Poole-Frenkel Effect and Schottky Effect in Metal-Insulator-Metal Systems

JOHN G. SIMMONS
Standard Telecommunication Laboratories, Harlow, Essex, England
(Received 3 October 1966)

Existing experimental data on the *bulk* conductivity of Ta_2O_5 and SiO films are shown to be consistent with the Schottky effect rather than the Poole-Frenkel effect. A discussion of the physical properties of vacuum-deposited insulators has led to a simple model in which the insulator is proposed to contain neutral traps and donor centers. This model is shown to resolve the above-mentioned "anomalous" Poole-Frenkel effect. Other simple models are discussed, but they do not exhibit the anomalous Poole-Frenkel effect.

1. INTRODUCTION

THE Poole-Frenkel effect (field-assisted thermal ionization) is the lowering of a Coulombic potential barrier when it interacts with an electric field,[1] and is usually associated with the lowering of a trap barrier in the bulk of an insulator,[2–5] as shown in Fig. 1. To experience the Poole-Frenkel effect, a trap is required to be positively charged—that is, it must be positively charged when empty and uncharged when filled, the interaction between the positively charged trap and the electron giving rise to the Coulombic barrier. It will be clear, also, that a donor or acceptor center will also manifest the Poole-Frenkel effect, although this does not appear to have been explicitly stated in the literature. Furthermore, a neutral trap—that is, a trap that is neutral when empty and charged when filled—will not manifest the Poole-Frenkel effect.

The Poole-Frenkel effect is analogous to the well-known Schottky effect, which is the attenuation of a metal-insulator barrier arising from electrode image-force interaction with the field at the metal-insulator interface. Denoting the barrier attenuation by $\Delta\phi$, we have for the Poole-Frenkel effect[1]

$$\Delta\phi_{PF}=\left(\frac{e^3}{\pi\epsilon_0 K}\right)^{1/2}E^{1/2}\equiv\beta_{PF}E^{1/2}, \tag{1}$$

and for the Schottky effect

$$\Delta\phi_s=\beta_s E^{1/2}=\tfrac{1}{2}\beta_{PF}E^{1/2}, \tag{2}$$

where e is the unit of electronic charge, ϵ_0 is the permittivity of free space, K is the *high*-frequency dielectric constant of the insulator, and E is the electric field strength in the insulator. Both of these effects give the conductivity a field dependence of the form:

$$\text{(Poole-Frenkel)}\qquad \sigma=\sigma_0\exp(\beta_{PF}E^{1/2}/kT), \tag{3}$$

$$\text{(Richardson-Schottky)}\qquad \sigma=\sigma_0\exp(\beta_s E^{1/2}/kT), \tag{4}$$

where σ_0 is the low-field conductivity of the system. It will be apparent that the Poole-Frenkel conductivity is observed only when the conduction process is bulk-limited, and the Richardson-Schottky conductivity when it is electrode-limited.

Although the functional dependence of the conductivity upon field strength is the same for the Schottky and the Poole-Frenkel mechanisms, one can differentiate quite readily between the two types of conductivity from their different rates of change of conductivity with field strength, viz., a plot of $\ln\sigma$ versus $E^{1/2}/kT$ results in a straight line of slope β_s or β_{PF}. These experimentally determined slopes can be compared with the theoretical β_s and β_{PF}, which can be calculated quite accurately provided that the high-frequency dielectric constant for the material is known. Alternatively, knowing that the conductivity is either bulk-limited or electrode-limited, one can calculate a value for the high-frequency dielectric constant of the material by equating the experimentally determined value for β to its appropriate theoretical equation: $(e^3/\pi\epsilon_0 K)^{1/2}$ for bulk limited conductivity and $(e^3/4\pi\epsilon_0 K)^{1/2}$ for electrode limited conductivity. The resulting value for K should satisfy the equation

$$K=n^2, \tag{5}$$

where n is the refractive index of the material. Equation (5) should be quite closely satisfied,[6] since in the determination of K the other parameters are known quite accurately.

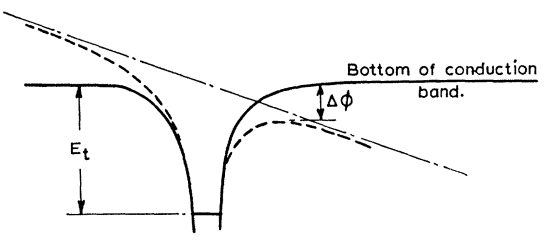

FIG. 1. Mechanism of Poole-Frenkel effect. The solid line represents the Coulombic barrier without a field. The dashed line shows the effect of an electric field on the barrier. The slope of the dash-dot line is proportional to the applied field.

[1] J. Frenkel, Tech. Phys. USSR **5**, 685 (1938); Phys. Rev. **54**, 647 (1938).
[2] C. A. Mead, Phys. Rev. **128**, 2088 (1962).
[3] H. Hirose and Y. Wada, J. Appl. Phys. **3**, 179 (1964).
[4] I. T. Johansen, J. Appl. Phys. **37**, 499 (1966).
[5] T. E. Hartman, J. C. Blair, and R. Bauer, J. Appl. Phys. **37**, 2468 (1966).

[6] This equation holds true provided that the electron does not acquire sufficient energy to produce an optical phonon.

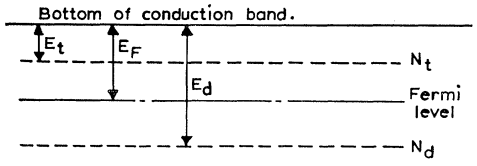

FIG. 2. Energy diagram showing shallow neutral traps and deep donor levels.

We will first discuss measurements made along the above lines, from which there emerges an apparent anomalous Poole-Frenkel effect. We will then go on to describe an insulator band model which resolves the anomaly.

2. EXISTING EXPERIMENTAL DATA

Several investigators have observed a field-dependent conductivity of the form given by (3) and (4) in what is apparently bulk-limited conduction in Ta_2O_5 [2] and SiO films.[3–5,7] Stuart[7] and Johanson[3] have noted, however, that the β coefficient of $E^{1/2}$ is compatible with the Schottky effect rather than the Poole-Frenkel effect. In Table I we have transcribed Stuart's[7] results for three SiO films of various thicknesses; β_{exp} is his experimentally determined coefficient. On closer examination of the results of Mead[2] and of Hirose and Wada,[3] although they claim Poole-Frenkel emission, it is apparent that their β_{exp} are actually compatible with Schottky emission. These authors base their conclusions on values of K which are typically four times too high for the high-frequency dielectric constants of the materials they use. From their experimentally determined β, Hartman *et al.*[5] deduce high-frequency dielectric constants of 3 and 12, assuming Schottky and Poole-Frenkel emission, respectively. A value of 3 is reasonable for the high-frequency dielectric constant of SiO, but 12 is out of the question, particularly in light of the fact that Hartman *et al.*[5] have determined the low-frequency dielectric constant of their films to be only 5.8 from capacity and multiple-beam interferometric measurements. In view of the above facts, it is almost certain that β is consistent with β_s of Eq. (4), rather than β_{PF} of Eq. (3). However, since the conductivity is bulk-controlled, it is most probable that the above phenomenon is due to an "anomalous" Poole-Frenkel effect; certainly the Schottky effect must be discarded as an explanation.

3. THE MODEL

In this section we discuss some of the properties of vacuum-deposited SiO films and propose a band model arising out of these discussions.

It is apparent that in films of SiO, because of its wide energy gap, in order to have any detectable current, even in the absence of traps, it is necessary to have donor centers to supply the necessary carriers. Also, the low thermal activation energy associated with the conductivity[2–5,7] eliminates the possibility of band-to-band excitation. The existence of the donors can arise from at least two sources. First, it is extremely difficult to evaporate compounds without dissociation of the molecules. SiO, in particular, is known to be notorious in this respect, and the process yields a film containing compounds varying from SiO to SiO_2 and also free Si.[8–10] The second source of donors is the contamination of the film from the crucible material. Thus it requires dissociation of only 1 molecule per million, or sublimation of the crucible at one millionth the rate of the evaporant, to yield an impurity density of the order $10^{17}/cm^3$. Furthermore, because of the amorphous nature of SiO and the tendency for compounds to dissociate at high temperature, vacuum-deposited SiO films must contain an extremely high trap density. A judicious study of conduction in thin-film vacuum-deposited insulators can only be accomplished in the light of these facts. We therefore propose a model based on neutral trapping centers and field-assisted thermionic emission from donor centers in order to explain the observed conduction phenomena in SiO films and Ta_2O_5 films.

The electronic structure of our model is shown in Fig. 2. The neutral traps are assumed to lie above the Fermi level. The donor level lies below the Fermi level; this assumption is reasonable in view of the fact that the conductivity of the SiO film continues to increase with increasing temperature above room temperature,[3–5,7] indicating that the donors are not fully ionized.

We locate the position of the Fermi level by equating the number of electrons missing from donor centers, i.e., the number of ionized centers, to the number of occupied traps, the number of electrons in the conduction band being negligibly small; therefore,

$$N_d e^{-(E_d-E_F)/kT}=N_t e^{-(E_F-E_t)/kT}, \tag{6}$$

from which

$$E_F=\tfrac{1}{2}(E_d+E_t)+\tfrac{1}{2}kT\ln N_t/N_d. \tag{7}$$

At zero field the number of free electrons n is given by

$$\begin{aligned} n&=N_c e^{-E_F/kT}\\ &=N_c(N_d/N_t)^{1/2}e^{-(E_d+E_t)/2kT} \end{aligned} \tag{8}$$

and

$$\sigma_0=e\mu N_c(N_d/N_t)^{1/2}e^{-(E_d+E_t)/2kT}. \tag{9}$$

TABLE I. Stuart's[a] results for SiO films of thickness $d\mu$.

$d\mu$	β_{exp}/β_s
3.3	1.05
7.0	1.03
13.7	1.00

[a] See Ref. 7.

[7] M. Stuart (to be published).

[8] G. Hass, J. Am. Ceram. Soc. **33**, 353 (1958).
[9] E. Ritter, Opt. Acta **9**, 197 (1962).
[10] G. W. Brady, J. Phys. Chem. **63**, 1119 (1959).

In the presence of a field the donor barrier (but not the trap barrier) is lowered by the Poole-Frenkel effect according to (1), so that the number of free electrons in the conduction band increases to

$$n=N_c(N_d/N_t)^{1/2}\exp\left[-\frac{E_t+(E_d-\beta_{\mathrm{PF}}E^{1/2})}{2kT}\right], \quad (10)$$

and the conductivity increases to

$$\sigma=\sigma_0\exp(\beta_{\mathrm{PF}}E^{1/2}/2kT)=\sigma_0\exp(\beta_s E^{1/2}/kT). \quad (11)$$

Thus, for an insulator with the electronic structure shown in Fig. 2,[11] the *bulk* conductivity is field-dependent in a manner usually associated with Schottky emission, although the Poole-Frenkel effect is the operating mechanism. Stated in an alternative way, if the conductivity of an insulator is field-dependent in a manner described by the Schottky effect [Eq. (4)], then the conduction process is not necessarily electrode-limited.

4. RELATIVE POSITIONS OF DONOR, TRAPS, AND FERMI LEVELS

It will be apparent that there are two possible positions for the Fermi level besides the one shown in Fig. 2: it may lie above the trap level or below the donor level. These combinations, together with the fact that the positions of the trap level and donor levels can be reversed with respect to each other, give an additional five combinations of trap, donor, and Fermi levels. These five combinations are shown in Fig. 3. It turns out, however, that the combination we have chosen to illustrate is the richest of the six possible combinations from the point of view of permissible relative densities of the donors and traps. For example, assuming nondegenerate positioning of the Fermi level with respect to the donor and trap levels, the other five combinations require one of the following three conditions for their existence: $N_d\gg N_t$, $N_d\ll N_t$, or $N_d\simeq N_t$, as shown in Fig. 3. There are no such conditions imposed on the combination shown in Fig. 2, since N_d is capable of being a good deal larger or smaller than N_t. This may be shown in the following manner: Starting with (6) we have

$$N_d/N_t=\exp[(E_t+E_d-2E_F)/kT].$$

Positioning the Fermi level within $2kT$ of both the donor and trap levels, i.e., $E_F=E_d-2kT$ and $E_F=E_t+2kT$, respectively, we get for the extremities of the ratio N_d/N_t:

$$N_d/N_t=\exp[\pm(E_d-E_t\mp 4kT)/kT].$$

[11] The β_s coefficient of $E^{1/2}$ would still obtain even if there were no traps in the insulator, that is

$$\sigma=e\mu(N_cN_d)^{1/2}\exp[-(E_d-\beta_{\mathrm{PF}}E^{1/2})/2kT].$$

Thus, the traps are not essential for the Poole-Frenkel "anomaly," but rather are a practical requirement.

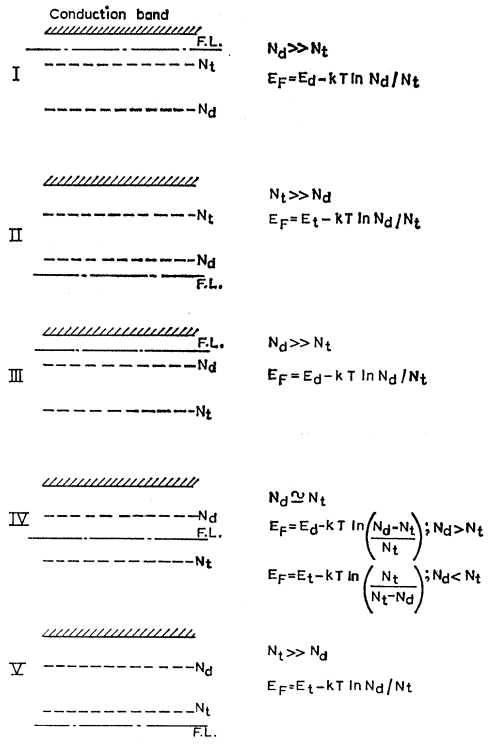

FIG. 3. Energy diagrams of various combinations of trap, donor, and Fermi levels other than that shown in Fig. 2. In calculating E_F, it was assumed that $N_t\gg n$, i.e., that trapping is effective at all times.

Thus, for $E_d-E_t=\frac{1}{2}$ eV and $T=300°$K, we find that any ratio of N_d/N_t between 10^7 and 10^{-7} can exist, which includes practically any value that one may meet with in practice. This, of course, also means that for the relative positions of trap and donor levels shown in Fig. 2, the Fermi level is almost certainly positioned as shown.

Let us substitute into Eq. (8) the values of E_F given alongside the energy diagrams in Fig. 3, taking into account the Poole-Frenkel effect as we did in (10). (We are assuming at present that in the case of II and V we are dealing with charged traps.) Then we readily see that the conductivity for all combinations obeys the 'normal' Poole-Frenkel law, Eq. (3). If in the case of combinations II and V the traps are assumed neutral, the conductivity will be field-independent.

Thus, the model shown in Fig. 2 is unique among the six combinations in that it is the only one exhibiting the anomalous Poole-Frenkel conductivity, and it covers the greatest range of relative donor and trap densities.

5. CONCLUSIONS

We have discussed existing experimental data on bulk conductivity of Ta_2O_5 and SiO films, and it is apparent that they are consistent with a field-dependent conductivity which fits the Richardson-

Schottky law rather than the Poole-Frenkel law. It has been shown that any model invoked to explain the above anomaly must of necessity include not only trapping centers but also donor centers. We have proposed a model on this basis in which we have shallow neutral traps and deep donors. This model exhibits a bulk conductivity which is field-dependent in a manner usually associated with the Schottky effect even though the Poole-Frenkel effect is the operating mechanism, thus resolving the "anomalous" Poole-Frenkel effect in Ta_2O_5 and SiO films. It is shown that this is the only simple system of a single trap[11] and donor level that will exhibit the anomalous Poole-Frenkel effect.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge stimulating discussions with Prof. Sir N. F. Mott. The encouragement and support given by Dr. P. White of these Laboratories is gratefully acknowledged. The author is also indebted to M. Stuart of these Laboratories for kindly permitting him to quote some of his results prior to publication.

PHYSICAL REVIEW VOLUME 155, NUMBER 3 15 MARCH 1967

Size Effects in the Longitudinal Magnetoresistance of Thin Silver Films

K. L. CHOPRA

Ledgemont Laboratory, Kennecott Copper Corporation, Lexington, Massachusetts
and
National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received 3 October 1966; revised manuscript received 9 November 1966)

Size effects in the longitudinal magnetoresistance of metal films have been observed at low temperatures and high magnetic fields. Partial specular reflection of conduction electrons is observed in silver films, provided the ratio α of the thickness to the effective-electron mean free path is smaller than 0.5. It is shown that the scattering coefficient (proportion of specularly reflected conduction electrons) can be determined from the size-effect data. Size effects for films with $\alpha>0.5$ are in agreement with total diffuse-scattering behavior. The dependence of the scattering coefficient on the value of α suggests that the nature of scattering depends on the angle of incidence of the electrons at the surface.

INTRODUCTION

THE scattering of conduction electrons from the surface of a metal film of thickness comparable in magnitude to the mean free path (l) has generally been considered[1] to be diffuse (inelastic). Recently, however, the studies of the thickness dependence of the electrical conductivity by Chopra and co-workers,[2–5] Larson and Boiko,[6] and Lucas[7] have established that the scattering in vacuum-evaporated gold and silver films is partially specular (elastic). An unambiguous determination of the fraction of specularly reflected electrons (the scattering coefficient p) from conductivity measurements on various films is difficult. The assumptions of a constant free path and a scattering coefficient for all the films is hardly justified, since each film has a characteristic value of l and also, presumably, of p. A meaningful scattering coefficient can be determined only for one film, either by changing l by varying the temperature[5] or by modifying the geometrical trajectories of the conduction electrons so as to change the amount of scattering. The latter corresponds to the galvanomagnetic size effects which are easily swamped by the large-bulk galvanomagnetic effects in noble metals. The bulk longitudinal magnetoresistance[8] generally increases to saturate to a small constant value at high magnetic fields. Deviations from this behavior caused by the geometrical size effects could, therefore, be observed and measured. The necessary condition to satisfy is: $l>t$ (film thickness)$>r$ (orbital radius of the electron trajectory under the applied magnetic field). This is now possible, due to the availability of high magnetic fields and epitaxially grown metal films of long mean free paths at low temperatures.[5,6]

Longitudinal magnetoresistance size effects are also expected to throw some light on the question as to what determines diffuse scattering. We know that although the polycrystalline and epitaxially grown continuous films have similar surface smoothness, the latter exhibit more specular reflection.[4,5] It is conceivable, as already suggested by Parrott,[9] that, in analogy with the reflection of light, specular reflection takes place only

* Supported by the U. S. Air Force Office of Scientific Research.

[1] E. H. Sondheimer, Advan. Phys. **1**, 1 (1952).
[2] K. L. Chopra, L. C. Bobb, and M. H. Francombe, J. Appl. Phys. **34**, 1699 (1963).
[3] K. L. Chopra and L. C. Bobb, Acta Met. **12**, 807 (1964).
[4] K. L. Chopra and L. C. Bobb, *Single Crystal Films* (Pergamon Press, Inc., New York, 1964), p. 371.
[5] K. L. Chopra, Phys. Letters **15**, 21 (1965).
[6] D. C. Larson and B. T. Boiko, Appl. Phys. Letters **5**, 155 (1964).
[7] M. S. P. Lucas, Appl. Phys. Letters **4**, 73 (1963).
[8] B. Lüthi, Helv. Phys. Acta **33**, 161 (1960).
[9] J. E. Parrott, Proc. Phys. Soc. (London) **85**, 1143 (1965).