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In-situ investigation of Bi thin film condensation by surface sensitive X-ray absorption spectroscopy at cryogenic temperatures

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Abstract. Reflection mode grazing incidence X-ray absorption spectroscopy at the Bi L₃-edge and simultaneous electrical resistivity measurements were used to investigate the microstructure of quench condensed thin Bi metal films on float-glass substrates at temperatures from 20 K to 300 K. While thin films of ≈ 6 nm thickness appear to be amorphous after deposition at 20 K, thicker films of about 18 nm show the well-known rhombohedral structure of bulk Bi. During a subsequent heat treatment, the amorphous structure of the thin films transforms irreversibly into the crystalline form for temperatures at (42 ± 2) K. This crystallisation is accompanied by an irreversible increase of the film resistivity by a factor of more than 2.7. The film density and roughness do not change within detection limits during the heat treatment.

1. Introduction

Thin Bi films quench-condensed on glass substrates at temperatures below approx. 50 K show several unique physical properties. For example, while bulk Bi has a positive temperature coefficient of resistivity (TCR) [1], negative TCR values are reported for thin Bi films [2]. Quench-condensed Bi films are superconducting with a critical temperature of about 10 K, while bulk Bi is a semimetal revealing no superconductivity down to the mK regime [3]. However, those outstanding properties are transformed into the bulk-like behaviour of bismuth if the films are heated above a critical temperature T_C , which is accompanied by a structural transition to the well-known rhombohedral structure. The value of T_C depends on the film deposition rate, the vacuum conditions and especially on the Bi film thickness, with typical values in the range from about 10 K to more than 50 K [3,4]. While films with a thickness of 60 nm are spontaneously transforming into rhombohedral structures even for temperatures below 4 K, the critical temperature may reach 70 K for a film thickness below 10 nm [4].

Quench-condensed films are generally metastable and thus their microstructure is difficult to characterize, because in situ investigations at low temperatures are necessary. Most investigations of quench-condensed films performed so far are based on electrical resistivity measurements only, some combined with low temperature scanning tunnelling microscopy (STM) [5]. However, STM only probes the outermost surfaces of the deposited films and provides no information of the inner film structure. Furthermore, STM is a local probe, i.e. only small surface areas can be probed. We have therefore studied metastable Bi thin film phases which are deposited on float glass substrates held at temperatures of 20 K under ultrahigh vacuum conditions using a combination of simultaneous surface

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sensitive grazing incidence X-ray absorption spectroscopy, X-ray reflectometry and electrical resistivity measurements.

2. Experimental details

The X-ray experiments were performed at beamline BL8 [6] using the synchrotron radiation emitted by the superconducting asymmetric in the DELTA storage ring (Dortmund, Germany) operating with 1.5 GeV electrons and injection currents of 130 mA. A photo of the setup at the beamline and a schematic representation of the experiment are given in figure 1. A double-crystal monochromator with two flat Si(111) crystals was used. Incident (I_0) and reflected (I_1) intensities were measured by nitrogen- and argon-filled ionization chambers, respectively. A third ionization chamber (I_2) was used for the measurement of a Bi-metal reference foil simultaneously with the reflection mode spectra of the sample. The incident X-ray beam (8 mm width) was collimated vertically by a 200 µm slit and enters the ultrahigh vacuum chamber via a differentially pumped Kapton window [7]. Bi films were evaporated from resistively heated tungsten boats in an ultra high vacuum of less than $5 \cdot 10^{-10}$ mbar with a deposition rate of (0.20 ± 0.05) nm/s. Film thicknesses as well as deposition rates were monitored by a calibrated quartz crystal thickness monitor. The deposition took place on thoroughly cleaned float glass substrates (40 mm length, 30 mm width), that were mounted on the oxygen-free Cu sample holder of the liquid helium cryostat (Model ST-400, Janis Research, Wilmington, USA). The electrical resistivity measurements were performed using a conventional four point probe technique simultaneously with the X-ray experiments. The whole setup was mounted on the multipurpose 6circle diffractometer of BL8, which allows a precise positioning of the sample surface in the X-ray beam [6]. Further details of the experimental setup are presented elsewhere [8,9].



Figure 1. Photo and schematic representation of the experiment setup at BL8 at the DELTA storage ring. The vacuum chamber with the cryostat is mounted in the swing of the diffractometer, which allows a precise adjustment of the sample in the monochromatic X-ray beam, which is reflected downwards at the samples surface. The monochromatized X-ray beam enters from the right.

3. Results and discussion

In figure 2(a) the electrical resistance of a Bi film with a thickness of 5.9 nm during annealing is presented. The resistance exponentially decreases during deposition at $T_D=20$ K, until a thickness t of about 4.5 nm is obtained, as can be seen in the inset in figure 2(a). Above this critical thickness t_c, no

substantial changes of the film resistance of about 0.46 k Ω can be measured with increasing thickness, indicating that the film is continuous from t_c on. Compared to the bulk metal, the thin films generally show a significantly increased specific resistivity ρ directly after deposition. For example, for a film of 5.9 nm thickness, a resistivity of 390 $\mu\Omega$ cm was observed, compared to a value of $\rho_{bulk} \approx 5.7 \,\mu\Omega$ cm for bulk Bi at 20 K [10]. This extremely high value is directly related to the size effects at low film thickness and the high structural disorder of the films. The latter is furthermore responsible for the negative TCR value of $-1.72 \,\mu\Omega$ cmK⁻¹ which was observed between the deposition temperature and an annealing temperature of T_c = 42 K.



Figure 2. (a) Left: Resistivity ρ vs. sample temperature T_S of a (5.9 ± 0.1) nm Bi film quench condensed at $T_D = (20 \pm 1)$ K (A) onto a float-glass substrate during annealing. The substrate was heated to about 83 K (B) with a constant rate of 2 K/min and finally cooled to 30 K (C) again. Inset: Resistance of the film vs. film thickness during deposition. (b) Right: Grazing incidence X-ray absorption spectra at the Bi L₃-edge (13419 eV) at an incidence angle of $\Theta = 0.3^{\circ}$ at different stages of the annealing treatment. The curves are vertically shifted by 0.01 with respect to each other.

While the linear and reversible behaviour of the electrical resistivity observed between the deposition temperature and about 40 K indicates that no structural changes take place in this temperature region, the irreversible increase at 42 K indicates the presence of a temperature induced phase transformation. The heat treatment was stopped at about 83 K, and the film was cooled again to 30 K, showing again a reversible and linear behaviour with a negative TCR of -0.65 $\mu\Omega$ cmK⁻¹. Both the different TCR's before and after annealing as well as the dramatic irreversible increase of the electrical resistivity at 42 K suggest the presence of substantial modifications in the film structure.

In figure 2(b), typical reflection mode grazing incidence X-ray absorption spectra measured at the Bi L₃-edge during deposition and annealing of the 5.9 nm thick Bi film are presented for an incidence angle of $\Theta = 0.3^{\circ}$. This grazing angle is in the vicinity of the critical angle of total reflection (Θ_C) of Bi, which amounts to about $\Theta_C = 0.24^{\circ}$ at 13000 eV photon energy. In general, the analysis of reflection mode EXAFS spectra is not as straightforward as conventional transmission or fluorescence mode EXAFS, because both the real (δ) and the imaginary part β of the complex index of refraction n(E) = $1 - \delta(E) - i^*\beta(E)$, contribute to the reflectivity fine structure depending on the actual grazing angle and the photon energy E, while only the imaginary part is directly linked to the absorption coefficient μ by $\mu\lambda/4\pi$, (λ being the X-ray wavelength). As a consequence, the amplitudes of the reflectivity fine structure oscillations change considerably if the grazing angle is varied, and even the structureless (atomic) background is influenced accordingly. For small grazing angles, i.e. $\Theta < \Theta_C$, the reflectivity is generally high even in the vicinity of the X-ray absorption edge, and the amplitudes of

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the EXAFS oscillations are quite small. In the case of incidence angles larger than Θ_{C} , the overall reflectivity is small and so is the amplitude of the EXAFS, while in the vicinity of the critical angle, the edge jump, i.e. the absolute decrease in reflectivity at the edge as well as the absolute amplitude of the fine structure oscillations have their maximum amplitudes (see e.g. [11]). As a further consequence of the described relations, the extraction of μ from the reflectivity data is required for a detailed EXAFS data analysis yielding coordination numbers, distances and the local disorder around the atom of interest is possible. While such a procedure, e.g. making use of a Kramers-Kronig transform may be applied in the case of homogeneous samples or thin films with a film thickness substantially larger than the penetration depth of the X-rays into the material (see refs. [12-15]), it cannot be applied in the case of the thin Bi films investigated here: In any case, the penetration depth of the X-rays will at least be comparable to the film thickness, so that some contributions of the substrate are to be expected. In the present situation, we have therefore generally used incidence angles close to the critical angle of total reflection of Bi, in order to enhance the weak fine structure modulations that are generally observed in the case of Bi, having in mind however, that the measured fine structures include contributions of both β and δ , and even destructive interference may occur. Furthermore, we will restrict our data analysis to a qualitative comparison, and we will not determine coordination distances or even coordination numbers here for the reasons state above.

As can be seen in figure 2(b), only extremely weak XAFS oscillations with a low oscillation frequency were observed directly after deposition at 20 K. Such features are typical for amorphous atomic structures. After annealing to $T_s = 83$ K, the amplitude of the oscillations increased significantly, indicating substantial modifications in the atomic environment of the Bi atoms. Crystallization has occurred, leading to an atomic ordering at short distances. Those structural changes are irreversible because spectrum (C) which was taken after cooling down again to 30 K, does not differ from the profile recorded at 83 K. This is in agreement with the electric resistivity measurements of figure 2(a). After further annealing to $T_s = 345$ K, no additional changes can be observed, except the typical reduction of the amplitude of the fine structure due to the increasing amplitude of the thermal vibrations of the atoms. According to specular X-ray reflectivity profiles recorded for fixed photon energy, the density as well as the film roughness do not change substantially during the thermal treatment of the thin Bi film [9]. Therefore the comparison of the spectra presented in figure 2(b) which were measured under identical conditions, namely identical incidence angles, seems to be suited to follow the changes of the thin film structure. The interpretation of an ordering on short atomic length scales is supported by the low value of kT_c of about ~ 3.6 meV, which is small in comparison to the activation energies of most diffusion processes, which typically amount to more than some tenth of an eV. For example, the activation energy for vacancy diffusion amounts to 0.3 eV [16], and that for grain growth to 0.47 eV [17]. Therefore, thermally activated annealing and diffusion processes should be negligible at 42 K, and the observed structural modifications have to be caused by athermal processes. Small assemblies of atoms can crystallize athermally, release the heat of crystallization and may thus stimulate further crystallization of the initially disordered films. When the annealing process was stopped at temperatures slightly above T_C, the film resistivity did not increase further but remained on a constant level, suggesting that the annealing processes are not self-sustaining. The described changes of the short range order structure of the Bi thin films during annealing can be further detailed by analysing the Fourier-transforms of the reflectivity fine structures - the amplitudes of the nearest neighbour peaks increase considerably after annealing if the non-normalized reflectivity fine structures are investigated [9]. Both a significant increase of the nearest neighbour coordination that could already be anticipated from the raw reflection mode EXAFS data presented in figure 2(b) as well as distinct signatures of coordination shells at larger distances are clear indications for the crystallization of the initially amorphous thin Bi film [9].

Here we focus on the thickness dependence of the film structure during the quench condensation. Films with a slightly increased thickness of t = 10 nm still show the same growth and crystallization behaviour as the thinner film with about 6 nm thickness, i.e. they reveal an amorphous film structure after their deposition at $T_D = 20$ K, however, with a smaller crystallization temperature of about 35 K.

The reflection mode EXAFS spectra recorded directly after deposition at 20 K and after annealing at 77 K are compared in figure 3(a) for a grazing angle slightly smaller than Θ_{c} .



Figure 3. (a) Left: Comparison of the reflection mode EXAFS spectra of a 10 nm thick Bi film recorded for $\Theta = 0.2^{\circ}$ directly after deposition at $T_D = 20$ K and after annealing at 77 K. (b) Right: Comparison of the normalized difference (1-R) to an absorption spectrum of a Bi metal foil at 20 K.

Like in the case of the of the 5.9 nm thick film, the differences between the as-deposited and the annealed 10 nm sample are obvious. Clearly developed fine structures are observed for the annealed film, while almost no oscillations are visible for the as-deposited Bi-film. As a measure of the films absorption, we have calculated the difference (1-R) for a more detailed analysis, keeping in mind however the limits of such a simple extraction procedure that may lead to erroneous amplitudes, especially due to the lack of a clear background signal and the influence of both the absorption and the dispersion on the form of the spectrum. The normalized quantities are compared to the normalized absorption of a polycrystalline Bi metal foil measured in transmission at 20 K in figure 3(b). As can be seen here, the overall shape of the spectra calculated from the reflectivity data is different from those of the transmission mode spectrum especially in the pre-edge region. This is a clear signature of the influence of the dispersion on the spectra. However, if the two spectra from the thin film are compared to each other, the increase of the amplitudes of the fine structure oscillations are obvious, and furthermore, the near edge spectrum of the annealed thin film sample and the polycrystalline Bi reference reveal absorption minima and maxima at the same energies, and with very similar intensities. In contrast, the features of the sample in its as-deposited state only show significantly weaker extrema located at different photon energies.

Even thicker films with a larger thickness of 18 nm grow into a crystalline modification during deposition at 20 K as can be clearly deduced from figure 4, where in-situ collected grazing incidence reflection mode spectra are presented for two individual films and an incidence angle of $\Theta = 0.24^{\circ}$. The first film was deposited at 20 K, and investigated directly after deposition as well as after an annealing to 300 K. The absorption fine structure of this sample shows clear signatures of the crystalline rhombohedral bulk Bi phase directly after deposition, and those structures remain almost unaffected during heating to 300 K. Because of the thermal vibrations, the amplitude of the EXAFS oscillations is slightly reduced at 300 K, however, the similarity of both spectra is obvious. Furthermore, a second sample was deposited on the glass substrate at 300 K and cooled to 20 K for the measurement. Such samples are well known to crystallize in the bulk Bi structure (see e.g. [17-19]) and the measured X-ray absorption fine structure resembles exactly that of the first 18 nm thick sample. Furthermore, the similarity with the spectrum of the sample of 5.9 nm thickness after annealing (stages B and C in figure 2(b)) and the annealed 10 nm sample (figure 3) qualitatively supports the results of the data analysis.

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Figure 4. Grazing incidence X-ray absorption spectra of two Bi films of 18 nm thickness for an incidence angle $\Theta = 0.24^{\circ}$ and different experimental conditions as indicated. The first film was deposited on float glass at $T_D = 20$ K and was investigated at 20 K directly after deposition and after annealing to 300 K. The second film was deposited at 300 K and cooled down to T = 20 K for the measurement.

4. Conclusions

Thin quench-condensed Bi films of different thickness were investigated by a combination of electrical resistivity measurements and in-situ surface sensitive reflection mode X-ray absorption spectroscopy. The results suggest that films with a thickness of less than about 10 nm grow in an amorphous structure for substrate temperatures of about 20 K, which is generally not expected for a mono-elemental film material. The X-ray absorption data measured in-situ further suggest that the amorphous structures crystallize during annealing. In agreement with the electrical resistivity measurements, the critical temperature decreases from about 42 K for films of 6 nm thickness to ca. 35 K for films of 10 nm thickness. A further increase of the film thickness to 18 nm leads to the formation of crystalline Bi films even for deposition temperatures as low as 20 K, which clearly demonstrates the importance of the film thickness for the structural evolution of the films during growth.

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