Silver sulphide growth on Ag(111): A medium energy ion scattering study

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ABSTRACT

The interaction of S_2 with Ag(111) under ultra-high vacuum conditions has been investigated by medium energy ion scattering (MEIS). 100 keV He$^+$ MEIS measurements provide a direct confirmation of a previous report, based on thermal desorption, that the growth of multilayer films of Ag_2S occurs through a continuous corrosion process. These films show a commensurate $(\sqrt{7} \times \sqrt{7})R19°$ unit mesh in low energy electron diffraction, consistent with the epitaxial growth of (111) layers of the high-temperature F-cubic phase of Ag_2S. The substantial range of co-existing film thicknesses found indicates that the growth must be in the form of variable-thickness islands. The use of 100 keV H$^+$ incident ions leads to a very rapid decrease in the sulphide film thickness with increasing exposure that we attribute to an unusual chemical leaching, with implanted H atoms interacting with S atoms and desorption of H_2S from the surface.

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1. Introduction

Adsorption at surfaces can lead to a range of strongly-bonded structural phases including chemisorbed overlayers, substitutional surface alloys, and surface compound phases in which adsorbate and substrate atoms intermix to form a local compound with a well-defined limited thickness. In a few cases, however, interaction with atoms or molecules from the surrounding gas or solution can lead to the formation of bulk compounds that have a well-defined epitaxial relationship to the underlying bulk substrate. Few of these special 'corrosion' systems have been studied in detail, in part because the methods of surface science, which specifically exploit surface specificity, are ill-suited to investigate these systems beyond the very earliest stages of compound formation. Medium energy ion scattering (MEIS) [1], typically using ~100 keV H$^+$ or He$^+$ incident ions, is a technique that can be used to explore both true surface phenomena (occurring in the outermost one or two atomic layers of a solid) but also to investigate the sub-surface region to thicknesses of a few hundred Ångström units. Here we report on the use of this technique to investigate the interaction of molecular sulphur in the form of S_2 with Ag(111).

Tarnishing of silver objects in the air is a well-known phenomenon that is attributed to silver sulphide formation at the interface between the silver and a thin water surface film containing air-borne sulphur compounds. An early investigation [2] concluded that the interaction of molecular sulphur with single-crystal films of Ag by electron micros-copy led to the formation of thick films of acanthite, the monoclinic phase of Ag_2S [3] that is stable at room temperature, and also identified some epitaxial metal–sulphide orientational relationships. However, the vacuum conditions associated with this study were poor. The first relevant ultra-high vacuum (UHV) investigation using modern surface science methods is a study of the interaction of S_2 with Ag(111) by Schwaha et al. [4]. Using low energy electron diffraction (LEED) they showed that at low coverage a 'complex' phase exists, initially attributed to a '($\sqrt{39}R16.1° \times \sqrt{39}R16.1°$)' unit mesh but more recently proposed to be more properly described in the matrix notation as $\begin{bmatrix} 3.67 & 0.00 \\ 3.00 & 3.50 \end{bmatrix}$ [5]. At a slightly higher coverage LEED revealed a $(\sqrt{7} \times \sqrt{7})R19°$ pattern, but this persists to much higher coverages. Auger electron spectroscopy (AES) showed a limiting ratio of the Ag and peak heights with increasing exposure to S_2, but temperature programmed desorption (TPD) showed that this was due to continuing growth of a compound film of fixed stoichiometry, rather than saturation of the surface at a lower coverage. Based on these observations, they attributed the $(\sqrt{7} \times \sqrt{7})R19°$ pattern to the formation of an epitaxial film of the high-temperature phase of Ag_2S (referred to as the γ-phase in the very limited report of its structure [6]). This bulk structural phase of Ag_2S has been characterised more fully by neutron scattering [7] and confirmed to have a face-centred cubic lattice with a lattice parameter of 6.27 Å. As such the S–S spacing in the (111) plane is 4.43 Å, an almost perfect match to the $\sqrt{(7/3)}$ spacing 4.41 Å required for epitaxial growth on Ag(111) with a $(\sqrt{7} \times \sqrt{7})R19°$ registry mesh.

In addition to these investigations of gas-phase interactions with molecular sulphur, the interaction of gas-phase H_2S, both under UHV conditions [8] and at ambient pressures [9], have been shown to lead to a $(\sqrt{7} \times \sqrt{7})R19°$ ordered surface phase, although it is unclear as to

whether this treatment can lead to multilayer compound formation. The same surface ordering has been observed by scanning tunnelling microscopy in electrochemical S deposition [10,11], and under these conditions it is clear that at an appropriate potential, multilayer growth can occur.

Despite the ubiquitous nature of the Ag(111)($\sqrt{7}\times\sqrt{7}$)R19°–S phase, and clear evidence from TPD and electrochemical current measurements that multilayer compound formation can be associated with this ordering, there has been only one reported investigation of the structure of this phase, and this was focussed on the earliest stages of multilayer growth [5]. This investigation, using the normal incidence X-ray standing wave (NIXSW) method [12], followed an earlier detailed investigation of the structure of the closely-related Ag(111)($\sqrt{7}\times\sqrt{7}$) R19°–CH$_3$S phase, [13] which concluded that the methylthiolate induces a reconstruction of the metal surface to yield a surface comprising 3/7 ML CH$_3$S species and 3/7 ML of reconstructed Ag atoms. This structure (with the methyl radicals omitted) is shown in Fig. 1. The later study of the Ag(111)($\sqrt{7}\times\sqrt{7}$)R19°–S surface [5] concluded that Ag$_2$S(111) grows on an interface that is rather similar to the thiolate structure, although the relative spacings and coverage of the S and Ag atoms in this region differ from that of the thiol structure (Fig. 2). NIXSW is not well-suited, however, to explore the properties of thicker layers.

Here we present the results of a new MEIS study of this system which provides mainly information on the stoichiometry and morphology of thicker Ag$_2$S layers up to ~50 Å average thickness. In the process of performing these experiments, however, we identified a novel form of ion-beam-induced modification that appears to be dominated by chemical, rather than kinetic, influence.

2. Experimental details

The experiments were performed at the Daresbury Laboratory UK National MEIS facility [14]. The ion accelerator fitted with a duoplasmatron ion source was used in the present experiments to produce a beam of H$^+$ or He$^+$ ions at a nominal energy of 100 keV. Ions scattered from the sample were detected by a moveable toroidal electrostatic analyser, the two-dimensional (2D) detector [15] of which provides 'tiles' of ion counts as a function of both ion energy and scattering angle over limited ranges of each. The general methodology for extracting from these raw data tiles both the scattered-ion/energy spectra at fixed scattering angle, and the angular blocking curves corresponding to scattering from a
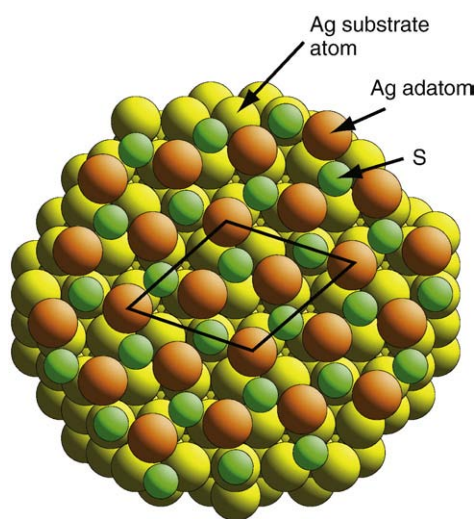

Fig. 2. Top and side views of a model of the early stages of growth of the ($\sqrt{7}\times\sqrt{7}$)R19° structure formed by Ag$_2$S on Ag(111). On the left is shown an area comprising only the first (2/7 ML) layer of S atoms with 3/7 ML of Ag atoms above, while on the right the first complete Ag$_2$S layer has grown on top of this interface structure. The Ag$_2$S is assumed to be a slightly-strained form of the high-temperature F-cubic phase with all Ag atoms in the tetrahedral sites.

single atomic species, has been described elsewhere [13,16]. The end-station comprises separate UHV chambers (typical pressures 2–5×10^{-10} mbar) for sample preparation and characterisation, for sample storage, and for the ion scattering experiments, with sample transfer between chambers being achieved under UHV conditions. The Ag(111) sample was prepared *in situ* by the usual cycles of 1 keV argon ion bombardment and annealing to 600 °C until a well-ordered clean surface was obtained as judged by a sharp (1×1) LEED pattern and AES. The Ag$_2$S overlayers were prepared by the same method as Schwaha et al. [4], namely through the use of a solid-state Pt/Ag/AgI/Ag$_2$S/Pt electrochemical cell that delivers a flux of almost entirely S$_2$ molecules [17,18]. The cell was operated at a temperature of ~180 °C with an applied potential of ~150 mV, with an associated pressure rise during operation to 4×10^{-9} mbar, and deposition was onto the Ag surface at room temperature. Auger electron spectroscopy was used to achieve an approximate calibration of the rate of deposition, assuming 'breaks' in the gradient of the S LVV Auger peak intensity as a function of exposure corresponded to completion of atomic layers. On this basis the deposition rate was estimated to be ~0.15 layers of Ag$_2$S per minute.

3. Sample characterisation and radiation damage

For deposition times of less than ~20 min the LEED pattern was characteristic of the 'complex' phase, only transforming to the expected ($\sqrt{7}\times\sqrt{7}$)R19° pattern at higher coverages. As this exposure is expected, on the basis of the deposition-rate calibration to correspond to an average thickness of ~3 layers, this result is superficially surprising. We note, however, that the 1/7th order diffraction beams that characterise the ($\sqrt{7}\times\sqrt{7}$)R19° pattern are also a sub-set of the diffracted beams of the complex phase, so the continued appearance of the diffraction pattern of the complex phase simply implies that some fraction of the surface remains at this lower

Fig. 1. Model of the ($\sqrt{7}\times\sqrt{7}$)R19° structure formed by methylthiolate, CH$_3$S–, on Ag (111). The full lines show the unit mesh while the 3/7 ML S headgroup atoms and 3/7 ML Ag adatoms of the reconstructed surface are also shown. This also forms the basis o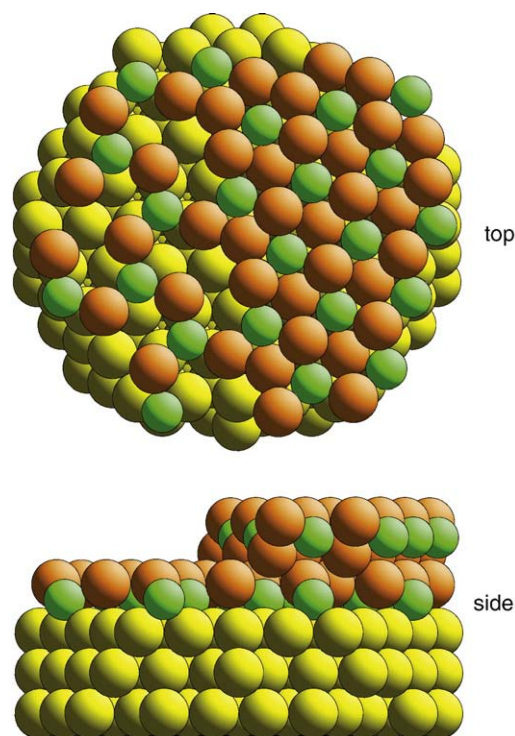f the model of Ag$_2$S growth on Ag(111).