Lithuanian Journal of Physics, Vol. **45**, No. 1, pp. 53–57 (2005)

TRANSPORT PROPERTIES AND STRUCTURE OF THIN Bi FILMS PREPARED AT CRITICAL SUBSTRATE AND ANNEALING TEMPERATURES

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Received 20 September 2004

The magnetoresistance (MR), sheet resistance ($R_\square$), and structure of vacuum-deposited thin bismuth films with 0.3 to 1.5 μm thickness prepared on noncrystalline dielectric amorphous substrate were investigated as a function of substrate (T_S) and annealing (T_A) temperatures. The investigations were mainly focused on films prepared at critical T_S and T_A temperatures, at which essential changes in film structure and magnetoresistance value were obtained. The existence of these temperatures is associated with the intensive growth of high-quality crystallites. The mechanism of this phenomenon is discussed. In the case of annealed 1–1.5 μm thick films, the size of these crystallites ranges from 50 to 200 μm. It was demonstrated that such films have large transverse magnetoresistance ranging up to 170% for 1.5 μm thick films at 293 K in 2.5 T magnetic fields.

Keywords: evaporation and annealing, bismuth, thin films, magnetoresistance

PACS: 68.03.Fg, 68.55.Jk, 73.50.Jt

1. Introduction

Bismuth is a semimetal with electronic properties related to its highly anisotropic Fermi surface and small effective carrier masses. The carrier mean free path is many orders of magnitude larger than in most metals. However, applications of bulk single crystals are limited by their low mechanical strength and the complicated technology required to prepare single devices. For this reason, more and more attention was directed towards the investigation of thin Bi films, which were extensively studied due to their quantum transport [1, 2], finite size [3, 4], thermoelectric [5] effects, anisotropy effect in the uniaxially deformed polycrystalline film [6, 7], and large negative magnetoresistance phenomenon in quantizing magnetic fields [8, 9]. It was demonstrated that thin Bi and Bi–Sb films can be used for the development of deformation and magnetic field sensors [2, 10].

High-quality single crystal (epitaxial) Bi films exhibit at low and room temperatures large magnetoresistance (MR) effects [2, 3, 11]. However, the fabrication of such films is expensive and complicated because it requires the use of molecular beam epitaxy growth techniques [11] or electrolytic deposition (electrodeposition) on oriented single-crystal substrates equipped with special annealing techniques [2, 12].

Thus, it is necessary to simplify the technological process by which Bi thin films are prepared, which enable one to fabricate films with properties similar to that obtained in bulk single crystals. A widely used inexpensive method for preparing Bi films is the condensation of bismuth vapour on to a dielectric substrate in high vacuum. However, thin Bi films deposited on noncrystalline substrates by this method contain a large number of structural defects and are affected by large mechanical strain. One of the possible measures for improving the quality of these films is to anneal them. But even at high annealing temperatures (near to the melting temperature of the film, T_M), the process of recrystallization of these films drags on for many hours. The possibility of obtaining films of high quality is limited. On the other hand, changes in the film structure and properties occuring at high temperatures are not clearly understood.

In this article, we report on the properties of thin bismuth films, produced by the annealing process at temperatures T_A close to the melting temperature T_M and demonstrate that there is a critical regime at which high-quality films can be grown.

ISSN 1648-8504

2. Experimental

Bismuth thin films were prepared by thermal vacuum evaporation onto substrates made from corning 7059 glass. The deposition of 99.999% pure Bi was performed by using a molybdenum boat at a pressure of 10^{-6} Torr and an evaporation rate $\sim$1.5 nm/s. The substrates were cleaned in detergent solution and rinsed in deionised water, after which they were dried and annealed in high vacuum at a temperature of 573 K. The distance between the Bi source and the substrate was about 10 cm. The film thickness d was varied from 0.3 to 1.5 μm.

In order to investigate how substrate temperature and annealing in vacuum affects the properties of these films, the temperature gradients of T_S and T_A were induced along an 8 cm length substrate strip. The gradient was created by irradiation from a flat-shaped heater, whose planar surface was directed at a certain angle to the strip plane. The temperature of the substrate (T_S) during deposition was from 293 to 470 K. The annealing investigations were performed on a thin film strip deposited at 390 K.

The annealing investigations were performed when the hottest end of the film strip was higher than the T_M of bulk bismuth (544.45 K). The electric sheet resistance $R_\Box$ (resistance per square of the films having the same thickness) and transverse magnetoresistance (MR) of the films were measured at room temperatures. Samples were in the shape of 2 mm wide strips cut off from an 8 cm long substrate perpendicular to the temperature gradient direction. The electrical contacts were made from thin silver films that were deposited onto Bi films using suitable masks. For substrate temperature measurements, copper–constantan thermocouples were glued to the substrate with talc-cement.

The magnetoresistance (MR) was measured in permanent magnetic fields with inductance of up to 2.5 T. MR was calculated by using the ratio

$$\frac{R(B) - R(B=0)}{R(B=0)},$$

where $R(B)$ and $R(B=0)$ are the film resistances at a certain magnetic field and the zero magnetic field, respectively. The structure and size of the crystallites were studied by means of an optical microscope.

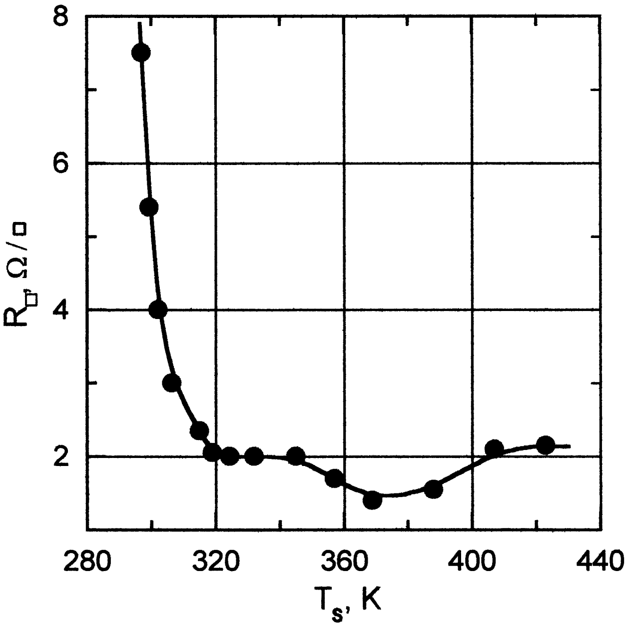

Fig. 1. The dependence of the sheet resistance $R_\Box$ of bismuth thin film with thickness $d = 0.8$ μm measured at 293 K on the substrate temperature T_S.

3. Results and discussion

3.1. The films deposited at 293 K < T_S < 420 K

It was found that thin Bi films with thicknesses greater than 50 nm, deposited at temperatures in the range 293 K < T_S < 380 K, were polycrystalline with a preferential [111] orientation [6]. Unusal changes in the thin film structure and electrical resistivity were found to occur in a certain range of T_S. Figure 1 shows the typical sheet resistance $R_\Box$ versus T_S dependence of films with thickness $d \approx 0.8$ μm measured at the room temperature. An abrupt drop of $R_\Box$ occured in the T_S temperature range of 293–320 K. This drop is associated with the growth of the crystalites and the decrease in the number of imperfections when T_S increases. However, further increase in T_S up to 345 K did not cause any visible changes in $R_\Box$. In the temperature range 345 K < T_S < 410 K, the $R_\Box$ versus T_S curve has regions of decrease and increase. It was found through the optical microscope investigation that the decrease of the value of $R_\Box$ is caused by fast growth of the crystallites when T_S increases. The biggest crystallites are found in the films deposited at $T_\mathrm{S} \approx 373$ K. They had a diameter of a few micrometres, which is much larger than the thickness of the Bi films. The changes in the film structure in the range 345 K < T_S < 380 K occurs because of increase of the dispersed liquid phase of Bi, which stimulated the growth of crystallites. At higher temperatures T_S (370 K < T_S < 410 K), where the concentration of the liquid phase increases, the mechanism of formation of the crystalline phase was changed. At T_S > 410 K, the crystalline phase was not formed directly from the vapour phase, but mainly from the dispersed liquid Bi phase. This induces changes in the crystalline structure of the Bi film. When T_S increases, polycrystalline spherical granules consisting of small, chaotically oriented crystallites begin to form and the film gradually changes to a new state.

It was found that at $T_S < 370$ K, the roughness of the film surface increased as d increased and that at $d > 1$ μm, the surface has dendrite-shaped structures.

3.2. The films deposited at $T_S > 400$ K

Figure 2 shows the typical dependence of $R_\square$ and MR at $B = 0.4$ T versus T_S for films with $d = 0.4$ μm measured at room temperature. As it can be seen, in the temperature range 380 K< T_S <435 K, the linear increase in MR is accompanied by a nonlinear decrease in $R_\square$. It demonstrates that MR depends mainly on the size and quality of Bi crystallites, while $R_\square$ is also affected by intercrystallite boundaries. At temperatures in the range 380 K< T_S <395 K, the surface of thicker films was matted and had a granular structure. At higher T_S, the film changes gradually to a monolayer polycrystalline structure and the surface glitters. Increasing T_S from 400 K to 435 K makes the structure of the film more perfect, as a result of increase in the size of the crystallites and decrease in the number of imperfections. At 435 K, it was found that the $R_\square$ abruptly drops and then slowly increases with increase in T_S (Fig. 2). However, these changes in $R_\square$ are not accompanied with any peculiarities in the MR versus T_S dependence, which was linear up to $T_S = 450$ K. This could be explained by assuming that in the temperature range 400 K< T_S <435 K, the film was transformed into a new heterogeneous state consisting of high-quality crystallites exhibiting large carrier mobility and, thus, large MR values. The decrease in MR at $T_S > 450$ K is caused by an increase in $R_\square$. This effect can be explained by assuming that at $T_S > 450$ K, small-insulated islets of liquid bismuth are formed during film growth. Investigations using an optical microscope showed that at $T_S > 460$ K, large single crystallites surrounded by Bi-free areas and islets of Bi (drops) appeared. The size of these crystallites was several tens of mm at $T_S > 470$ K. The biggest crystallites were found when T_S was about 480 K. Such film structures are caused by a strong decrease in the concentration of crystallization centres and by an increase in recrystallization process during which crystallite growth was accompanied by material transition from the liquid phase to the crystalline phase.

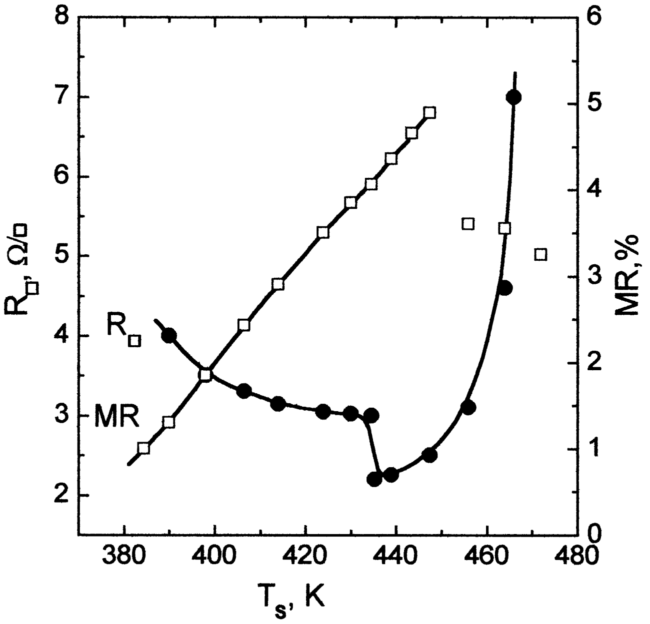

Fig. 2. The dependence of the sheet resistance $R_\square$ (full points) and magnetoresistance (MR) at $B = 0.4$ T (open points) of the bismuth thin film with thickness $d = 0.4$ μm measured at 293 K versus the substrate temperature T_S.

It was found that an increase of d from 0.3 to 1.5 μm increases the value of MR. At $d < 1$ μm, the MR versus d dependence is sublinear and tends to saturation when $d > 1$ μm. This is due to the surface scattering influence on the mobility of the charge carriers.

3.3. Annealing effects

As demonstrated above, the deposition of thin bismuth films at necessary values of T_S is an effective way to obtain high-quality Bi films. However, to prepare films having an extra-high quality structure, the film has to be annealed. It is known that the film melting temperature T_M is dependent on its thickness and the degree of defectiveness of its crystalline structure. We assume that at T_M, the growth of the crystallites is not interrupted, only the conditions of their growth changes. In order to verify these assumptions, the effects of annealing on the structure and MR of the films annealed at temperatures $T_A > T_S$ was investigated. The films were plated at $T_S \approx 390$ K. They were kept in vacuum for 30 min at the temperatures $T_A > T_S$.

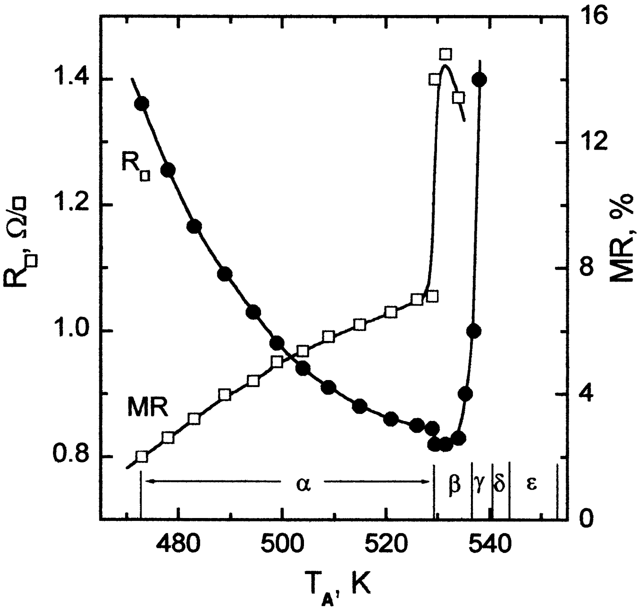

Fig. 3. The dependence of the sheet resistance $R_\Box$ (full points) and magnetoresistance (MR) at $B = 0.4$ T (open points) of the bismuth thin film with thickness $d = 1.2$ μm measured at 293 K versus annealing temperature T_A.

So much time was necessary to stabilize the gradient of T_A.

Figure 3 shows the $R_\Box$ and MR versus T_A dependence for films with $d = 1.2$ μm at $B = 0.4$ T and $T = 293$ K. It was found that, depending on T_A, the film exhibited different surface structures. The surface of the film annealed at a T_A ranging from 370 to 390 K was slightly matted, however, at higher T_A, i. e. up to 530 K, it was flat and had a characteristic metallic reflection. In this T_A range (α), $R_\Box$ decreased as T_A increased, while MR increased from 2% to 7% (Fig. 3). For T_A ranging from 530 to 536 K (β region), extra-high quality films consisting of large (up to 200 μm long) crystallites, whose trigonal crystallographic axes were oriented at small angles to the surface of the substrate, were obtained. In this case, after a small drop of $R_\Box$ at $T_\mathrm{A} = 530$ K, increases in the annealing temperature did not influence $R_\Box$, however, the value of MR increased abruptly. Further increase in T_A demonstrated that the film was transformed into a state containing small spherical islets of hardened bismuth located between large single crystallites. When T_A was changed from 536 to 540 K (γ region), large increases in $R_\Box$ were accompanied by small decreases in MR. Annealing at $T_\mathrm{A} > 540$ K showed that two regions (δ) and (ε) with different film structures can be obtained. It is typical of region δ that films annealed at 540 K$<$ $T_\mathrm{A} < 546$ K consist of big crystallites having different configurations in a background of small spherical bismuth islets. Films annealed at T_A ranging from 546 to 566 K (region ε) consisted mainly of spherical bismuth islets ("tropes") of almost the same size.

The increase in film quality annealed at $T_\mathrm{A} \approx 530$ K is associated with changes in the recrystallisation process. At the melting temperature T_M, only part of the crystallites begins to disintegrate. In this case, melted crystallites create favourable conditions for growth of the crystallites having more ordered crystalline structure. Measurements of MR performed at 293 K in 2.5 T magnetic fields for films with $d = 1.5$ μm showed that it was up to 170%. This value was larger for these films in comparison with thicker (10–20 μm) films in which the influence of surface scattering of charge carriers on their mobility was negligible. It should be noted that the MR for $d = 10$ μm suitably annealed single-crystal films fabricated by electro-deposition onto a Si(100) wafer with a thin Au underlayer [2] and epitaxial Bi films grown by MBE on semiinsulating CdTe substrate [11] at 293 K in 2.5 T was 95% and 109%, respectively.

4. Conclusions

It was demonstrated that, by changing the substrate and annealing temperature of vacuum-deposited thin Bi films prepared on a glass substrate, it is possible to obtain conditions at which these films exhibit large transverse magnetoresistance. The highest quality films were produced when the annealing process was performed at temperatures near the film melting temperature. At such conditions, crystallites having less perfect structure are transformed to the liquid state and serve as a source of formation for large, more ordered crystallites. The results show that Bi films prepared by this method on noncrystalline substrate are sufficiently high quality to be used in variety of technical and practical applications, e. g., for development of high-sensitivity magnetic field sensors operating at room temperature.

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Bi PLONŲ SLUOKSNIŲ, GAUTŲ ESANT KRITINĖMS PADĖKLO IR ATKAITINIMO TEMPERATŪROMS, TRANSPORTO SAVYBĖS IR STRUKTŪRA

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Santrauka

Naujos Bi sluoksnių fizikinių savybių panaudojimo perspektyvos skatina pastovų domėjimąsi ir jų plonais sluoksniais, kurių pagrindinis privalumas – labai paprasta ir pigi jų gamybos technologija. Nežiūrint didelio skaičiaus darbų, skirtų šių sluoksnių savybėms tirti, dar ir dabar yra nemažai esminių, mažai tirtų klausimų.

Pateikti Bi plonų sluoksnių ant amorfinių padėklų, gautų vakuuminio garinimo būdu, esant padėklo temperatūrai (T_S) artimai kritinei, tai yra, tame T_S intervale, kuriame sluoksnio savybės kinta iš esmės, tyrimų duomenys. Tokių T_S sričių yra dvi. Viena jų, esanti 345 K$<$ T_S $<$410 K intervale, susijusi su sluoksnio susidarymo iš garų fazės mechanizmo pasikeitimu, t. y. perėjimo nuo mechanizmo “garų fazė – kieta fazė” prie mechanizmo, kai kieta fazė susidaro per dispersinę skystą Bi fazę. Šios T_S srities pradžioje, iki 373 K, kurioje vyrauja pirmasis mechanizmas, dispersinės skystos Bi fazės buvimas skatina kristalitų augimą bei jų fizikinių savybių gerėjimą didėjant T_S. Kristalitų matmenys toje srityje siekia kelis mikronus. Antroji sritis, $T_\mathrm{S} > 435$ K, susijusi su staigiu kristalizacijos centrų mažėjimu didėjant T_S ir skystos Bi fazės sričių susidarymu. Toje srityje kristalitų matmenys gali pasiekti kelias dešimtis mikronų.

Sluoksnio kristalinės būsenos ir fizikinių savybių priklausomybės nuo atkaitinimo temperatūros (T_A) tyrimais parodyta, kad, T_A priartėjus prie sluoksnio tirpimo temperatūros (T_M), kristalitų matmenys, didėjant T_A, ima staigiai didėti. Toje T_A srityje kristalitų skersmuo gali pasiekti kelis šimtus mikronų. Didelė magnetovarža (MR) žymi gerą tokių sluoksnių kokybę. Šioje srityje MR vertė priklauso nuo sluoksnio storio ir, kai $d > 1{,}5$ μm, priartėja prie monokristalinių sluoksnių MR verčių. Aiškinama, kad tas reiškinys atsiranda dėl to, kad polikristalinių sluoksnių tirpimas dėl skirtingo kristalitų susitvarkymo laipsnio yra nevienalytis, todėl, kai T_A artima T_M, tik dalis kristalitų lieka stabilūs, o kiti pradeda tirpti. Tokia padėtis sudaro palankias sąlygas stabiliems kristalitams augti nestabilių kristalitų sąskaita. MR priklausomybė nuo sluoksnio storio tiesiogiai susijusi su paviršiaus sąlygota krūvininkų sklaida. Sluoksnio storiui pasiekus krūvininkų laisvo kelio ilgį (apie 1,5 μm kambario temperatūroje), ši sklaida tampa nežymi. Tinkamiausio atkaitinimo režime gautų sluoksnių savybės, esant toms pačioms sąlygoms, yra artimos monokristalinių sluoksnių savybėms. Todėl jie gali būti pritaikomi praktikoje.