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Synthesis, structure and electrophysical properties of polycrystalline bismuth films

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Thin bismuth films provide a wide range of practical applications. Owing to a high magnetoresistive effect bismuth layers can be used as components of magnetic field sensors [1]. Many of today's conventional thermoelectric materials are bismuth-based compounds, for example Bi_2Te_3 [2]. The present work is focused on establishing correlation between electrophysical properties of polycrystalline bismuth films prepared by different methods and their microstructure. The films were fabricated by melt spinning and electrochemical deposition techniques.

Electrochemical bismuth deposition was performed from aqueous electrolyte containing 0.174 mol/l $Bi(ClO_4)_3$ and 3 mol/l $HClO_4$ onto plates made of a one-sided flexible foil-coated laminate. 70 µm thick Bi films were electrodeposited at room temperature and electrolyte stirring under galvanostatic regime with a current density of 2.5 A/dm^2. In the melt spinning technique, bismuth (99.9999 %) was melted and then spilled on the cold surface of rotating cylinder made of a polished copper.

Grain structure analysis (electron backscatter diffraction technique) showed that relatively fine-crystalline films (grain size l_G is 0.5–1.5 µm) were formed by electrochemical deposition. Annealing of these films at 540 K for 5–6 h led to a significant growth of the grain size (up to 10–50 µm). Melt spinning technique provided immediate formation of the coarse-grained Bi films (l_G ~ 5–15 µm). Electrophysical characteristics such as resistivity, magnetoresistance, Seebeck coefficient and Hall coefficient of the prepared bismuth films were measured in 4–300 K temperature range under magnetic fields up to 8 T. Relative magnetoresistance $\Delta\rho/\rho_o$ at 4 K under magnetic field 8 T reached 4500 for annealed electrodeposited films, whereas $\Delta\rho/\rho_o$ did not exceed 12 for as-prepared electrodeposited films. Temperature dependence of the resistivity was found to be strongly influenced by Bi grain size. Semiconductor-like behavior was observed for the samples with grain linear size l_G comparable to a charge carrier's mean free path l. Metal-like behavior was inherent to the samples with $l << l_G$.

Mobilities and concentrations of electrons and holes were calculated using Lax model for electrons and parabolic dispersion law for holes. Electron and hole concentrations were found to be practically independent of the film fabrication method and were around 10^{24} m^{-3}, increasing five to seven times at the temperature growth from 25 to 300 K. Mobilities for the electrochemically deposited samples were close to 1 m^2/(V·s) and depended only slightly on the temperature in the studied range. For the other types of Bi films, mobilities were approximately 10 m^2/(V·s) at helium temperatures and declined by an order of magnitude at room temperature.

The observed differences in electronic properties of the Bi films under study can be explained by a profound effect of grain boundaries on charge carriers scattering. For fine-crystalline films (as-prepared electrodeposited films) the grain-boundary scattering plays a significant role, which results in a weak temperature dependence of mobility and a decrease of resistivity with increasing the temperature due to a rise of the charge carrier concentration. In case of coarse-crystalline films (electrodeposited films after annealing and films deposited by melt spinning) a contribution of the temperature-dependent scattering by phonons enhances strongly. As a result, the charge carrier mobility decreases, and the resistivity droningly rises with the temperature increase.

References

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