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XPS study of adsorption and desorption of a Bi thin film on the fivefold icosahedral Al-Pd-Mn surface

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We have employed x-ray photoelectron spectroscopy to characterise the growth and thermal stability of a Bi thin film on the fivefold icosahedral Al-Pd-Mn surface. The growth can be characterised as Stranski-Krastanov, in agreement with previous STM studies. As a function of annealing temperature, the multilayer desorbs first and thereafter coverages of 1 ML and 0.5 ML are stable for significant temperature ranges.

Keywords: bismuth; aluminium-palladium-manganese; x-ray photoelectron spectroscopy; scanning tunnelling microscopy; quasicrystal; surface; adsorption

1. Introduction

There have been numerous studies in recent years of the growth of thin films on quasicrystal surfaces [1–4]. The surfaces of quasicrystals offer a unique template for epitaxial growth, and several pseudomorphic systems have been discovered [5–7]. The study of such systems can provide insight on the influence of quasiperiodic order on their physical properties and on their potential for technological application.

The semi-metal bismuth (Bi) adsorbed on the fivefold surface of *i*-Al-Pd-Mn was one of the first systems found experimentally to form a quasiperiodic pseudomorphic monolayer [5]. A scanning tunnelling microscopy (STM) study of the initial growth showed that the atoms first adsorb in a pentagonal arrangement at sites above truncated pseudo-Mackay clusters [8]. After approximately 0.5 ML coverage (one monolayer (ML) corresponds to an adsorbate layer which completely covers the surface), the nucleation sites become exhausted and further Bi adatoms occupy sites interstitial to the clusters to form a complete monolayer. Further deposition above a monolayer leads to the formation of {100}-pseudo-cubic Bi islands [9]. The most stable islands form with heights of 4 and 8 ML.

In our recent study [10] atomic resolution STM images confirmed the structure of these pseudo-cubic, nano-scale islands. It was found that with time the pseudo-cubic islands transformed to larger, hexagonal islands, orientated with the {111}-pseudo-cubic ({0001}-hexagonal) plane parallel to the surface. This orientation is the preferred epitaxial allotrope observed for deposited Bi [11]. By increasing the flux of Bi it was possible to increase the density of pseudo-cubic islands and prevent the transformation to the hexagonal phase. These surfaces were in turn utilised to compare their reactivity to molecular adsorbates [10, 12].

In this article, we describe the results of an X-ray photoelectron spectroscopy (XPS) study of the growth of Bi on the fivefold surface of *i*-Al-Pd-Mn, and of the stability of the overlayer as a function of substrate temperature. We establish the desorption temperature ranges for the multi-layer and monolayer regimes.

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2. Experimental Details

The sample surface was oriented perpendicular to the fivefold axis. The nominal composition of the sample was $\text{Al}_{70.5}\text{Pd}_{19.5}\text{Mn}_{8.5}$. After insertion into a UHV chamber it was cleaned by sputtering with Ar^+ ions at grazing incidence. Surface order was subsequently restored by annealing for 2 hours at a temperature of 923 ± 10 K. It has been shown that the resulting surface can be considered as a bulk termination [13].

The x-ray source employed an Al anode target (x-ray energy line $\text{Al K}\alpha = 1486$ eV). A hemispherical analyser was used for photoelectron detection. XPS scans were recorded at 15° off normal emission. The angular acceptance of the analyser is $\pm 8^\circ$. The surface was checked for contamination by an XPS scan after every anneal. The base pressure in the chamber was 5×10^{-10} mbar. STM data were taken using an Omicron STM-1 equipped with a chemically etched tungsten (W) tip.

The amount of Bi deposited on the surface was calibrated using XPS intensity measurements of the Mn $2p$, Pd $3d$, Al $2s$, Al $2p$ and Bi $4f$ core-level photoemission peaks as the dose was increased. The estimated coverage was therefore a dose equivalent to the monolayer (quoted as monolayer equivalent - MLE). A Shirley background was fitted to the peaks and the the the peaks were then fitted with a Gaussian-Lorentzian sum, from which the total area was deduced to represent the peak intensity. The order of the clean surface was confirmed by observation of a distinct, fivefold low energy electron diffraction (LEED) pattern. The stability of the film structures was determined by incremental desorption of the film. This was performed by directly heating the sample with a multilayer present and monitoring changes in the photoemission peak intensities. The sample temperature was measured using a previously calibrated optical pyrometer.

3. Results and discussion

STM scans obtained from the clean surface show a flat step and terrace substrate morphology. A quasiperiodic Bi layer wets this surface. Further deposition on this wetting layer, leads to two different allotropes (Figure 1) depending on the growth conditions. Initially, $\{100\}$ -pseudo-cubic islands are observed, as shown in Figure 1 a). This structure was formed using a Bi flux of $0.16 \text{ MLE min}^{-1}$. The stepped, pseudo-cubic $\{100\}$ islands are composed of 4, 8 or a larger number of multilayers.

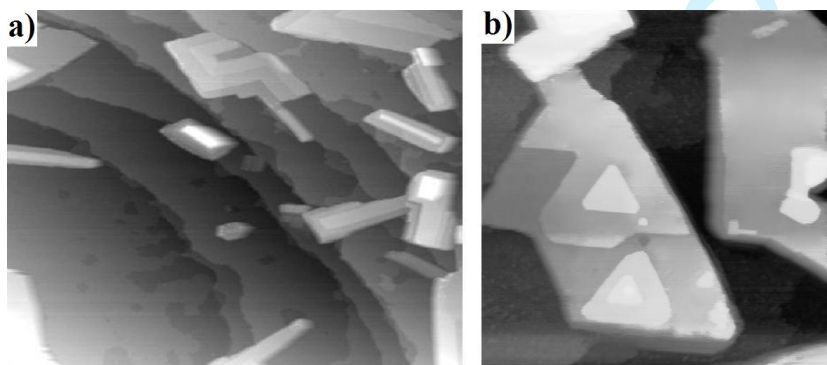


Figure 1. STM images taken of the fivefold surface of Al-Pd-M after Bi deposition. Bi multilayer islands of two different allotropes are present on the quasicrystalline wetting layer. Coverage of Bi is estimated at 4.1 ML. a) $395 \text{ nm} \times 500 \text{ nm}$ image displaying the stepped, rectangular $\{100\}$ -pseudo-cubic orientated Bi islands. b) $200 \text{ nm} \times 200 \text{ nm}$ scan displaying the stepped, $\{111\}$ -pseudo-cubic structure islands.

The {100}-pseudo-cubic islands are found to transform to the stable, {111}-pseudo-cubic phase over time (Figure 1 b)). Occasionally a mixture of the two phases was observed. Details of these STM results, and of the factors influencing the morphological transition, have been published elsewhere [10].

As mentioned in Section 2, the evolution of the core-level photoemission peaks was monitored as an increasing amount of Bi was adsorbed to determine the growth mode. Figure 2 displays the variation in substrate (Al 2p) and film (Bi 4f) intensity after each deposition. The peak areas were normalised to the maximum intensity reading on each curve so that they may be compared on the same plot. A change in gradient of the curve at a dose of around 11 min indicates the completion of the monolayer preceding formation of the islands.

LEED patterns obtained from a complete deposited monolayer of Bi displayed principal spots in a 1×1 pattern. Such a result indicates pseudomorphic growth [5]. The LEED pattern for the Bi monolayer showed greater contrast than that of the clean surface. This observation has previously been suggested to be due to the larger electron scattering cross-section of the heavier Bi atoms rather than surface reconstruction or differing instrument parameters [5].

A linear variation in intensity with increasing deposition and lack of further breaks in the deposition curve is evidence for a Stranski-Krastanov (initial layer plus island growth) type growth mode of Bi [14]. This observation is consistent with the STM results discussed above.

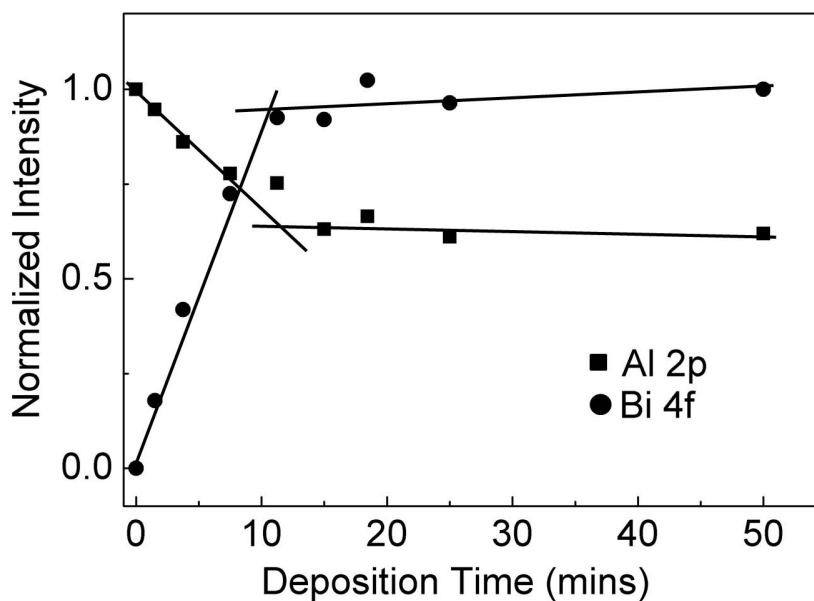


Figure 2. Variation in Al 2p and Bi 4f intensity as a function of deposition time, showing line segments of different gradients. The Al 2p intensity is normalized with respect to the clean surface and Bi 4f intensity is normalised to the peak intensity and after 50 mins Bi deposition.

Figure 3 shows the desorption curve obtained by heating the sample with a coverage of 56 MLE of Bi. The sample was heated to each temperature for a duration of 10 minutes and then allowed to cool for 5 minutes before spectra were recorded. The plot shows that the multilayer desorbs between 520-620 K. This range agrees with previous studies which found the multilayer completely desorbed at 620 K leaving a monolayer [9]. The ratio of intensities of Pd 3d to the Bi 4f peak matches well with that of the monolayer transition in the deposition curves.

The monolayer coverage is relatively stable for a large temperature range of 620-800 K. The monolayer desorbed at 820 K leaving ≈ 0.5 ML on the surface. This coverage correlates with the previously determined point at which saturation of the pentagonal nucleation sites occurs and the pure growth regime begins [8]. At 900 K the Bi peak intensity is reduced to the background count indicating that all the adsorbate atoms have desorbed. This temperature is significantly higher than that reported in a previous study where the monolayer was estimated to desorb between 670-870 K [5]. However this estimate was inferred from an observed structural change without any direct chemical information.

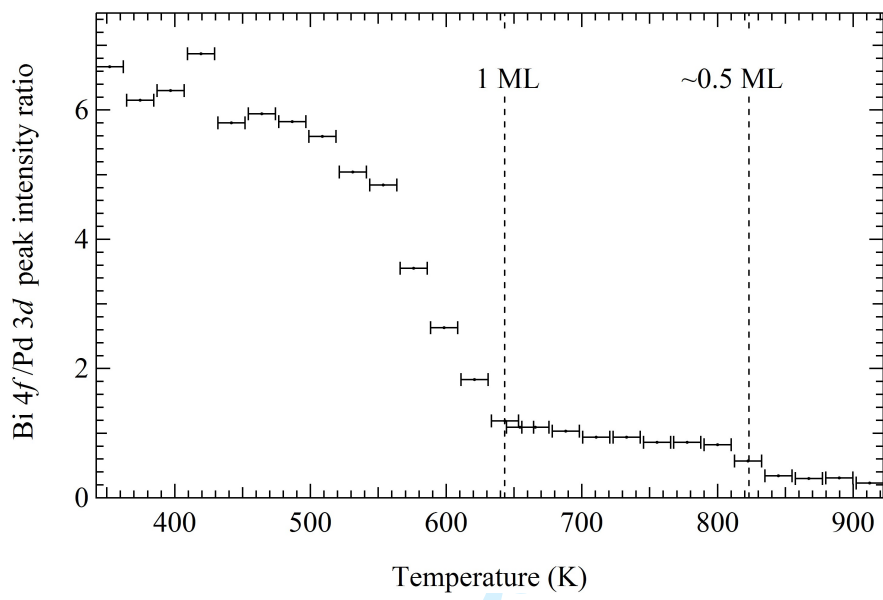


Figure 3. Desorption of Bi from the fivefold *i*-Al-Pd-Mn substrate: the plot shows the ratio of the Bi 4*f* to Pd 3*d* photoemission peak intensity as a function of increasing sample temperature.

4. Summary

XPS has been utilised to study Bi films adsorbed on the fivefold *i*-Al-Pd-Mn surface. The deposition curve supports a Stranski-Krastanov growth mode for Bi on the quasicrystal. The two plateaux in the desorption curve show the relative thermal stability of the monolayer and sub-monolayer coverages. The coverage of around 0.5 ML that is stable for a large high temperature range corresponds to the point at which the initial nucleation adsorption sites are saturated. The sub-monolayer coverage was found to desorb at 900 K leaving the clean substrate.

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