temperature and high fields, such oscillations in C_S may be observable.

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OBSERVATION OF SURFACE AND IMPURITY STATES IN SILICON BY OXIDE LAYER TUNNELING*

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Conductance and differential capacitances have been measured as a function of frequency and of bias on a number of silicon-silicon oxide-aluminum sandwiches. The results indicate that information about the density and energy of states near the silicon-silicon oxide interface may be deduced from these measurements. Conductance is due to electron tunneling transitions between the aluminum and silicon. This is believed to be the first reported evidence of tunneling to a semiconductor through an oxide film.

Samples are prepared by thermally oxidizing the freshly cleaved (111) surface of a single-crystal silicon specimen. Aluminum is evaporated onto the resulting oxide film. The oxide thickness is judged to be 40 to 60 Å based on capacitance measurements. Because of charge trapped in "outer states" in the oxide,[1] the bands of the p-type silicon used in the present experiments are bent downward at the surface forming a depletion layer. This intrinsic region is essential to the success of the experiment, since otherwise the tunnel current would be nearly Ohmic. The extent of band bending is evident from the position of the band edges relative to zero bias in both figures.

The problem with sample preparation is growing an oxide layer thin enough to permit tunnel current to dominate the conductance and thick enough such that nearly all of the applied bias appears across the oxide rather than the depletion region. This is particularly critical with higher resistivity silicon at low temperatures. When the above conditions are met, the existence of other transport processes is easily ruled out. The films are too thin for space-charge limited current. Virtual temperature independence of the qualitative features eliminates Schottky emission. The fact that an estimated 20% increase in oxide thickness reduces the conductance three orders of magnitude without seriously altering the detailed features of the curves removes the possibility of Ohmic conduction. In addition, the results are readily interpreted in terms of es-

tablished tunneling theory and the well-known properties of silicon.

The tunnel current may be written as[2]

$$j_x = \frac{4\pi e}{\hbar} \sum_{k_t} \int_{-\infty}^{\infty} |M_{ab}|^2 \rho_a \rho_b (f_a - f_b) dE, \quad (1)$$

where M_{ab} is the matrix element for the transition, ρ_a and ρ_b are initial- and final-state densities, and f_a and f_b are occupation probabilities. The sum is taken over all transverse wave numbers, k_t, subject to the condition that k_t is the same for initial and final states.

When tunneling occurs between the metal and either the valence or conduction band of the semiconductor, the density-of-states factors are cancelled by reciprocal factors in the squared matrix element if a single-particle WKB approximation is made. The matrix element may be expressed as

$$|M_{ab}|^2 = (1/4\pi^2)(1/\rho_a \rho_b) \exp(-2K), \quad (2)$$

where $K = \int |k_x| dx$ taken over the forbidden path in the oxide band gap. The band gap should not be thought of as a vacuum layer, and $|k_x|$ will not be expected to vary rapidly with energy near

the center of this gap. An idea of the effect of a semiconductor band edge may be obtained by suppressing the dependence of K on energy and bias and solving Eq. (1) using (2). The current is

$$j_x \approx [m_t e^2 \exp(-2K)/4\pi^2 \hbar^3 K']$$

$$\times (V - V_c)\{1 - \exp[-2K' e(V - V_c)]\}, \quad (3)$$

where V is bias, V_c is the bias corresponding to a band edge, m_t is the transverse effective electron mass, $K' \equiv (\partial K/\partial E_t)$ evaluated at $E_t = 0$, and $E_t = \hbar^2 k_t^2/2m_t$. Thus the conductance (dj_x/dV) will rise linearly from zero at a band edge and approach a constant value (Ohmic) deep in the band. The effect of the variation in K will be superimposed. This behavior is consistently observed. In obtaining (3) we have assumed a band extremum at $k = 0$ and a temperature of $0°K$.

In the case of tunneling from the metal to an impurity band or interface state, the factor ρ_b will not be cancelled by the matrix element so that the conductance will depend primarily on the density of states apart from changes in barrier height. The problem of tunneling from an isolated state (in the present case, an interface state) may best be thought of in terms of transi-
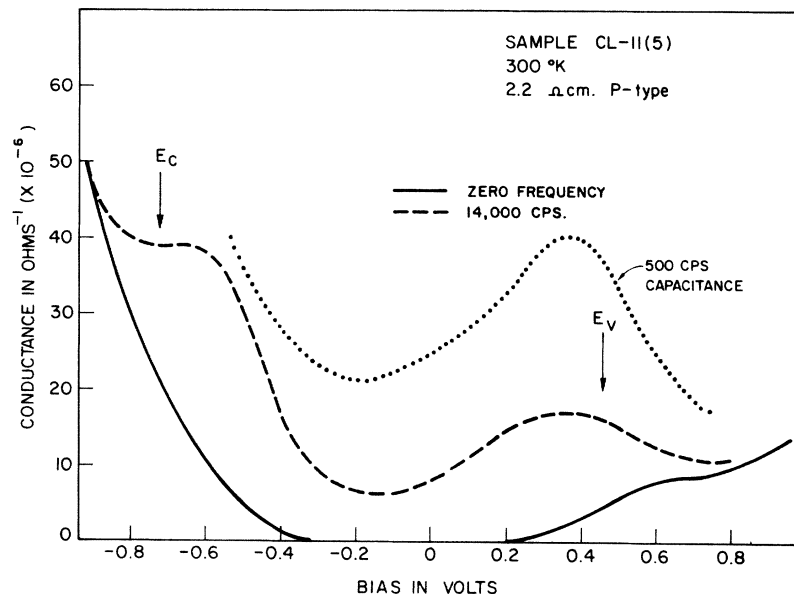

FIG. 1. Conductance (dI/dV) vs bias at $300°K$. The zero-frequency conductance is taken from current-vs-bias measurements. The approximate voltages corresponding to band edges are labeled E_v and E_c. The low-frequency capacitance is shown for comparison. Its peak value is 1600 $\mu\mu f$. Sample area is 0.41 mm^2.
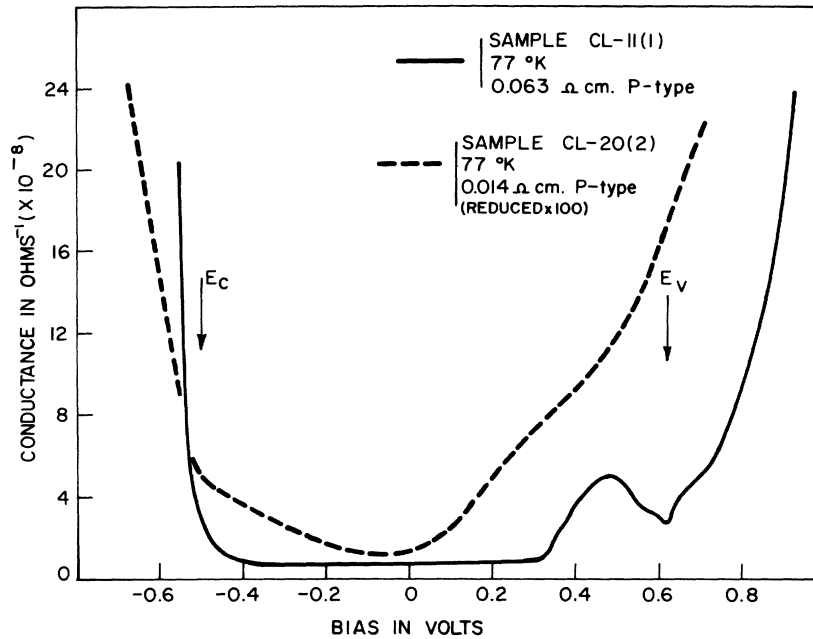
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FIG. 2. Conductance (dI/dV) vs bias at 77°K. The approximate voltages corresponding to band edges are labeled E_v and E_c.

tion probability per unit time,

$$w_a = \frac{2\pi}{\hbar}\sum_{k_t} |M_{ab}|^2 \rho_b, \tag{4}$$

from which a lifetime may be derived. Since the term exp(-2K) will still be in the matrix element, the lifetime $(w_a)^{-1}$ will depend strongly on oxide thickness. The conductance due to such states will be frequency dependent for frequencies of order w_a.

Little dc current is transmitted via the interface states (Fig. 1). They remain essentially filled up to the energy of the Fermi level in the metal. For frequencies $\ll w_a$, the current is capacitive and limited by the number of available states. Thus the small-signal ac differential capacitance is proportional to the density of interface states as shown by the dotted line in Fig. 1. At frequencies $\gg w_a$, the states will not be able to charge appreciably during one cycle, and current will be in phase with the ac voltage. The conductance then will be proportional to density of states and independent of frequency as shown by the dashed line of Fig. 1. The high-frequency capacitance will be due to the depletion region and oxide layer in series, and its variation with bias will serve to monitor changes in width of the depletion region. This is an important consider-

ation since it indicates how much of the total bias appears as band bending.

The density of interface states is obtained directly from the low-frequency capacitance curve of Fig. 1. It is ~2×10^{12} states/eV cm^2 at the peak. The second peak in capacitance is obscured by diffusion capacitance, but its position is indicated by the peak in high-frequency conductance. The densities and the positions of the two peaks are in good agreement with the findings of Statz et al.[3] from field-effect measurements.

As mentioned, the dc current is scarcely affected by interface states and serves to probe the bulk properties of the material (intrinsic and impurity bands). Impurity bands were detectable only in heavily doped samples. Figure 2 shows the conductance (dI/dV) taken from dc measurements of two samples at 77°K. The more lightly doped sample (~10^{18} impurities/cm^3) clearly shows its boron impurity band. The width of the forbidden band (1.1 eV) may be read directly from this curve. The valence band edge is no longer well defined with ~10^{19} impurities/cm^3 (dashed line).

The curves shown in Figs. 1 and 2 are typical of a large number obtained from samples in this range of resistivity. It is hoped that planned refinements in procedure and extension to other materials will yield more detailed information.

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ELECTRICAL CONDUCTIVITY ANOMALY IN VANADIUM SESQUIOXIDE

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Recently we have found that the large electrical conductivity anomaly associated with the Curie point of doped, semiconducting barium titanate originates at the grain boundaries of the polycrystalline material and is not displayed by single crystals of identical composition.[1]

With this unequivocal grain-boundary phenomenon in mind, our attention was drawn to reported similarities in the properties of vanadium sesquioxide, V_2O_3.[2-4] This material also has a large conductivity anomaly, occuring at a suspected Néel point at 168°K. The temperature coefficient of conductivity at the anomaly is positive, however; in doped $BaTiO_3$ it is negative.

With the exception of Morin's work,[2] this anomaly in V_2O_3 has been observed only in polycrystalline material. Morin's specimens were single crystals, but of such small size (0.1 mm) as to permit only a two-point conductivity measurement. Thus, if the anomaly were of grain interface or of surface origin, it could have been erroneously attributed to the bulk material as the result of such a measurement. This has occurred in the case of $BaTiO_3$.[1]

We undertook to make a four-point dc conductivity measurement on a single crystal (see Fig. 1). The V_2O_3 specimen was sawn from a Verneuil-grown boule from Linde Air Products Co. X-ray diffraction and metallographic examination identified the selected portion as V_2O_3 free of extraneous phases. The tendency of the material to shatter on undergoing the large volume change of the
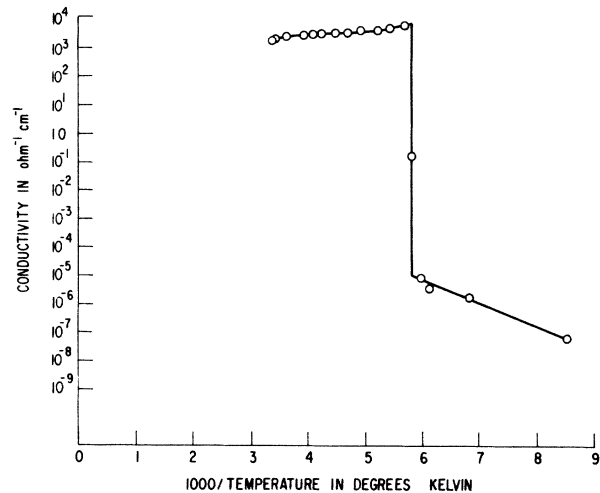

FIG. 1. Direct-current conductivity vs reciprocal temperature for unoriented V_2O_3 crystal (cooling curve).

phase transition made it necessary to limit the size of the parallelopiped specimen to about $5 \times 2 \times 0.5$ mm. Rubbed-on indium-gallium amalgam electrodes were used.

The conductivity anomaly was observed and, in fact, was two orders of magnitude greater than previously reported. We conclude that this is not a grain-boundary effect.

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