Phase transitions of ultrathin Bi films on insulating substrates: Bismuth on Sapphire

ESRF	**Experiment title: Phase transitions of Quantum Size Effect driven metallic nanostructures on insulating substrates: Bismuth on Sapphire.**	**Experiment number**: MA 2475
Beamline:	**Date of experiment**: from: 01/07/2015 to: 07/07/2015	**Date of report**: 09/09/2015
Shifts: 18	**Local contact(s)**: Maciej Jankowski	*Received at ESRF:*

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Report:

Although the common phenomenon of melting and solidification have been studied for centuries, phase transitions of nanoscale Bi films are yet not fully understood as Bi shows such exotic properties at the smallest scales. Bi is a semi-metal with a very long (~30nm) Fermi wavelength and has therefore historically been studied for quantum size effects (QSE). As Bi is an allotrope material, showing different crystal structures, different (electronic) properties can be driven by choice of the substrate. A slight change in the geometrical structure of Bi can result in dramatic changes in its electronic bands [1]. Opening a gap in ultrathin Bi films is of utmost importance for future thermoelectric applications as well as for electronic applications. For this, insulating substrates for these unique thin film structures are indispensable, however not studied so far, as conducting substrates are dictated by the electron microscopy and diffraction techniques currently used in the field.

Therefore, the aims of this study were to study the growth of ultrathin Bi film structures and their phase transitions on insulating sapphire (α-Al_2O_3(0001)) substrates, to gain a deeper understanding of the growth observed with emphasis on the emergence and evolution of QSE driven thin film structures [2]. First, we focused on the growth of ultrathin Bi films studied by surface SXRD to determine the thickness together with oscillations indicative of the QSE. By elevating the sample temperature we observed shifting interference fringes in the SXRD curves indicative of the QSE as has been demonstrated for determining the QSE for Pb on sapphire [3]. Secondly, for slightly thicker films we observed phase separation of the mixture of Bi(003) and Bi(102) domains grown at RT, which transforms into a full Bi(102) layer at 200°C. Upon supercooling of a liquified Bi film, recrystalization results in a full Bi(003) film.

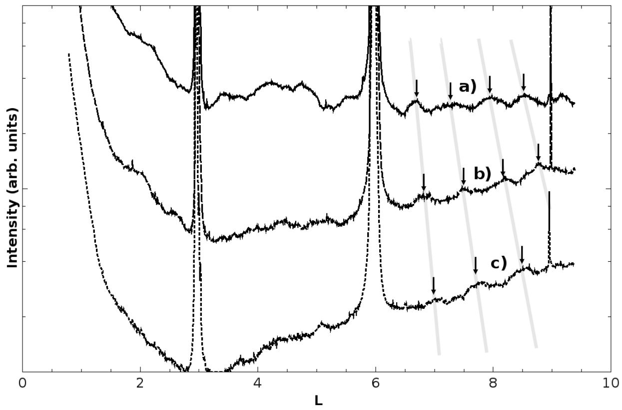

Figure 1: SXRD curves for a 0.5MLE Bi film deposited at RT on sapphire. The SXRD curves reveal shifting oscillations between L=6 and L=9 when elevating the sample temperature from RT (a), to 100°C (b) and 200°C (c).

Sapphire substrates were prepared by annealing for several hours at ~1050°C in a tube furnace and their cleanliness was verified by ex-situ Tapping-Mode Atomic Force Microscopy (TM-AFM) and X-ray Photoelectron Spectroscopy (XPS) at the University of Twente. After introducing the sapphire sample into the diffractometer vacuum chamber at ID03 (base pressure $1x10^{-10}$mbar), we continued substrate preparation by repetitive cycles of Ar sputtering followed by annealing (600°C) and cooling in an O-rich background pressure (~$1x10^{-7}$mbar) verifying the surface cleanliness by use of SXRD and HK maps. Bi was evaporated by an electron beam evaporator at a rate of ~2.5 monolayer equivalent (MLE) per minute, where the sample was at RT. The precise thickness of the Bi film was determined post-factum using the SXRD data.

X-ray reflectivity curves, see Fig. 1, obtained from submonolayer coverages of Bi deposited at RT and the same thin film annealed to 100°C and 200°C show a sharp Bragg peak from the sapphire substrate at L=6 (in substrates reciprocal lattice units). The oscillations, arising from interference fringes, found between L=6 and L=9 arise from the atomic layered structure of the Bi film. As the number of interference fringes is an estimate of the average film thickness, we found that for increasing the substrate temperature, the average film height decreases. From conservation of material, the grown islands are therefore expected to decrease their area which is in contact with the substrate. However, this increase in roughness of the film, and, as we expect here, island formation, will result in less pronounced oscillations in the reflectivity curve.

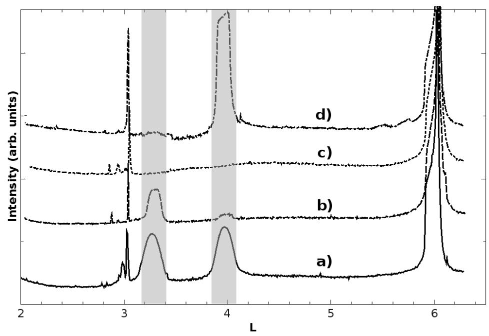

Figure 2: SXRD curves right after deposition of a 15nm thick Bi film on a sapphire substrate (a) revealing 42% Bi(003) coverage and 58% Bi(102) coverage. Annealing this film to 200°C, nearly all domains are transformed into Bi(102) domains (b). After cooling down from the Bi liquid phase (c), all Bi is found to recrystallize into Bi(003) domains.

When growing thicker Bi films, beyond the thickness where the QSE is able to reveal itself, Bi films show two different superstructures: Bi(102) and Bi(003) at similar ratios, see Fig. 2(a). Upon annealing to 200°C, a phase transition occurs for the Bi(102) phase, restructuring into the Bi(003) phase, see Fig. 2(b). Studying this single Bi(003) superstructure using HK-maps, we find this Bi film to have random rotations with respect to the substrate and revealing diffraction rings in the HK-maps corresponding to in-plane lattice distances for the Bi(003) structure, see Fig. 3(a). From the integrated intensity from the HK map plotted for 2θ, plotted in the inset of Fig. 3(a), it is clear that the Bi(003) has a slight in-plane lattice misfit with respect to the underlying sapphire substrate.

Upon elevated temperature, the Bi film liquifies as revealed in the SXRD curve in Fig. 2(c). Upon cooling, the liquid recrystalizes into a full Bi(102) superstructure. The HK-maps, and integrated intensity for 2θ, see Fig. 3(b), reveal the Bi(102) in-plane distance to match that of the underlying sapphire substrate.

The melting of the Bi(102) film is experimentally measured throught the diffraction intensity at L=3.25 while recording the sample temperature, see Fig. 4. Upon melting the Bi(003) superstructure, we find the phase transition from solid to liquid to occur very swift, within our resolution of the temperature measurement of 1°C, and above the bulk melting temperature of Bi being 271.4°C. Although supercooling of Bi thin films has been described in literature [4], superheating of Bi is unanticipated, but expected to be driven by the substrates influence on the thin film [5]. Upon cooling the liquid, recrystalization occurs at 106°C where this phase transition occurs slower (over 6°C), indicative of the nucleation and ripening of nanocrystals [2,3].

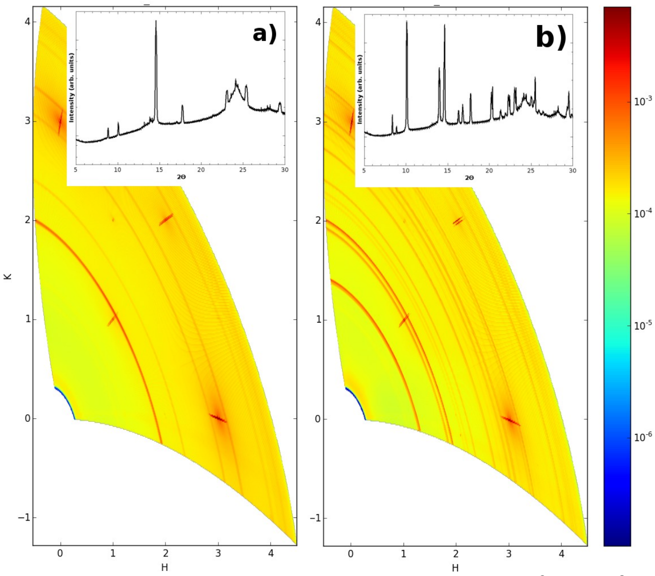

Figure 3: In-plane HK-maps together with calculated 2θ-scans for a 15nm thick Bi film on sapphire heated to 200°C (a) and cooled from the liquid phase down to RT (b) revealing the phase transition from a pure Bi(003) at 200°C to a Bi(102) phase after resolidification.

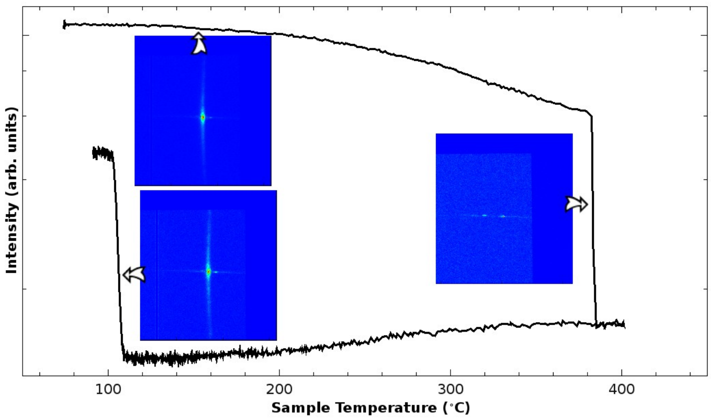

Figure 4: Melting and solidification curve for a 15nm thick Bi film on sapphire by tracing the intensity at L=3.25. Bi bulk melting is expected at 271°C.

References

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