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Surface properties of semiconductors

Nobel Lecture, December 11, 1956

First let me say that while I am very proud to be one of the recipients of the Nobel Award in Physics, I am nevertheless well aware that I am only a representative of many others, without whose work and effort I would not be here today. May I mention first my teachers and in particular the late Prof. Benjamin H. Brown at Whitman College, who originally inspired me to take up physics and who also taught my mother and father. Then there are all the many workers in the field of semiconductors on whose shoulders we have stood. Finally and more closely connected with our work are all of our colleagues at the Bell Telephone Laboratories whose efforts and cooperation made our work possible. In particular here I would like to mention R. S. Ohl, J. H. Scaff and H. C. Theurer, whose pioneering work on silicon made a new class of semiconductors available to physicists. It was Scaff and Theurer who, as metallurgists, supplied the silicon and germanium with which we worked, and Ohl who first discovered a p-n junction in a melt of silicon prepared for him by the other two. One needs indeed to be very humble about accepting such an award when he thinks how fortunate he was to be in the right environment at the right time, to take advantage of all that had been done before. Let me here express my gratitude to all of these people.

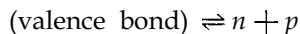
I would like to start by emphasizing the importance of surfaces. It is at a surface where many of our most interesting and useful phenomena occur. We live for example on the surface of a planet. It is at a surface where the catalysis of chemical reactions occur. It is essentially at a surface of a plant that sunlight is converted to a sugar. In electronics, most if not all active circuit elements involve non-equilibrium phenomena occurring at surfaces. Much of biology is concerned with reactions at a surface.

If surfaces are so important, what do we know about them? What is a surface! What properties does a surface have that a physicist can measure? Of the various states of matter - solid, liquid, and gaseous - physicists have long understood and explained the behavior of gases and are now, thanks to quantum mechanics, making considerable progress with simple homoge-

neous solids. Liquids are still quite obscure and surfaces still more so. It was Irving Langmuir, a previous Nobel Laureate, who gave us the first model of a surface, namely clean tungsten in high vacuum, and who further explored some of the simple adsorption phenomena that take place at such a surface*. The main physical measurement by which he could characterize his surface was the electronic work function or potential jump at the tungsten surface and the changes in this potential due to adsorption of various foreign atoms or molecules. He could also measure heats of evaporation of these components. All this points up the essential properties of a surface, namely: (i) it is a boundary across which the concentration of one or more components changes greatly, and (ii) there is a potential jump or energy change associated with the surface. In the case of a metal all these phenomena take place in a few ångströms, making such a surface difficult to analyze. The behavior of a tungsten surface has for some time been a model for the understanding of all surface phenomena. When one comes to some of the dirtier and often more interesting surfaces these have been too remote from clean tungsten for it to serve well in understanding their behavior.

The main point of this story is that now as a result of the progress that has been made in the understanding of semiconductors we have another model of a surface, namely a p-n junction in a single crystal of a semiconductor such as silicon or germanium, and that this model is in a sense at the opposite extreme from clean tungsten. It can also be said that most surfaces lie in between these two models and either model may be used for understanding the multitude of surface phenomena, whichever is best.

In particular one can understand the complicated and dirty germanium gas surface at least qualitatively in terms of the p-n junction model. Let us first consider our p-n junction model. It occurs in one of the simplest, purest and now best understood solids. For example a single crystal of germanium, its atoms held together by well-understood covalent bonds, serves as a medium in which electrons and holes can exist in equilibrium. The existence of these components depends on the thermal dissociation of valence bonds namely



* The present author got his start working under J. A. Becker who was one of the early contributors and is still actively working in the field of metal surfaces.

The law governing this reaction is the mass action law

$$np = K \quad (1)$$

where n and p represent the concentration of electrons and holes in equilibrium at a given temperature. The constant K depends primarily on the absolute temperature (T) and energy (E_g) necessary to dissociate a valence bond creating a hole electron pair:

$$K \sim \exp - (E_g/kT) \quad (2)$$

where k is Boltzmann's constant. The proportionality constant in this last equation can be approximately derived from fundamental physical constants and the density of the crystal. The parameter characterizing the semiconductor is the energy E_g necessary to dissociate a hole electron pair. It is approximately three quarters of an electron volt for germanium, one electron volt for silicon and ranges in other semiconductors from a few tenths to several electron volts.

The main point here is that while the product of the equilibrium concentrations is always a constant at a given temperature, the magnitude of either concentration can be varied over extreme ranges by solution of impurities in the semiconductor lattice. Substitutional solution of a fifth-column element in the lattice of silicon or germanium, as discussed by Shockley in the previous lecture, makes n very large and p correspondingly small, the product remaining constant. Likewise the solution in the lattice of a third-column element makes p large and n small.

Consider now a p-n junction, a crystal of germanium, one side of which is n-type ($n_1 > p_1$) and the other side p-type ($p_2 > n_2$). At the contact between the two regions we have the situation that n_1 must be greater than n_2 and likewise p_2 greater than p_1 since $n_1 p_1 = n_2 p_2 = K$. Because of this concentration difference, electrons will tend to diffuse from 1 to 2 and holes from 2 to 1. This will charge region 1 positive and region 2 negative until an electric potential difference is built up just sufficient to make the field flow balance the diffusion flow. The crystal will then be in equilibrium. This potential is given by

$$V = (kT/e) \ln (n_2/n_1) = (kT/e) \ln (p_1/p_2) \quad (3)$$

Associated with this potential is a space-charge double layer at the boundary, between the two regions. The charge density ρ is related to the potential by Poisson's equation

$$\frac{d^2V}{dx^2} = -4\pi\rho/\epsilon$$

where ϵ is dielectric constant of the medium. The extent of this space-charge double layer is large compared to that in a metal. In germanium it has a characteristic length of about 1×10^4 cm.

This is our model of a surface, a phase boundary across which the concentration of the components differ greatly, the associated potential jump, at the surface and the necessary charge double layer. Its properties can be studied by changing the concentration of the components on each side of the surface from their equilibrium values. When one does this, that the potential difference across the surface changes in a manner with Eq. (3) and this change in potential can be measured. If p'_1 and n'_2 are the non-equilibrium concentrations of holes and electrons on sides 1 2 then the change in potential is given by

$$\Delta V = (kT/e) \ln (p'_1/p_1) = (kT/e) \ln (n'_2/n_2)$$

Note that it is the change in concentration of the minority carrier on side of the boundary that is controlling factor. Likewise, by changing from the equilibrium to the non-equilibrium state, one can measure the flow of charge into or out of the sample or the corresponding change in charge.⁴ the double layer. By a consideration of rate processes going on at this interface, one can also write down a current balance equation for this surface.

$$I = I_s \left[\frac{p'_1}{p_1} - 1 \right]$$

where I_s is the so-called saturation current and is determined by rates of recombination and thermal generation of electrons and holes on both sides of the surface. The non-equilibrium condition may be obtained by flow of current across the surface, in which case I is this current, or by generation of electron hole pairs in the neighborhood of the junction, for example by light, in which case I is the rate of generation of pairs by light multiplied by

the electron charge (e). If both means are used then I is the sum of both currents. Note that one can eliminate p'_2/p_1 from Eqs. (5) and (6), getting the well-known rectifier equation.

We see that the physical properties of this surface which can be measured are the changes in potential, changes in concentration occurring at the surface, and rates of return to equilibrium. These are in general the things one can measure for any surface.

Let us now consider a germanium surface in a gaseous ambient. By the Kelvin method one can measure a contact potential difference between it and a reference electrode. Any change in the potential jump at the surface will give a corresponding change in the contact potential. If the equilibrium at the surface is upset by shining light on the surface the resulting potential change can be measured. This is the surface photo-effect. If the germanium is the proper shape, thin and long, one can also measure the photo conductivity, and from this deduce the change in minority carrier concentration for a given illumination. On a large sample of germanium one can measure the lifetime of electrons and holes in the body of the germanium and then, from the transient behavior of the thin sample, the surface rate of recombination of holes and electrons. As a result of all these studies, one finds that there is in general a space-charge double layer at the germanium surface. It is as if the germanium surface was of a given type, p or n, depending on the nature of the ambient gas and that the germanium interior must be in equilibrium with its surface. All the qualitative phenomena that one would find at a p-n junction, if one maintained say side 1 at a given fixed n-type and varied side 2 from p^+ to n^+ , are found at a germanium gas interface. For example in the case of an n-(p^+) junction the photo e.m.f. is such to make the n-side more negative. As one changes the p^+ side from p^+ to just the same degree of n-ness as side 1, the photo e.m.f. goes to zero and when side 2 is made n^+ the photo e.m.f. changes sign. This e.m.f. is largest in magnitude for n-(p^+) case. If side 1 had been p-type, similar changes would occur when side 2 was varied from p^+ to n^+ but now the photo e.m.f. is largest for the p-(n^+) case. This is also quite an accurate description of the germanium-gas surface. Moreover the magnitude and sign of the photo effects at the extremes can be predicted if one knows the density of holes and electrons, the body lifetime and the surface recombination for the sample in question. Furthermore the experimental results agree with theory.

From the above results one would predict that, since the surface of a germanium crystal in a gaseous ambient may be of a different type from the

interior, the electrical conductivity of the surface should be different from the interior, and, as the surface changes in type, this conductivity should change. In a thin-enough sample these changes can be measured. Along with the changes in surface type, there must also be a change in the charge double layer. One can of course induce such a change in the charge double layer by applying an electrical field perpendicular to the surface, and one can measure the change in conductivity induced by this field. This is the field effect which was predicted by Shockley but which at first one was unable to detect.

As a result of measurements of this change of conductivity with field and of the other changes at the surface with change in gaseous ambient, it is found that there are slow and fast changes at the surface. For example, if one illuminates the surface of germanium suddenly, the contact potential changes quickly to a new value, then slowly decays back towards the original value. Likewise with the surface conductivity when one suddenly applies the field. There are of course changes in the charge double layer at the surface corresponding to the change in surface photo-effect and surface conductivity. From these results one gets the concept of slow and fast states at the surface wherein this charge resides. The fast states are so to speak in good connection with the germanium body and can get into equilibrium or steady state with the body very quickly, in a microsecond or less. On the other hand the slow states are poorly connected with the interior. It takes seconds or minutes for them to adjust to changes induced by light or field. These may not even be states at all but changes in adsorption equilibrium or steady state with the surrounding gas.

The next step is that, from our knowledge of the properties of germanium, one can calculate, from the changes in conductivity, the potential difference across the space layer from the surface into the interior. One can also calculate the change in charge in the space-charge layer. As one changes the germanium surface from p^+ to n^+ , the conductivity should go through a minimum. If in an experiment one can find this minimum, one knows the potential difference across the space-charge layer and, from the change in conductivity from this minimum, one knows the change in this potential. Further, from the field-effect experiment, one can determine the total change in charge at the surface, and from the change in conductivity, how much of this change in charge occurred in the space-charge layer. The charge across the surface must of course add up to zero when there is no field at the surface. If Σ_b , Σ_f and Σ_s are the charges in the space-charge barrier layer, the fast states and the slow states respectively, then

$$\Sigma_b + \Sigma_f + \Sigma_s = 0$$

In the case of an applied field, the sum of these charges must be equal to the field-induced charge. By calculating Σ_b and measuring changes in total charge under slow and fast conditions one can obtain values for both Σ_f and Σ_s . One can also determine the potential change across the space-charge layer and the total change in potential across the surface. For this type of surface one has the chance of taking the surface apart and measuring the individual parts in some detail. What remains to be done is to determine at the same time the chemical changes that occur at this surface and to understand the relation between the physical and chemical changes. When this is accomplished - and I think it will be soon - the germanium surface will be the most thoroughly understood of all surfaces.

As an example of what already has been accomplished if one measures on the same surface at the same time certain quantities as a function of gas ambient, one can deduce the distribution in energy and capture cross-sections of the fast states or traps for electrons and holes. These quantities are the photoconductivity, the decay lifetime, the change of conductivity with field and the surface photo-effect. From these measurements and a knowledge of the body properties of the germanium sample one can then deduce (i) the change of charge in the fast states with respect to the surface space-charge layer potential difference at zero added carrier concentration, (ii) the change of charge in the fast states with added carrier concentration at constant surface potential, and (iii) the surface recombination, all as a function of ambient gas or surface potential. These quantities all depend on the fast trap distribution in energy and on the surface potential. The second depends also on the ratio of the capture cross section for holes and electrons and the third depends as well on the product of the capture cross sections. The relations are integral equations and not easy to solve in general. One question is whether the trap distribution is discrete or continuous. An examination of all the pertinent data indicates that, at least for energies near the middle of the region between the valence and conduction bands, the distribution of traps in energy is continuous and that it is fixed and independent of gaseous ambient or germanium type, for a given surface treatment. One can calculate approximately the ratio of the cross sections obtaining $\sigma_p/\sigma_n \cong 150$ and the product $\sigma_p \times \sigma_n \cong 2.4 \times 10^{-31} \text{ cm}^4$ giving $\sigma_p \cong 6 \times 10^{-15} \text{ cm}^2$, $\sigma_n = 4 \times 10^{-17} \text{ cm}^2$. Not only are these values reasonable but they suggest that the fast trap is acceptor-like, that is, negatively charged when occupied by an

electron and neutral when empty. The attraction between the hole and the negatively charged trap thus explains the larger cross section for hole capture.

In conclusion, one can say that the physical nature of the germanium surface in a gas depends primarily on the surface treatment and the nature of the gas, and not on the type, p or n, of the body material. The reaction of the surface with the gaseous ambient, in particular the Bardeen-Brattain cycle of oxygen and water vapor, is an example of a low-grade catalytic reaction. The understanding of such a simple surface will ultimately contribute to understanding of other surface phenomena, especially catalysis. It was the original attempts to understand surface phenomena of this nature that led to the discovery of the transistor effect. Since then many people have contributed to the present understanding. Some of these are the work of Bardeen and his group at the University of Illinois, Henisch and his group at the University of Reading, Kingston and his co-workers at Lincoln Laboratory, Aigrain and Dugas at the École Normale, Many and his group at the Hebrew University, Israel, and that of my colleague - Garrett. Equally important is the work of Walter Brown on the field effect and, while not specifically dealt with here, his earlier work on channel conduction along with the similar work of Statz and his group at Raytheon.