Metallization and manifestation of the quantum size effect in the system of a bismuth film in a polar medium

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In the system of a bismuth film in a polar medium (an electrolyte) the carrier density in the film exceeds that in bulk bismuth by two or three orders of magnitude. A nonmonotonic dependence of the external photoemission current on the potential drop at the bismuth-electrolyte interface, caused by a quantum size effect, has been observed for the first time.

The quantum size effect accompanying the imposition of a strong external field on thin bismuth films is of considerable research interest.[1,2] Strong fields (10^7–10^8 V/cm) difficult to produce by other methods can be produced with the help of "nondischarging" ions in the Helmholtz layer at the interface between a bismuth film and an electrolyte. Under these conditions, electrons are pumped into the conduction band (a metallization occurs) at potentials more negative than the zero-charge potential of the bismuth electrode. Ion surface densities $\rho_s \simeq 10^{13}$–10^{14} cm^{-2} are achieved experimentally. At a film thickness $L \simeq 10$ nm the corresponding electron density is 10^{19}–10^{20} cm^{-3}, or two or three orders of magnitude higher than the density in bulk bismuth. At sufficiently large values of ρ_s it becomes possible to test for a quantization of the transverse motion of conduction-band electrons by studying photoemission.

Thin films were produced by deposition of bismuth vapor (99.999% pure) in a vacuum (1 mPa) on mica heated to 80 °C. The films synthesized under these conditions have a single-crystallite structure over their thickness; the trigonal axis runs perpendicular to the surface.[3] Experiments were carried out with films of two types: films with a constant thickness and wedge-shaped films. The differential capacitance was measured by a pulsed method[4] with a pulse 5×10^{-6} s long. This method made it possible to determine the capacitance and series resistance of the sample and to simultaneously monitor the state of the film during the measurements. A capillary filled with the working solution was pressed against the surface of the film for the capacitance measurements, and measurements were taken at various points on the wedge. The photoemission was measured during steady illumination of the electrode (DRSh-1000 mercury vapor lamp, $\lambda = 365$ nm) during an adjustable jump in the potential φ, reckoned from the potential of a saturated calomel electrode. The measurements were taken in a 0.5M KCl solution, with N_2O used as an electron acceptor.[5]

Figure 1 shows the differential capacitance per unit surface area, C, as a function of the film thickness. At thicknesses greater than 80 nm the values of C do not depend on the thickness and are approximately equal to the capacitance of bulk bismuth electrodes. At thicknesses below 80 nm the differential capacitance falls off with decreasing thickness. The reason for this decrease is a decrease in the degree of metallization (i.e., in the carrier density) in the thin film. Figure 2 shows the external photo-

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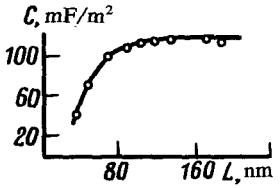

FIG. 1. Differential capacitance versus the film thickness. Pulse length of 5×10^{-6} s.

emission current j versus the potential φ (in the coordinates $j^{0.4}$-φ) found for bismuth films 20, 29, and 170 nm thick. At film thicknesses greater than 40 nm this dependence can be described by the five-halves law,[5] in agreement with data on bulk bismuth in the literature.[6] There are some important distinctions in the photoemission behavior of the thin films ($L<40$ nm): Some characteristic steps appear on the potential dependence of the photocurrent, and the length of these steps increases with decreasing film thickness. The five-halves law holds for a parabolic dispersion law in the conduction band of the external medium when there is a nonsingular behavior of the state density in the band near the Fermi surface involved in the photoemission.

The appearance of the steps on the j-φ curves (Fig. 2) is a consequence of a quantization of the motion in the direction perpendicular to the surface of the film. For corresponding calculations we work from the expression for the spectrum in Ref. 7, extrapolated to $E>E_g$:

$$\left(E-\frac{E_g}{2}-\frac{p_1^2}{2m_{1+}}\right)\left(E+\frac{E_g}{2}+\frac{p_1^2}{2m_{1-}}\right)=E_g\left(\frac{p_2^2}{2m_2}+\frac{p_3^2}{2m_3}\right), \tag{1}$$

where $m_{1+}=m_{1-}=m_e$, $m_2=m_3=10^{-2}m_e$, and E_g is the width of the band gap. To determine the degree of metallization we should substitute $p_{1,2}=\pi\hbar n_{1,2}/d$ ($d\gg L$, $n_{1,2}$ are integers) and linearize (1) with respect to n_1 and n_2 under the constraint $n_1n_2/d^2\sim\rho_s$. These calculations lead to the following expression for the minimum distance between the bottom of the conduction band and the Fermi level:

$$\Delta E_F=\pi\hbar\rho_s(\pi^2\hbar^2/4m_1+E_g/2m_3\rho_s)^{1/2}\simeq 1\text{eV}. \tag{2}$$

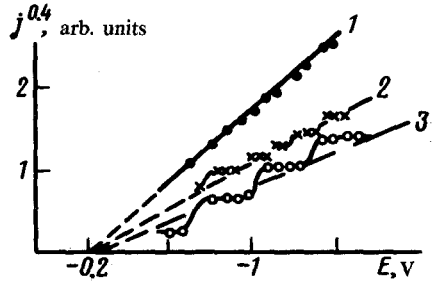

FIG. 2. The dependence $j^{0.4}$-φ for bismuth films of several thicknesses. 1) 170; 2) 29; 3) 20 nm.

Here $\rho_s \simeq 10^{13}$ cm^{-2} ($\rho_s = C\varphi$, $C \simeq 10$ μfm/cm^2, $\varphi \simeq 0.1$ V). The ratio $E_g/2m_3 = (2 \pm 0.5) \times 10^{16}$ erg/g was found from the φ dependence of j (Fig. 2), since we can find an expression for the step length $\Delta\varphi$ from spectrum (1): $\Delta\varphi = (\pi\hbar/L)(E_g/2m_3)^{1/2}$. The value which we find for $E_g/2m_3$ for a film 20 nm thick is an order of magnitude greater than the corresponding value for bulk bismuth.[7] The discrepancy may be due to a deviation of the spectrum from (1) at $E > E_g$ or an increase in E_g in the thin films.

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