Superconductivity of Nanostructured Pb₇Bi₃ Films Doped by Ce

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By means of electrochemical deposition from electrolytes, containing salts of Pb and Bi (0.03 mol/l and 0.02 mol/l respectively) thin films of intermetallic Pb₇Bi₃ have been fabricated. The superconducting transition temperature of the films was measured to be around 7.8 K. The deposition of the films with thickness of 50–100 nm was performed via passing rectangular current pulses with given amplitude and length. It was shown that adding salt of Ce into the electrolyte leads to a significant growth of the T_c for the deposited films reaching its maximum at the salt concentration of 0.06 mol/l. X-ray analysis data revealed the single phase of Pb₇Bi₃ films with hexagonal structure (SG) having a textures parallel to (101) plane. The morphology of the film surface is characterized by nanocluster structure with typical grain size around 70–80 nm. For the films, fabricated with adding salt of Ce, together with the intermetallic phase of Pb₇Bi₃, the second phase containing Bi is detected. At the same time, the typical grain size is reduced to 20–30 nm. Additionally, the suppression of the superconductivity in the grown films is investigated. The influence of the composition and structure on the superconducting critical temperature is discussed for both types of the fabricated films.

Keywords: Superconductivity, Nanostructured, Pb₇Bi₃ Films, Electrodeposition.

At present times, vacuum sputtered layers of metallic superconductors (Nb, Al, Pb, MoGe etc) are used as the superconducting elements of new electronic schemes.¹ In some of the tasks related to the use of normal metals a method of electrodeposition from solution is implemented. A good example of that is growing nanosized threads in porous matrix,² or creating multilayer structures with many interchanging layers.³ Many technological problems connected with the technique of superconducting materials vacuum sputtering could have been avoided if the method of electrodeposition from solution was used instead. However, electrodeposition of Nb layers from solutions under regular conditions is still an unaccomplished task, and frequently used lead layers with nanometer thickness oxidize easily, losing their superconducting properties. At the same time intermetallic Pb₇Bi₃ is more resistant to oxidation and has a superconducting transition temperature T_c = 7.8 K, yet the known methods of electrodeposition of PbBi alloy using water electrolytes do not guarantee any reproducibility of layers phase composition and properties. Our approach to obtaining metallic alloy layers consists of using electrolytes on the basis of complex-forming aproton-dipolar solvent, which allows us to obtain films from alloys (including intermetallic compounds ones) both in electroless process⁴ and using the method of pulse electroplating.⁵

The distinctive feature of thin films obtained under such conditions is their nanocrystalline structure. The main goal of the present study is the development of the PbBi electrodeposition techniques of nanocrystalline films and investigation of their superconducting properties. PbBi films with the characteristic thickness of 20–100 nm were grown from the solution on brass and copper substrates using pulse electroplating. The sample of 5 cm² was used as a cathode whereas platinum foil had the role of the anode. Rectangular current pulses were sent through the electrolyte solution, the amplitude of 100–400 mA and pulse length 3–50 msec were controlled via density was varied in the range of 50–100 mA/cm². The electrolyte contained ions of Pb²⁺, Bi³⁺ or Pb²⁺, Bi³⁺ and Ce³⁺ in organic aproton-dipolar solvent.⁵
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The transport and superconducting properties of the obtained films were measured using standard 4-point scheme. The resistance of the films was examined at different temperatures from 300 K down to the superconducting transition around 7.8 K and then the critical field $H_c$ was measured at 4.2 K. SEM Supra V50 and Siemens D500 systems were used for the investigation of the film composition, morphology and X-ray analysis (Cu Kα-radiation) respectively.

Figure 1 shows the diffraction pattern of Pb/Bi-71/29 at.% film, grown on brass substrate by pulse electroplating, the film thickness is 80 nm. The X-ray analysis reveals the single phase surface Pb7Bi3, which has a hexagonal close-packed structure (SG.P63 mmc) having the following lattice parameters $a = 3.5058 \text{ Å}$, $c = 5.7999 \text{ Å}$ respectively, and texture parallel to (101) plane. The film surface morphology is presented in Figure 2.

The dependence of the film resistance versus temperature is quite predictable, see Figure 3(a), and demonstrates the superconducting transition around $T_c = 7.8 \text{ K}$, which agrees well with the data for bulk intermetallic Pb7Bi3. The PbBi film doping with Ce was performed by adding sols of Ce into the electrolyte. The maximal critical temperature $T_c$ of 10.3 K (Fig. 3(b)) was obtained at Ce salt concentration around 0.06 mol/l, while the additional increase of the salt concentration does not result in further $T_c$ growth.

At 4.2 K, well below the superconducting transition, the critical field $H_c$ is reached around 7 kOe if the external magnetic field is applied perpendicular to the film surface (Fig. 4).

The composition of the Pb/Bi-71/29 at.% film with $T_c = 10.3 \text{ K}$ was determined. The diffraction pattern indicate the presence of Pb7Bi3 phase and around 10% of a secondary phase with the central reflex corresponding to Bi ($T_c$ for Bi 6.17 K therefore the basic contribution to superconducting transport properties is done by phase Pb7Bi3).
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Fig. 3. (a) Temperature dependence of resistance for Pb-Bi film. (b) Temperature dependence of resistance for Pb-Bi+Ce film.

The morphology of the film surface is characterized by the nanocluster 20–30 nm grain structure (Figs. 2(a, b)), which indicates a significant grain size decrease, see Figure 2 for comparison. Such structure formation is obviously caused by adding Ce atoms. A $T_c$ increase for the film doped with Ce can be related to its nanocluster structure. It was previously theoretically predicted that the critical temperature increase can occur in metallic ordered nanocluster systems.\(^7\) The influence of Ce doping on superconducting properties of electrodeposited PbBi films is not entirely clear, in particular the film nanoclustered structure should be studied in more detail.

References and Notes


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