Concerning the nature of carrier scattering by the surfaces of bismuth films

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Results are presented of an investigation of the size effect in the electric conductivity and the thermoelectric power of bismuth films whose surfaces are coated with thin tellurium or lead layers. The decisive role played by the charge state of the bismuth film in its scattering ability relative to the carriers is established.

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When the sample dimensions are commensurate with the carrier mean free path, carrier scattering by geometric surfaces becomes significant. This leads to a size effect in the kinetic coefficients, as observed, for example, in thin films.[1] The degree of manifestation of the size effect depends on the scattering ability of the surface relative to the carriers. In the Fuchs theory of the size effect[2] this ability is characterized by a phenomenological specularity coefficient (equal to zero for complete diffuse scattering and to unity for specular scattering). Usually the character of the carrier scattering by a surface is associated with its geometric relief (roughness).[3,4] This point of view, however, does not explain the noticeable differences in the character of surface scattering of carriers of opposite signs, observed in bismuth and in antimony.[5,6] Thus, for example, it was established in[5] by the method of transverse magnetic focusing that the specularity parameter of an antimony surface is equal to 0.8 for electrons and to 0.1 for holes. These results can be attributed to the fact that the surface has a charge (captured, for example, by the surface state) whose electric field acts on the carriers as they move near the surface. If the surface is negatively charged, then the electrons are reflected from the potential barrier produced by the charge without reaching the geometric surface of the sample. At the same time, a negative charge not only fails to prevent holes from reaching the surface, but even deflects them towards the surface, from which they are diffusely scattered. Thus, the presence of a negative charge on the surface specularizes it, so to speak, relative to the electrons, but increases the scattering of the holes from the surface.

The effect of the surface charge and of the band bending it produces in the surface layer on the size effect in the electric conductivity of semimetal such as bismuth and antimony was considered in[7]. The theory there explains a number of pecularities of the size effect in the electric conductivity (for example, its saturation), which have been observed in bismuth.[8-10] However, no direct and controllable investigations have been made of the influence of the charge state of the surface and of the band bending it produces on the size effect in bipolar materials.

One of the methods of producing a controllable band bending near a sample surface is to deposit on this surface a layer of matter having a different electron work function (the method of applying a transverse electric field cannot be used for bismuth or antimony).[11] It is important that the coating be in perfect physical contact with the sample surface. The band bending in the surface layer can then be calculated by the theory of contact phenomena.[12]

The character of the surface scattering of carriers manifests itself most noticeably in the electric conductivity of the samples. From the conductivity data, however, it is impossible to deduce separately the character of the scattering of each group of carriers. This can be assessed from the change in the magnitude and sign of the thermoelectric-power, since its electron and hole components add up algebraically, with proportionality coefficients equal to the partial conductivities.

We have investigated the electric conductivity and the thermoelectric power of bismuth films whose surfaces were modified by thin layers of tellurium and lead. The choice of these modifiers was dictated by the fact that the work functions of electrons from tellurium and lead are respectively larger (4.73 eV) and smaller (4.0 eV) than that of bismuth (4.4 eV).[13] If we assume that this ratio of the work functions is preserved also for films, then a negative charge (upward bending of the bands) should be produced on a bismuth film surface modified by tellurium, and a positive charge (downward bending) if lead is used.

The samples were obtained by condensation from the vapor phase at room temperature in a vacuum of 10^{-6} mm Hg. A film of the modifying material was first deposited on a mica substrate, followed by condensation of a bismuth film of specified thickness as the sublayer. Simultaneously with the three-layer samples (sandwiches) we produced also "witness" films of the bismuth and of the modifying elements. The tellurium and lead condensation rate was 5–7 Å/sec, and that of bismuth 50 Å/sec. The bismuth film thickness was estimated from the known rate and time of their deposition. The resistivity was measured by a four-probe method. The thickness of the sublayer and of the coating was 30–50 Å and their combined resistance 10^6–10^7 Ω.

Electron-diffraction investigations of thin-layer bismuth–tellurium sandwiches (200 and 200 Å) have shown that there is no interaction that produces intermediate compounds of bismuth and tellurium. Diffractometric investigations have established that the samples are polycrystalline with practically random grain orientation.

The dependences of the resistivity and of the thermoelectric power of tellurium–bismuth–tellurium and lead–bismuth–tellurium sandwiches, as well as of bismuth films on mica (their "witnesses") on the thickness at room temperature are shown in Fig. 1. In the case of bismuth films on mica these dependences take the customarily observed form. For the three-layer sandwiches, however, there is no size effect in the resistivity, and there is even some tendency of the resistivity to decrease in the region of small thicknesses. The dependence of the resistivity of three-layer lead–bismuth–lead and tellurium–bismuth–tellurium sandwiches are similar, but the resistivity of the latter is higher. These samples exhibit more noticeable differences in their thermoelectric powers. The thermoelectric power of tellurium–bismuth–tellurium samples is negative and greatly exceeds in absolute value that of bismuth film, reaching maximum values 90–92 μV/K at a sample thickness 2000–3000 Å (this, incidentally, shows that there is no diffusion of the tellurium into the bismuth under the sample-preparation conditions, since doping of bismuth by tellurium decreases the absolute value of the thermoelectric power).[14] This coefficient changes more steeply with thickness than for

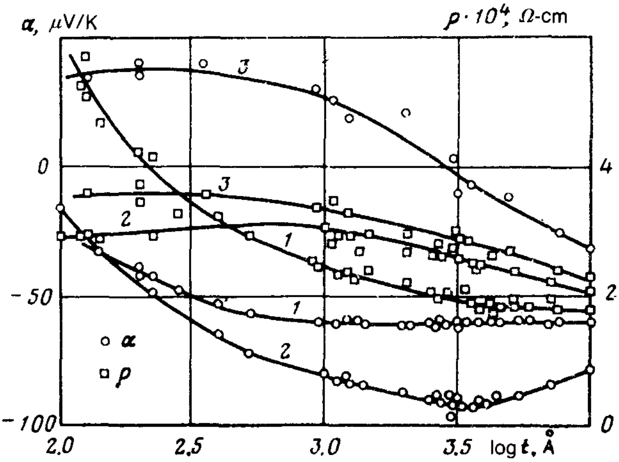

FIG. 1. Thickness dependences of the thermoelectric power (α) and of the resistivity (ρ) of bismuth films on mica (1) and of tellurium-bismuth-tellurium (2) and lead-bismuth-lead (3) sandwiches.

bismuth films. The thermoelectric coefficient of lead–bismuth–lead samples is positive at small thicknesses (40 μV/K), begins to decrease at 1000 Å, reverses sign at a thickness 3000 Å, and then assumes slowly increasing values.

The results attest to a substantial influence of the contact potential-difference field and of its direction on the probability of carrier collision with the surface. In the tellurium–bismuth–tellurium samples, the contact potential-difference field bends the electron trajectory away from the surface and the hole trajectory towards the surface. As a result of the more intense scattering of the holes, their mobility decreases more significantly than that of the electrons, and more the thinner the bismuth films. It can be stated that in thin bismuth films whose surfaces are modified by tellurium the electron transport is mainly effected by electrons specularly reflected from the surface, while the hole conductivity is appreciably suppressed. The pattern is reversed for lead–bismuth–lead samples. The sign of the thermoelectric power of these samples points to a predominantly *p*-type conductivity up to a thickness 3000 Å. Since the bulk mobility of the holes is less than that of the electrons, the resistivity of the lead–bismuth–lead samples is larger than that of the tellurium–bismuth–tellurium samples. If the bismuth film in the sandwich is thin, the effect of carrier enrichment or depletion of the surface layers can also come into play. This can explain some lowering of the resistivity and of the thermoelectric power of the samples. On the whole, however, the observed singularities have a dimension more commensurate with the carrier mean free path (2000–3000 Å) than with the depth of the space-charge layer (300 Å),[11] i.e., they are mainly connected with the influence of the charge state of the surface on the effective mean free path rather than on the carrier density.

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