Mutual charging of small metallic particles

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Direct experimental proof of mutual charging of small metallic particles of different size is obtained for the first time. This phenomenon is caused by the size dependence of the Fermi energy attributable to spatial quantization of the electron levels. The potential contrast method in scanning electron microscopy was employed to establish the existence of charged regions in an island film. Transmission electron microscopy was also employed to demonstrate that particle dimensions in the charged regions were an order of magnitude below standard dimensions. Relative charging of small particles is manifested as diode properties of the island film whose particle sizes vary monotonically in the direction of current flow. In order for such properties to be exhibited, charge transfer from particle to particle must occur through a substrate having semiconductor properties. A theoretical analysis of the observed phenomenon is carried out. Specifically, a theory of charged region screening by small particles of opposite charge is given.

INTRODUCTION

According to existing theoretical concepts, if small metallic particles forming an ensemble are of different size, thermodynamically-equilibrium mutual charging of the particles will occur in such an ensemble. This is caused by the dependence of the Fermi energy μ on particle size. Under equilibrium conditions the electrochemical potentials of the particles will be identical. In order to achieve such a condition the electrons must make the transition from particle to particle through the surrounding medium.

The primary physical cause of the Fermi level dependence on particle size R is the spatial quantization of the electron levels. In the quasiclassical range $k_F R \gg 1$ if the distance between levels δ is small compared to T, spatial quantization will be manifested as an addition to the expression for the level density proportional to the surface area S (k_F is the Fermi momentum).

The most complete solution to the problem of level density with a square dispersion law was obtained in Ref. 1. Using this expression we can easily find the correction μ_1 to the Fermi energy μ_0 proportional to $S/V \sim 1/R$ for an infinite spectrum (V is the system volume).

The sign of this correction will depend on the boundary conditions for the electron wave function on the particle surface.[2] If the energy of the electron in the surface atoms is the same or higher than that of the bulk atoms, the Fermi level grows with increasing particle size ($\mu_1 > 0$). If the surface contains a layer of atoms whose electron energies lie below those in the interior, the Fermi energy diminishes with diminishing R ($\mu_1 < 0$).

At an electron concentration n so great that the band character of their spectrum becomes significant, the sign on μ_1 will also depend on n (Ref. 3). If the Fermi level arises with diminishing R for small n, with large n it grows.

In the low-temperature range $\delta \ll T$ the Fermi energy will have a nonmonotonic dependence on R. Oscillations of μ as a function of R have been investigated previously for the case of thin films,[4] while Nagaev[5] demonstrated that in spherical bodies these oscillations are quasistochastic and have a giant amplitude.

As noted previously, the sign of the charge of the smaller particle relative to the larger particle is fixed in the high-temperature range. This charge may be either positive or negative, depending on the boundary conditions and the concentration. In the low-temperature range the signs of these charges may oscillate as a function of the difference of their radii. It should also be noted that in an ensemble consisting of many particles the mutual charging of the particles is a cooperative phenomenon. Indeed, the charge of each particle, which is based on equilibrium of the electrochemical potentials of this particle and the remaining particles, will depend on the size and position of all these remaining particles.[3]

We will provide estimates of the size-dependent shift of the Fermi energy. If the energy spectrum of the crystal contains no surface band, then regardless of its size the quantity μ_1 is of the order of $\mu_0/k_F R$. If we have $R = 50$ Å, then $|\mu_1|$ will reach 0.3 eV. When there is a surface band below the bottom of the bulk band, $|\mu_1|$ may be even greater.

We can then easily obtain an estimate for the particle charges q by generalizing the approach of study Ref. 3 to an ensemble consisting of a random number of particles. Assuming a large distance between particles compared to their radii we obtain the following expression for the average squared charge q^2 with an equilibrium distribution of particle radii over the interval $[L - l, L + l]$:

$$\overline{q^2} = \mu_1^2(L)\, l^2 \varepsilon^2 / 3 e^2, \tag{1}$$

where ε is the permittivity of the medium surrounding the particles. In deriving (1) we assumed $\mu_1(R) \propto 1/R$. As follows from (1) for $L \sim 50\text{–}100$ Å and $l/L \sim 0.5$ the average charge equals 1–2 electrons for $\varepsilon = 1$ and on the order of 100 electrons for $\varepsilon = 100$.

To date there has been no direct experimental confirmation of mutual charging in an ensemble of small particles. Essentially there are not even any experiments confirming the size dependence of the Fermi energy of small particles, although there are experiments that demonstrate the size dependence of the work function χ (this was first observed in Ref. 6). It is, however, important to emphasize that the size dependence of μ generally does not derive from the size dependence of χ. Indeed it is sufficient to assume an electro-

static energy of order $e^2/2\varepsilon R$ for such a dependence; this energy is acquired by the particle after the electron leaves it. The initial size dependence of χ was in fact treated in this manner. The fact that μ_1 also makes a contribution to the size dependence of χ was only noted in Ref. 2:

$$\chi = \chi_0 - \mu_1 + e^2/2\varepsilon R,$$
$$\mu_1 \propto 1/R, \tag{2}$$

where χ_0 is the work function of a bulk specimen.

Physical situations where χ reveals a size dependence while μ does not and vice versa are also possible, as indicated by (2). Boundary conditions for which μ_1 vanishes, for example, correspond to the first case. The fact that such boundary conditions do exist derives from the previously noted variation in the sign of μ_1 as the surface electron energy diminishes. The second case corresponds to the equality $\mu_1 = e^2/2\varepsilon R$. It is also clear that the sign of the size dependence of χ may be quite different from that of μ. Indeed if the size dependence of χ were determined by the quantity μ while the correction μ_1 were positive, then χ would diminish with increasing R. Due to the electrostatic term, however, χ could at the same time increase as a functions of R.

Mutual particle charging likewise does not follow from the size dependence of χ. Indeed, the charges that arise on particles of different radii R_1 and R_2 are proportional to $\mu(R_1) - \mu(R_2)$. These vanish for $\mu_1 = 0$ although the size dependence of χ does not vanish. A comparison of the experimental data on the size dependence of χ and on mutual charging establishes the fundamental possibility for separating the contributions of the kinetic energy and the electrostatic energy to the size dependence of χ.

An experiment[7] that observed a silver particle coagulation rate in plasma four orders of magnitude greater than that would be determined by the Van der Waals forces represents indirect evidence of the existence of mutual charging of small particles. The effect can be attributed to the fact that substantially stronger attractive forces with Coulomb asymptotic forms occur between the silver particles under conditions of mutual changing. This explanation is supported by the fact that the coagulation rate of carbon particles, between which mutual charging is absent, does not increase.

The present study is evidently the first to provide experimental data directly confirming the existence of mutual charging of small particles, i.e., an actual size dependence of the Fermi energy. We describe and analyze two types of experiments. The first experiment employs electron microscopy to observe the potential distribution throughout the film and to detect charging of the region where the smallest particles are concentrated. The calculation carried out in this case identified the properties of the screening of this charged region by other particles when mobile charge carriers are absent.

The second experiment employed electrical measurements and revealed rectification properties of an island metallic film deposited on an insulating substrate so that particle sizes diminish monotonically in one direction. The diode properties of such a system are naturally explained by the nonlinearity of the I-V characteristic (IVC) of the metallic particles with different energy levels separated by the semiconductor interlayer.

1. VISUAL OBSERVATION OF MUTUAL CHARGING OF SMALL PARTICLES

We begin with a presentation of the results from visual observation of charged regions in island films. The studies were carried out at 300 K on island gold films fabricated by thermal deposition on the (001) cleave faces of an NaCl crystal. Since the crystal surface was nonideal due to the cleaving process (for example edge irregularities occur on the surface), the small-particle formation conditions differed throughout the surface. Therefore the island film may have had areas where particle sizes differed significantly from the average particle sizes. Electroneutrality does not hold in such regions in accordance with the concepts outlined above.

The studies were carried out using a scanning electron microscope and an electron-beam energy spectrometer.[8] This method employs a comparison of the energy spectrum of the secondary electrons of the probed region to the reference spectrum of the secondary electrons. Electrodes were attached to the film and the spectrum of the grounded electrode was used as the reference spectrum. The secondary electron spectrum may deviate from the reference spectrum for two reasons. First any deviation of the local potential of the probed region from the reference potential will cause an energy shift of the local spectrum relative to the reference spectrum equal in magnitude to this potential, which is then registered as a signal (the vertical beam deflection during its horizontal sweep). Second, electrically neutral substrate defects may also serve to distort the spectrum, and these also produce a signal. However, the apparent potential associated with such defects can easily be differentiated from the true potential by the behavior of the signal in an external electrical field applied to the electrodes.

Figure 1 shows the potential contrast signal plotted as a function of the coordinate along the scanning line. Curve 1 corresponds to the case where no voltage is applied to the film. The features appearing on this curve have different physical origins. Indeed when a voltage is applied to the film (curves 2 and 3 are obtained by applying a 0.5 and 1 V vol-
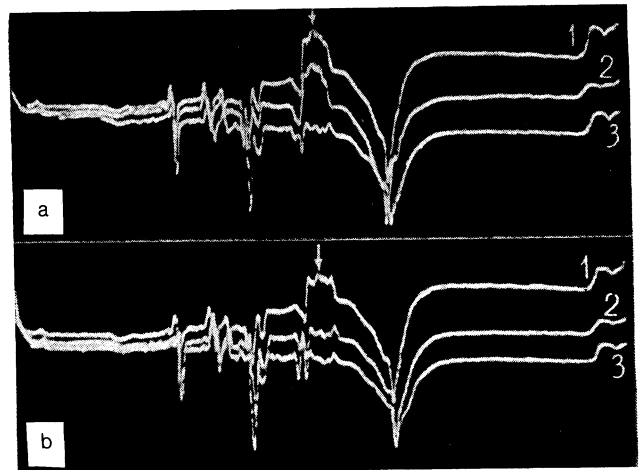

FIG. 1. Potential contrast curves (a) for an island gold film deposited on the (001) cleaved face of an NaCl crystal at $T \approx 300$ K and a film voltage $U_f = 0$ (curve 1), 0.5 (2) and 1 V (3); the left electrode is grounded. b—repeat measurements showing the reproducibility of results.

tage to the film, respectively) the feature labeled by the arrow vanishes while the other features remain. When the voltage is removed the feature indicated by the arrow reappears. The potential contrast curves are recovered in their entirety in repeated measurements (compare Fig. 1a and 1b), are stationary in time and are independent of the energy and intensity of the probe electron beam. This suggests that they reflect the natural properties of the film and do not derive from changes in its state during the measurement process. Specifically, film charging by beam electrons is excluded.

Therefore the potential contrast curves as a function of the coordinates reveal two types of feature. Features of the first type remain unchanged upon application of voltage to the film. Consequently they are not related to film charges and are wholly determined by its morphology. The second type (it is the only one labeled by the arrow in Figs. 1a, b), on the other hand, exists when no voltage is applied to the film although it vanishes when the voltage level is raised. Consequently it can be attributed to the electrical charges that accumulate in a specific region of the film. Given the electroneutrality of the film, they must be screened by charges of opposite sign in the adjacent regions.

A drawback of this approach is that the measurements are carried out along a single scanning line. If a given step is selected and the spectral shift of the secondary electrons is converted into a digital signal and is then used to modulate the luminance of a television cathode ray tube, it is possible to carry out measurements across the entire surface with the results output as equipotential lines.[8]

Figure 2 shows the equipotential lines from the application of a $U_f = 3$ V voltage to the film as alternating dark and light lines. The potential difference between two neighboring light (dark) lies is 0.3 V. If a film were to contain no charged regions the equipotential lines would form a family of parallel lines. However, Fig. 2 clearly reveals a film region surrounded by a closed equipotential line (as indicated by
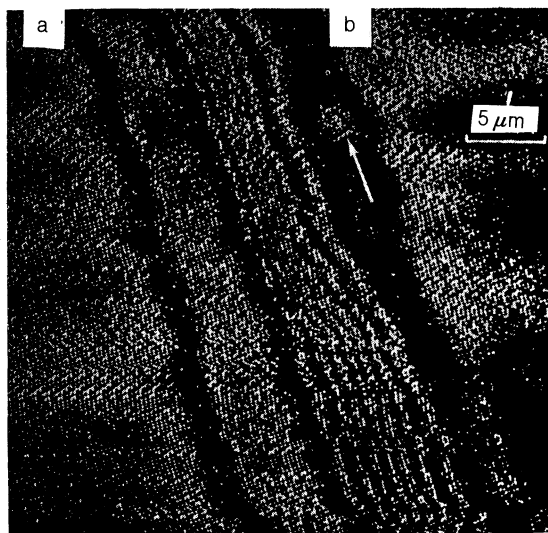
the arrow). This behavior of the potential can be attributed solely to charges in this region. In order to avoid confusion it should be emphasized that the results shown in Figs. 1 and 2 were obtained on different specimens. The fact that, unlike the first specimen (Fig. 1), the external field applied to the second specimen (Fig. 2) does not break down the charged region can be attributed to its geometrical proximity to the "B" electrode which is used to stabilize the specimen (the center of the region is negatively charged, while the "B" electrode is positively charged). Changes in electrode polarity will cause the charged region to vanish; this effect was observed in many specimens. It is important that the charged region shown in Fig. 2 does not vanish when the external field is removed, i.e., like the region in Fig. 1 it is produced by the intrinsic properties of the film.

The specimen whose equipotential lines are shown in Fig. 2 was also analyzed by scanning electron microscopy. It was established that particle size within the charged region amounts to a few tens of angstroms, while it is an order of magnitude higher outside this range. Hence the natural explanation is to attribute the charge region to the difference in the Fermi energies of the electrons in the localization range of the smallest particles and in the remaining film.

A theoretical analysis of the charged regions due to the difference in particle size will be examined in Sec. 3.

2. THE DIODE PROPERTIES OF ISLAND FILMS WITH A PARTICLE SIZE GRADIENT

The mutual charging effect can also be used in practice. If a dispersive metallic film is deposited on a dielectric substrate with the size of film islands varying monotonically from one electron to another, such a film will have diode properties due to the mutual charging of the particles. Indeed the charge-induced initial potential relief of the film is added to (or subtracted from) the applied voltage depending on its polarity, thereby producing asymmetry in the conductivity of such films. A necessary condition for this phenomenon is that the electrical conduction of the medium through which charge transfer from particle to particle occurs, i.e., the substrate (see Sec. 4), be of semiconductor nature.

Oblique deposition was used to fabricate films with an island size varying monotonically from one contact to another. However, this fabrication technique remains difficult to implement. Films with a sharp island size gradient were deposited using a different technique; this technique employs a mask.

The I-V characteristic shown in Fig. 3 corresponds to an island gold film with island sizes varying from several tens to several hundreds of angstroms. The characteristic is given for the ± 0.1 V range since the asymmetrical behavior of its branches corresponding to different voltage polarities across the film is particularly clearly expressed in this region; this is consistent with the theoretical analyses outlined above. The forward current direction is the direction where current flows from large islands to small islands, as would be expected with the charge sign established above for the small particles. At higher voltages both branches of the I-V characteristic converge and are accurately superimposed. In the initial section of the I-V characteristic the rectification ratio for the gold films exceeded a quantity of order 10 in individual cases.
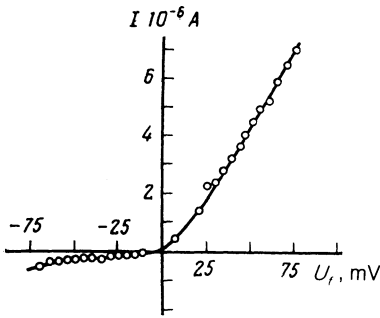

FIG. 2. The equipotential lines in an island film, $U_f = 3$ V, $T \approx 300$ K. The contact-island film boundaries are designated A and B.

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FIG. 3. The I-V characteristic of a film with asymmetric inhomogeneous island structure ($T \approx 300$ K).

3. MUTUAL CHARGING OF SMALL METALLIC PARTICLES WITH AN IRREGULAR SPATIAL DISTRIBUTION BY SIZE

An irregular size distribution is unavoidable in any ensemble of small particles. Since the Fermi energy μ of the particle depends on its size a trend towards equalization of the electrode chemical potentials will cause electrons to travel from particle to particle through the surrounding medium (a small but finite conductivity is assumed). In Ref. 3 the calculation of the electrical charges in the particle system was limited by the smallness of this number. Such a calculation will be carried out below for an arbitrarily large number of particles. We will assume, in accordance with the commonly encountered experimental case (see Sec. 1) that there are clearly differentiated regions containing concentrated particles of sizes substantially smaller than throughout the remaining film.

Naturally the charge within the smallest particle accumulation region will be irregularly distributed, and a compensating charge layer will be formed outside this region.

In some sense it is possible to state that the large particles screen the small particles. However, the potential distribution in a small-particle system is significantly different from the ordinary screening problem in a conducting medium where such screening results from the change in concentration of mobile large carriers near the screened charges. Here such screening results from the change in the charges of immobile particles. Unlike the standard situation, here the screening length cannot include kinetic parameters, while the coordinate dependence of the potential is different then in ordinary screening.

Strictly speaking, a very small but nonzero number of mobile electrons must exist between the particles in the medium in order to support charge transfer from particle to particle to equalize their electrochemical potentials. This will result in ordinary field screening. However in the analysis below the corresponding screening length will be assumed to be large compared to both the size of the region and the screening length for the case of screening by the compensating charge. Hence we will neglect ordinary screening.

A calculation will be carried out below in order to clarify the nature of charge and potential distribution in such a system. Obviously such a calculation will be simply a model calculation due the random shape of the region and the arbitrary particle size distribution. However the estimates obtained from this calculation will also be applicable to actual island films.

The model used below corresponds to a spherical region of radius ρ containing randomly distributed particles of radius R_1 and Fermi energy $\mu_1 = \mu_1(R_1)$. Particles of radius R_2 are distributed randomly outside the region. Such a model better reflects the properties of composite systems than those of island films, for which a model of charged spheres in three-dimensional space would be more appropriate. However, we can expect that this model will provide at least a semiquantitative reflection of the properties of the island films. Convincing evidence in favor of this assertion derives from the similarity of results obtained for the three-dimensional and one-dimensional model when particles of radius R_1 form a plane-parallel layer. For the numerical calculations carried out below for the island films the permittivity of the medium ε will refer to the half-sum of these quantities for the substrate and a vacuum.

The conditions of electrochemical potential equality between the particles can be given as

$$\mu_1/e + q_i/\varepsilon R_1 + \varphi_1(r_i) = \mu_2/e + q_j/\varepsilon R_2 + \varphi_2(r_j) = \text{const}, \quad (3)$$

$$\sum_i q_i = -\sum_j q_j. \quad (4)$$

Here q_i is the charge of a type 1 particle at point r_i, $\varphi_1(r_i)$ is the potential at this point produced by all remaining particles, q_j and $\varphi_2(r_j)$ are the corresponding quantities for the type 2 particles. The equality (4) accounts for the electroneutrality of the system.

At rather high concentrations n_1 and n_2 of particles 1 and 2 spherically symmetric distributions of the charges and the potentials can be assumed, allowing for the slow decay of the Coulomb potential. Then

$$\varphi_k = \frac{n_1}{\varepsilon} \int_0^\rho \frac{q_1(r')d^3r'}{|r'-r|} + \frac{n_2}{\varepsilon} \int_\rho^\infty \frac{q_2(r')d^3r'}{|r-r'|}, \quad k=1,2. \quad (5)$$

Then using familiar electrostatic theorems we obtain from (5)

$$\varphi_1(r) = \frac{n_1}{\varepsilon r} \int_0^r q_1(r')d^3r' + \frac{n_1}{\varepsilon} \int_r^\rho \frac{q_1(r')d^3r'}{r'}$$

$$+ \frac{n_2}{\varepsilon} \int_\rho^\infty \frac{q_2(r')d^3r'}{r'}, \quad r<\rho; \quad (6)$$

$$\varphi_2(r) = \frac{n_1}{\varepsilon r} \int_0^\rho q_1(r')d^3r' + \frac{n_2}{\varepsilon r} \int_\rho^r q_2(r')d^3r'$$

$$+ \frac{n_2}{\varepsilon} \int_r^\infty \frac{q_2(r')d^3r'}{r'}, \quad r>\rho. \quad (7)$$

As we see from (7) subject to (4) $\varphi_2(\infty) = 0$.

The integral equations (3), (6), and (3), (7) can be reduced to exactly solvable differential equations by double differentiation with respect to the spatial coordinate:

$$\Delta q_1 = \varkappa_1^2 q_1, \quad \varkappa_1 = (4\pi n_1 R_1)^{1/2} \quad (8)$$

and

$$\Delta q_2 = \varkappa_2^2 q_2, \quad \varkappa_2 = (4\pi n_2 R_2)^{1/2}. \quad (9)$$

Their solution subject to the finiteness of the charge, the electroneutrality condition (4), and the vanishing of $q_2(\infty)$ is given by the expressions

$$q_1 = A \frac{\text{sh}(r\varkappa_1)}{r},$$

$$q_2 = \frac{C}{r} \exp\{-\varkappa_2(r-\rho)\},$$

$$C = -\frac{n_1\varkappa_2{}^2}{n_2(1+\varkappa_2\rho)\varkappa_1{}^2}[\varkappa_1\rho\,\text{ch}(\varkappa_1\rho)-\text{sh}(\varkappa_1\rho)]A, \qquad (10)$$

$$A = \frac{\mu_2-\mu_1}{e} \frac{R_1(1+\varkappa_2\rho)\varepsilon}{[\varkappa_1\,\text{ch}(\varkappa_1\rho)+\varkappa_2\,\text{sh}(\varkappa_1\rho)]}.$$

[The expressions for the potential and not the charge ordinarily take the form of (10) in the ordinary screening problem.]

As we see from (10) for $\varkappa_1\rho \gg 1$ virtually the entire charge of the internal region is concentrated within its boundaries and diminishes outside the boundaries over a length $\sim\varkappa_1^{-1}$ with the thickness of the charged region depending solely on the geometrical parameters R_1 and n_1 and dropping off with increasing particle concentration as $n_1^{-1/2}$. The particle charge at the internal boundary of the region is equal to

$$q_1(\rho) = \frac{\varepsilon(\mu_2-\mu_1)R_1(1+\varkappa_2\rho)}{e\rho(\varkappa_1+\varkappa_2)}, \qquad (11)$$

i.e., its typical order of magnitude is the same as the particles that do not form regions but rather are distributed randomly among particles of normal size [this is easily observed by setting φ_1 and φ_2 equal to zero in (3)].

The potential decays over the screening length $\varkappa_2^{-1}$ along the outside of the boundary; this screening length vanishes as $n_2 \to \infty$. The particle charge will also vanish: $q_2(\rho) \propto n^{-1/2}$.

Using (10) and (6), (7) we obtain the following expressions for the potential at the center and along the boundary of the region:

$$\varphi(0) \approx (\mu_2-\mu_1)/e,$$

$$\varphi(\rho) = \frac{\mu_2-\mu_1}{e} \frac{\varkappa_1\rho\,\text{ch}(\varkappa_1\rho)-\text{sh}(\varkappa_1\rho)}{\varkappa_1\rho\,\text{ch}(\varkappa_1\rho)+\rho\varkappa_2\,\text{sh}(\varkappa_1\rho)}. \qquad (12)$$

As we see from (12) the potential remains nearly constant throughout the entire anomalous region for $\varkappa_1 \gg \varkappa_2$. On the other hand it jumps sharply within this region for $\varkappa_2 \gg \varkappa_1$. The experimental data in Fig. 1 more closely correspond to the first case.

4. ASYMMETRY OF THE I-V CHARACTERISTIC OF METAL-SEMICONDUCTOR-SECOND METAL SYSTEMS

This section will attempt to explain the rectification properties of island films with the particle size gradient described in Sec. 2. These can naturally be attributed to the difference in the Fermi energies of particles of different size. However this differential is itself insufficient. As we know, a direct contact between two metallic strips with different Fermi energies will behave like an ohmic resistance. It is of fundamental importance that is in this case particles with different work functions will make contact through a semiconductor, whose role in this case is played by the substrate. As is well known, a metal contact with a semiconductor has rectification properties if the carriers in the contact layer of the semiconductor are depleted. In the present case

the situation is clearly quite different. The metal, on the contrary, increases the electron concentration in the contact region of the semiconductor.

In order to simplify the discussion we will consider a system consisting of two metallic particles. Here the stopping layer lies between the two contact layers of the semiconductor. If both metallic particles were identical this layer would be quite symmetrical with respect to these particles and would have a symmetrical shape. It is clear that such a layer cannot produce a symmetry in the I-V characteristic. However if the particles are different the stopping layer is asymmetrical and hence the I-V characteristic ceases to be symmetrical. Therefore we are talking about a new rectification mechanism compared to existing mechanisms.

If the system consists of an ensemble of particles with monotonically varying sizes then this can obviously be considered to be a system of metal-semiconductor-metal cells in series with an identical stopping direction and hence the qualitative arguments outlined above apply to such a system as well.

We will provide a mathematical description of the I-V characteristics of the metal–semiconductor–other metal system below. In order to simplify the discussion both metal strips and the intervening semiconductor will be assumed to be plane-parallel wafers, which makes it possible to treat the system as one-dimensional.

We first find the distribution of the potential φ_0 when the current vanishes. Consequently the following constant electrochemical potential condition must be satisfied:

$$e\varphi(-\infty)+\mu_1 = T\ln\frac{n(x)}{n_s}+e\varphi(x)=\mu_2+e\varphi(\infty), \qquad (13)$$

where μ_1 and μ_2 are the Fermi energies of metals 1 and 2, e is the carrier charge, and n_s is the carrier concentration in the semiconductor far from the contact.

Consistent with (13) the potential φ_0 within the semiconductor is found from the Poisson equation

$$\frac{d^2\varphi_0}{dx^2} = -\frac{4\pi e n_s}{\varepsilon}\exp\left(-\frac{e\varphi_0}{T}\right). \qquad (14)$$

Equation (14) assumes that the intrinsic carrier concentration is small compared to the concentration that arises in the semiconductor due to contact metal doping.

The boundary conditions on (14) consist of continuity of the potential and its derivative at the semiconductor boundaries ($\pm l$), and the analysis accounts for the fact that within the metal the potential obeys an exponential law with a characteristic Thomas-Fermi length.

It is obvious that $e\varphi_0$ within the interval $[-l,l]$ will pass through an extremum. If we designate the extremum point as x_0, then from (14) we have

$$\frac{d\Phi}{dx} = \pm\frac{2}{r}\{\exp[-\Phi(x)]-\exp[-\Phi(x_0)]\}^{1/2}, \qquad (15)$$

$$\Phi = e\varphi_0/T, \quad r = \varepsilon T/2\pi e^2 n_s,$$
$$\Phi(x) = \Phi(x_0)+2\ln\cos[(x-x_0)/R], \qquad (16)$$
$$R = r\exp[\Phi(x_0)/2].$$

The selection of signs in (15), (16) is determined by the fact that the potential $\Phi(x)$ is negative and passes through a maximum at x_0 under contact doping conditions. The position of the point x_0 itself is found from the boundary condi-

tions outlined above. Without dwelling on a detailed analysis of these conditions we will provide the quite obvious result:

$$x_0 \propto \mu_1 - \mu_2. \tag{17}$$

We now address current flow. This is given by the expression

$$j = u[e(n+v)(F+f) - Td(n+v)/dx], \tag{18}$$

where u is electron mobility, $F = -\partial\varphi_0/dx$, f is the current-generating field, and $v(x)$ is the change in carrier concentration compared to its equilibrium value n during current flow. Allowing for the fact that f and v are related by the Poisson relation, we obtain from (18), recalling (15), (16) and the relation between F and dn/dx under equilibrium conditions, the following expression:

$$j = \left[\hat{L}f - \frac{\varepsilon u}{8\pi} \frac{d}{dx} f^2 \right],$$

$$\hat{L} = u \left[en_s \left(\frac{r}{R} \right)^2 \cos^{-2} \left(\frac{x-x_0}{R} \right) \right. \tag{19}$$

$$\left. + \frac{\varepsilon T}{2\pi eR} \operatorname{tg} \left(\frac{x-x_0}{R} \right) \frac{d}{dx} - \frac{T\varepsilon}{4\pi e} \frac{d^2}{dx^2} \right].$$

The boundary conditions on differential equation (19) are given by the equalities $v(\pm l) = 0$ (Ref. 9) or subject to the Poisson equation

$$\left. \frac{df}{dx} \right|_{\pm l} = 0 \tag{20}$$

The I-V characteristic is obtained by numerical integration of (20) and (19); an analytic solution of even the linearized equation (19) is impossible. However, it is also possible to establish the nonlinearity of the I-V characteristic without solving (19) based on the following arguments.

The operator $\hat{L}$, which is linear, cannot produce nonlinearity of the I-V characteristic. The nonlinearity can be produced only by the second term in (19) with the necessary condition that the system be asymmetrical. Indeed, as follows from (19),

$$j = \frac{1}{2l} \int_{-l}^{l} dx \hat{L}f - \frac{\varepsilon}{16\pi l} [f^2(l) - f^2(-l)]. \tag{21}$$

In a symmetrical system $f^2(l) = f^2(-l)$. Hence with a change in the sign of j the quantity $f(x)$ also simply changes sign and the total voltage drop

$$\delta\varphi = \int_{-l}^{l} f(x) \, dx$$

keeps its absolute value. If the system is asymmetrical, i.e., $x_0 \neq 0$, the voltage drop will depend on the current flow direction. With small f the nonlinear term in (19) can be accounted for in perturbation theory. If x_0 is also small, then

$$f^2(l) - f^2(-l) \sim x_0 \propto \mu_1 - \mu_2$$

and the difference in the voltage drops $|\delta\varphi(j)| |\delta\varphi(-j)|$ remains of the same order upon reversal of the direction of current flow.

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