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Growth and oxidation of Cr films on the W(1 0 0) surface

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Abstract

The growth and oxidation of Cr films on the W(1 0 0) surface have been studied with low energy electron microscopy (LEEM) and diffraction (LEED). Cr grows in a Stranski–Krastanov (SK) mode above about 550 K and in a kinetically limited layer-by-layer mode at lower temperature. Stress relief in the highly strained pseudomorphic (ps) Cr film appears to be achieved by the formation of (4×4) periodic inclusions during the growth of the third layer between 575 and 630 K and by growth morphological instabilities of the third layer at higher temperature. Kinetic or stress-induced roughening is observed at lower temperature. In the SK regime, three-dimensional (3D) Cr islands nucleate after the growth of three Cr layers. 3D island nucleation triggers dewetting of one layer from the surrounding Cr film. Thus, two ps Cr layers are thermodynamically stable. However, one and two layer ps Cr films are unstable during oxidation. 3D clusters, that produce complex diffraction features and are believed to be Cr_2O_3, are formed during oxidation of one Cr layer at elevated temperature, $T \geqslant 790$ K. The single layer Cr film remains intact during oxidation at $T \leqslant 630$ K. 3D bulk Cr clusters are formed predominantly during oxidation of two ps Cr layers.

Keywords: Growth; Surface morphology; Oxidation; LEEM; LEED; Chromium; Tungsten

1. Introduction

The magnetic properties of ultrathin films are a topic of considerable current research activity. One of the many recurring themes is the interplay between structure and magnetism. Due to the often strong interaction with the substrate, films may be coherently strained or, more extremely, they may adopt a structure that differs from their natural bulk form. Stabilization of strained or non-bulk structures offers the possibility to identify new magnetic phenomena and to develop a deeper understanding of magnetism. This general motivation for studying films of ferromagnetic materials applies equally well to anti-ferromagnetic materials.

In this paper, we report on the growth and oxidation of Cr films on the W(1 0 0) surface. While Cr is anti-ferromagnetic in bulk bcc form, early theoretical work predicted that Cr may have ferromagnetic properties if its lattice constant could be increased by about 20% [1]. Although this extreme condition may never be achieved, the growth of highly strained pseudomorphic (ps) Cr films on W(1 0 0) has been reported [2]. Ps Cr on W(1 0 0) has (lateral) tensile strain of nearly 10%. This large strain is expected to have some effect on the anti-ferromagnetic properties of Cr. Cr film growth was studied previously below 400 K with low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) [2]. We extend earlier studies by examining growth above 400 K using complementary low energy electron microscopy (LEEM) and diffraction. Besides magnetic phenomena, another interesting observation that provided a separate motivation for this work is that $c(2 \times 2)$ ordered surface alloys form when some metals, including Cu, Ag and Au, interact with the W(1 0 0) surface at elevated temperature [3–5]. Investigations of the interaction of other metals, such as Cr, with W(1 0 0) at elevated temperature

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may contribute to the understanding this alloying phenomena.

The oxidation of Cr on W(1 0 0) is aimed at formation of chromium oxides. Chromium dioxide, CrO_2, is a half-metallic ferromagnetic material with a Curie temperature of 390 K and a spin polarization at the Fermi level of close to 100% [6,7]. Due to its special spin polarization properties, CrO_2 is an attractive material for spin transport. However, CrO_2 is metastable at atmospheric pressure and has been shown to irreversibly reduce to Cr_2O_3 at temperatures between 525 and 740 K [8,9]. This imposes the demand for rigorous synthesis conditions and also limits the potential applications of CrO_2. On the other hand, Cr_2O_3 is widely used as a catalyst in many applications and as a constituent in anti-corrosive materials [10,11]. In terms of oxide growth, the W(1 0 0) surface appears to be a favorable substrate for CrO_2 epitaxy. CrO_2 has rutile structure with tetragonal Bravais lattice. The lattice constant is $a_{CrO_2} = 4.42$ Å with $c/a = 0.66$ (c-axis repeat distance of 2.92 Å) [12]. The CrO_2 lattice constant is closely matched to the separation of next-neighbor sites (the diagonal of the surface unit cell) on W(1 0 0), $\sqrt{2}a_W = 4.47$ Å. Epitaxy of CrO_2 on W(1 0 0) in this orientation with c-axis normal to the substrate surface could produce a $c(2 \times 2)$ diffraction pattern.

These investigations of Cr growth and formation of Cr-oxides on a macroscopic W(1 0 0) surface also have relevance to spin polarized scanning tunneling microscopy (SP-STM) techniques. The earliest substantial report of SP-STM imaging described results obtained with ferromagnetic CrO_2 crystalline tips [13]. Anti-ferromagnetic Cr-coated W(1 1 0) probe tips have also been demonstrated that have the advantage over ferromagnetic tips of vanishing dipole field [14]. Cr or CrO_2 coated W(1 0 0) tips may also produce useful spin polarized tunneling effects.

2. Experimental details

The growth and oxidation of Cr films were investigated with LEEM and LEED. The imaging principle and contrast mechanisms of LEEM have been described previously [15–17]. The complementary diffraction and imaging capabilities of LEEM also permit direct comparison of real and reciprocal space features of the same sample area. LEEM imaging of growth was performed using an incident electron energy of $E = 7.3$ eV. This energy corresponds to a nearly out-of-phase interference condition between adjacent terraces that are separated by a monatomic step on the W(1 0 0) surface, which results in strong step contrast features in LEEM images [16]. The W sample was oriented to within 0.1° of the [1 0 0] direction. It was cleaned by annealing at 1200 K in an oxygen pressure of 1×10^{-7} Torr and flashing to 2000 K. The sample temperature was measured by a W/Re3%–W/Re25% thermocouple that was attached to the sample holder immediately adjacent to the side of the sample. The growth experiments were performed by depositing Cr on the surface at various fixed temperatures. Cr was deposited reproducibly from an electron beam heated rod in a deposition source that was equipped with water cooling and flux monitor by proportional ion current measurement. The pressure rose to the mid-10^{-10} Torr range during Cr deposition. The deposition rate referenced to the ps monolayer (ML) was in the range from 0.18 to 0.25 ML/min. The results did not depend noticeably upon deposition rate in this range.

3. Results

3.1. Growth

The growth of Cr on the W(1 0 0) surface was investigated in the temperature range from 430 to 840 K. A uniform decrease of the LEEM image intensity was observed initially during Cr deposition, which evolved further as intensity oscillations (Fig. 1). These oscillations are caused by periodic island nucleation, growth and completion of atomic layers [17].[1] The presence of two prominent intensity peaks positioned at equal time intervals during Cr deposition identifies layer-by-layer growth of at least two complete layers in most of the temperature range studied. LEEM step contrast [16], which is sensitive to atomic scale roughness, is also weakened or lost at (atomically rough) half-integer layer coverages during growth and returns strongly at times that correspond to the completion of the (atomically smooth) first and second layers. This is shown explicitly in panels (a)–(e) in Figs. 2–5 for growth of the first two layers in the temperature range 630–740 K. The surface evolved in a very similar way during intensity oscillations at other temperatures. The uniform appearance of the surface during growth of the first two layers at all temperatures therefore implies the presence of a high density of very small islands that are not resolvable with LEEM. The absence of superstructure diffraction spots in LEED also indicates that the first two Cr layers grow pseudomorphically at all deposition temperatures (Fig. 6(a)).

In contrast to the growth of the first two layers, island and step flow growth of the third layer were clearly resolved with LEEM between 575 and 690 K (panels (f)–(h) in Figs. 2–4). The third Cr layer grew pseudomorphically except for small features that appeared black in LEEM images. These features were identified with LEED to have a (4×4) periodic structure (Fig. 6(b)). The (4×4) structure was formed during growth at temperatures between 575 and 630 K (Fig. 2), but was strongly suppressed during growth at lower temperature and was also absent at 650 K and above (Fig. 3–5).[2] The (4×4) structure

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[1] Strong image intensity oscillations are expected to occur at out-of-phase imaging conditions during growth, if the island nucleation density is high and island growth before coalescence does not exceed the coherence length (~400 Å) of the electron beam.

[2] The (4×4) structure also transformed reversibly to the pseudomorphic (1×1) structure during heating with a transition temperature between 630 and 650 K. The (4×4) structure was stable and grew somewhat during cooling to room temperature.