Observation of (6×2) and close-packed $c(8\times2)$ structures of dysprosium on W(100)

N. Moslemzadeh,[1,*] S. D. Barrett,[1,2] and J. Ledieu[1]
[1]*Surface Science Research Centre, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom*
[2]*Department of Physics, University of Liverpool, P.O. Box 147, Liverpool L69 7ZE, United Kingdom*
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Low-energy electron diffraction (LEED) results have showed that Dy films grown on W(100) at room temperature are highly disordered. By growing Dy on W(100) at 470 K, an epitaxial relation was found for Dy/W(100) in which Dy(0001)‖W(100) and Dy$[11\bar{2}0]$‖W[010]. Annealing to 770 K improved significantly the quality of the LEED pattern. The Dy hexagonal lattice is slightly distorted along the [010] and [001] axes of the W(100) substrate, resulting in a $c(8\times2)$ commensurate unit cell. The lattice constants of the Dy overlayer have been found to be extended by 0.7% (along W[010]) and by 1.5% relative to the Dy bulk lattice constant. Scanning tunneling microscopy (STM) studies of the annealed film showed that this annealing temperature for Dy/W(100) will produce flat and well-ordered films of $c(8\times2)$ structure. STM studies have shown that Dy also forms a (6×2) structure in some regions of the surface.

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I. INTRODUCTION

The electronic structure of a material is intimately related to the geometric structure. Any structural change at a surface will give rise to a redistribution of valence-band electrons. This valence state changes can cause not only a modification of surface core levels,[1–3] but also a modification of the atom sizes, which can cause surface reconstructions or can affect the growth mechanism in thin-film growth.[4] Therefore it is important to study electronic structure and geometrical structure together. Producing flat and well-ordered films of Dy on tungsten surfaces is one of the major aims of this study. This is very important for future applications of these films in complementary experiments such as magnetic properties investigations which can bring them closer to the practical applications. Low-energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS), and scanning tunneling microscope (STM) experiments have been carried out on the Dy/W(100) system to obtain such information about the morphology of the films. However, little is known about the geometric structure of Dy on different W surfaces. Ciszewski and Melmed[5] used field electron emission from a sharp W tip which had W(100) facets. The substrate, which was a polyfaceted crystal, was heated during deposition to give the adsorbate atoms sufficient energy to migrate over the substrate. One of their observations was the epitaxial relationships of (0001)Dy‖(001)W with $[01\bar{1}0]$Dy‖[001]W. These epitaxial relationships were found only where the substrate was held at 800–930 K during the growth. However, the W surface was not macroscopically flat and had a very small effective area, and so their conclusion regarding growth cannot necessarily be extrapolated to atomically flat surfaces. The most relevant structural study of the work in this study on Dy/W(100) is the Gd/W(100) system studied by White *et al.*[6] with STM and LEED, in which a $c(8\times2)$ overlayer was observed. This was very similar to a close-packed layer with hexagonal symmetry, but with a small surface-induced strain, giving rise to the description of ''pseudohexagonal.''

II. EXPERIMENTAL DETAILS

The x-ray source was a water-cooled Henke type with twin anode source (Mg-Al), and the electron energy analyzer was a hemispherical Vacuum Generator MDS50 type. The base pressure of the chamber was 8×10^{-11} mbar, and during evaporation, the pressure remained below 1×10^{-10} mbar.

The W crystals were prepared by backfilling the chamber with $\sim10^{-6}$ mbar O_2 and heating the sample to 1800 K for 30 min to remove C, followed by cycles of flashing briefly to 2500 K, when the pressure reached $\sim10^{-10}$ mbar. This process was repeated until the surface was judged to be clean and well ordered by LEED and XPS. The substrate temperature was measured using an optical pyrometer and a C-type thermocouple.

Evaporation of Dy was carried out by a well-degassed WA Technology Knudsen cell (*K*-cell) evaporator which contained Dy of 99.99% purity. This type of evaporator is able to keep the evaporation temperature constant within ±1 °C. Having an enclosed cell makes this type of evaporator well suited for evaporating Dy, which has a relatively high vapor pressure (70 Pa at its melting point of 1685 K).[7]

The Dy coverage was calibrated using the known deposition rate of the source (which was regularly checked and remained stable over the experiments) and by the intensity of the W $4f$ levels in XPS. Due to the high reactivity of rare-earth metals,[8] the sample was flashed every 30 min and new films were grown to ensure that the films were clean during the experiment.

LEED experiments were carried out using a Vacuum Generators system mounted onto the analytical chamber, and the STM experiments were performed using a commercial Omicron Vakuum Physik STM operated at room temperature (RT) in an ultrahigh-vacuum chamber different from that of the XPS experiments. The base pressure of the chamber was 2×10^{-11} mbar, and during evaporation, the pressure remained below 9×10^{-11} mbar.

The STM images were obtained in constant-current mode and represented as gray tone images. The data presented by

U and *I* in the figure captions refer to sample bias voltage and tip current, respectively. The *xyz* piezoelectric system was calibrated by measurements of graphite with known periodicity. The error in measurements was found to be ~4% in the *x, y*, and *z* directions. All image processing was carried out using IMAGE SXM.[9]

The crystallographic directions assigned to the images were determined by the orientation of the LEED patterns, and splitting of spots indicated terraces of 30 Å width on the clean W(100) surface.

III. RESULTS

A. LEED

The LEED patterns of 1–3 ML of Dy grown on W(100) at RT showed high background intensity with W spots and a very faint and broad pattern of two hexagonal-shaped domains of Dy spots rotated by 90° relative to each other. Spots of one of the Dy hexagonal domains were matched to the W spots in the [001] direction and the other domains to those in the [010] direction. This was very similar to the pattern of Gd/W(100),[6] but with a very high background. The pattern did not show significant change by growing at different temperatures. However, the growth at 470 K was the best temperature of those tested (RT and 470, 570, 670, and 770 K). However, even at 470 K, the background intensity was high and the Dy spots were very faint.

These observations indicate that the surface of the Dy films grown on W(100) is highly disordered. As one of the aims of this study is to find the conditions under which clean and well-ordered films can be produced, annealing was carried out at different temperatures. By annealing the films (grown at RT) to different temperatures up to 820 K it was found that the background intensity decreased and hexagonal spots of Dy became sharper. However, only one domain of Dy remained in the pattern after annealing, whose spots matched the W spots along W[001].

The best annealing temperature was found to be 770 K. The LEED result of annealing 3 ML of Dy to this temperature is shown in Fig. 1. The W spots were still clear in this picture. This annealing caused an increase (decrease) in Dy (W) intensity in XPS, indicating a flattening of the Dy film. By increasing the annealing temperature from 770 to 820 K, the intensities of the Dy (W) LEED spots and the XPS signal of Dy (W) decreased (increased) slightly. However, the LEED pattern still consisted of sharp W and Dy spots and no change in background intensity could be seen. These observations are attributed to accumulation of the Dy film and the formation of ordered islands of Dy. By increasing the annealing temperature to above 820 K, the background increased in the LEED pattern and the Dy spots started to become broad and faint. Simultaneously, the XPS signal of Dy (W) started to decrease (increase). This is an indication of evaporation of the Dy film.

Careful measurements of angles and ratios between reciprocal vectors of the Dy surface lattice has been made on the LEED pattern indicated that the Dy hexagonal lattice is slightly distorted along the [010] and [001] axes of the W(100) substrate. These results, together with consideration

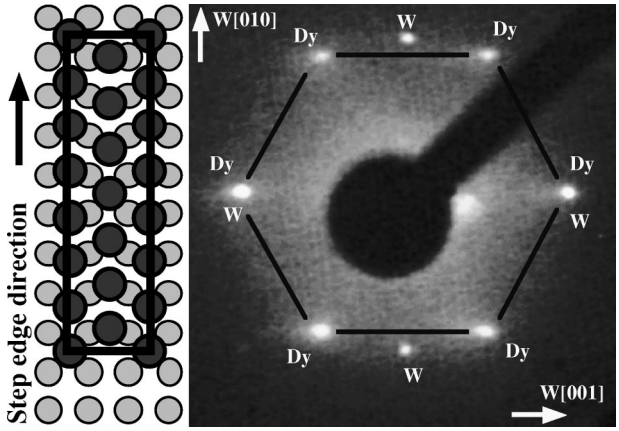

FIG. 1. LEED pattern taken at 110 eV beam energy of 3 ML Dy grown at RT on W(100) and annealed at 770 K. A schematic diagram of a possible Dy $c(8\times2)$ structure on W(100) is shown as an inset at the left, in which gray circles are W and dark circles are Dy. To indicate the registry of each Dy atom in the unit cell, the Dy circles have been drawn smaller than their actual size relative to the W circles.

to minimize the misfit between the Dy and W lattices, indicated that Dy forms a $c(8\times2)$ commensurate cell with respect to the W substrate (Fig. 1). In this case the interatomic distances of the Dy overlayer are found to be extended by 0.7% along W[010] and by 1.5% along W[001] relative to the bulk Dy(0001), which is itself expanded by 5% relative to ideal close packing. Therefore, the unit mesh of the Dy overlayer is expanded by 1.9% relative to the basal plane of the Dy. It is interesting to note that in the case of Dy (bulk lattice constant $a=3.592$ Å) both $a_{1_{\mathrm{Dy}}}$ and $a_{2_{\mathrm{Dy}}}$ are extended, while in the case of Gd (Ref. 6) (bulk lattice constant $a=3.634$ Å) $a_{1_{\mathrm{Gd}}}$ is extended and $a_{2_{\mathrm{Gd}}}$ is contracted. Therefore, the Gd surface lattice expands in area by only 0.1%, which is significantly smaller than that of Dy. Because of the relatively large expansion of the Dy film compared to the bulk, this structure needs a large amount of energy to overcome such a strain. This is why a $c(8\times2)$ LEED pattern is clear only after 470 K growth (not RT). As a result of the anisotropy in strain, it is now clear that dominance of one

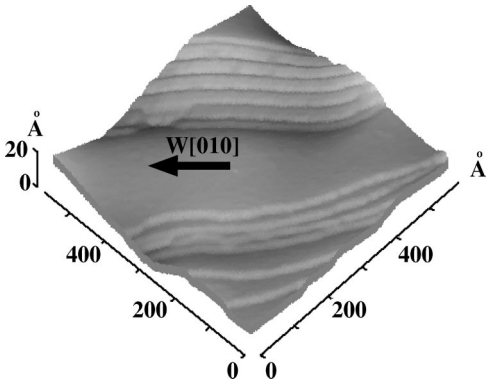

FIG. 2. STM image of Dy/W(100) in constant-current mode of 5 ML Dy annealed to 750 K, corresponding to the $c(8\times2)$ structure. $U=1$ V, $I=1$ nA.

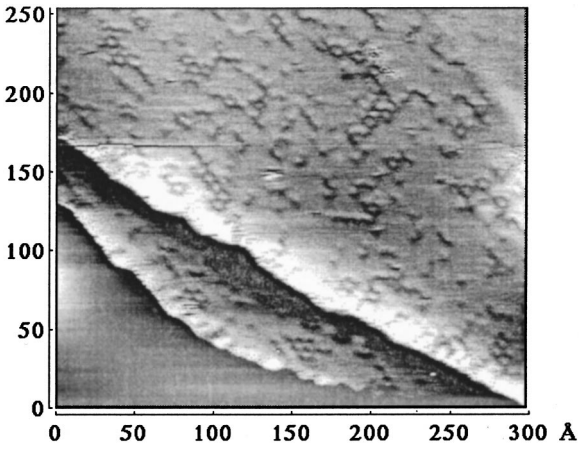

FIG. 3. STM image of one of the terraces shown in Fig. 2. The defects on the surface, such as missing rows and atoms, resulted in atomic resolution in the image. $U=-0.8$ V, $I=2$ nA.

domain over the other on annealing depends on the size (average width ~25 Å) and direction (W[010]) of the terraces of the substrate. That is, for finite-sized terraces the domain with smaller strain along the step edge direction has lower energy than the other domain.

Although from a thermodynamic point of view structures with larger interatomic distances are less stable, it seems that the surface (and interfacial) free energy of the extended Dy area successfully competes with the strain energy of the Dy film.

B. STM

An STM image of a surface giving the same pattern as shown in Fig. 1, the Dy/W(100) system annealed to 750 K, is shown in Fig. 2. The film consists of flat and large terraces of Dy (compared to those of W) which are along the step edge direction of the substrate, i.e., W[010]. Step heights have been measured and found to be (multiples of) 2.82 Å as expected for single (multiple) steps of Dy(1000) layers. The

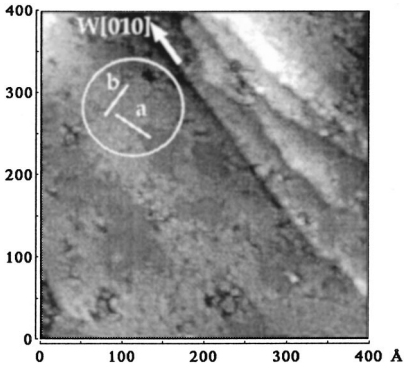

FIG. 4. STM image of a region with atomic resolution of Dy film produced by annealing 5 ML Dy to 750 K. The vertical displacement along the direction shown by line (a) between non-close-packed and close-packed areas (dark patches) is 0.7 Å. The vertical corrugation between atoms along the direction shown by line (b) is 0.2 Å. The circles indicates the region shown in Fig. 5. $U=-0.5$ V, $I=0.5$ nA.

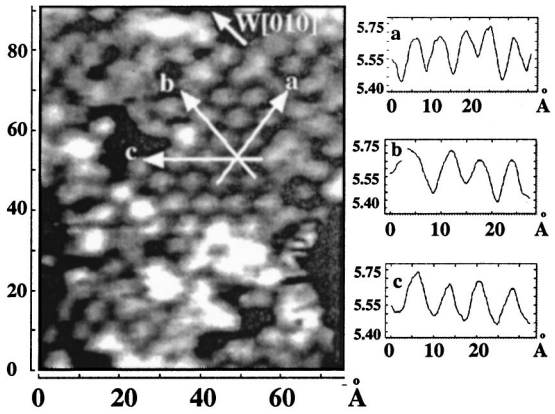

FIG. 5. Enlarged view of the area shown by the circle in Fig. 4. The insets show profiles of atomic rows along lines shown by *a*, *b*, and *c*. The corresponding interatomic distances are 6.6, 6.3, and 7.5 Å, respectively.

average sizes of terraces was found to be at least 5 times larger than the average size of terraces on the clean W(100) surface. Further attempts to achieve atomic resolution of the close-packed $c(8\times2)$ structure were not successful due to low corrugation of the surface. Figure 3 shows an image of one of such terrace. It is clear from this image that defects on the surface, such as missing rows and atoms, resulted in increasing corrugation of nearby areas, which led to atomic resolution in the image.

By further investigation of different areas on the film a small region with atomic resolution was found (Fig. 4). This area consists of regular Dy atomic rows along steps which is consistent with the LEED orientation of the close-packed $c(8\times2)$ (see Fig. 1). However, the distances between adjacent Dy atoms were different from those of the close-packed $c(8\times2)$ structure. For example, the apparent interatomic distance was 6.4 Å along the step direction, which is larger than the case for close-packed $c(8\times2)$. This leads to an increase of corrugation to 0.2 Å between adjacent Dy atoms, which makes it possible to achieve the atomic resolution. It is possible to recognize a distorted hexagonal pattern for this structure. Figure 5 shows a closer view of the area shown by the circle in Fig. 4. Profiles along lines (a), (b), and (c) indicate that atomic distances along these directions are 6.6, 6.3, and 7.5 Å, respectively. These measurements show that Dy

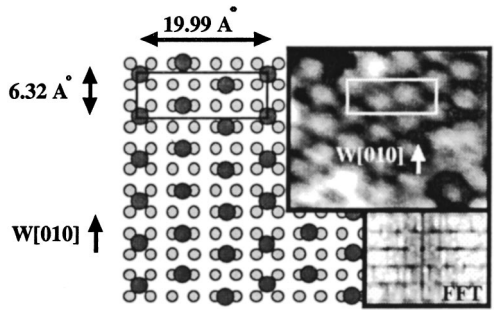

FIG. 6. (6×2) model corresponding to the structure in Fig. 5 (shown as inset in the right top). An FFT of this model is shown as an inset in the bottom right of the image.

forms a distorted hexagonal overlayer in this area with an apparent interatomic spacing 2 times larger than the bulk value of Dy. A model for this structure is shown in Fig. 6. Such a large lattice constant is unlikely to occur and a fast Fourier transform (FFT) of this proposed structure shows maximum intensities at positions that do not correspond to those of the LEED spots in Fig. 1. It is possible that the 0.2 Å corrugation is a consequence of a reconstruction of a close-packed structure involving vertical displacements of alternate atoms.

In summary, LEED studies have shown that Dy films grown on W(100) at room temperature are highly disordered. By growing Dy on W(100) at 470 K, an epitaxial relation was found for Dy/W(100) in which Dy(0001)‖W(100) and Dy$[11\bar{2}0]$‖W[010]. Annealing to 770 K improved significantly the quality of the LEED pattern. The Dy hexagonal lattice is slightly distorted along the [010] and [001] axes of the W(100) substrate, resulting in a $c(8\times2)$ commensurate unit cell. In this model the lattice constants of the Dy overlayer have been found to be extended by 0.7% (along W[010]) and by 1.5% relative to the Dy bulk lattice constant. STM studies of the annealed film showed that this annealing temperature for Dy/W(100) will produce flat and well-ordered films of $c(8\times2)$ structure. STM studies also showed that Dy formed a (6×2) structure over a small part of the surface.

*Corresponding author. FAX: 0044 151 7080662. Electronic address: moslemza@liv.ac.uk

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