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Real-space study of the growth of magnesium on ruthenium

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ABSTRACT

The growth of magnesium on ruthenium has been studied by low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM). In LEEM, a layer-by-layer growth is observed except in the first monolayer, where the completion of the first layer in inferred by a clear peak in electron reflectivity. Desorption from the films is readily observable at 400 K. Real-space STM and low-energy electron diffraction confirm that sub-monolayer coverage presents a moiré pattern with a 12 Å periodicity, which evolves with further Mg deposition by compressing the Mg layer to a 22 Å periodicity. Layer-by-layer growth is followed in LEEM up to 10 ML. On films several ML thick a substantial density of stacking faults are observed by dark-field imaging on large terraces of the substrate, while screw dislocations appear in the stepped areas. The latter are suggested to result from the mismatch in heights of the Mg and Ru steps. Quantum size effect oscillations in the reflected LEEM intensity are observed as a function of thickness, indicating an abrupt Mg/Ru interface.

1. Introduction

Magnesium is a commonly available non-toxic metal. From a technology point of view, its hydride MgH_2 has been proposed as a lightweight hydrogen carrier, even if kinetic and thermodynamic limitations have restricted its use. From a fundamental point of view, Mg together with Be and Al have been studied as part of the so-called free-electron-like metals with quite ideal metallic bonding. The simple electronic structure of Mg and its nearly ideal hexagonal close-packed lattice, with a c/a lattice parameter ratio of 1.624 compared to the ideal value of 1.633, simplifies fundamental studies. However, its low sublimation temperature limits the preparation of high quality single crystals in ultra-high vacuum (UHV). Fortunately, Mg is known to grow as highly perfect thin films on many substrates. On some of them, the interface with the substrate is very sharp. With the appropriate substrate, quantization of the Mg sp-bands has been observed up to a thickness of several nanometers [1].

There are only a limited number of studies on the growth of Mg on refractory metals, most of them on W(110) [1,2]. On W(110), a real-space study by low-energy electron microscopy [2] found a very high quality layer-by-layer growth. The quality of such thin films is so good that is has been used to study how the bulk electronic structure develops as a function of thickness [1] and influences chemical reactivity [3].

Over et al. [4] characterized the epitaxial growth of Mg over Ru (0001) using LEED, work function changes and temperature programmed desorption (TPD). They reported that magnesium grows over Ru(0001) in an incommensurate manner, i.e., keeping its own in-plane spacing. This was understood to be due to the large mismatch between the respective in-plane lattice spacings (around 18%). The result is an overlayer film without significant strain. A moiré was observed in the LEED pattern, starting at coverages as low as $\theta = 0.05$. θ is the areal density of the Mg normalized to that of Ru(0001). From $\theta = 0.05$–0.65 ML the LEED indicated a (5×5) periodicity with a Mg–Mg distance of 3.35 Å (4% expansion with respect to the Mg bulk value). When the coverage was increased to $\theta = 0.65$–0.75 ML, a compression of the Mg overlayer was observed, with the LEED pattern changing gradually to a (7×7) periodicity with a final Mg–Mg distance of 3.13 Å (slightly compressed with respect to the bulk distance of 3.21 Å). When $\theta = 0.75$ ML there were no further changes in the LEED patterns and the authors concluded that a complete monolayer of Mg covered the substrate. From TPD measurements the authors described several peaks. For a coverage of less than one monolayer of Mg, there were three main TPD peaks: α at 750 K, which is observed for small Mg coverages, β at 580 K, corresponding to the compressed phase (7×7) and γ at 500 K, which is present for higher Mg coverages. This last peak shifts to higher temperatures when the coverage is higher than one monolayer. Specifically the authors assigned the peak γ at 550 K to the desorption of the 2nd ML, the peak γ' at 530 K to the desorption of the 3rd one and the peak γ'' at 510 K to the desorption to the 4th and subsequent layers. From these results it can be deduced that the first Mg layer interacts more strongly with the support than the subsequent layers interact with Mg layers. The same group published later [5] a LEED-IV fit providing a crystallographic structure of the first 3 ML of Mg over Ru(0001). They used the (5×5) symmetry for the analysis of the first Mg overlayer. The

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second and third overlayers were treated within a mirror approximation, giving the films a $7/6 \times 7/6$ structure.

A few works have described STM imaging of epitaxial Mg grown at room temperature up to 2 ML. Pezzagna et al. [6] described recently the growth of continuous Mg films over the semiconductor GaN (0001) using STM and reflection high-energy electron diffraction (RHEED). The in-plane lattice mismatch with Mg is only 0.3%. In agreement with this small mismatch, they did not observe a moiré pattern on the Mg surface. They reported hexagonal shaped Mg islands with a height of 2.80 Å (slight larger than the interlayer spacing of close-packed planes in bulk Mg, 2.60 Å). When the coverage was lower than 0.4 ML the islands displayed atoll-like shapes. Increasing the Mg coverage changed the shape of the islands, making their shape more compact. The appearance of the islands depended also on the STM imaging bias. With 4 V the islands looked flat. However, if the bias was lowered to 0.5 V there was a detectable corrugation at their surface of 0.06 Å(6 pm). Submonolayer Mg over Si (001) was characterized by Hutchinson et al. [7] at room temperatures using STM. Deposited magnesium formed rows that are roughly perpendicular to the substrate dimer rows.

In this paper we present a real-space STM and LEEM study of the growth of Mg films up to 10 ML on Ru(0001). Since this substrate does not alloy with Mg under growth conditions and both materials have the same crystal structure, the growth processes are simplified and the Mg films closer approach bulk material. The knowledge of how Mg grows over Ru(0001) is a key part of our group's efforts in understanding the relationship between the atomic structure of ultrathin films and their hydrogenation/dehydrogenation ability as a hydrogen storage material [8]. In the present work we obtain LEED data in a LEEM microscope that confirms the results obtained previously by Over and coworkers. New insight is obtained from present real space data of the Mg growing acquired using two complementary microscopic techniques (LEEM and STM). In thin films, STM reveals corrugations at the same periodicities as the moiré between the Mg and Ru lattices. In thicker films, we find stacking faults between Mg regions and screw dislocations in regions of high Ru step density.

2. Experimental details

The magnesium growth on ruthenium was performed in two different UHV chambers with two Ru(0001) single crystals as substrates. The first chamber has a commercial LEEM (Elmitec III). The microscope can monitor growth in real time, or during heating/cooling of the substrate between 200 and 1600 K. The second houses a low-energy electron diffractometer and a home-made STM [9]. The STM is controlled by commercial RHK electronics and the open-source Gxsm STM software [10,11]. For analysis, we used the packages Gwyddion [12] and ImageJ [13] for STM and LEEM images, respectively. The base pressure of both UHV systems is below 1×10^{-10} mbar. In the LEEM system, the Ru(0001) substrate was cleaned by exposure to 1.5×10^{-8} mbar of O at 890 K, followed by brief flashes to 1600 K. In the STM system, the substrate was cleaned by repeated exposure and flash cycles (exposure to 20 s at 1.3×10^{-7} mbar at room temperature and flashing to 1600 K). Mg was deposited from a Mg rod heated by electron bombardment. During the film growth the pressure remained in the low 10^{-10} mbar range. Typical deposition rates were 1 ML/min. A monolayer is defined as a bulk-like Mg layer [4].

The LEEM images directly the electrons reflected by the surface under observation. Thus, the measurement of the averaged reflected intensity, either as a function of deposition time, or as a function of the incoming electron energy, is extracted by averaging the image intensity from a suitable region (box). When imaging the diffraction pattern, the relevant data is the integrated intensity and position of each spot. When measuring the spatial position of a diffracted spot in LEED, a 2-dimensional Gaussian function was fitted to the spot position.

3. Results and discussion

3.1. Growth in LEEM

The low-energy electron microscopy view of the first stages of Mg growth on Ru(0001) is shown in Fig. 1. The LEEM snapshots are selected from a sequence acquired while continuously imaging the surface during the magnesium deposition. Growth of first-layer islands cannot be imaged directly by LEEM. At first, only a uniform decrease of the reflected electron intensity is detected and the substrate steps become less visible. In Fig. 1g the spatially averaged reflected intensity is plotted as a function of the deposition time. After reaching a minimum, the reflected electron intensity increases again. Completion of the first layer is indicated by the maximum of the reflected intensity. At the same time, in the real-space images, the substrate steps are suddenly visible again. Nevertheless the Mg-covered substrate terraces are not imaged like the bare Ru substrate. The fine-scale contrast in Fig. 1b suggests that there are structures in the monolayer whose size is close to the resolution limit of the LEEM, which for our instrument is about 100 Å. The same observation (lack of first monolayer LEEM island contrast, with the substrate steps clearly visible at close to the compact monolayer) has been reported for Mg/W(110) [2] and ascribed to the formation of small islands.

The nucleation of the second layer, by contrast, is clearly observed, and proceeds through well-defined island growth. The nucleation density increases slightly for the next layers. At the electron energy of

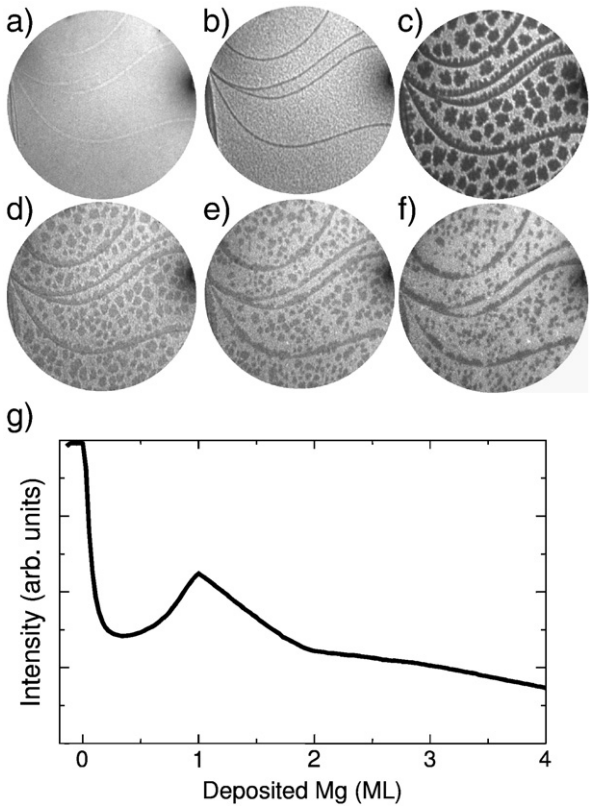

Fig. 1. (a–f) LEEM snapshots from a sequence acquired while growing Mg on Ru(0001) at 373 K. The field of view (FOV) is 7 μm and the electron energy is 5 eV. a) shows the bare substrate. b) corresponds with the substrate just before the appearance of the 2 ML islands. c), d), e) and f) show islands 2, 3, 4, and 5 ML thick respectively. The first ML islands cannot be distinguished in LEEM [b)], but the surface looks rough when compared with the Ru substrate [a)]. In g) the average reflected intensity is plotted versus time. The first peak corresponds to the completion of the first ML [b)].