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Stabilizing face-centred-cubic magnesium

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Abstract

Experiments aimed at the stabilization of the metastable face-centred-cubic (fcc) phase of Mg which was found by calculation of the epitaxial Bain path (EBP) are described. Ultrathin films of Mg up to 14 Å thick are grown on a W{001} substrate and found to be pseudomorphic. A quantitative low-energy electron diffraction analysis finds the crystal structure of these films to be body-centred tetragonal with axial ratio $c/a = 1.39$. Consideration of where this structure fits on the calculated EBP confirms that it is a strained state of the fcc phase, which has therefore been stabilized by pseudomorphic epitaxy.

1. Introduction

First-principles total-energy calculations of the epitaxial Bain path (EBP) for tetragonal states of Mg [1] have revealed the existence of a face-centred-cubic (fcc) phase with energy only about 1 mRyd/atom higher than that of the hexagonal close-packed (hcp) ground state of Mg. The calculated elastic constants of this phase satisfy the stability conditions for fcc crystals [1], hence the phase is metastable.

The present paper describes experiments aimed at stabilizing this phase in the form of ultrathin films grown pseudomorphically on a suitable substrate. We recall that pseudomorphism is the special case of epitaxial growth in which a growing film assumes the same in-plane lattice parameters as the substrate. If the substrate surface has lattice parameters equal or close to the calculated parameters of a metastable phase of the film material, then this phase has a good probability of being stabilized, at least for a small number of atomic layers, owing to the fact that the film is anchored to the substrate surface by the pseudomorphism. Previous work has shown that this procedure can indeed be successful for stabilizing metastable phases (fcc Ti on Al{001} [2], and δ-Mn on W{001} [3]), and in some cases even for stabilizing unstable phases by constrained epitaxy (body-centred-tetragonal (bct) V on Ni{001} [4] and on Cu{001} [5], and bct Pd on W{001} [6]).

In the present case, the first-principles calculations [1] have shown that the lattice parameter of fcc Mg is about 4.5 Å; more precisely, that the parameters of the corresponding bct cell are $a = 3.14$ Å and $c = 4.44$ Å when calculated with the local-density approximation (LDA), and $a = 3.20$ Å and $c = 4.51$ Å when calculated with the generalized gradient approximation

(GGA) [1]. These results suggest that a suitable substrate for possible pseudomorphic growth of fcc Mg should have a square-net surface with a mesh edge between 3.1 and 3.2 Å. The {001} surface of tungsten, which is body-centred cubic (bcc) with $a = 3.1652$ Å, fulfils the requirement.

We report here the results of experimental attempts at stabilizing the fcc phase of Mg in ultrathin pseudomorphic films grown on W{001}. The procedure consists in depositing small amounts of Mg on an atomically clean W{001} surface in ultrahigh vacuum; testing that the Mg film is pseudomorphic with the substrate; and then determining its lattice parameters. These parameters are: a, the in-plane lattice constant, which is identical to that of the W{001} substrate if the film is indeed pseudomorphic; and c, the periodicity in the direction perpendicular to the substrate surface. A perfect fcc crystal would have the axial ratio $c/a = \sqrt{2}$, but a pseudomorphic film is usually strained, because the a-parameter of the substrate surface almost never matches exactly the in-plane parameter of the film material. Hence, the film is stretched (or compressed) within the plane and consequently compressed (or stretched) in the perpendicular direction: the crystal structure is bct with c/a close to, but different from, $\sqrt{2}$.

The technique used for the determination of the c-parameter is the well-tested quantitative low-energy electron diffraction (QLEED) method. Once c is known, both the ratio c/a and the volume/atom $V = a^2c/2$ can be calculated, and the result is then plotted on the calculated EBP. The location of the experimental point on the EBP usually indicates whether or not the structure of the grown film is a strained form of the fcc phase.

We describe in section 2 the experimental procedures and in section 3 the QLEED structure analysis, while in section 4 we give a discussion and the conclusions.

2. Experiment

The experiments were carried out in a stainless-steel chamber pumped with a sputter-ion pump and capable of reaching base pressures of about 1×10^{-10} Torr or lower. The substrate was a W{001} platelet with approximate dimensions $8 \times 9 \times 0.5$ mm^3. The initial cleaning procedures of the substrate surface were lengthy and elaborate, owing to the presence of C impurities in the bulk of the platelet, and are described in detail in [3]. But thereafter the re-cleaning procedure was rather simple: a series (4 to 5) of Ar-ion bombardments at room temperature for about 6–12 h each (5×10^{-5} Torr of Ar gas, about 1 μA of ion current, 375 eV of ion energy), followed by anneals at 1200 °C for 5–10 min each time.

Auger electron spectroscopy (AES) was used to test the chemical composition of the W surface, and the cleaning process was continued until AES revealed no impurities (C and O) above the noise. The anneals produced a 1×1 LEED pattern with low background and sharp spots, typical of a clean well-annealed W{001} surface at room temperature.

The deposition source consisted of electrically heated tungsten spirals containing small pellets of 99.95% pure Mg. Deposition rates were usually small, between 0.2 and 0.8 Å min^{-1}. The surface coverage was determined from AES scans in the conventional way (see, e.g., [2]) from the ratio of the Mg line at 45 eV to the W line at 169 eV. It should be noted that a film thickness determined in this way is an *equivalent* thickness, i.e., the thickness of a flat and uniform film that would produce the same AES intensities as observed. The actual film is not expected to be, and most certainly is not, uniformly flat. The accuracy of the quoted thickness values is not estimated to be very high, perhaps around ±50%.

The LEED optics used was of the reverse-view type. The intensities of the diffracted beams were measured with a conventional computer-controlled TV-camera system [7].

The growth procedure was typically the following. With the substrate kept at room temperature:

(1) deposit approximately 2–3 Å of material;
(2) determine the coverage with AES;
(3) check the LEED pattern and collect the intensity-versus-voltage (so-called $I(V)$) curves for a few diffracted beams;
(4) compare the $I(V)$ curves with those measured before the last deposition.

In this work, after all depositions the LEED pattern remained essentially 1×1, with the major diffracted beams geometrically at the same locations as those of the substrate (albeit with increasing background), which confirms that the growing film was pseudomorphic. Some weaker extra beams appeared after the film grew beyond about 8 Å, and will be discussed below. The $I(V)$ curves changed visibly in the early stages of deposition, as expected when growing pseudomorphic films, and continued to change until the films were about 9–10 Å thick. Thereafter the $I(V)$ curves no longer changed, a situation that we refer to as one of 'stable' $I(V)$ curves. Generally, the background is high at this stage, and continues to worsen with increasing surface coverage until the LEED pattern is obliterated, for thicknesses of about 15 to 20 Å. An important goal for our purposes is to grow a film that produces stable but still measurable $I(V)$ curves, because this stability means that the incident electron beam does not 'see' the substrate; hence the intensity calculations needed for the structure analysis can be done with the simplifying assumption that the film is semi-infinite, disregarding the presence of the substrate. All $I(V)$ curves were recorded for normal incidence of the primary electron beam.

After obliteration of the LEED pattern the film was sputtered away until the clean substrate surface was attained, then another film was grown and its stable $I(V)$ curves measured. The sequence was repeated four times to ensure reproducibility of the experimental $I(V)$ curves.

3. Structure analysis

The calculations of the diffracted LEED intensities were done with the CHANGE computer program written by Jepsen [8], including 81 beams and 5 phase shifts up to 400 eV. The Mg potential was obtained from the collection of Moruzzi *et al* [9]. The real part of the inner potential was initially set at 10 eV and adjustable during the analysis, and the imaginary part was 4 eV; the root mean square amplitude of thermal vibrations was $(\langle u^2 \rangle)^{1/2} = 0.126$ Å.

The calculations were done for a semi-infinite film of pure Mg{001} with in-plane lattice constant equal to that of W{001}, $a_0 = 3.1652$ Å, as required by the pseudomorphism. The calculations were done for many values of the bulk interlayer spacing d_{bulk}: from 1.80 to 2.6 Å, initially in steps of 0.2 Å, later in steps of 0.1 or even 0.02 Å, in each case varying the *change* in first interlayer spacing Δd_{12} from -0.5 to $+0.5$ Å in steps of 0.05 Å. The $I(V)$ curves calculated for each d_{bulk}-value were compared with the experimental curves both visually and by calculation of the Zanazzi–Jona R-factor r_{ZJ} [10]. For the best parameters thus found we then tested possible changes Δd_{23} in the second interlayer spacing.

The best agreement between calculated and observed $I(V)$ curves was found for the following parameters (lengths in Å):

$$d_{bulk} = 2.2, \qquad \Delta d_{12} = 0, \qquad \Delta d_{23} = -0.2, \qquad r_{ZJ} = 0.17.$$

For reasons to be discussed later, the error bars are estimated to be large, ± 0.15 Å for d_{bulk} and ± 0.2 Å for Δd_{12} and Δd_{23}. The $I(V)$ curves calculated with the above parameters are compared to the experimental ones in figure 1.

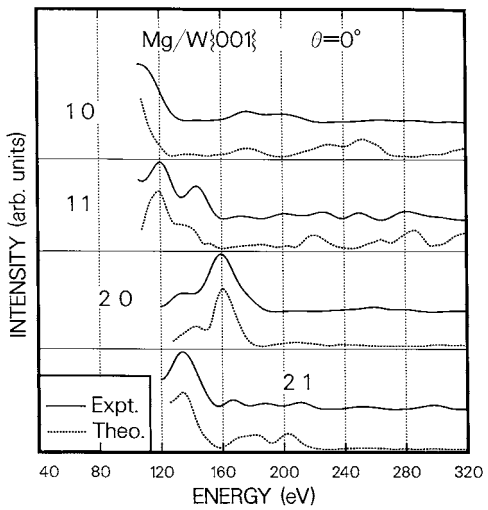

Figure 1. Experimental (solid) and calculated (dotted) $I(V)$ curves for a Mg{001} film on W{001}.

4. Discussion

The best R-factor value found above is not as low as we would have expected. Visual comparison between theoretical and experimental $I(V)$ curves, in figure 1, shows that the major peaks are well reproduced, but the smaller peaks are not.

A factor playing an important role in the fit of theory to experiment, in this work, is the presence of the extra spots in the LEED pattern, which are reproducibly observable on Mg films thicker than about 8 Å. These extra beams are located near, but not on, the 10-type beams and between the 10- and the 11-type beams, apparently arranged on a hexagonal mesh superimposed on the square mesh of bct Mg. A photograph of the LEED pattern at 90.2 eV (an energy at which the extra spots are most intense) is reproduced in figure 2.

Since the ground state of Mg is hcp, the hexagonal symmetry of the extra spots' arrangement suggests that they may be connected with hcp Mg. However, our measurements find that the mesh constant of this arrangement is about 2.8 Å, a value that is inconsistent with the possibility of a coexisting film of hcp Mg (lattice constant $a = 3.2094$ Å). Contributions from impurities seem unlikely, since the only impurities detected, C and O, have AES peaks which emerge from the noise during film deposition and reach intensities of only about 0.04 and 0.005, respectively, smaller than the Mg peak of a 14 Å thick film. Furthermore, the lattice parameters of possible oxides or carbides of Mg are also inconsistent with 2.8 Å (MgO: 4.21 Å; MgC_2: 4.86 Å; $MgCO_3$: 4.62 Å). Hence, the origin of the extra spots remains unclear.

However, an important consideration for our present purposes concerns the effect that the extra spots may have on the $I(V)$ curves used in the QLEED analysis. We note that the extra spots in the vicinity of the 10-type beams (figure 2) are too close to the corresponding 10 beams to allow measurement of the latter's intensities alone. The result is that the measured $I(V)$ curves of the 10 beams of fcc Mg contain small components (the intensities of the extra spots are generally small) coming from the extra spots. The 11-type beams seem also to contain some small spurious contributions (very weak extra spots, not visible in the photograph reproduced in figure 2, are present in the pattern very near the 11 and the $\bar{1}\,\bar{1}$ beams, and do not seem to be

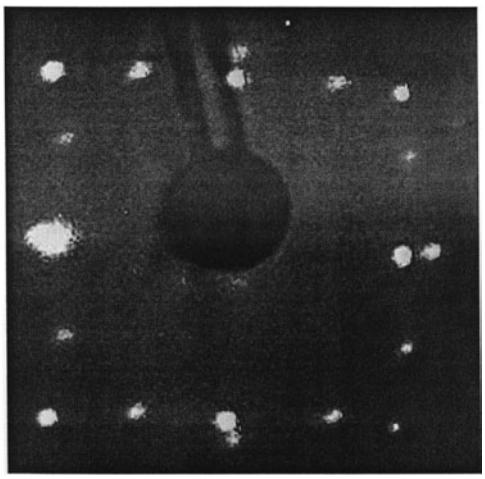

Figure 2. A photograph of a LEED pattern from a 14 Å Mg film on W{001} for 90.2 eV electron energy. In addition to the square-net spots produced by bcc Mg{001}, extra spots are visible near the 10-type and between the 10- and 11-type beams.

part of the hexagonal pattern). The 20 and 21 beams of fcc Mg are less affected by the extra spots, and in fact the visual fit of these beams is somewhat better than that of the others. It seems reasonable to conclude that the differences between theoretical and experimental $I(V)$ curves in the range of low intensities is due in part to the presence of the extra spots.

An overall conclusion can nevertheless be reached upon consideration of all experimental facts, namely: the Mg films grown in this work are (i) crystalline; (ii) pseudomorphic to the W{001} substrate; hence (iii) they have an in-plane square net; and (iv) their bulk interlayer spacing is $d_{bulk} = 2.2$ Å. We conclude therefore that the crystal structure of the Mg films grown here is bct with parameters $a = 3.6152$ Å and $c = 4.4$ Å ($=2 \times d_{bulk}$ as determined above).

This structure is undoubtedly a strained state of some 'mother' equilibrium phase; hence the next question is: what is the mother phase?

To answer this question we resort to the calculated EBP of tetragonal Mg, and in particular to the plot of normalized volume/atom V/V_0 versus axial ratio c/a, reproduced from [1] in figure 3. We recall that this curve was drawn by dividing the theoretical values of V^{theor} of each state on the curve by the theoretical volume/atom $V_0 = V_0^{theor} = 21.83$ Å^3 of the metastable fcc phase (for the LDA calculation), and that the shaded portion of the plot is the region of intrinsically unstable states. From our experimental results we calculate $c/a = 4.4/3.1652 = 1.39$ and $V^{exp} = a^2c/2 = 22.04$ Å^3. In order to enter this experimental point on the EBP we should divide the V^{exp} by the experimental value V_0^{exp} of the fcc phase. Such a value, of course, is not available. The best that we can do is to 'correct' the theoretical value of $V_0^{theor} = 21.83$ Å^3 by using as a guide the corresponding values of the stable hcp phase, for which the experimental volume is known; see [1]. For hcp Mg: $V_0^{exp} = 23.24$ Å^3 and $V_0^{theor} = 21.6$ Å^3. Using the ratio between these values, we estimate an 'experimental' value of the fcc phase $V_0^{exp} = 23.4$ Å^3, hence $V^{exp}/V_0^{exp} = 0.94$. This experimental result is plotted in figure 3 as an open circle, with estimated error bars.

The most important part of this result is that the experimental point lies on the same side of the intrinsically unstable region of the EBP as the metastable fcc phase. This observation indicates that the structure of the Mg films grown was indeed a strained state of the fcc phase,

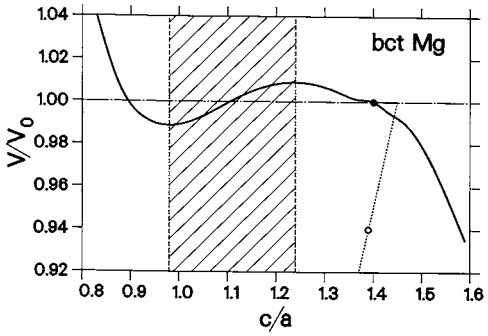

Figure 3. The EBP of tetragonal Mg calculated in [1], displaying reduced the volume V/V_0 versus the axial ratio c/a of the tetragonal states of Mg (V_0 is the theoretical value of the volume/atom of the fcc phase of Mg). The full circle marks the position of the metastable fcc phase as calculated. The shaded area covers a region of intrinsically unstable states. The open circle is the experimental point obtained from the bulk interlayer spacing 2.2 Å found with the QLEED analysis. The error bars are calculated from an estimated accuracy of ± 0.15 for the bulk interlayer spacing of the Mg film.

which was therefore the 'mother' phase. We conclude that the metastable fcc phase of Mg was stabilized by the pseudomorphism in the ultrathin films grown on W{001}.

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