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Transient-Capacitance Measurement of the Grain Boundary Levels in Semiconductors

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The transient response of a grain boundary to a voltage pulse is discussed in terms of the basic capture and emission processes at the boundary states. This model is used to interpret the deep-level transient spectroscopy spectrum of a low-angle tilt boundary with a known dislocation structure in a germanium bicrystal. A characteristic level is found at 0.42 eV below the bottom of the conduction band; the number of states at this level is about 10^9 cm^{-2} and their capture cross section for electrons is 5×10^{-12} cm^2.

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With few exceptions,[1-3] the electrical properties of grain boundaries in semiconductors have been investigated from steady-state measurements only: The barrier height is determined from the capacitance and from the current-voltage characteristics,[4,5] and the grain-boundary density of states can then be derived by an appropriate deconvolution scheme.[6] However, both the density of states and the capture cross sections can be obtained more directly from the transient response, after voltage pulses have been applied across the boundary.[3,7] In this Letter we first give a description of the transient response in the model generally accepted for a grain boundary.[4] We then describe the experimental results obtained in the case of a low-angle tilt boundary in a germanium bicrystal.

Figure 1(a) shows the well-known energy band structure at a grain boundary in n-type material.[4] As discussed in a previous paper,[8] at low enough temperatures the boundary charge is screened by the ionized impurities in the depleted regions on both sides of the boundary. Changes in the occupancy of the boundary levels can be detected from the concomitant changes in the grain boundary capacitance. Provided the hole contribution can be neglected, the conduction electrons are solely involved in the capture and emission processes at the boundary states. If we consider the latter as a discrete set of levels (which will be justified below), the emission rate from a level at energy E_0 is given by[9]

$$e_n = 2N_c \sigma \bar{v}_{\rm th} \exp[-(E_c - E_0)/kT], \qquad (1)$$

where σ is the capture cross section of the boundary level, N_c is the effective number of states in

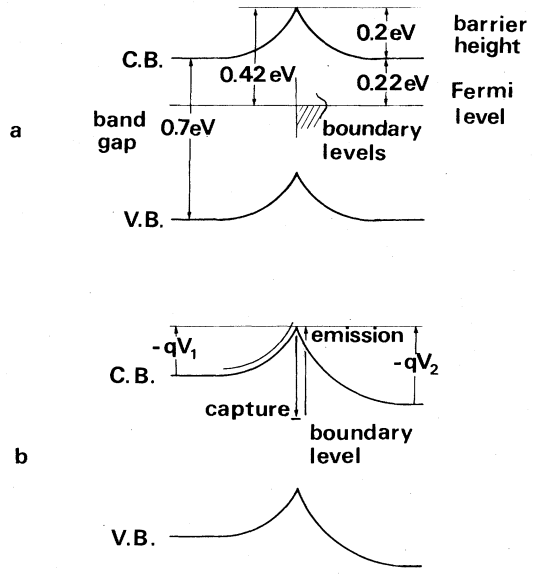

FIG. 1. Band bending near a grain boundary (a) at thermodynamic equilibrium and (b) under bias. The numerical values are justified in the text.

the conduction band (energy E_c), and $\bar{v}_{th}$ is the thermal velocity of the electrons. According to the thermoelectronic emission theory, the capture rate is given by[9]

$$c_n = n\sigma\bar{v}_{th}[\exp(qV_1/kT) + \exp(qV_2/kT)], \quad (2)$$

where n is the free-carrier density in the bulk of the grains, q is the (positive) elementary charge, and V_1 and V_2 are the (negative) potential barrier heights for electrons coming, respectively, from the left- and from the right-hand sides of the boundary [Fig. 1(b)]. At equilibrium, c_n and e_n adjust so that the occupancy f_B of the boundary levels obeys the Fermi distribution law. Consider now the case where a voltage pulse is applied across the boundary and the bias is then returned to zero. While the pulse is being applied, c_n is increased compared to equilibrium so that f_B (and therefore V_1 and V_2) changes with time according to the equation

$$df_B/dt = c_n(1 - f_B) - e_n f_B . \quad (3)$$

Equation (3) also applies to the relaxation transient with the appropriate expression for c_n. Suppose now that the pulses are strong enough to vary the barrier height by a large amount compared to kT/q. Then, emission processes are primarily involved in the relaxation transients and the energy of the boundary traps can be obtained from the temperature dependence of the emission rate as given by Eq. (1). Negative capacitance transients are expected with majority-carrier traps, since filling these levels results in increasing the width of the depleted layer, whereas positive transients should be associated with minority-carrier traps.

The capture cross section can be derived from the change in the transient amplitude with increasing pulse width [Eqs. (2) and (3)]. The pulse height should be large compared to kT/q, and the pulse width small enough to make sure that capture predominates over emission throughout. On the other hand, the trap density is obtained from the transient amplitude under saturating conditions, i.e., with long pulse duration. The transient amplitude is not expected to be a simple exponential function of time, since V_1 and V_2, and therefore c_n, depend on the occupancy of the boundary levels. Indeed, we have observed non-exponential transients in various cases by direct inspection of the grain-boundary capacitance response.

We have studied the properties of a low-angle (3.5°) tilt boundary in an n-type, P-doped (2×10^{13} cm^{-3}) germanium bicrystal.[10] The tilt axis is $[1\bar{1}0]$ and the boundary plane is (111). The dislocation structure of the boundary has been investigated by electron microscopy, and found identical to that reported by Bourret and Desseaux[11] on similar samples. The capacitance transients are analyzed by the deep-level transient spectroscopy (DLTS) technique,[12] following the method described in Ref. 13. Figure 2 shows a typical boundary spectrum, together with a spectrum of the bulk traps obtained using a Schottky diode on one of the grains. A level with the same signature (peak G1, 0.22 eV) is found in both cases. An obvious explanation is that the traps within the screening layer are also filled by voltage pulses applied across the boundary, and therefore show up in the boundary spectrum.[7]

Prior to any conclusion about the boundary levels, the spectrum must be corrected for an effect due to the bulk resistance of the sample (R_s) in series with the boundary capacitance (C_s).[15] This effect occurs because the quality factor of our sample (given by $Q = R_s C_s \omega$, where ω is the pulsation of the 1-MHz signal delivered by the capacitance meter) lies in the vicinity of unity. As a result, the transient amplitude is reduced by the factor $(1 - Q^2)/(1 + Q^2)^2$. In our case, Q varies with temperature in such a way that even the sign of the spectrum is reversed in the high-temperature range. The deconvolution

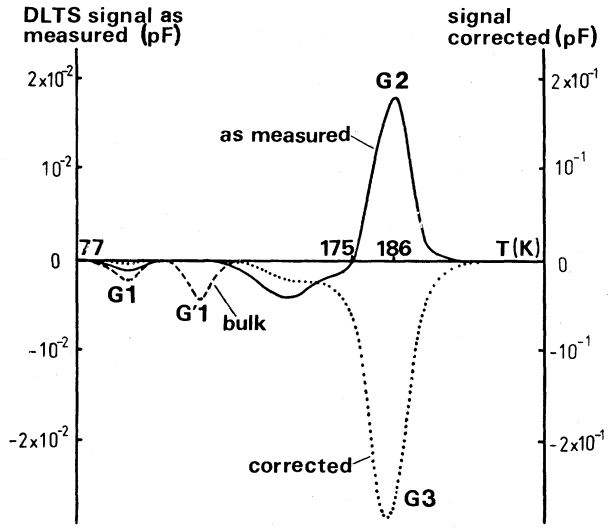

FIG. 2. Boundary spectrum as measured (full line) with pulse rate 10 s^{-1}, pulse width 200 μs, and pulse height 0.5 eV, and after correction for the sample series resistance effect (dotted line) and bulk trap spectrum (dashed line). The peak G'1 (0.38 eV) is observed in the bulk spectrum only. It could be associated with the acceptor level of copper (Ref. 14) diffused in the process of making the Schottky diode.

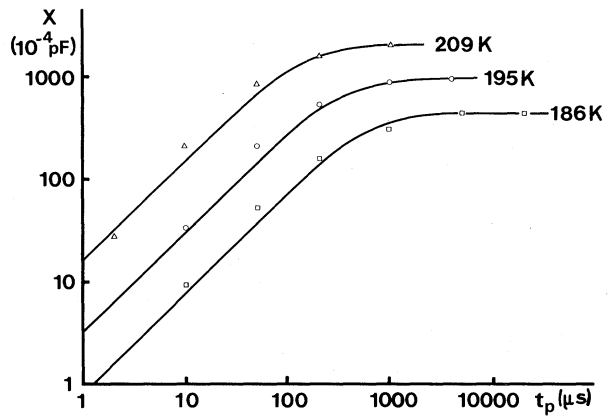

FIG. 3. Amplitude of the DLTS signal X (G2) as a function of pulse width t_p at various temperatures (logarithmic scale). Full lines are empirical fits with the law $X = X_0[1 - \exp(-c_n t_p)]$. The shift in the saturation amplitude as the temperature increases is explained by the effect of the sample series resistance.

procedure is based on varying the shape of the spectrum by means of an additional series resistance, as discussed in Ref. 15. The corrected spectrum (Fig. 2) consists of a broad negative peak, corresponding to majority-carrier traps only.

In performing the signature of the traps, care was taken to apply strong enough pulses so that the barrier height was varied by more than kT/q and the larger part of the relaxation transients could be analyzed in terms of emission only. Associated with the peak G2, an energy level has been found at 0.42 eV below the bottom of the conduction band. It is interesting to compare this figure with the data deduced from zero-bias capacitance and conductance measurements. The latter have given a value of 0.2 V for the barrier height at temperatures about 200 K, where the peak G2 was observed. At that temperature, the band gap is 0.7 eV and the Fermi level lies at 0.22 eV below the bottom of the conduction band. When put together, these figures provide a picture of the grain boundary [Fig. 1(a)] quite similar to Bardeen's model for the potential barrier at a semiconductor surface.[16] Levels deeper than 0.42 eV are not detected since they are already filled at equilibrium. Shallower levels, corresponding to the shoulder on the peak G3 in the corrected spectrum, are currently investigated.

The capture cross section of the traps at 0.42 eV has been measured from the amplitude of the DLTS signal X as a function of the pulse width t_p. By analogy with the case of localized bulk traps, the experimental points have been fitted with the law $X = X_0[1 - \exp(-c_n t_p)]$ (Fig. 3). Such a law is only approximate since it takes no account of the dependence of the barrier height on the occupancy of the boundary levels. The saturation amplitude X_0 yields $\sim 10^9$ traps $\cdot cm^{-2}$. This figure should be compared with the net charge density in the boundary plane which, according to steady-state measurements, is about 10^{10} electrons $\cdot cm^{-2}$. If one assumes one dangling bond every lattice distance along the dislocations and if the bonds are not reconstructed, then one finds $\sim 10^{13}$ states $\cdot cm^{-2}$. Thus, either a small fraction only of the boundary levels are measured by our experiment, or there is much less than one state per lattice distance along the dislocations. The capture rate deduced from the slope of $X(t_p)$ at $X = 0$ varies with temperature with an apparent activation energy of 0.2 eV. According to Eq. (2), this temperature dependence could be due (i) to the variation of σ with temperature and (ii) to the thermal activation of the electron flow over the potential barrier. Assuming the capture cross section to be temperature independent, one finds a value of $\sim 5 \times 10^{-12}$ cm^2.

In conclusion, we discuss the question whether

the boundary states form a band or a discrete set of levels. In the first case one expects every captured electron to fall down to the lowest non-occupied level. The reverse should happen during the emission process, the shallower levels being emptied first. Considering the temperature dependence of the emission rates, the longer the pulses, the more the spectrum should extend into the low-temperature region. The observed capacitance transients show no evidence for a broadening of their temperature scale. This, in addition to the observed dependence of the transient amplitude on pulse duration, is evidence for the model of the boundary states as a discrete set of levels, capable of being filled or emptied independently.[7]

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Velocity Distributions of Sputtered Excited Atoms

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The first direct measurements are reported of the velocity distributions of sputtered atoms in excited states with electronic configurations completely different from the ground state. In contrast to previous work, the measured distributions for both the singlet and triplet metastable D states of Ba atoms showed no energy thresholds and had most probable energies similar to those of sputtered ground-state atoms.

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Ever since the discovery[1-3] of the sputtering of excited atoms during ion bombardment of solids, there have been numerous attempts to measure their velocities by monitoring the Doppler broadening[2,4,5] or the spatial distribution[6-10] of the emitted light. In all these experiments the "mean" and/or "threshold" kinetic energies of the excited atoms were measured. With one possible exception,[4] the sputtered atoms were found to have mean kinetic energies of hundreds of electron volts and threshold energies greater than 10 eV. Because these values are significantly higher than most probable energies of a few electron volts of the ground-state sputtered atoms and ions, they have placed strong boundary conditions on the possible mechanisms of excited-atom formation.[11] Recently, Pellin, Wright, and Gruen,[12] using the Doppler-shift laser fluorescence (DSLF) technique,[13,14] found that the velocity distributions of sputtered Zr atoms in the excited a^3F_3 and a^3F_4 levels were identical to that of the ground-state a^3F_2 atoms. Although this result apparently contradicts the findings of all the other experiments, it was argued[15] that these excited levels (0.07 and 0.2 eV) are essentially ground states because of both their low energies and the fact that they are the fine-structure components of the same electronic configuration.

In this Letter we report the first definite experimental evidence that sputtered excited atoms

