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Observation of inverted island-substrate step structures in heteroepitaxial growth: Gd on W(100)

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Scanning tunneling microscopy has been used to study the growth of Gd on W(100) in which an inverted island-substrate step structure is seen for deposition at elevated temperatures. This results in lower step heights than would be the case if the islands followed the step morphology, and a reduction of the exposure of high-energy Gd faces. Deposition at lower temperatures results in flat islands whose size is related to the deposition temperature, with the data supporting a local Stranski-Krastinov growth mechanism. Low-energy electron diffraction indicates that the islands are terminated by the Gd(0001) face and that a (8×2) overlayer is formed. [S0163-1829(97)52140-0]

Over the last few years there have been a number of studies on the magnetic properties of epitaxially grown thin films. To date, most of the work has focused on 3*d* transition metals, with relatively little work being performed on 4*f* rare-earth metals. This is despite many unusual magnetic properties of these materials, such as a surface-enhanced critical temperature where the surface maintains magnetic order at higher temperatures than the bulk.[1] However, rare-earth metals are extremely reactive and difficult to clean, thus creating difficulties in obtaining experimental data. Recently attention has focused on the formation of thin films of rare earths on transition metals to overcome such problems. In particular, the growth of Gd films on tungsten single-crystal surfaces has attracted considerable attention.[2–8] To fully understand the properties of such structures, a detailed relationship between surface structure and magnetism is required. To date most of the studies have focused upon the Gd/W(110) system, in which a Gd(0001) termination of the film was reported. However, the growth mode by which Gd films formed on this surface remains a matter of debate. A recent scanning tunneling microscopy (STM) study[3] showed that a Stranski-Krastinov (SK) (layer plus islanding) growth mode occurred upon annealing to 710 K, while at lower temperatures layer by layer, Frank–Van der Merwe growth occurs, and at room temperature (RT) a rough disordered overlayer is observed. Traditionally, growth modes have been determined from thermodynamic equilibrium arguments, as determined by Young's equations,[9] and will depend on the surface free energy of the adsorbate γ_a, the interfacial energy γ_i, and the substrate γ_s.

However, as has been illustrated by the intensive research over the past few years into the structures formed by metal-on-metal growth, the situation is much more complicated than predicted from such considerations, in part due to effects such as strain energies, and the fact that many films are grown under conditions far from equilibrium. STM has proved to be a valuable technique in determining many of these surprising growth mechanisms, which include surface alloying even of immiscible metals[10] and subsurface growth modes.[11–13]

In this paper we report the growth of Gd on W(100) using STM and low-energy electron diffraction (LEED). Initially, at low deposition temperatures, poorly ordered islands are formed. Moderate annealing of the substrate to about 400 K results in the islands coalescing to form more ordered structures, and at higher coverages large islands are formed which are up to three layers thick. The size, density, and thickness of the islands are seen to be dependent on the deposition temperature. Nucleation of the second layer only occurs after the first layer is almost complete. This suggests that a local Stranski-Krastinov growth mechanism exists. LEED patterns indicate that the Gd islands on W(100) are terminated by a (0001) overlayer. Due to the lattice mismatch between W and Gd, a pseudohexagonal (8×2) structure is seen. Higher annealing temperatures reveal an inverted substrate-island morphology, previously unobserved in metal heteroepitaxial growth, in which a down step on the substrate results in an up step on the Gd island above it. By comparing the step heights of W(100) and the interlayer distance on Gd, such structures result in a smoother termination of the Gd islands.

These experiments were performed using a commercial Omicron STM operated at room temperature which was mounted in an ultrahigh vacuum chamber (base pressure 5×10^{-11} mbar), and containing standard facilities for sample cleaning and characterization. The W(100) crystal was prepared by initial annealing in partial pressures of oxygen (5×10^{-7} mbar) followed by cycles of flash annealing to 2200 K until judged clean and ordered by LEED and STM. Gd

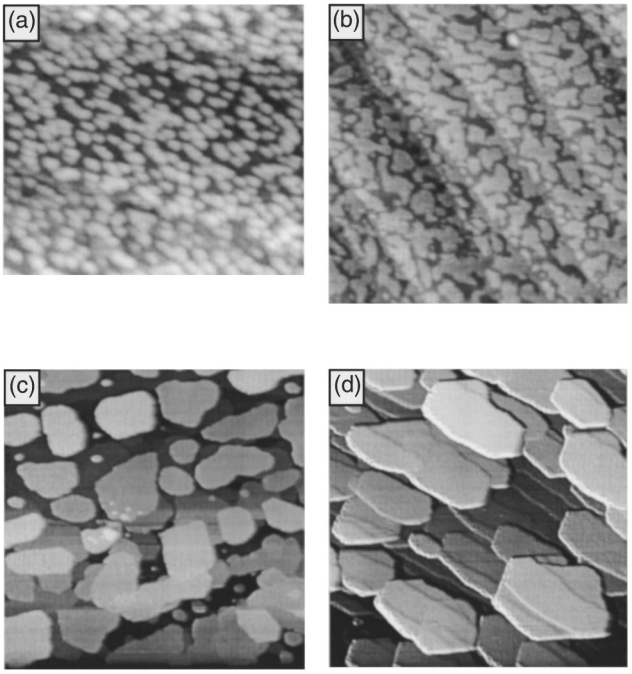

FIG. 1. (a) 500×450 Å^2 image of W(100) after 0.5 ML Gd deposition at RT, showing the appearance of small islands on the surface. (b) Typical image of the surface shown in (a) following either annealing to or deposition at 400 K (1000×1000 Å^2). (c) 2000×2000 Å^2 image after 1.5 ML Pd deposition at RT showing the formation of large islands on the terraces, above an incomplete first layer. (d) 2000×2000 Å^2 image after annealing a 3 ML film to 800 K. Large islands can be seen in which the steps on the island are inverted to the corresponding steps on the substrate.

evaporation was carried out by resistively heating a conical tungsten filament which contained Gd, with the source being allowed to stabilize before exposure of the sample, as described elsewhere.[4] Pressure during deposition remained below 5×10^{-10} mbar. All STM images were recorded in the constant current mode. The coverage was calibrated using the known deposition rate of the source which was regularly checked and remained stable over the course of the experiments.

Figure 1 shows a series of STM images recorded at a variety of Gd coverages and annealing temperatures. An image corresponding to a low coverage ($\theta_{\mathrm{Gd}}=0.6\pm0.1$ ML) deposition at RT is shown in Fig. 1(a). Poorly ordered islands are seen on the terraces which correspond in height to one Gd interlayer separation. The typical diameters of these islands is on the order of 20 Å. Such structures result in a rough morphology which increases further upon deposition at RT. However, upon slight annealing to approximately 370 K the islands coalesce, resulting in a much smoother structure as shown in Fig. 1(b), which corresponds to a coverage of approximately 0.8 ± 0.1 ML. The larger islands appear to have no preferential shape or orientation and are the same height as the structures imaged in Fig. 1(a). However, there does appear to be a preferential nucleation at the step edges as all these sites have Gd islands extending out from them, a feature seen on a number of metal heteroexpitaxial systems.[14] Despite the Gd coverage being only 0.2 ML from a full monolayer, no evidence is seen of any second layer nucleation on the islands at this coverage.

Continued deposition at similar temperatures (400 K) up to 1.5 ± 0.2 ML gives rise to the structures shown in Fig. 1(c). Larger islands which range in diameter from 200 to 400 Å are seen. The heights of the islands are 5.8 ± 0.3 Å, corresponding to two Gd layers, and the islands occupy 70% of the surface area. Again, no specific orientation of the islands or their edges is seen at these temperatures. As mentioned earlier, growth modes were initially determined from thermodynamic equilibrium arguments, as determined by Young's equations,[9] and will depend on the surface free energy of the adsorbate γ_a, the interfacial energy γ_i, and the substrate γ_s, as shown below,

$$\triangle\gamma=\gamma_a+\gamma_i-\gamma_s. \tag{1}$$

Although γ_a and γ_s are well known for most systems, γ_i is difficult to obtain, thus causing some uncertainty. Furthermore, effects such as strain energy will also further complicate the situation, as is illustrated by the many complicated growth modes that have been reported for metal heteroepitaxy.[14] However, in many of these cases there is not a great difference between γ_a and γ_s. In contrast the differences between the surface energies of Gd and W are considerably larger, being 0.935 and 3.488 J m^{-1}, respectively.[15] In the case of Volmer-Weber three-dimensional islanding growth, this occurs when $\triangle\gamma>0$ and, on the basis of the above values, would appear unlikely.[16] Thus from a simple consideration of the surface energies one would expect either a layer-by-layer or a Stranski-Krastinov growth mode as reported by Tober *et al.*[3] From the STM images a layer-by-layer growth mode is quite clearly ruled out by the fact that multilayer islands are imaged in Fig. 1(c). By calibration of the evaporator there is insufficient Gd to allow for the full completion of the initial layer before nucleation of the second, even allowing for a slight error/variation of the source. Furthermore, this is also confirmed directly by the STM data of Fig. 1(c), which shows second layer islands existing above an incomplete first layer, thereby not supporting a full SK growth mode. However, the coverage at which the second layer nucleates is quite high as evidenced by Fig. 1(b) and thus, in places, there will be a local coverage of 1.0 ML. These local regions may be large enough such that nucleation of the second layer is preferable to the energy cost of diffusion of Gd atoms across large distances at RT to complete the remaining initial layer over the entire surface, creating a local pseudo-first-layer-plus-islanding growth mechanism.

Annealing both the higher and lower coverage films to 800 K again results in more coalescing of the islands than is observed for the RT deposition and lower annealing temperatures of 400 K. The typical size of the islands increases up to 700 Å, although a few smaller islands are still present as illustrated in Fig. 1(d). Furthermore, they have now taken on a hexagonal shape with well-defined edges. Figure 1(d) reveals a striking feature when the Gd islands traverse a step. Whereas the step on the substrate goes down, the corresponding step on the Gd island goes up resulting in an *inverted island-substrate step structure*. We will discuss this phenomenon in greater detail later in the paper.

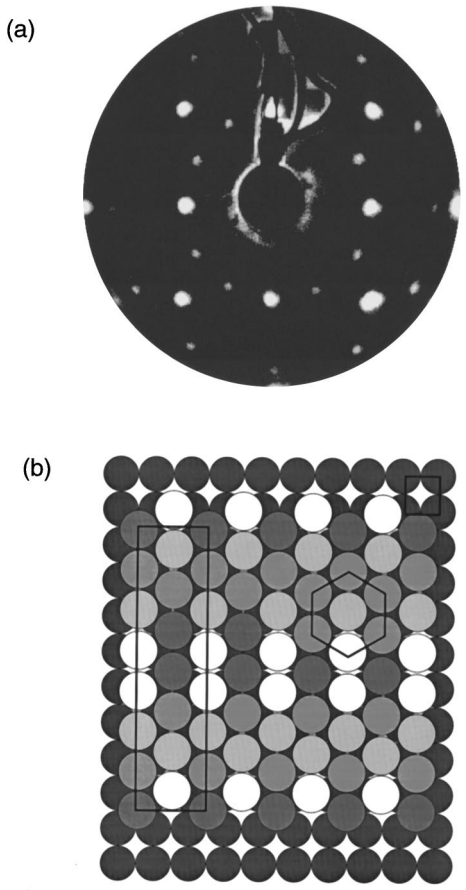

FIG. 2. (a) LEED pattern recorded at 100 eV following deposition of 3 ML Gd at RT. The W(100) first order spots can be made out (square lattice) in addition to the hexagonal spots induced by Gd. The LEED pattern indicates that a (0001) termination of the Gd overlayer exists which has an (8×2) periodicity with respect to the W(100) substrate. (b) Simple ball model of the (8×2) pseudohexagonal overlayer as determined from the LEED pattern of (a).

Attempts to resolve the atomic structure of the islands using STM proved difficult. In part, this is due to the rough morphology which is induced by a large number of islands. Indeed, even on single-layer metal islands atomic resolution with the STM has been difficult to achieve on other systems compared to flat surfaces.[17] However, by careful examination of the LEED pattern, information can be gained on the atomic structure of the islands and interface. Figure 2(a) shows a LEED pattern recorded at 100 eV from 3 ML of Gd deposited at RT. The principal order spots which form a square lattice corresponding to the W(100) substrate can be seen in addition to two hexagonal structures which are rotated 90° with respect to each other corresponding to the Gd structures. The orientation and periodicity of the hexagonal spots indicate that the islands are terminated by the Gd(0001) face and consist of two domains with a $c(8\times2)$ periodicity with respect to the underlying W(100) lattice. This results in a uniaxial strain of the Gd(0001) face of the islands from the ideal value, resulting in a pseudohexagonal overlayer. A (0001) termination of the Gd islands is not surprising, as this is the close-packed face and has the lowest surface energy. Indeed, even on Gd single crystals other faces undergo extensive reconstruction to form (0001) type terminations.[18] Based on this evidence the proposed model for this structure is illustrated schematically in Fig. 2(b). A (0001) termination of Gd has also been reported for films formed on the W(110) surface, in which a (7×14) overlayer was formed.[3] Similar structures have been reported for other systems, for example, Ag/Cu(110).[19]

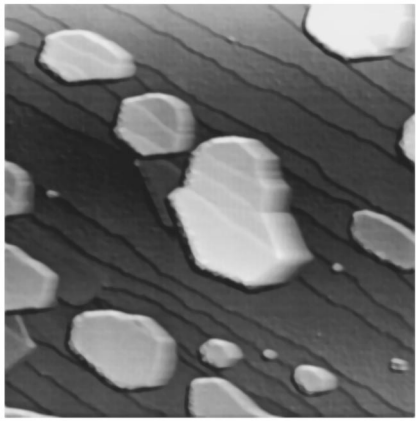

FIG. 3. (a) 2000×2000 Å^2 STM image of 1.5 ML Gd annealed to 800 K. This shows more clearly the step structure of the islands and steps. The steps on the substrate are consistent with a W(100) step (1.58 Å) while the steps on the island are 1.31 Å.

We now focus in greater detail on the *inverted island-substrate step structure* of Fig. 1(d). Figure 3 shows STM images of Gd, in which the island density is fairly low in order that the relationship between the islands and substrate steps be more clearly visible. The hexagonal shape of the islands is much clearer, with the angles between the edges being $120°\pm5°$. By comparing the amount of Gd within the islands and the coverage calibrated from the evaporator there should be more Gd on the surface than can be accounted for in just the islands if an SK growth exists. The coverage determined from calibration of the evaporator is 3.8 ML. The island density averaged over number of images recorded at different locations on the surface is 30%, while the average island height corresponds to nine Gd layers. Thus it can be seen that the islands correspond to 2.7 ML. The remaining Gd can be accounted for through an SK growth as evidenced by no nucleation of second layer growth for coverages approaching 1 ML shown in Fig. 1(b). The SK growth mechanism is also consistent with that recently reported for Gd on W(110),[3] and also in agreement with a simple consideration of the surface energies.

By carefully measuring the step heights on the islands it is found that they are 1.3 ± 0.1 Å. Although initial intuition would suggest a similar morphology to the substrate, the origin of this inverted step structure can be explained by considering the step heights of the W(100) substrate and the Gd interlayer distance. If the Gd islands followed the same morphology of the substrate then the step height would be 1.58 Å (i.e., the value of the substrate steps). The Gd interlayer distance is 2.89 Å. Thus if the islands have an inverted step, then the height is reduced by 0.27 Å to a value of 1.31 Å. This is illustrated schematically by the model of Fig. 4. Such a restructuring would lead to a reduced surface energy

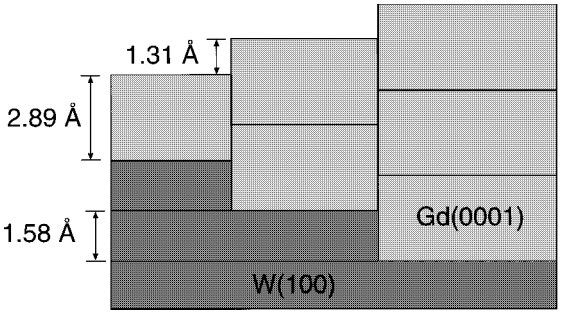

FIG. 4. Proposed model for the inverted island-substrate step morphology imaged in Fig. 3, which shows how the inverted steps reduce the exposure of the high-energy faces of the Gd islands. The W substrate is shown by light shaded blocks and the Gd overlayer by dark shaded blocks.

by decreasing the amount of the high-energy step face. As mentioned earlier, even on Gd single crystals the other faces will relax or reconstruct to form a (0001)-type termination. The fact that the change in step height of the inverted step structure is quite small would indicate that the energy gained by adopting such a structure is low. This is consistent with the fact that in order to obtain such structures, which would require significant mass transport, a high annealing temperature is necessary.

In summary, we have studied the growth of Gd on W(100) using STM and LEED. The STM results show that an islanding growth mode exists, with the islands coalescing upon annealing the substrate. LEED indicates that a two-domain Gd(0001) structure which has a (8×2) periodicity is formed. With progressively higher annealing temperatures an increase in the size of the Gd islands is seen. Upon annealing to high temperatures (800 K) an inverted island-step structure is observed, which results in a smoother termination of the Gd islands than if they followed the substrate morphology, resulting in a lower surface energy.

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