Structural and electronic properties of ultrathin films of Gd, Tb, Dy, Ho, and Er

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Single-crystal ultrathin films of Gd, Tb, Dy, Ho, and Er were grown epitaxially on W{110} in ultrahigh vacuum. Comparison with single-crystal data available for Tb shows that while the purity of the films may be higher, the crystallinity, i.e., the long-range order, is less well developed in the films than in bulk single crystals.

The study of bulk and surface properties of the rare earths has been hampered for years by the enormous difficulties encountered in the preparation of high-purity single crystals and clean surfaces thereof.[1-3] Some of these difficulties may be at least partially circumvented by replacing the bulk single-crystal samples with single-crystal thin films, which, when grown in ultrahigh vacuum, may contain lower amounts of the interstitial C, N, O impurities and perhaps also less of some of the substitutional (Fe, Pd) impurities than their bulk counterparts.

Single-crystal thin films of Y were successfully grown on Nb{110} and Nb{111} by Kwo, Hong, and Nakahara, who in fact succeeded in fabricating ultrathin and coherent superlattices in the Nb{110}/Y(0001) system.[4] Multilayers of Y on Dy and of Y on Er were successfully grown by Rhyne, et al.[5] Epitaxial thin films of Gd(0001) were also successfully grown, on W{110} substrates, by a number of workers.[6-10] The epitaxial conditions achieved in these studies are such that it appears likely that all hexagonal-close-packed rare earths may possibly be grown in the form of single-crystal thin films on the {110} faces of the refractory metals Nb, Mo, Ta, and W. One of the goals of the work reported here was to test whether in fact that is the case, at least for four of the rare earths following Gd in the periodic table, namely, Tb, Dy, Ho, and Er, and for W{110} as a substrate. A second goal was to examine whether the single-crystal (0001) films that are grown on W{110} are in fact wholly equivalent, from the crystallographic point of view, to bulk (0001) samples. The experimental tools used in these studies were low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and ultraviolet photoemission spectroscopy (UPS).

All thin films studies in this work were grown in ultrahigh vacuum on a W{110} substrate. A tungsten platelet with the major surfaces oriented along a {110} crystallographic plane to within ±0.5° was depleted of carbon content, prior to its installation in the experimental chamber, by a sequence of heating and cooling treatments in an oxygen atmosphere. The treatments involved passing a current of about 250 A through the platelet, thereby raising its temperature to about 2000 °C, for approximately 20 sec, then allowing the platelet to cool to room temperature for 5 min, the surrounding atmosphere being pure oxygen at 10^{-6} Torr. This cycle was repeated continuously for a period of about 48 h, whereupon the

platelet was mounted in the experimental chamber.

After attainment of base pressure ($\approx 1 \times 10^{-10}$ Torr) in the experimental chamber the W{110} surface was subjected to argon-ion bombardments (5×10^{-5} Torr, 600 eV, 7 μA) followed by brief (15 sec) flashes at approximately 1500 °C. After several cycles of ion bombardments and anneals the W{110} surface was free of oxygen and carbon impurities as determined by AES. LEED produced a 1×1 pattern with sharp spots and low background.

For all rare earths concerned the sources were small pellets of pure material (purchased from the Materials Preparation Center of the Iowa State University in Ames, Iowa) inside tungsten spiral baskets that were heated electrically. After suitable outgassing, each source was heated, for the actual deposition, to about 1350 °C, thereby producing a deposition rate of about 1–2 Å/min. During deposition the substrate was heated to 500 °C.

The coverage of the W{110} substrate by the rare earth involved was determined from the ratio $R = I_{\mathcal{R}(E_n)}/I_{W(169)}$ between the intensities of the AES lines of the corresponding rare earth ($\mathcal{R}$) at E_n eV and of W at 169 eV, respectively, with the formula

$$R = R_\infty \frac{1 - e^{-d/\lambda_{E_n}}}{e^{-d\lambda_{169}}}, \tag{1}$$

where $R_\infty = I_{\mathcal{R}(E_n)}^\infty / I_{W(169)}^\infty$; I^∞ denotes the intensity of the AES line from a very thick sample of the $\mathcal{R}$ (W) at E_n (169) eV; the λ's are the inelastic mean free paths of electrons with E_n (169) eV energy; and d is the thickness of a $\mathcal{R}$ film assumed to be uniform over the W{110} surface. The values of E_n were, for the rare earths involved in the present work, Gd, Tb, Dy, Ho, and Er, the following: 138, 146, 151, 157, and 131 eV, respectively. The corresponding values of R_∞ were taken from Ref. 11 and the corresponding values of the λ's from Ref. 12 ($\lambda = 6.4$, 6.6, 6.7, 6.8, and 6.3 Å for Gd, Tb, Dy, Ho, and Er, respectively).

The AES scans were done with a cylindrical mirror analyzer. The thicknesses of the $\mathcal{R}$ films as determined with Eq. (1) are quoted, below, in layer equivalents (LE), representing the number of *uniformly distributed* layers of rare-earth metal that would produce the same value of the ratio R in Eq. (1) as that measured in the actual ex-

periments. The conversion from d in Å to d in LE was done by assuming an interlayer distance of 2.8 Å, applicable, on the average, to all rare earths involved in the present experiments. The error bars in the determination of film thickness are estimated to be about ±50%.

In the initial stages of deposition, for all rare earths considered in this work, the LEED patterns were very complex with large numbers of extra spots (see also Ref. 6). No attempts were made at the classification of any of these patterns. Both the AES scans and the LEED patterns exhibited W signals only up to coverages of about 10 LE, when the LEED patterns turned into the sixfold 1×1 patterns characteristic of the basal plane of the corresponding rare earth—thicker films produced no tungsten AES signal.

The orientation of the rare-earth lattice with respect to the W{110} surface was similar to that found by Kwo, Hong, and Nakahara[4] for Y on Nb{110}, namely, the so-called Nishiyama-Wasserman (NW) orientation:[13] $\mathcal{R}(0001)\|W(011)$ and $\mathcal{R}[01\bar{1}0]\|W[011]$. The periodicities in these directions are about 6.30 Å for the $\mathcal{R}[01\bar{1}0]$ and 4.47 Å for W[011], so that there is no direct 1:1 match, but there is a 5:7 coincidence-lattice match (in the case of Y on Nb{110} the match was 3:4, Ref. 4).

However, the 1×1 LEED patterns were of mediocre quality: the spots were strong but broad with a relatively high background. In the only case where we had direct experience with LEED studies of bulk single crystals, the case of Tb(0001) (Ref. 14), we could establish that the LEED pattern from the bulk single crystal was of better quality (sharper spots, lower background) than that from the epitaxial film.

All rare-earth films investigated here were short lived with regard to surface purity. Both AES and UPS showed that the carbon and especially the oxygen signal increased noticeably in times of the order of $\frac{1}{2}$ to 1 h even at pressures of 1 to 2×10^{-10} Torr, and even more rapidly when the surface was exposed to the electron beam from the AES unit or to the photon beam from the synchrotron ring. Consequently, during data collection, especially during the photomission experiments, the films were sputtered away from the W{110} surface and regrown approximately every hour.

LEED $I(V)$ spectra under normal-incidence conditions were collected from all rare-earth films grown in this work. However, quantitative intensity analyses were not carried out, both because the quality of the LEED patterns was not considered good enough for such a purpose, and because in the present case the values of the in-plane lattice constants were not precisely known [in nonpseudomorphic epitaxy such values may not be exactly equal to those of the corresponding bulk crystals (cf. Ref. 7)]. But the $I(V)$ spectra were nevertheless useful for characterization and intercomparisons.

Figure 1 depicts the 10, 11, and 20 normal-incidence spectra from all films studied (all films were at least 15 to 20 LE thick). The similarity of all curves for the same beam from different rare earths was expected because the dominance of ion-core scattering in LEED makes it difficult to distinguish between isostructural elements with not-too-different atomic numbers. What Fig. 1 tells

us is that all films had approximately the same atomic structure, in accordance with the fact that all six rare earths considered here crystallize with the hexagonal-close-packed (hcp) structure. Just how close the structure of the films was to that of the bulk material could be examined only in the case of Tb(0001), for which a quantitative LEED analysis of bulk single-crystal data was recently reported.[14] Figure 2 juxtaposes the normal-incidence spectra from the single crystal and from the film. The curves for the same beam are obviously very similar to one another, but not identical. It is difficult at this point to decide which of the two sets is more typical of pure and well-crystallized material: the bulk single crystal was well ordered, but contained small amounts of impurities,[14] whereas the thin film was perhaps purer, but undoubtedly with less long-range order.

The electron-distribution curves (EDC's) collected in photoemission experiments from Gd, Dy, Er, and Tb are shown in Fig. 3. The Ho data were not judged to be representative of clean material (a strong oxygen-derived peak at about 6 eV below the Fermi level was always present in the EDC's from the Ho films) and were therefore omitted from the figure. We note that all curves exhibit a peak at approximately −0.5 eV (the zero of energy corresponds to the Fermi level). On single-crystal Y(0001) (Ref. 15) and Tb(0001) (Ref. 16) and on Gd(0001) films[17] such a peak has been associated with a surface state located in a band gap of the projected band structure at $\bar{\Gamma}$ [in the case of Gd(0001) this surface state was
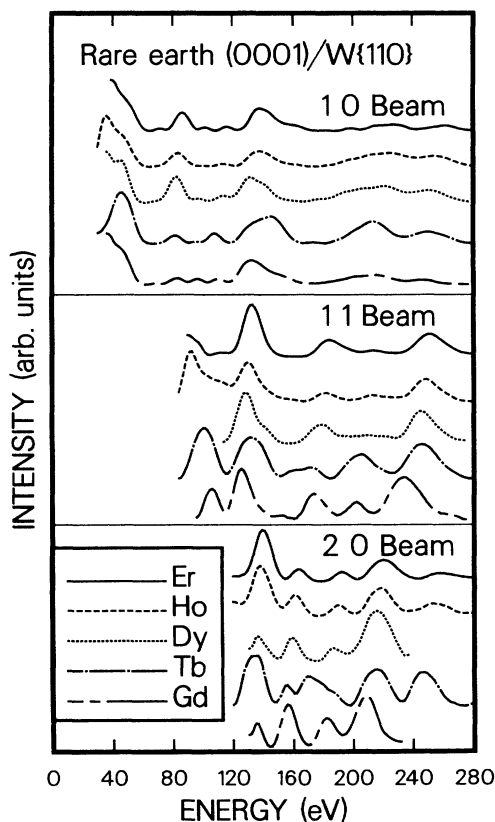

FIG. 1. Normal-incidence LEED $I(V)$ spectra from single-crystal thin films of rare earths as indicated.
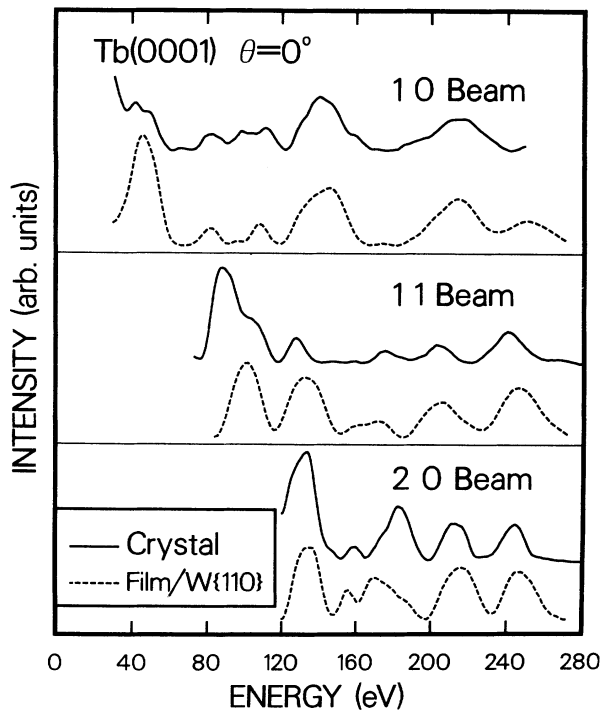
FIG. 2. Comparison between normal incidence $I(V)$ spectra from bulk Tb(0001) (solid) and from a Tb(0001) thin film grown on W{110}.

also predicted by band-structure calculations].[18] Thus the curves in Fig. 3 indicate that such a surface state exist also on Dy(0001) and Er(0001), and probably in all heavier rare earths.

Comparison of the Tb curve in Fig. 3 with the corresponding EDC measured on bulk single-crystal Tb(0001) (Ref. 19) shows the following differences: (1) the surface-state peak at about -0.5 eV is much sharper and more intense in the single-crystal data; (2) the peak centered at about -2.6 eV, which is due to the $4f$ electrons, is visibly broader in the thin-film data; (3) the peak at -4 eV in the thin-film data does not appear in the single-crystal data—it was probably due to unknown and otherwise undetected impurities in the thin film. This comparison indicates that the Tb single-crystal data published in Refs. 16 and 19 are more representative of the pure and well-crystallized material than the data collected from the Tb thin films grown in this work.

In conclusion, we have shown, by low-energy electron diffraction, that not only Gd, but also Tb, Dy, Ho, and Er single-crystal films can be grown epitaxially on W{110}, all in the NW orientation with a 5:7 match between the
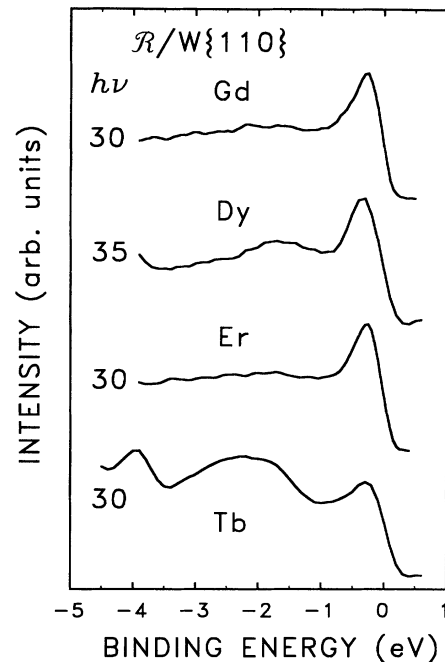

FIG. 3. Normal-emission electron distribution curves from single-crystal thin films of Gd, Dy, Er, and Tb measured with photon energies $h\nu$ (in eV) and $(75\%s+25\%p)$-polarized light. The zero of energy is taken at the Fermi energy.

$\mathcal{R}[01\bar{1}0]$ direction and the W[011] direction. All films had similar structure, as expected, which in the case of Tb(0001) was confirmed to be the hcp structure of the bulk material, and all films had satisfactory purity, in particular, no signal of metallic contaminants detectable by AES. However, it appears that the crystallinity, i.e., the long-range order, is definitely less perfect in the films than in bulk single crystals. This fact may be due to the lack of direct 1:1 lattice match that was detected by LEED. On balance, therefore, we suggest that if one is interested in studying the intrinsic properties of the rare earths, both bulk and surface, one may indeed profit from preliminary studies of single-crystal thin films grown on tungsten substrates, but one should confirm the results with studies of high-purity bulk single crystals.

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