Nucleation and growth of noble metals on transition-metal di-tellurides

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Abstract

Transition-metal di-tellurides (α- and β-MoTe₂ and WTe₂) were used as substrates for nucleation and growth studies of noble metals. They represent a group of chemically closely related compounds with different surface topographies. Nucleation and growth of Ag and Au at room temperature were studied by means of UHV-STM, AFM and TEM. The results revealed that the growth and orientation of these metals are influenced by the topography of the substrate surfaces. Contrary to the growth on atomically flat α-MoTe₂, there is an enhanced diffusion and nucleation along the periodic surface troughs on β-MoTe₂ and WTe₂. The topography of their (001) surfaces is responsible for the orientation of metal (112) planes being parallel to the substrate surface.

Keywords: Atomic force microscopy; Electron microscopy; Epitaxy; Gold; Growth; Molybdenum di-telluride; Scanning tunneling microscopy; Silver; Tungsten di-telluride

1. Introduction

The layered transition-metal di-tellurides (TMD) are formed by two-dimensional Te–metal–Te sandwiches with strong covalent bonds inside and weak van der Waals' (vdW) interaction between the sandwiches. They usually cleave along the vdW gaps exposing low energy (001) chalcogen terminated surfaces. The undistorted TMD materials, such as α-MoTe₂, have atomically flat surfaces, while others, like, e.g. β-MoTe₂ and WTe₂, crystallise in distorted forms [1,2] and their (001) surfaces are periodically corrugated along their [010] directions [3]. Both β-MoTe₂ and WTe₂ (001) surfaces are similar in topographies and have almost equal in-plane lattice constants.

Noble metals usually grow in the island (Volmer–Weber) mode with their (111) planes parallel to the atomically flat TMD surfaces [4]. By contrast, very few studies have been carried out on how these materials grow on the corrugated surfaces. While in a recent study the growth of Au on β-MoTe₂ [5] has been investigated, the aim of this work was to find out possible different behaviour of Ag due to its expected reactivity with the substrate.

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2. Experimental

All TMD crystals were grown by chemical vapour transport with I₂ as the transport agent. Their structures were confirmed by X-ray diffraction (XRD) analysis. The crystals were cleaved by adhesive tape just before introducing them into the UHV preparation chamber. STM investigations in the constant current mode were performed by using an Omicron UHV-STM system at an operating pressure between 10⁻¹⁰ and 10⁻¹¹ mbar. Electrochemically etched tungsten tips were used throughout this work and the tip quality was pre-examined by scanning graphite prior to each experiment. Ag and Au of 99.999% purity were deposited onto these crystals at room temperature from a resistively heated Mo boat at pressures of about 10⁻⁹ mbar. Samples were transferred between the STM and the preparation chamber without exposing them to atmosphere.

To compare with STM results, AFM experiments in both contact and lateral force modes were performed with a Digital Instruments Nanoscope III SPM system using silicon nitride cantilevers in air. Mica was used for adjustment of the AFM scanner and to check the quality of the cantilever. The substrate–deposit orientational relationship was determined by transmission electron diffraction (TED) in a Philips EM301 transmission electron microscope.

3. Results and discussion

3.1. Nucleation and growth

Unlike on atomically smooth TMD surfaces, the enhanced one-dimensional diffusion of the metal adatoms along the surface troughs plays an important role in nucleation and growth of both Ag and Au on β-MoTe₂ and WTe₂ (001) surfaces. Due to this directional diffusion, nuclei formed in the surface Te troughs. The initial stages of growth were thus characterised by small randomly distributed clusters, elongated along the [010] direction of TMD (Fig. 1). In case of Ag on β-MoTe₂, these clusters continued to grow into atomically flat anisotropic islands elongated in the same direction (Fig. 2a). At approximately 30 ML of Ag the entire surface becomes covered by rectangulo-shaped, well oriented Ag islands as shown in the AFM image of Fig. 2b.

3.2. Orientation

Selected area TED patterns, acquired from the thinnest measurable metal islands on both β-MoTe₂ and WTe₂ surfaces, revealed the substrate–deposit orientational relationship (Fig. 3a) as: (112)[110]Au(Ag) || (001)[010]β-MoTe₂ (WTe₂).

This is locked-in due to similar topographies of the (112) planes of Ag (Au) and the (001) planes of β-MoTe₂ (WTe₂) as shown in the schematic computer drawing of Fig. 3b. STM evidence of this orientational relationship is given in Fig. 4 with parallel Ag and Te atomic rows.

3.3. Reaction

Contrary to Au, Ag reacted during deposition with Te atoms on both β-MoTe₂ and WTe₂ surfaces forming Ag₂Te as determined by TED. Chemisorption and reaction of Ag with the
Fig. 2. (a) STM image ($I_t=0.83$ nA, $U_p=0.5$ V, 160 x 100 nm²) of atomically flat, about 200 nm long and 2 ML high Ag islands aligned along the [010] direction on the (001) β-MoTe₂ surface. (b) AFM image of approximately 30 ML thick Ag layer on β-MoTe₂ with well oriented rectangularly shaped islands (2.2 x 2.2 µm²).

substrate was proved also by its different behaviour during scanning. While the small Au islands were easily removed by repeated scanning, Ag islands remained stable during several subsequent scans due to chemisorption. In certain cases only one monolayer high chemisorbed Ag islands can be observed (Fig. 5).

The reaction between Ag and Te was more pronounced on WTe₂ and resulted in a massive destruction of the substrate surface. Due to the formation of Ag₂Te, holes were formed on the

Fig. 3. (a) TED pattern of Ag deposited on β-MoTe₂ showing their epitaxial relationship and (b) the corresponding computer drawing.
WTe$_2$ surface, whose size and depth increased with increasing amount of Ag.

4. Conclusions

Because of the enhanced diffusion of adatoms along β-MoTe$_2$ and WTe$_2$ surface troughs, both Ag and Au grow in the form of elongated islands. Both metals grow with their (112) planes parallel to the (001) surfaces of β-MoTe$_2$ and WTe$_2$ due to their topographic similarities. Ag reacts with Te on both substrate crystals and forms Ag$_3$Te. Due to this reaction a massive destruction of the WTe$_2$ surface takes place even at room temperature depositions.

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