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Meetings

Physics of Semiconductor Surfaces

THE current interest in the surface properties of semiconducting materials has its origin largely in earlier attempts (e.g., 1938-47) to understand rectification phenomena at contacts between semiconductors and metals. To account for the lack of correlation between rectification properties and the thermionic work functions of the surfaces concerned, Bardeen suggested in 1947 that the free surface of a semiconductor is associated with a potential barrier arising from the presence of surface states. Electrons accommodated in these states would act as an electrostatic screen and would protect the barrier (in varying degree, depending on the density of surface states) from interaction with external charges. This would make the barrier independent of (or, at any rate, insensitive to) differences between the work functions of one contacting metal and another. Since then, surface states and associated phenomena have been the subject of intensive research, and the interest is no longer confined to contact rectification. Surface properties influence the performance and, notably, the stability of a variety of semiconductor devices, and independent arguments have established the importance of surface states in a whole range of catalytic phenomena and oxidation processes. The investigations are thus supported by important practical as well as theoretical interests.

To survey the progress made during the last ten years or so, a "Conference on the Physics of Semiconductor Surfaces" was held at the University of Pennsylvania, June 4th-6th, 1956. It was sponsored by the University, by the Office of Naval Research, and by the Lincoln Laboratory of MIT and was organized by a committee under the co-chairmanship of J. L. Jackson, R. H. Kingston, and P. H. Miller, Jr. 123 research workers participated by invitation, including many from abroad. The detailed proceedings of the Conference are being published by the University of Pennsylvania Press under the general editorship of R. H. Kingston. The present report is intended as a summary and is, as always in such circumstances, inescapably personal and necessarily incomplete.

Since surface properties are sensitive to contamination, two complementary lines of research have developed. In the conference program these were designated respectively as "clean surfaces" (free from contaminants and approaching perfect structure) and "real surfaces" (as encountered in practice and covered at

least by an oxide film). Most of the investigations have been carried out on germanium (though certainly not all of them) since the bulk properties of this material are reasonably well understood.

The session on "clean surfaces" was under the chairmanship of J. Bardeen. C. Herring gave a general introduction to the theory of surface states, distinguishing between those which arise from surface imperfections and those associated with the perfect lattice. He discussed the origin of Tamm and Shockley levels and dealt with some of the practical complications which have to be envisaged, e.g., strain and the interaction of surface imperfections with one another.

Among the important problems under discussion was, of course, that of obtaining a really clean surface. This can be done, for instance, by cleaving a crystal in high vacuum, but experimental results of this kind were not available in time for the conference. Alternatively, a "real" surface can be subjected to a number of sputtering and annealing cycles, as described by R. E. Schlier and H. E. Farnsworth, who also showed how the resulting surfaces can be sensitively examined by means of low-energy electron diffraction.

Some recent measurements of the thermionic work function, photoconductance, surface conductance, and (transverse) field effect in ultra-high vacuum were discussed by P. Handler. A model was presented which accounted for the strong dependence of the observed effects on chemisorbed oxygen in terms of the unfilled germanium orbitals at the surface. R. H. Kingston then gave a brief historical review of the critical experiments which have served to establish our present picture of surface structure: the discovery of the inversion layer and injection, the demonstration of field effects, first studies of the oxide layer on germanium, and investigations of the surface conductance under static as well as transient conditions.

The sessions on "real surfaces" were under the chairmanship of A. F. Gibson and H. K. Henisch. Studies of lateral conduction within the inversion layer of a barrier call for a knowledge of the effective carrier mobility. This important quantity has to be calculated, and J. R. Schrieffer reviewed his analysis of the scattering and averaging problems involved. P. C. Banbury, G. G. E. Low, and J. D. Nixon dealt with the effect of capacitively applied fields on the surface conductance and surface recombination, with particular reference to the changes occurring within the first few hundred microseconds. The results have led to an evaluation of the capture cross section of surface states for majority carriers in *n*-type and *p*-type material. The surface states involved in these phenomena are designated as the "fast" states, to distinguish them from those which give rise to changes over a period of minutes or so. A. Many, E. Harnik, and Y. Margoninski described experiments in which the surface recombination velocity was measured as a function of barrier height, giving good agreement with theoretical expectations. Capture cross sections could again be evaluated. B. H. Schultz presented results on hole storage in a semiconducting



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plate as a function of plate thickness. The effective carrier lifetime was found to increase with diminishing plate thickness. Hole storage with delayed recombination is thus possible at the surface. Experiments of this kind, together with recently obtained information on the capture cross sections of surface states should soon make it possible to analyze the transient behavior of the surface recombination process in detail. There is as yet only partial agreement as regards the energetic distribution of these states, which implies some uncertainty as to whether the surfaces used in different experiments are really of identical structure. To clarify the problem of energy distribution, W. L. Brown, W. H. Brattain, C. G. B. Garrett, and H. C. Montgomery added capacitance measurements to the techniques more commonly employed, making use of the fact that the capacitance is not influenced by the carrier mobility. Capture cross sections of "fast states" were again deduced, in this case from measurements on transients performed throughout an oxidation cycle.

H. Statz, G. A. de Mars, L. Davis, Jr., and A. Adams, Jr. reported experiments on the static and transient surface conductance of germanium and silicon and estimates for the energy distribution of the fast states which are also believed to be responsible for surface recombination. Certain interesting anomalies were observed in the presence of organic vapors. Experiments on the "slow states" which are thought to be located on the outside of the oxide film were reviewed by S. R. Morrison. The observed time relations are generally nonexponential and an analysis can be made in terms of the barrier height which governs the probability of charge transfer from the bulk material to these "slow states". The time constants involved have been studied in detail by M. Lasser, C. Wysocki, and B. Bernstein and were found to increase with increasing oxide thickness. The surface can in fact be stabilized by growing a thick oxide film. Problems connected with noise generation at semiconductor surfaces were reviewed and discussed by A. L. McWhorter, who also presented results which indicate that the fluctuating charge density in "slow states" is responsible for the so-called excess or $1/f$ noise found in germanium. The absolute magnitude of the $1/f$ noise in devices still represents an unsolved problem. In recent models, mentioned by Petritz, the noise energy is derived from the applied field. R. L. Petritz and W. W. Scanlon then presented experimental results relating to thin films of lead sulphide and also to surfaces on bulk crystals. These surfaces are evidently highly sensitive to changes of external environment.

A special session was devoted to problems connected with adsorption and catalysis, under the chairmanship of P. Agrain. In his introductory lecture, P. B. Weisz gave a general survey of catalytic phenomena. He also discussed some of the interesting results which arise from the fact that many large periodic structures (e.g., some organic molecules) have common energy levels and can, in a sense, be likened to semiconducting crystals. A contribution by K. Hauffe dealt with cata-

lytic processes which involve an electron exchange between the semiconductor surface and the surrounding gas, and with the dependence of these processes on the Fermi level at the surface. The general aim is, of course, to relate the observations on reaction kinetics to our knowledge of Fermi potentials, space charge distributions, and thermionic work functions. G. M. Schwab distinguished between donor reactions involving electron transfer to the catalyst, and acceptor reactions involving electron loss from the catalyst. He showed how information concerning the rate-determining step can be obtained from experiments in which the kinetics of a reaction are analyzed as a function of donor or acceptor impurity content. G. W. Pratt, Jr. and H. H. Holm reported observations of thermionic work functions on gold, germanium, and silicon as a function of the ambient atmosphere. It was shown that the slow changes of work function which can be stimulated by electrostatic fields or by illumination in a gas atmosphere are related to the changes of surface conductance observed by other workers and interpreted in terms of the "slow surface states".

The last session of the Conference was devoted to surface oxidation, under the chairmanship of W. H. Brattain. In the opening lecture, N. Cabrera pointed out that oxide formation depends initially on nucleation and only in the later stages on diffusion, two processes which may have very different activation energies. The presence of impurities and of surface imperfections, e.g., places where dislocations terminate, plays an important part in the formation of oxide nuclei, as, indeed, it does in etching treatments and perhaps also in certain forms of catalysis. M. Green, J. Kafalas, and P. H. Robinson described experiments in the course of which germanium crystals were first crushed in high vacuum and in which the subsequent oxygen uptake was kept under observation as a function of time, temperature, and pressure. The results have led to a proposed model for the structure of the first oxide layer. Its quantitative confirmation depends on the accuracy with which surface areas can be measured by independent methods, e.g., krypton adsorption. J. T. Law and P. S. Meigs have studied the oxidation rate of different crystal faces on germanium and have found that a protective surface film is formed after a few minutes at 700°C, after which the oxygen uptake ceases. The pressure dependence of the oxidation rate is entirely different below 500°C and above 550°C and different rate-controlling mechanisms have been suggested for these ranges. Above 550°C the oxidation rate becomes independent of crystal orientation. The session ended with concluding remarks by J. Bardeen on the Conference as a whole.

That there should have been so little overlap between numerous contributions on so narrow a subject bears eloquent testimony to the amount of planning and judgment exercised by the Committee. To the guest from abroad, the high standard maintained throughout and, amongst other things, the young average age of the participants were impressive features of the Con-

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ference, with important and highly encouraging implications for the future. A banquet was held in the University Museum on the evening of the second day. It was a splendid occasion, cordial, hilarious, full of good fellowship and warmth which left only the surrounding Egyptian statues unmoved.

H. K. Henisch
University of Reading

Solar Energy

INTEREST in the direct utilization of solar energy is increasing rapidly. At a symposium in Wisconsin in 1953 and again in India in 1954 there was an attendance of about forty. At the conference on solar energy utilization in Arizona last November there were nearly a thousand registrants including 130 scientists from 31 foreign countries. The Ford Foundation, the Rockefeller Foundation, UNESCO and several agencies of the United States Government made possible the participation of the foreign guests.

The conferences were sponsored jointly by the newly-formed Association for Applied Solar Energy, the Stanford Research Institute, and the University of Arizona. Leaders in the organization plans were Merritt L. Kastens, Henry B. Sargent, and Louis W. Douglas. The conference attracted a great variety of people—physicists, chemists, biologists, engineers, and many observers, writers, industrialists, and businessmen who were keeping an eye on new developments in a field of expanding potentialities.

The conference was divided into three parts: The Scientific Basis at Tucson; The World Symposium on Applied Solar Energy at Phoenix; and the Solar Engineering Exhibition at Phoenix.

There was a great demand for places on the scientific programs at Tucson and it was necessary to hold several meetings simultaneously, morning, noon, and evening. It was unfortunate that these programs had to overlap in time and that there was insufficient time for discussion, but the program committee under the chairmanship of Edwin F. Carpenter did an effective job in making available many last-minute contributions. Over one hundred papers describing frontier researches were emphasized at Tucson, while thirty reviews and summaries, stressing practical applications, were given at Phoenix.

The Tucson program dealt with thermal, photochemical, and electrical processes. The thermal processes included flat-plate collectors, high-temperature furnaces, solar stoves, house-heating and cooling, solar power, and solar distillation of saline water; the photochemical processes covered algal culture and higher plants and nonbiological systems; and the electrical processes contained papers on thermal, photogalvanic, and photovoltaic systems.

There were many controversies, such as that between the advocates of flat-plate collectors for heating water and other liquids and the advocates of converging reflectors which can give higher temperatures. It may