to imperfections in the specimen crystal or may not be explained by the suggestion of Bozorth and Walker,[7] but may be characteristic of the annealed state of these alloys. The domain pattern obtained after cooling at the rate of about 200 centigrade degrees/hr from 855°C with an external magnetic field of about 550 oersteds applied along the length of the specimen crystal [Fig. 1(c)] is also shown for comparison. Thus our expectation that the domain structure in the annealed state of f.c.c. solid solutions and of b.c.c. solid solutions (with $K<0$) should be fine and complicated, and accordingly our supposition that the perminvar-type magnetic properties are due to the stabilization of domain walls by the induced uniaxial anisotropy, has been verified, and it may be said that these properties are really common to the annealed state of such solid solutions.

Finally, the above considerations and observations seem to indicate, further, that in general the domain structure of a ferromagnetic crystal may be fine and complicated at temperatures immediately below the Curie temperature, and it grows larger and becomes simpler with decreasing temperature. However, in the solid solutions concerned, the growth of domains may be suppressed appreciably at high temperatures since their domains can grow only by an accompanying redistribution of atoms by diffusion, and the domain structure is fixed strongly at lower temperatures by the induced uniaxial anisotropy.

PHYSICAL REVIEW VOLUME 102, NUMBER 5 JUNE 1, 1956

Slow Surface Reaction on Germanium

S. Roy Morrison*
Sylvania Electric Products, Inc., Bayside, New York

(Received November 28, 1955)

An experimental study of the long decay time levels has shown that the reaction between the levels and the bulk germanium depends on the number of carriers in the germanium, on the oxygen pressure, and exponentially on the temperature. It is therefore suggested that the rate-limiting process is electron transfer over a surface barrier. A simplified model, based on this mechanism, yields adequate agreement with the present results and also with those obtained by Kingston.

I. INTRODUCTION

The field effect, i.e., the change of conductance of a semiconducting filament of germanium when an electric field is applied normal to the surface, has been studied by many investigators.[1–4] In the present work, we have been concerned more with the "polarization" of the field effect, a phenomenon which has to date been studied mainly by Kingston and McWhorter[5] and by Low.[4] If a field, E, is applied normal to the surface of a flat filament, an excess charge will be induced on the surface and the conductance along the specimen will therefore change (field effect). However, if the field is maintained, the conductance will in time return to its initial value (polarization of the field effect). This latter effect has been the subject of the present investigation. It is ascribed to a reaction which involves the transfer of the induced charge into nonconducting surface states. The reaction is reversible.

It will be shown that two other disturbances, namely temporary illumination and temporary changes in temperature, cause a similar reaction to occur. In both cases the equilibrium charge density in surface states is displaced. Upon removing the stimulus, a return to equilibrium is observed which shows itself as a slow change in *dark* conductance.

II. EXPERIMENTS ON THE FIELD EFFECT

The sample used for most of the measurements had a p-type impurity density of the order of 10^{13} cm^{-3}, which implies intrinsic conduction above about -16°C. The sample dimensions were $0.2\times2\times10$ mm, the capacity between the field effect probe and the sample was the order of 2 $\mu\mu$f. At all temperatures the surface was p-type, as determined from the sign of the field effect.[2] The measurements of conductance were made using the potentiometer probe technique. The sample was etched with 10% HF, 90% HNO_3, and was aged for four weeks in air, to promote the formation of a stable oxide, before measurements were made.

Results of measurement on the field effect and its polarization as a function of temperature are shown in Fig. 1. The field is applied at time zero. The value of the equilibrium conductance was determined by measurements on a thick filament of germanium, cut from the same crystal to match the characteristics of the sample

---

* Now at Honeywell Research Laboratories, Hopkins, Minnesota.

[1] W. Shockley and G. L. Pearson, Phys. Rev. **74**, 231 (1948).

[2] J. Bardeen and S. R. Morrison, Physica **20**, 873 (1954).

[3] H. C. Montgomery and W. L. Brown, Phys. Rev. **98**, 1565(A) (1955).

[4] G. G. E. Low, Proc. Phys. Soc. (London) **68**, 10 (1955).

[5] R. H. Kingston and A. L. McWhorter, Phys. Rev. **98**, 1191(A) (1955); A. L. McWhorter, Phys. Rev. **98**, 1191(A) (1955); A. L. McWhorter, thesis, Massachusetts Institute of Technology, May, 1955 (unpublished).

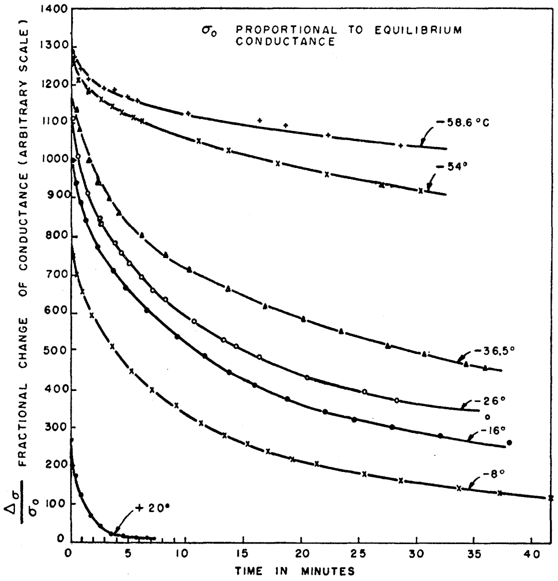

Fig. 1. Polarization of field effect at various temperatures.

as closely as possible. The graphs are plotted in this form to increase the spread between the various curves at short times. The field was applied with the sample positive, the metallic probe negative. Qualitatively similar results have been obtained using *n*-type germanium.

It is observed in Fig. 1, as reported earlier by Kingston,[5] that the value of $\Delta\sigma$ does not vary with time in a simple exponential manner. Kingston, observing this at room temperature, interpreted it as indicating that the surface levels are associated with a distribution of decay times. An alternative model, suggesting that the surface levels involved are monoenergetic and have a uniform decay characteristic will be discussed below.

III. EXPERIMENTS ON SURFACE EFFECTS OTHER THAN THE FIELD EFFECT

After either illumination or a temporary temperature change, the conductance returns to its equilibrium value in a manner very similar to that described above. In fact, if the magnitude and duration of the disturbance is adjusted to give the same initial change in surface conductance, the return to equilibrium is identical for the three disturbances. Such results are shown in Fig. 2. The disturbances are applied at time zero. With the field effect, the disturbance (the field) is kept on and the complete experiment is recorded. With the other effects, the disturbance is applied only for a short interval of time (of the order of two minutes), and in Fig. 2 this interval of time is deleted, making it appear that the disturbance is both applied and removed at time zero. The results of Fig. 2 are interpreted as indicating that the reactions occurring are identical, independent of whether caused by field effect, heating, or light. From the direction of the change in conductivity, it is apparent that the influence of illumination or heating in oxygen causes the surface levels to become more negatively charged, and the runs shown in Figs. 1 and 2 correspond to the reverse transition during which electrons are returning to the bulk germanium.

Although they have no direct bearing on the argument to be presented here, two other experimental observations should be recorded. Firstly, the positive field effect polarization (probe positive) has also been examined. It results in the transfer of electrons to the surface, and the recovery back to equilibrium after the field is switched off follows the same curve as those in Fig. 2. Secondly, the effect of ozone has been investigated. It likewise causes the transfer of electrons to the surface, but in an irreversible manner. When the ozone is removed, the conductance does not recover its original value, but maintains a higher level. The equilibrium conductance may be recovered if the sample is degassed at room temperature in vacuum.

The experiments on heating suggest a simple monoenergetic surface level. For if there were a distribution of energies at the surface, or if the levels were distributed within the oxide layer, one would expect the electron distribution among the levels to be different at room temperature and at −44°C. Hence a different electron distribution should be quenched in after the heating experiments from that observed after the illumination experiments. Since the recovery curves are identical, it is apparent that the electron distribution at time zero is identical for the two cases. The simplest explanation for this identity is a monoenergetic surface level.

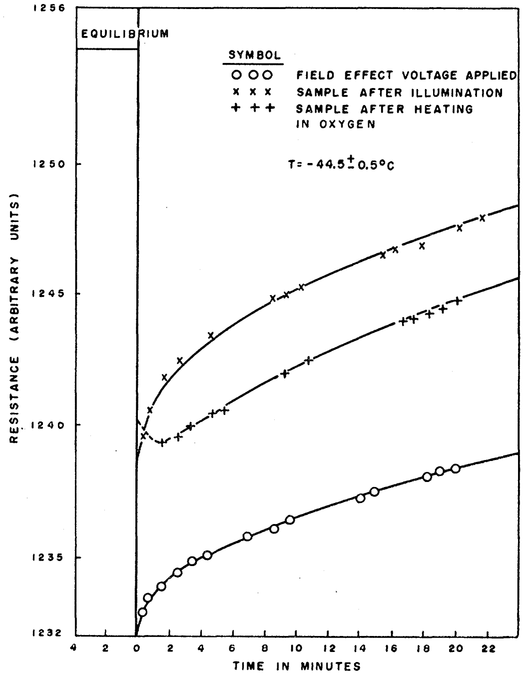

Fig. 2. Recovery of resistance to equilibrium following various disturbances.

Other experiments, designed to determine the influence of oxygen on the reaction, are shown in Fig. 3. The transfer of electrons to the surface, if it involves the adsorption of oxygen, should depend on the oxygen pressure. In the present experiments the specimen was maintained under illumination, except for brief dark periods required for the determination of the dark conductance after various time intervals. These measurements were made as a function of oxygen pressure. The results of Fig. 3 show that the initial rate of change of dark conductance increases as the oxygen pressure increases. It is also proportional to the measured photoconductivity. This means that the initial reaction rate is proportional to the number of holes (or electrons) in excess of equilibrium.

The experiment thus indicates that the phenomena under investigation are, at any rate in part, controlled by oxygen adsorption. Experiments at much lower pressures could in principle have served to test this impression, but were rendered impossible by the more complicated behavior of the surface under these conditions. It was found that if the pressure was reduced below about 1 mm, an irreversible process occurred under illumination, reminiscent of the reaction observed under ozone. This completely masked the reversible reaction. It is planned in future work to investigate this phase more closely. As discussed above, the experiments indicate that we are concerned with surface states of only one energy. Also, since the reaction rate is proportional to the number of free carriers (Fig. 3) and also to the number of surface levels, it may be concluded that electron exchange between the bulk germanium and the surface states constitutes the rate-determining process.

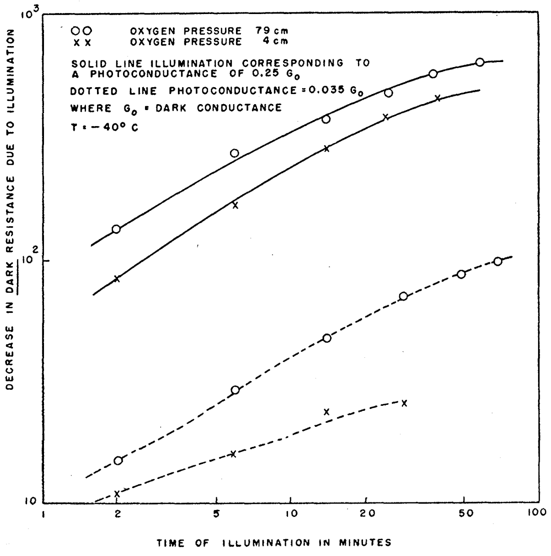

FIG. 3. Transfer of electrons to the surface by illumination.

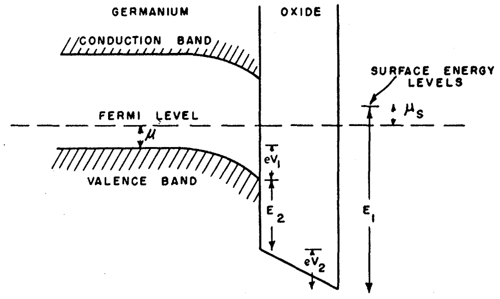

FIG. 4. Band structure at germanium surface assuming monoenergetic surface levels.

IV. THEORETICAL CONSIDERATIONS

The following analysis is concerned with the development of a model in which the rate determining process is electron transfer across a potential barrier. In view of the above conclusions, it is of interest to examine the relevant aspects of Melnick's adsorption theory[6,7] since this is based on similar electronic transfer concepts. Elovich[8] and others[9] have given an empirical description of *irreversible* adsorption processes in accordance with

$$dN_s/dt = a\exp(-bN_s), \tag{1}$$

where N_s is the surface density of adsorbed atoms (ions); a and b are constants. Melnick[6,7] showed that if N_s, the number of adsorbed ions, is large, a small change ΔN_s causes a change in the surface barrier height ΔV_0 proportional to ΔN_s. As a first approximation it may be assumed the rate of electron transfer depends exponentially on the barrier height, whence

$$d\Delta N_s/dt = a\exp(-b\Delta N_s). \tag{2}$$

In our case, the equation must be modified, for if we are dealing with an adsorption process, the experiments show that the process is reversible. If N_s is the equilibrium density of adsorbed ions, a small deviation ΔN_s from this value will thus be removed at a rate

$$d\Delta N_s/dt = a[\exp(-b\Delta N_s) - 1]. \tag{3}$$

It will now be shown that detailed considerations of a more specific barrier model leads to an equation of this form.

Figure 4 shows the barrier model[10] which is used as the basis of the present arguments. Since the experiments were carried out on *p*-type material, we assume that we are concerned with hole transfer. If electrons are transferred, the model must be reversed. The surface levels involved may be due to adsorbed ions, but the analysis should apply equally to surface levels arising from other

---

[6] D. Melnick, thesis, Physics Department, University of Pennsylvania, 1954 (unpublished).

[7] S. R. Morrison, Advances in Catalysis **7**, 259 (1955).

[8] S. Elovich, J. Phys. Chem. (U.S.S.R.) **13**, 1761 (1939).

[9] N. Thon and H. A. Taylor, J. Am. Chem. Soc. **75**, 2747 (1953).

[10] As with other work based upon the barrier concept,[6] the model is based upon a uniform surface barrier. It is apparent that surface irregularities will cause the barrier to be somewhat nonuniform. We have assumed that the surface barrier is the dominant variable in contrast to McWhorter's[5] assumption that the heterogeneity of the surface is the dominant variable, in the capture of electrons at the surface.

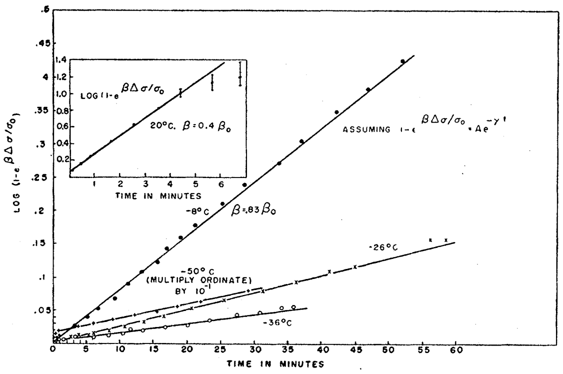

FIG. 5. Polarization of field effect at various temperatures.

causes. In this model we assume that any charge which may exist at surface states located on the germanium-oxide interface remains constant throughout the experiment. Most experimental evidence to date suggests that such levels are present in small density[2,11] and do not appreciably affect the conductance.

For small changes in n_s, the charge in the surface level, it is reasonable to assume that E_1 and E_2 are constant, and that V_1 and V_2 change. The experiments of Bardeen and Morrison[2] have indicated that for an extrinsic sample most of the change occurs in V_1, the Schottky barrier. However, for generality, the possibility that V_2 changes appreciably will be considered. If V_1 and V_2 have the same sign, to be expected if the density of interface levels is small, the rate of change of n_s in the simplest case will be

$$dn_s/dt=A_1\exp[-e(V_1+V_2)/kT]-A_2, \tag{4}$$

where the factors involving E_1 and E_2 have been incorporated into A_2 and A_1. One of the terms of (4) refers to hole transfer to the surface, the other to hole transfer to the bulk. Which of these terms represents adsorption depends on the sign of V_1 and V_2. If the density of surface states is sufficiently high, A_1 and A_2 will be very slowly varying functions of n_s and are here regarded as constant.

In equilibrium, $dn_s/dt=0$. For sufficiently small departures from equilibrium, Δn_s is proportional to the accompanying charge in barrier height, $\Delta(V_1+V_2)$. Applying these conditions to Eq. (4) yields Eq. (3). A change in the number of adsorbed ions will cause a proportional change in the conductance, and Eq. (3) reduces to the form

$$d\Delta\sigma/dt=B[1-\exp(-\beta\Delta\sigma/\sigma_0)] \tag{5}$$

the integration of which yields

$$1-\exp(\beta\Delta\sigma/\sigma_0)=A_0\exp(-\gamma t), \tag{6}$$

where $\gamma=-\beta B/\sigma_0$, A_0 is the constant of integration. Here β is related to the capacity between the surface states and the bulk germanium, γ is related to A_2 and hence to the equilibrium height E_1. These relations will be discussed in more detail below.

The results of Fig. 1 have been fitted to Eq. (6) and are plotted for several temperatures in Fig. 5. It is evident that the curves can be brought into agreement with Eq. (6) by a suitable choice of the constants. The use of these arbitrary constants reduces the importance of the agreement considerably. However, it will be shown below that the values of the "arbitrary" constants β and γ, which are in principle calculable from the model, are of reasonable magnitude and have the expected characteristics.

The quantity β can be shown to have the following form:

$$\beta=-\frac{e\sigma_0}{kT}\frac{d(V_1+V_2)}{d\Delta\sigma}$$

$$=-\frac{e}{kT}\left(\frac{C_1V_a\sigma_0}{\Delta\sigma_i}\right)\left[\frac{n_s}{KK_0(N_A+\alpha p_0)}+\frac{1}{C}\right], \tag{7}$$

where V_a is the dc voltage applied to the field effect probe, C_1 the capacity per square meter between the field effect probe and the sample, $\Delta\sigma_i$ the value of $\Delta\sigma$ at time zero (in Fig. 1), K the dielectric constant of germanium, K_0 that of free space, N_A the impurity density, $p_0=p-N_A$, where p is the hole concentration in the bulk material, and C is the capacity per square meter of the oxide layer, between the surface traps and the bulk germanium. The first term arises from Schottky barrier changes, the second from changes in V_2. It is observed that if $N_A\gg p_0$, the first term in the brackets is constant, but at a higher temperature such that the sample is intrinsic the first term becomes smaller, and the last factor approaches $1/C$. The value of β required for the three low temperature curves exhibited in Fig. 5 was $\beta_0=-(1.47/T)(\sigma_0/\Delta\sigma_i)$. At higher temperatures, the value of β required is noted on the figure in terms of the quantity β_0.[12] It is observed that the expected relaxation of the value of β occurs as the sample becomes intrinsic above -16°C. Evidently at low temperature the $1/C$ term, involving the variation of V_2, is negligible, and from Eq. (7) the value of n_s may be calculated. This turns out to be about 4×10^9 cm^{-2}. From the Schottky barrier theory, this would correspond to a barrier height of about 0.1 volt. The value of β has been extrapolated according to Eq. (7) to the limit at high temperature, yielding an estimate of C, and hence the oxide thickness. The latter turned out to be

---

[11] Statz, Davis, and De Mars, Phys. Rev. 98, 1566(A) (1955).

[12] From the value derived for β and from Eq. (6) it follows that the decay should approach an exponential form with lifetime $1/\gamma$ if $\Delta\sigma_i/\sigma_0\lesssim200$ in Fig. 1. This is observed in the room-temperature curve of Fig. 1. However, there seems to be a discrepancy between the present results and those of McWhorter[5] who reports a nonexponential decay independent of $\Delta\sigma_i$, through a factor of 10 variation in $\Delta\sigma_i$. It is not clear at this time why this discrepancy exists. However, it is certainly conceivable that the effects of a nonuniform surface, such as McWhorter suggests, may in some circumstances dominate over the barrier effects we have discussed, particularly when $\beta\Delta\sigma$ is small.

between zero and 100 A, to the estimated accuracy of the extrapolation.

The constant γ in Eq. (6) can be shown to follow the relation

$$\gamma = C_3 \exp[-(E_1-\mu)/kT], \tag{8}$$

where $(E_1-\mu)$ is the height of the surface barrier above the Fermi level, as in Fig. 4. C_3 is slowly varying with temperature compared to the exponential. From the slopes of the curves in Fig. 5, the value of γ as a function of temperature can be obtained. If γ is plotted according to Eq. (8), as shown in Fig. 6, the height of the surface barrier E_1 turns out to be about 0.5 ev.

V. DISCUSSION

In this work we have presented evidence that electron transfer over a surface barrier is the rate-limiting step in the reaction studied. An analysis similar to that of Melnick, who developed the rate equations for irreversible adsorption with the same rate-limiting step, has been used and extended to reversible reactions. The experimental results can be explained using this simple class of models, involving a monoenergetic set of surface levels, with a single decay characteristic. For one specific model of this class, it has been shown that the model produces reasonable values for the parameters.

Kingston and McWhorter[5] have interpreted some field-effect measurements involving the same reaction in terms of surface levels with a continuous distribution of time constants. Using the distribution of lifetimes so obtained, they found it possible to predict the $1/f$ noise spectrum so often observed in semiconductors and thin metal films. In an earlier communication,[13] the author has shown that the electron transfer model will also predict this noise spectrum. The latter would be expected to be more general, as Melnick-Elovich adsorption behavior is a very common manifestation.

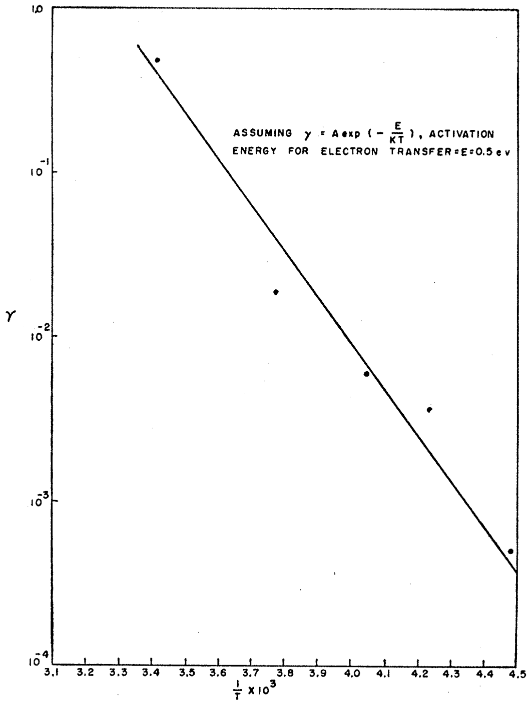

FIG. 6. Plot of γ, the time constant against inverse absolute temperatures.

ACKNOWLEDGMENTS

The author is grateful to his co-workers at the Sylvania Physics Laboratory at Bayside and at Ipswich, and to Professor P. H. Miller at the University of Pennsylvania, for the benefit of many stimulating discussions regarding the concepts presented in this paper.

---

[13] S. R. Morrison, Phys. Rev. 99, 1904 (1955).