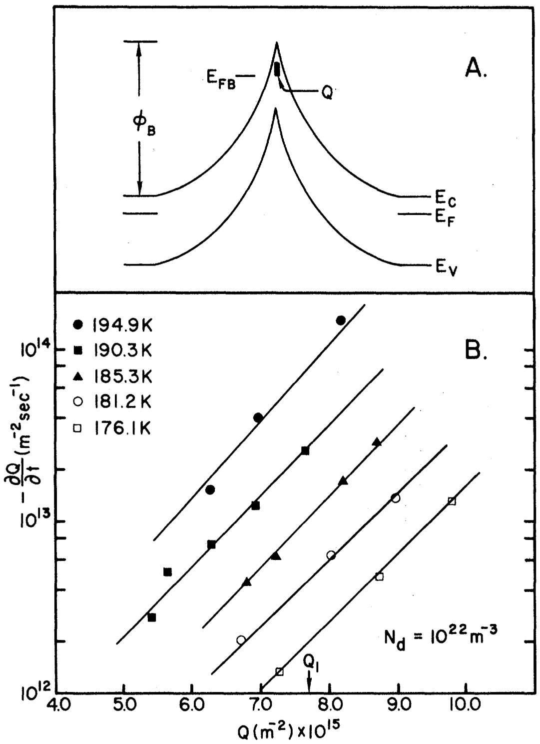

FIG. 1. (a) The electron energy diagram for a grain boundary in an n-type semiconductor which has a large amount of nonequilibrium trapped charge. This gives rise to barrier heights φ_B much larger than the equilibrium value. E_{FB} is the neutral (unjoined) Fermi level; see Ref. 2 for details of the double-barrier model. (b) Values of the charge decay rate $\partial Q/\partial t$, deduced from capacitance recovery measurements at five temperatures on a single grain boundary in silicon. The equilibrium value of Q is $\simeq 4.7\times 10^{15}$ m^{-2} in this temperature range.

To investigate this possibility further we exposed grain-boundary barriers to ~15 V for brief periods to inject charge in excess of thermal-equilibrium values, and then monitored the rise of C_0 (decay of this charge) as a function of time. The results for a sample having $N_d = 10^{22}$ m^{-3} are shown in Fig. 1(b) plotted versus the total number density of negative charges in the barrier. The strong dependence of the release rate on Q (and on T) suggests a substantial spread in trap energies.

To analyze this situation we can write that the time dependence of the decay of the charge trapped at states lying between energies E and $E+dE$ should be

$$\frac{\partial[q(E)dE]}{\partial t} = \frac{-q(E)dE}{\tau(E)}, \qquad (3)$$

where emission theory predicts[2]

$$\tau(E) = \tau_0 \exp[\beta(E_c - E)], \qquad \beta = (kT)^{-1}.$$

As long as φ_B is at least several times kT greater than its equilibrium value, we can neglect charge flowing into the barrier, and the total charge flow becomes

$$\frac{\partial Q}{\partial t} = -\int_{E_F}^{E_M} \frac{q(E,t)dE}{\tau(E)}, \qquad (4)$$

where E_M is the initial filled trap state level and E_F the equilibrium Fermi level in the barrier. This expression can be considerably simplified if we assume that thermal equilibrium is maintained among the charge states in the barrier; we thus expect that $q(E,t)$ is given by

$$q(E,t) = \frac{N_T(E)}{1+\exp\{\beta[E - E_1(t)]\}}, \qquad (5)$$

where $E_1(t)$ is (roughly) the energy of the highest filled trap state at time t. Approximating the Fermi function by its $T=0$ limit and $N_T(E)$ by a constant, we obtain

$$\frac{\partial Q(E_1)}{\partial t} = -N_T \int_{E_F}^{E_1} \tau_0^{-1} \exp[\beta(E - E_c)]dE. \qquad (6)$$

In practice we measure the release rate at energies at least several times kT larger than E_F. In this case

$$\frac{\partial Q(E_1)}{\partial t} \cong -kTN_T\tau_0^{-1} \exp[-\beta(E_c - E_1)]. \qquad (7)$$

In addition, using the assumption that N_T is a constant above E_F, we can write

$$Q = Q_0 + N_T(E_1 - E_F), \qquad (8)$$

where Q_0 is the equilibrium charge density. Thus

$$\frac{\partial Q}{\partial t} = -kTN_T\tau_0^{-1}\exp[\beta(E_c - E_F + Q_0/N_T)] \times \exp(\pm \beta Q/N_T). \qquad (9)$$

We thus find the exponential dependence of $\partial Q/\partial t$ upon Q displayed by the data of Fig. 1(b). The values of N_T calculated from the slopes of the lines in this figure range from (6.44 to 6.79) $\times 10^{16}$ m^{-2} eV^{-1}. In Fig. 2 these numbers are compared to $N_T(E)$ deduced[8] from I-V measurements on the same sample via the Pike-Seager deconvolution scheme. Excellent agreement is observed and the approximation that N_T is constant appears to be a reasonable one. The fact that N_T found from zero-bias charge decay agrees so well with N_T determined from dc transport da-

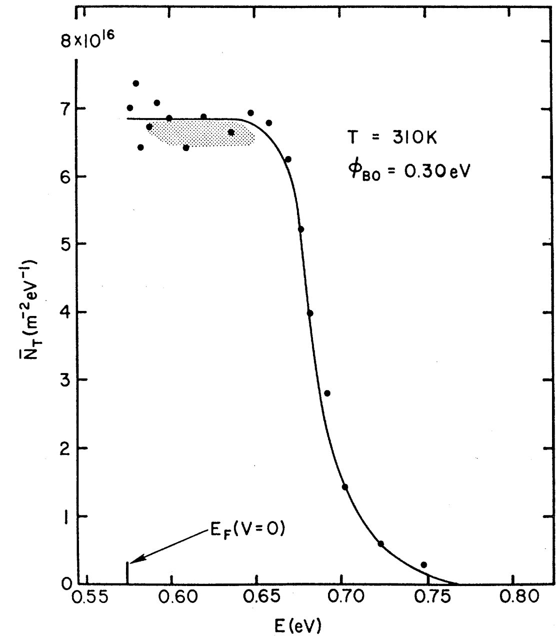

FIG. 2. Density of grain-boundary states for a single silicon grain boundary with $N_d = 10^{22}$ m^{-3}. The zero of energy is the valence-band maximum. The filled circles show the $\bar{N}_T$ deduced by deconvoluting current-voltage data at 310 K. $\bar{N}_T$ is the density of states, N_T, averaged over ~kT in energy and is the direct outcome of the deconvolution procedure (see Ref. 2 for details). The shaded area shows the range of values of N_T deduced from the capacitance recovery measurements.

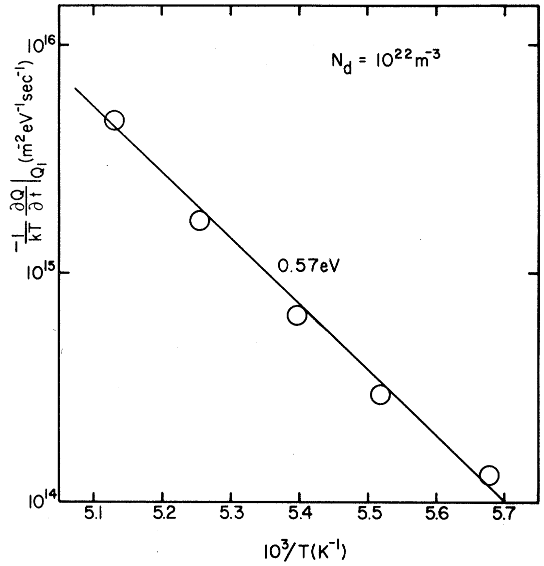

FIG. 3. Values of $(kT)^{-1}\partial Q/\partial T$ at a charge density of 7.7×10^{14} m^{-2} plotted versus $1/T$, and taken from the data in Fig. 1(a). The deduced slope [see Eq. (7) in the text] is 0.57 eV and the intercept value is 2.4×10^{30} m^{-2} eV^{-1} sec^{-1}.

ta up to high bias is a strong indication that thermal emission dominates at all measured biases.

Using Eq. (7) we can now find the energy $E_c - E_1$ by plotting $(kT)^{-1}\partial Q/\partial t$ evaluated at $Q_1 = Q(E_1)$. Choosing Q_1 to lie in the center of the measured data range yields the plot in Fig. 3. In order to compare this activation energy with other data obtained on this sample, it is useful to estimate how far the equilibrium Fermi level, E_F, lies below E_1. This can be computed from Eq. (8) since Q_0 is known to be $\sim 4.7\times10^{15}$ m^{-2} in the temperature range of interest here[8]; this yields $E_1 - E_F \simeq 40$ meV. From Fig. 3 $E_c - E_1 = 0.57$ eV, we thus deduce that $E_c - E_F = 0.61$ eV. An independent estimate of this energy comes from the activation energy of the zero-bias conductance which is found experimentally[8] to be ~0.62 eV for this sample. Considering the approximations made in reducing the data, this agreement represents good verification of the predictions of emission theory. The prefactor τ_0^{-1} deduced from the data in Fig. 3 is $\sim 3.7\times10^{13}$ sec^{-1}, which is roughly twice the optic phonon frequency in silicon.[9] This appears to be a reasonable prefactor for emission from a trap in silicon.[10]

We have thus shown that the decay rate of nonequilibrium barrier charge appears to proceed via simple electron emission from the localized grain-boundary states to the conduction band. Although recombination with holes either generated at the grain-boundary plane or swept into this region by the depletion region field could also contribute to this charge decay, the good agreement of experimental results with electron emission theory suggest that the recombination mechanism is of negligible importance. The agreement found here plus other recent results[8] suggest that the double-depletion-layer/thermal-emission model of barrier formation and transport provides a good description of grain-boundary barriers in silicon bicrystals. Thus any additional potential barriers associated with possible second-phase segregation or deformation-induced band-gap changes are of negligible importance to carrier transport across these boundaries.

This work was supported by the U. S. Department of Energy under Contract No. DE-AC04-76-DP00789. Sandia Laboratories is a U. S. Department of Energy facility.

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[6]Both the silicon samples and the doping were generously provided by J. Cleland and his group at Oak Ridge National Laboratory.

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