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Nonlinear Response in the Metallic Field Effect*

H. J. Juretschke and L. Goldstein†

Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

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We observe that charging the interface of a silver film on mica at a frequency ω modulates the conductance of the film at both ω and 2ω . Relative magnitudes and phases of the observed modulations, and their dependence on a superimposed dc charge, are consistent with a field-effect model assuming scattering of conduction electrons by surface charges, if the latter occur in patches that scatter the electrons coherently.

Recently, Berman and Juretschke¹ concluded that the metallic field effect in thin films of silver on mica results from the change of scattering of conduction electrons at the silver-mica interface caused by the applied surface charge. Surface scattering by localized charges should give a field effect proportional to Nz^2 , where N is the number of scattering centers and z is the number of elementary charges of each center. The observed field effect $\delta\Sigma/\delta q$ in silver is negative and reverses with the sign of the applied charge. This behavior implies that for scattering of conduction electrons the silver-mica interface appears normally positively charged and to a level much larger than the charge that can be applied externally. The experiment also indicated that the normally present positive charge increases with increasing temperature.²

Further experiments³ on the same system have provided the following new information:

(1) A field voltage $V_1(\omega)$ at frequency ω produces field-effect signals at ω and 2ω for frequencies ω around a few hundred hertz.

(2) The field-effect signal at ω is proportional to V_1 . The signal at 2ω is proportional to V_1^2 , and 90° out of phase.

(3) At a given temperature, a dc field voltage V_0 superimposed on $V_1(\omega)$ causes a linear change in the amplitude of the field effect signal at ω ,

but has no effect on the second-harmonic amplitude. A positive dc bias increases the field-effect amplitude.

(4) The response to dc bias is slow and equilibrium may be reached only after several minutes.

These facts support our basic interpretation of the metallic field effect. Furthermore, they allow identifying some specific aspects of the operative mechanism.

Surface scattering by charged centers can give rise to harmonics in the conductance Σ in two simple ways. First of all, surface charging can change N . Since N is always positive, harmonics are generated if the ac amplitude sweeps through the condition corresponding to a neutral surface. Alternatively, harmonics appear if the applied ac charge changes the occupation z of each center while N stays fixed. In this case we expect a change of conductance of the sample

$$\begin{aligned} \delta\Sigma &\propto -N(z_0 + z_1 \sin\omega t)^2 + Nz_0^2 \\ &= -2Nz_0z_1 \sin\omega t + \frac{1}{2}Nz_1^2(\cos 2\omega t - 1), \end{aligned} \quad (1)$$

where the ac and dc charges per unit surface are Nez_1 and Nez_0 , respectively. Equation (1) has all the dependences listed above under observations (1) and (2). Furthermore, it predicts that the fundamental signal amplitude varies linearly with V_0 (or z_0) while the second-harmonic amplitude is

independent of V_0 , which agrees with observation (3). Equation (1) contains one additional prediction. Let us write the field effect per unit ac charge, normalized to the bulk mobility [in silver $\mu_0 = 64 \Omega^{-1} (\text{C}/\text{cm}^2)^{-1}$], as

$$\frac{1}{\mu_0} \frac{\delta \Sigma}{N e z_1} = -A(\omega) \sin \omega t + A(2\omega) \cos 2\omega t. \quad (2)$$

Then Eq. (1) demands the relation $dA(\omega)/dz_0 = 4A(2\omega)/z_1$, or, since the dc and ac charges per center are proportional to the corresponding voltages (assuming that N remains constant),

$$dA(\omega)/dV_0 = 4A(2\omega)/V_1. \quad (3)$$

Experimental values found for silver films around 800 Å thick for the terms entering in Eqs. (2) and (3) are

$$A(\omega) = 2.2 \pm 0.2, \quad (4a)$$

$$dA(\omega)/dV_0 = (2.7 \pm 0.4) \times 10^{-3} \text{ V}^{-1}, \quad (4b)$$

$$A(2\omega)/V_1 = (5.7 \pm 0.8) \times 10^{-4} \text{ V}^{-1}. \quad (4c)$$

Within the limits of error, these numbers satisfy Eq. (3). Hence the field-effect model based on Eq. (1) appears to be valid, and we are justified in exploring some of its further consequences. [The alternate model leading to harmonics is in conflict with the observed strict V_1 dependence of $A(2\omega)$]. In terms of this model, the numbers given in Eq. (4) lead to specific answers about the silver-mica interface. Typically, ac voltages of 80 V (rms) give rise to a surface-charge amplitude $N e z_1 = 1.6 \times 10^{-7} \text{ C}/\text{cm}^2$. Using the ratio $A(\omega)/A(2\omega) = 4z_0/z_1$, we find a resident dc charge density $N e z_0 = 1.4 \times 10^{-6} \text{ C}/\text{cm}^2$, corroborating that the silver-mica interface is normally strongly charged to about $+6 \times 10^{-3}$ electron per surface atom. The data of Ref. 1 indicate how this charge density changes with temperature. The increase of the field effect $A(\omega)$ with positive dc bias, at a given temperature, is in the same direction as the change of $A(\omega)$ with increasing temperature, with 2.4 V ($3.4 \times 10^{-9} \text{ C}/\text{cm}^2$) corresponding to 1°C rise in temperature.

The overall change in conductance induced by the above value of $N e z_1$ is very small: $\delta \Sigma = -2.2 \times 10^{-5}/\Omega$. Similarly the total effect of $N e z_0$ on the conductance, as expressed in Eq. (1), is small: $\delta \Sigma = -9 \times 10^{-5}/\Omega$. This is much smaller than the change in Σ due to the total surface scattering ($\sim -0.7/\Omega$). Hence we conclude that surface-charge scattering, while responsible for the metallic field effect, is far too small to account for the observed diffuse scattering on metal surfaces.

Finally, we can make an estimate of the average scattering cross section per electronic charge of each charged center. The Sondheimer specularly Q has the explicit charge dependence of the cross section S_0 given by $Q = Q_0 - N z^2 S_0$.⁴ Using the z of Eq. (1) we have $\delta Q/N z_1 = -z_0 S_0$. The value of $\delta Q/N z_1$ can be found by using Eq. (4a) and writing $\delta \Sigma/N z_1 = (\delta \Sigma/\delta Q)_{Q_0} \delta Q/N z_1$. From the details of this transformation² we deduce the value $\delta Q/N z_1 = -5 \times 10^{-17} \text{ cm}^2$. From the range of voltages for which the V_1 dependence of $A(2\omega)$ is known, one can estimate that $N \leq 10^{10}/\text{cm}$, or $z_0 \geq 10^3$. Hence the specific cross section for diffuse scattering has the value $S_0 \leq 5 \times 10^{-20} \text{ cm}^2$. This value is much smaller than the cross section of a single screened electron charge.

On the basis of the foregoing, we obtain the following description of the localized charges seen by conduction electrons at the mica-silver interface: The interface is positively charged to a density of about 6×10^{-3} electron per surface atom. This density increases with temperature at a rate of 1.5×10^{-5} electron per surface atom per $^\circ\text{C}$. The charges occur in patches, with at least 10^3 electrons per patch, and the scattering of conduction electrons by the charges in each patch is coherent. The very small cross section for diffuse scattering per electron in each patch suggests that the charge arrangement within each patch is highly regular. As the temperature changes, the number of patches remains constant or varies only slowly, and both dc and ac charges applied externally primarily change the occupation of each patch. The difference in response time to dc bias (or also temperature changes) and to ac bias indicates that each patch contains at least two types of states of differing relaxation time. Both states exist in each patch because they give a coherent signal upon addition of dc and ac charges.

The experiments do not identify the origin of the resident surface charge $N e z_0$ seen by the conduction electrons. However, it is likely that it represents one end of a surface dipole distribution similar to that associated with the patches of differing work function on a thermionic emitter. Such patches may occur at the interface because of steps in the mica, or because of stress fields set up by grain boundaries and dislocations.

Extrapolation of the silver data to low temperature indicates that the mica-silver interface remains positive even near 0°K , and sufficiently so that an applied dc bias cannot reach or cross the state of charge neutrality. One has to look at oth-

er metal-mica interfaces, such as gold-mica, in order to study the region of near zero charge. Here it will also be interesting to look for the other mechanism leading to a nonlinear response in the field effect.

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†Present address: The Aerospace Corp., Los Angeles, Calif. 90045.

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Scaling Theory of Melting Temperatures of Covalent Crystals

J. A. Van Vechten

Bell Laboratories, Murray Hill, New Jersey 07974

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The melting temperatures of IV-IV, III-V, and some II-VI crystals are predicted with an accuracy generally better than 10%. Only empirical data for Si are used to fix scaling constants.

Calculations of thermodynamic properties based on assumed interatomic potentials are generally presented for systems, such as rare gases, where pairwise central forces are dominant. From these studies has emerged the notion of scaling for a class of similar materials. The simplest example of scaling is probably the use of reduced volumes, temperatures, and pressures in the Van der Waals equation of state (the law of corresponding states), which describes many gas-liquid transitions quite accurately.¹

It is often stated that in the presence of covalent (directional) forces, it is not feasible to construct an equation of state capable of predicting thermodynamic properties. Here it is shown that for $s-p^3$ hybridized covalent bonding, a microscopic model for the solid-liquid phase transition can be constructed based on scaling of the bond energies in the dielectric theory of $A^N B^{8-N}$ crystals. Given the heat and entropy of fusion for Si, as well as its Debye temperature, Θ , and the pressure at which Si transforms to the β -tin structure, the theory predicts the phase diagrams of tetrahedrally coordinated $A^N B^{8-N}$ compounds over a wide range of temperatures and pressures. The present discussion is confined to the melting points at low pressure, i.e., less than 1 kbar.

It may, perhaps, be fair to say that the last substantial advance in the theory of melting occurred in 1910 when Lindemann's criterion was proposed.² According to Lindemann, a crystal with a given structure melts when the mean amplitude \bar{x} of thermal vibration of one of its con-

stituent atomic species reaches a critical value x_0 . He also proposed that x_0 is a constant fraction of the mean interatomic spacing for all solids. For most solids x_0 ranges from 0.2 to 0.25 times the atomic radius.³ The equation relating the melting temperature T^F and the Debye temperature according to this criterion is, for monatomic crystals,

$$T^F = x_0^2 M \Theta^2 / 9 \hbar^2, \quad (1)$$

where M is the atomic mass.

The present theory differs from Lindemann's criterion in two important respects. Firstly, the Lindemann theory is of limited value for practical purposes because it requires a knowledge of the Θ for the material in question. As it is much more difficult to determine Θ than T^F , one cannot generally predict T^F from Eq. (1). However, it is common practice³ to use T^F and Eq. (1) to estimate Θ . This will be done in the present treatment where T^F will be calculated self-consistently from

$$T^F = \Delta H^F / \Delta S^F, \quad (2)$$

where ΔH^F and ΔS^F are the enthalpy and entropy of fusion. The estimated value of Θ enters the calculation through Debye-Waller factors⁴; these factors affect the calculated value of T^F by only about 15%. Secondly, Lindemann's criterion is independent of the nature of the liquid phase. In the present theory, it will be assumed that the liquid phase is metallic. This assumption is known to be correct for Si, Ge, and many III-V