# GROWTH AND DYNAMICS OF Bi THIN FILMS ON InAs(111) SURFACES

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## 1. Introduction

A new class of materials, the topological insulators, has opened a wide field of research. Bismuth, is the heaviest group-V semimetal; so its large spin-orbit splitting combined with the loss of inversion symmetry at the surface may result in a band structure which is not spin degenerate [1]. It is one of the key ingredients of this topological insulator family. With the aim of improving technological applications, especially the electronic devices, it is of highest importance to control the preparation of these materials as thin films.

The InAs (111) surface specific feature is that it has two different surface terminations: In termination (face A) and As termination (face B). Both faces show a specific reconstruction. By core-level photoemission we have identified a difference of chemical reactivity between A and B faces. Bi growth on A-faces tends to lead to a high quality monocrystal for films with a thickness of 10 monolayers.

In this work, the structural, chemical and electronic properties of Bi thin films deposited on InAs(111) have been investigated using soft x-ray photoemission electron microscopy (PEEM). PEEM allowed us to get snapshots, in both real space and reciprocal space, of the clean surface and of the changes it undergoes after Bi deposition and upon annealing. We found that the nature of the InAs surface plays a crucial role in the Bi growth mode. A morphology of circular patterns controlled by Bi atoms mobility is observed on the A side. The B side shows no particularly organized morphology due to a stronger chemical interaction between Bi and As atoms.

## 2. Experimental

The substrates were cut from a 0.5 mm thick n-type InAs(111) wafer (Wafer Technology Ltd., UK) doped with S with a carrier concentration of $3x10^{18}$ $cm^{-3}$ and polished on both sides, one being cation (In) terminated, the A side, and the other anion terminated (As), the B side, due to the lack of inversion symmetry of the InAs crystal. Both InAs(111)A and B surfaces were prepared by repeated cycles of ion bombardment ($Ar^+$, 600 eV) and annealing at 400° C. Bismuth was deposited from a Knudsen cell at a rate of about 0.5 BL/min.

The experiments were performed at the Nano ESCA beam line of the Elettra synchrotron radiation facility [2]. Using synchrotron radiation(p-polarised light) both element specific images and small-spot chemical state images can be recorded by photoelectron spectroscopy; k-space imaging by angle-resolved photoelectron spectroscopy (ARPES) can be done as well. The ARPES spectra were taken with a photon energy hν of 43 eV, as well as

most Bi 5dand In 4d PEEM images; some In 3d , As 4d and Bi 5dcore level PEEM images were recorded at $h\nu$ = 100 eV. The spatial resolution was better than 1 μm. The energy resolution was about 0.3 eV. All measurements have been made at room temperature.

## 3. Results and discussion

### 3.1. Clean InAs(111) surfaces

The LEED patterns show a (2 x 2) reconstruction for the A side and a non-reconstructed surface for the B side in agreement with previously reported investigations (see e.g. Ref. [3]). Identical electron energy bands in the Γ–M direction are observed for both sides (not shown). The bands are in agreement with previously published ARPES spectra [4], namely, very close to the Fermi energy ($E_F$) and in the vicinity of the Γ point we observe the presence of an electron accumulation layer for both surfaces [4], [5]. The analysis of the In 4d and As 3d core level photoelectron spectra reveals the same components as those previously reported in Ref. [6]; thus these spectra are not shown here.

### 3.2. Bi/InAs(111) interfaces

Bismuth was then deposited on such prepared A and B sides. Epitaxial growth on the A side leads to a high-quality Bi monocrystal already after deposition of several BL of Bi whereas, for the same coverage, the B surface induces formation of islands. However, after deposition of ≈30 BL the crystal quality is almost the same for both sides. For this reason, films with this thickness were initially prepared for our studies.

As an example, we show in Fig. 1 the results for the deposition on the B side. The mercury lamp image shows a "granularity" on a scale of 1 μm. More quantitative information can be obtained from the threshold spectra across the whole field of view and the result is mapped in Fig. 1(a). The histogram of the work function distribution shown in the inset to Fig. 1(a) is centred on4.37 eV with a full width half maximum of 50 meV. This is a strong evidence for a chemically uniform surface. The nearly uniform work function across the field of view suggests that the contrast is rather of topographical nature.

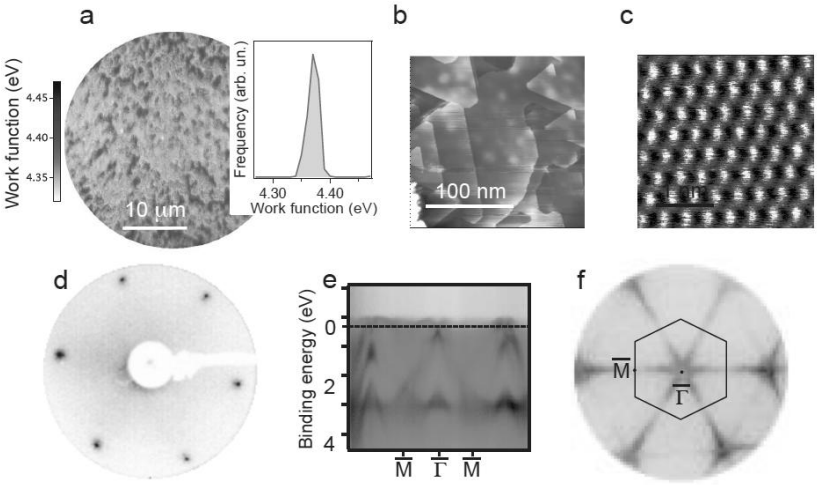


Fig. 1: *30 BL Bi/InAs(111)B: (a) Work function map taken with the mercury lamp and work function histogram (inset); (b) STM image showing terraces with a six-fold symmetry; (c) STM image showing the hexagonal arrangements of the Bi atoms on a terrace; (d) Bi/InAs(111)B-(1 x1) LEED pattern (at 33 eV); (e) ARPES in the Γ–M direction; (f) Fermi surface [the Bi(111) surface Brillouin zone with relevant high symmetry points is shown]*.

This is confirmed by scanning tunnelling microscopy (STM),which shows [see Fig. 1(b)] six-fold symmetry patterns at a scale of 100 nm corresponding to Bi(111) terraces. This

observation is very similar to the one done on films of $Bi_2Se_3$(which has the same crystalline structure as Bi) grown by molecular beam epitaxy on $SrTiO_3$ (111) substrates [7]. The STM image[Fig. 1(c)] shows a perfect hexagonal arrangement of closed-packed Bi atoms, without any presence of allotrope structures.

The excellent crystallinity of the terraces is also confirmed by the sharp Bi/InAs(111)-(1 x 1)LEED pattern [Fig. 1(d)] as well as by the well-defined energy bands and Fermi surface obtained by ARPES [Figs. 1(e) and (f), respectively] that are identical to those observed for the (111) surface of bulk bismuth (see e.g. Ref. [8]).One can recognize the hexagonal electron pocket at the centre of the Fermi surface, surrounded by six "petal" hole pockets along the Γ–M directions.

3.3. Annealed Bi/InAs (111) A interface

The deposited films were then annealed. We stepwise increase the temperature, looking at the surface morphology by recording at each step the PEEM image matrix over the threshold-close valence band with the mercury lamp. An important change in the images starts to appear at an annealing temperature of ~ 230°C [see Fig. 2(a)]. This is not unexpected because this temperature is close to the melting point of bismuth, which means that the mobility of Bi atoms is then greatly enhanced, some evaporation not being excluded. One notes that the long-range homogeneity observed in Fig. 1(a) has been broken and that small terraces of the original surface gain in size, spanning now a few 100 $\mu m^2$.

At the same time, the observed modification due to the enhanced mobility of Bi atoms does not alter the crystal quality of the remaining film because the large terraces still retain the six-fold symmetry. This is further demonstrated in Figs. 2(b and c) showing that the film has the all-over characteristics of the electronic band structure and of the Fermi surface of Bi (111) [see also Figs. 1(e and f) for comparison]. So, the thickness of the terraces must be large enough to stand for a bulk crystal and the structure is that of the original film.

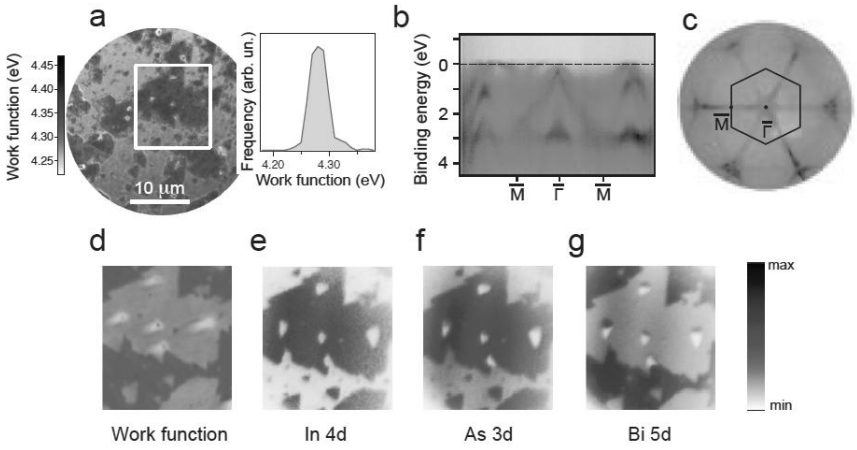


Fig. 2: *30 BL Bi/InAs(111)A sample after annealing at 230◦C: (a) Work function map and work function histogram; (b) ARPES in the Γ–M direction; (c) Fermi surface [the Bi(111) surface Brillouin zone with relevant high symmetry points is shown for reference]; (d) work function image for the region indicated by the white frame in (a); (e–g) In 4d, As 3d and Bi 5dPEEM corresponding energy filtered images of the white frame area.*

The annealing brings as well other new features with it. In the middle of the terraces one remarks small white triangular regions that can be attributed to the formation of Bi clusters as will be proven by Bi 5d core level PEEM. This is better seen in Fig. 2(d), which is the energy filtered work function image at $E - E_F = 4.7$ eV of the region shown on the work

function map by a white frame [Fig. 2(a)]. Here we have chosen $E - E_F$ such that the thickness of the Bi layer scales the darkness of the colour. In all other figures [Figs. 2(e–g)] corresponding to PEEM images recorded at the maximum intensity of the In 4d, As 3d and Bi 5d photoelectron signals the white shadows are observed as well. One can also remark that the white triangles are present only on the thinner Bi terraces (light blue colour in the work function image). Clearly, at the given annealing temperature and due to higher atom mobility, bismuth has the tendency to deplete the surface of the substrate and agglomerate in clusters. We attribute these white triangles to the drop shadow (absence of photoemission intensity) resulting from the presence of clusters, as the triangles exist in the same place whatever the core-level or valence-band energy-filtered PEEM image is considered. Moreover, a closer inspection of element-sensitive images in Figs. 2(e–g) reveals the presence of Bi clusters appearing as small dark dots at the upper part of the triangles in Fig. 2(g).

When going from Fig. 2(d) to Figs. 2 (e and f), the contrast is reversed, testifying the presence of In and As in about the same proportion on the light blue central terrace of Fig. 2(d). Note that the slight variation of photoemission intensity across the terrace is due to an inhomogeneity of the synchrotron light and not to a concentration gradient across the sample. The contrast is again reversed in Fig. 2(g), measured at the maximum of the Bi $5d_{5/2}$core level photoemission, indicating a small concentration of bismuth inside the terrace, except on the spots above the white triangles, as discussed above. On the contrary, outside the terrace, there is a massive Bi signal, corroborating our attribution of Bi film thickness in the various regions.

Raising the annealing temperature to 300° C, i.e. above the melting temperature of Bi, switches the atom dynamics to another regime and affects significantly the topography of the surface. The first qualitative observation on the work function map [Fig. 3(a)] indicates that the domains with six-fold symmetry have been replaced by an array of micrometer-sized circular patches with a spot at their centre. Upon repeated annealing at the same temperature, each of them during about 10 min, the patches decrease in size as well as in density, until complete disappearance, only the central spots staying in place [see Figs. 3(b and c)].

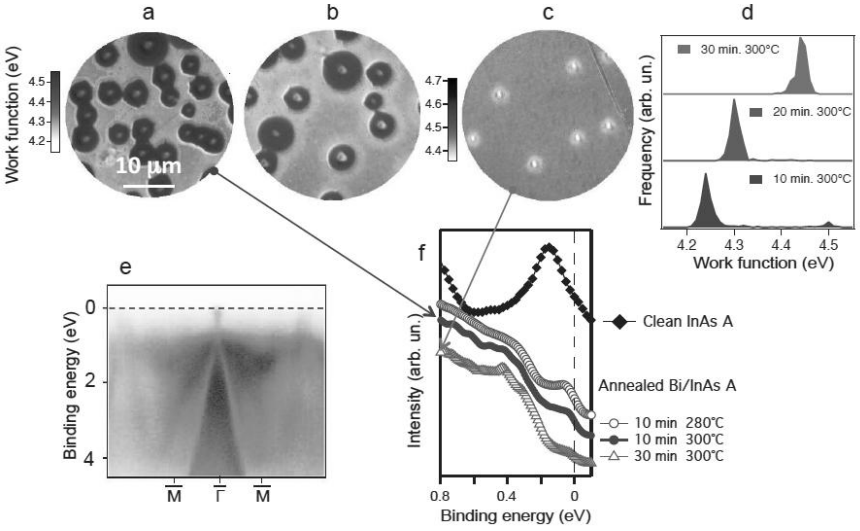


Fig. 3: *30 BL Bi/InAs(111)A sample after annealing at 300°C: (a) Work function map after a first 10 min annealing; (b) and (c) further annealing for 10 and 20 min; (d) work function histograms corresponding to samples (a–c); (e) ARPES spectrum in the Γ–M direction of the surface shown in (a); (f) energy distribution curve close to the Fermi level for the surfaces in (a) and (c). For comparison, the spectra corresponding to the clean InAs(111)A surface and to the 30 BL Bi/InAs(111)A surface annealed at 280°C are also shown.*

The work function histograms obtained after successive annealings are shown in Fig. 3(d). The corresponding ARPES data, averaged over the whole image[Fig. 3(e)], reveal that the band structure is no more that of bismuth but is related to that of InAs as also testified by a clear signature of the accumulation layer. The evolution of the ARPES spectrum can be more precisely followed through the energy distribution curve at the Γ point. In Fig. 3(f) we plot the energy distribution curves corresponding to the images shown in Figs. 3(a) and (c). For reference, we show also the energy distribution curve of the Bi/InAs (111)A surface annealed at 280° C and that of the clean InAs (111)A surface. One can see that the intensity of the feature due to the accumulation layer decreases when going from the InAs (111)A surface to the most annealed Bi/InAs (111)A surface. At the same time, the band dispersion in 2-dimensional ARPES data looses in contrast (not shown). This leads to the first conclusion that the annealing above the melting temperature of bismuth progressively destroys the crystallinity of the surface.

It is important to keep in mind that our PEEM images are measured at room temperature and therefore show a frozen atomic configuration of the surface at higher temperatures. Our results indicate that during the annealing at temperatures slightly above the melting point of Bi, the major part of the surface formed by one Bi BL sitting on the In top layer is preserved and, at the same time, in arbitrarily scattered (homogeneously distributed) points of the surface, probably where defects are present, a formation of Bi-As compounds is initiated. This necessitates more Bi atoms than available in one Bi bilayer and the Bi reservoirs are the clusters which were formed during the annealing of the film. The reaction between Bi and As is then fuelled by a flux of mobile Bi atoms leaving the cluster and sliding on top of the Bi bilayer which is sticking to the surface. As the flux of atoms is isotropic, the patches maintain a circular shape with the cluster in their centre. Implicitly, the rate of the reaction between Bi and As is lower than the velocity of surface-melted Bi atoms. Prolonged annealing favours a progressive advance of the frontier between an amorphous-like mixture of Bi-As-In compounds and the pristine InAs crystal covered by one Bi bilayer.

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**References:**

[1] S. Agergaard, et al., *New J. Phys.***3**, 15 (2001).
[2] C. M. Schneider, et al., *J. Electron Spectrosc. Related Phenom.* **185**, 330 (2012).
[3] E. Hilner, E. Lundgren, A. Mikkelsen, *Surf. Sci.* **604**, 354 (2010).
[4] L. Ö. Olsson, et al., *Phys. Rev.* **B 53**, 4734 (1996).
[5] P. D. C. King, et al., *Phys. Rev. Lett.* **104**, 256803 (2010).
[6] K. Szamota-Leandersson, et al., *Surf. Sci.* **605,** 12 (2011).
[7] J. Chen, et al., *Phys. Rev. Lett.* **105,** 176602 (2010).
[8] T. Hirahara, et al., *Phys. Rev. Lett.* **97** 146803 (2006).