

Normal-State Electron Tunneling Only Qualitatively Understood

From an experimentalist's point of view, the field of electron tunneling owes its present lively state to the discovery of the p-n tunnel diode by Leo Esaki in 1957 and of tunneling through oxide layers by John C. Fisher and Ivar Giaever in 1960. The results in the oxide system became even more remarkable when the electrodes against the oxide were made superconducting by Giaever in 1960. In the five years that followed, a happy combination of theory and simple experiments led to confirmation of the Bardeen-Cooper-Schrieffer gap and square-root singularity in the electronic density of states, the fascination of the Josephson effect and the measurement of the details of the electron-phonon interaction.

However, in the past two years, interest has again cycled to p-n diodes, metal-semiconductor conductor contacts and metal-insulator-metal (M-I-M) junctions in the normal state. As a result a conference on nonsuperconducting electron tunneling was held at Prouts Neck, Maine, during 3-5 Sept. The meeting was arranged in the style of a Gordon conference with morning and evening sessions. In keeping with the Gordon conference tradition, no further publication of proceedings is contemplated. Previous conferences, which considered tunneling into both superconducting and normal electrodes, were held at Philadelphia (1961) and Risø (1967).

The result of this conference can be summarized briefly: Tunneling in normal systems, for experimentalists and theorists alike, is in some trouble unless one is satisfied with a purely qualitative understanding of the field. Remembering the successful application of tunneling to superconductivity, we may find this conclusion surprising. The origin of the difficulties of the normal state was summarized by Doug Scalapino (University of California, Santa Barbara) in his impressions at the end of the conference. The superconducting experiments probe properties of the electrodes over distances comparable to the coherence length, generally large enough to sample bulk effects (maybe not in the

case of transition metals and type-II materials), whereas the normal-state experiments are affected by the nature of the tunnel barrier, sometimes only a few atom layers thick, and by the metal electrodes within a screening length of the oxide-metal interface. Thus tunneling has become a problem of surface physics.

The first topic dealt with at the conference was: How well can the overall conductance-versus-voltage dependences be explained by single-particle tunneling theory? Next, interactions of the tunneling electron with the oxide, or impurities or particles in the oxide, led to discussion of "zero-bias anomalies." Finally, observations of interactions within the electrodes, the many-body or self-energy effects, were reported and the theory of these effects received considerable discussion.

Single-particle tunneling. The calculation of single-particle tunneling currents through a potential barrier requires an exact knowledge of the barrier potential as a function of distance. As Gerald Mahan (University of Oregon) pointed out in the opening talk, this is poorly known in p-n diodes and only guessed at in M-I-M junctions; therefore, the metal-semiconductor contact (Schottky barrier on degenerate material) has received the most attention recently. He showed that a calculation of the tunneling current could be made, based on uniform charge density in the depletion region, which results in a parabolic potential barrier. Experiments in which the barrier height and thickness are determined by independent measurements give an absolute conductance in "better than an order of magnitude" agreement with the calculation. The experiments also show the correct voltage dependence of the conductance. This agreement holds only when the surface-barrier contacts are made by cleaving the semiconductor in vacuum. Mahan's gloom with respect to M-I-M junctions was questioned by Carver Mead (Cal Tech) who presented a detailed investigation of aluminum-aluminum-nitride metal junctions. Combining capacitance

and current-voltage measurements on a series of junctions with different nitride thicknesses, he and collaborators have determined the E versus k relationship for the electron over the whole of the forbidden gap of the insulator. This result raised the inevitable question: What "band structure" can we associate with such thin layers, and is the insulator crystalline or amorphous? The extension of such careful analysis to other systems will be of interest.

For M-I-M systems, the tunneling conductance at low voltages (less than 200 mV) is not constant but has a roughly parabolic dependence on voltage. As reported by J. M. Rowell (Bell Labs), calculations based on simple trapezoidal barriers also show that the minimal conductance only occurs at $V = 0$ for symmetrical barriers. However, no comparison of calculated and measured conductance has been made for junctions with barrier parameters determined independently.

Returning to an older barrier problem, phonon emission in p-n diodes, Charlie Duke (University of Illinois, Urbana) concluded that the theory of Kleinman offers a good description of the effect. New measurements of such phonon-assisted tunneling in a very wide gap material with complex lattice dynamics, silicon carbide, were reported by Phil Stiles (IBM).

Impurities. Although most oxide junctions contain unknown impurities, the addition of intentional impurities to the barrier is a relatively recent development. Two talks on the very interesting effects of adding metallic particles were given by Hansrudi Zeller (GE) and John Lambe (Ford). Although different in concept and results, the two experiments both raise a puzzling question. In the work described by Zeller (performed in collaboration with Giaever) the well known agglomeration of very thin metal films is used to introduce an array of particles (about 10 nm or less in diameter) into the oxide of a tunnel junction. The current flows as electrons tunnel to the particles, localize, and then tunnel to the other electrode. However, if a particle is about 5 nm in diameter,

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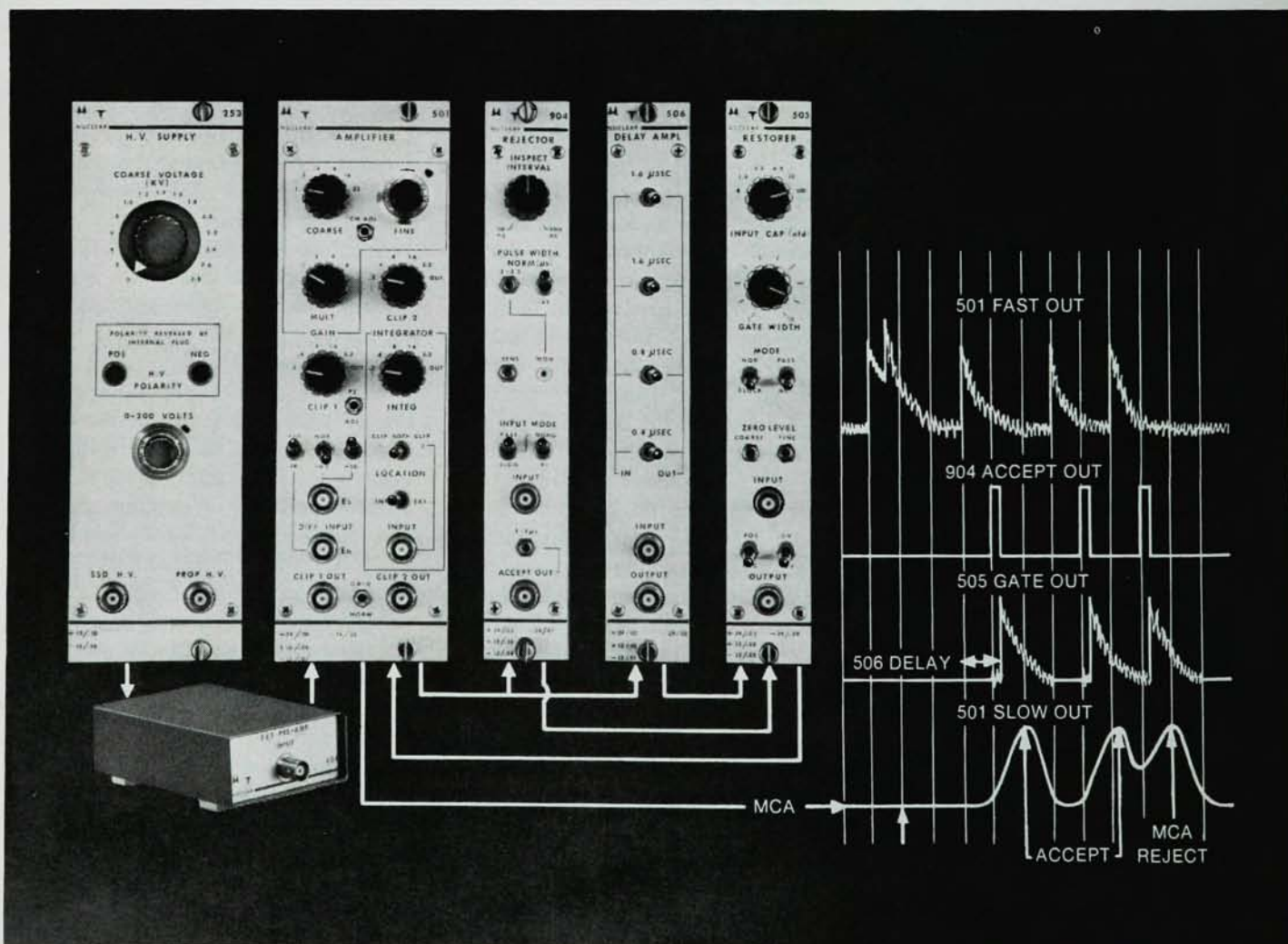
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the addition of one electronic charge requires a charging energy (Δ_c) of approximately 10 meV. For a single particle the junction conductance would show a step at Δ_c . For a distribution of particles the conductance rises rapidly as a function of voltage; that is, the resistance shows a strong peak at $V = 0$. Zeller frequently pointed out that this picture can be generalized to explain all "zero-bias resistance peaks," by claiming that "states" exist in the barrier with a density given by dG/dV . This explanation, of course, is possible, but it appears dangerous to assume that it is always correct, and hence to lose interest in the problem. For example, an alternative explanation of the conductance dip near $V = 0$ in metal-semiconductor contacts involves the excitation of phonons in the semiconductor depletion layer.

The theory of Duke and others was compared to experiment by Tom Caruthers (University of Chicago) and, although the energy range of the observed structure is correct, a disagreement in line-shape was apparent. Further discussion of the various excitation processes observable in metal-semiconductor contacts was given by Matthew Mikkor (Ford) and William Thompson (IBM). The possibility of observing organic impurity vibrations was a point of disagreement in these two talks.

Let us return now to the physics of particles. A small globule brought close to a metal electrode will, by tunneling, lose or gain electrons until its highest filled electron level is within the charging energy (Δ_c) of the Fermi level in the electrode. In order to explain the data Zeller assumes that, over all the particles of a given size, the highest filled level is uniformly distributed within $-\Delta_c$ to $+\Delta_c$ of the Fermi level. In other words, there is no preferred alignment of the particle level with the electrode, because partial electronic charge cannot be exchanged. However, it is just such an alignment that is essential to the new work described by Lambe. He and Bob Jaklevic (Ford) studied the metal-oxide-particle-oxide-metal system where one oxide is too thick to permit tunneling. The properties of the device are probed using capacitance measurements, that is by making electrons hop on and off the particle through the thinner oxide. The resulting capacitance-voltage depen-

dence, which shows symmetrical structure about $V = 0$, is explained on the basis of some degree of alignment of particle "Fermi level" with that of the electrode. Even more dramatically, if a voltage (or series of voltages) is applied to the device at room temperature and maintained during cooling, then at low temperatures the capacitance-versus-voltage structure is removed from $V = 0$ and shifted to the "forming" voltage (or voltages). This result implies that realignment of particle and electrode "Fermi levels" is induced by the applied voltage. The necessary transfer of partial charge to the particle is achieved by "polarization" of the oxide. Although details of this polarization were not understood, results described by John Adler (University of Alberta) may be relevant. In a study of the excitations of molecular impurities in aluminum-oxide tunnel junctions he found that the relative strengths of the various vibrational modes could be changed by applying a voltage to the junction at room temperature. If this change implies a motion, or rotation, of polarized molecules then it is equivalent to rearrangement of charge in the oxide.

So far, all tunneling layers between metal films have been thermally grown oxides. However, Giaever described his fabrication of junctions using evaporated semiconductors such as germanium, zinc sulfide and cadmium sulfide. By oxidation, any pinholes in the semiconducting layer were filled with oxide of the base metal. That tunneling was taking place through the semiconductor was confirmed by observing conductance structure at the correct energy for excitation of LO phonons in the semiconductor. In the case of cadmium sulfide Giaever showed that the tunneling characteristic could be changed by shining light on the junction; a "tunable tunneling matrix element."

Zero-bias anomalies. As mentioned above, the question of zero-bias anomalies was discussed frequently at the conference. One of the best understood of these is the conductance-peak anomaly. This anomaly is categorized by a conductance obeying the law

$$G \propto \log \frac{(eV)^2 + (k_B T)^2}{E_0^2}$$

where eV is the voltage, $k_B T$ the temperature, and E_0 a cut-off parameter. The conductance is also strongly dependent on magnetic field. An explanation for this effect had been ad-



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vanced by Appelbaum and Anderson, based on the electron spin-flip scattering of magnetic impurities in the barrier region. David Losee and Edward Wolf (Eastman Kodak) presented data on a number of different vacuum-cleaved degenerate semiconductor Schottky-barrier junctions, in which they ascribe the origin of the magnetic impurities in their systems to the neutral donors at the edge of the depletion layer. They found good agreement between their data and the Appelbaum theory if they suitably extended the theory to include the lifetime broadening of the magnetic level as well as a g -shift. Work on these anomalies in metal-doped insulator-metal junctions was reported by Adrian Wyatt of Nottingham University and also Paul Nielsen of Chicago.

Many-body effects. The influence of many-body effects on nonsuperconducting electron tunneling generated considerable discussion. In the past, tunneling has been a powerful probe of the many-body interactions in superconductors. This is because of the strong momentum dependence of the electron self-energy in a superconductor, which makes the structure seen in the conductance large, and the superconductor's large coherence length, which makes the superconducting wave functions near the metal-oxide interface only weakly dependent on the details of this surface. Both these effects no longer operate in nonsuperconducting tunneling. There the self-energy is predominantly frequency dependent, leading to small (1%) structure in the conductance. The effective "coherence length" is the order of the Fermi wavelength, so that the exact form of the metal-oxide interface (or semiconductor-Schottky barrier depletion layer) has an important influence of the structure one sees on the conductance.

Craig Davis (Ford) presented work, done in collaboration with Duke, on the influence of the electron self-energy, (resulting from the electron-optical phonon interaction in semiconductors) on the conductance of Schottky barriers. The self-energy in this case is purely frequency dependent. He emphasized that no structure in the conductance would be predicted unless the momentum dependence of the tunneling matrix element is taken into account. This momentum dependence is uniformly ignored

in superconducting tunneling; so we see again the important difference between the two types of tunneling.

The standard approach to tunneling calculations, the tunneling Hamiltonian, came under attack in work presented by Joel Appelbaum and Bill Brinkmann (Bell Labs). They argued that the tunneling Hamiltonian predicts the incorrect form for the transition matrix elements because it first calculates the coupling between the electrodes and then considers the influence of the many-body effects. To rectify this problem they proposed a theory that considers the transition rate between exact many-body states of the electrodes. If the transition rate is calculated by the WKB approximation, they find they can recover the conventional formula for the current, but with the transition matrix element replaced by one that is predominantly frequency dependent. In general, they find that the current depends on the electron Green's function in the vicinity of the barrier. They showed, for the particularly simple example of the electron interacting with magnetic impurities (zero-bias conductance peak), that the size as well as the sign of the zero-bias anomaly depends on the relative position of the impurity and the junction interface.

The theoreticians therefore concluded that the surface can have a profound influence on the self-energy effects observed in the conductance of metal-insulator-metal junctions. It was also obvious that experimentally great variations in junction properties (presence of zero-bias conductance peak, for example) are obtained by altering oxidation procedures. This result indicates that, in future, tunneling experiments must be increasingly tied to surface studies of the metal electrodes, with such tools as low-energy electron diffraction, field emission, Auger spectroscopy and optical studies.

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The conference was sponsored by the Ford Scientific Laboratory, by the National Science Foundation, and by the Air Force Office of Scientific Research. As stated above, no proceedings are to be published, but those interested in further reading on the subject will find an excellent up-to-date review in: C. B. Duke, Tunneling in Solids, Academic Press, New York (1969) (Solid State Physics, Supplement 10).

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