

On the surface

Dr Steve Barrett from the University of Liverpool, UK, has been studying rare earth metals for 20 years. Here he explains how preparation of the surface layer is crucial to the functionality of these scarce elements.

Studies into the properties of rare earth metals have been active since the 1960s. However, because the information gathered was effectively averaged over all possible orientations of the surface crystallites, possibly weighted by preferential orientation due to surface energy minimisation, it was difficult to draw meaningful

conclusions regarding the surface structure or its properties.

The creation of single crystal surfaces did not become routine until the 1980s, when the first studies of the geometric and electronic structure of single crystal rare earth metal surfaces were published. Studies of the magnetic structure

Closely packed

All but two of the rare earth metals adopt the hexagonal close-packed (hcp) crystal structure, or structures closely related to it. Cutting the hcp crystal structure parallel to its principal planes produces the surface structures shown in Figure 1. The surface unit cells (indicated by the parallelograms drawn in bold) are hexagonal for the (0001) surface and rectangular for both the $(11\bar{2}0)$ and $(10\bar{1}0)$ surfaces. It can be seen that the (0001) surface is close-packed and that the $(11\bar{2}0)$ and $(10\bar{1}0)$ surfaces have large unit cells due to their very open structures. As a consequence of this, the inter-layer spacings of these surfaces are relatively small compared to those of the (0001) surface.

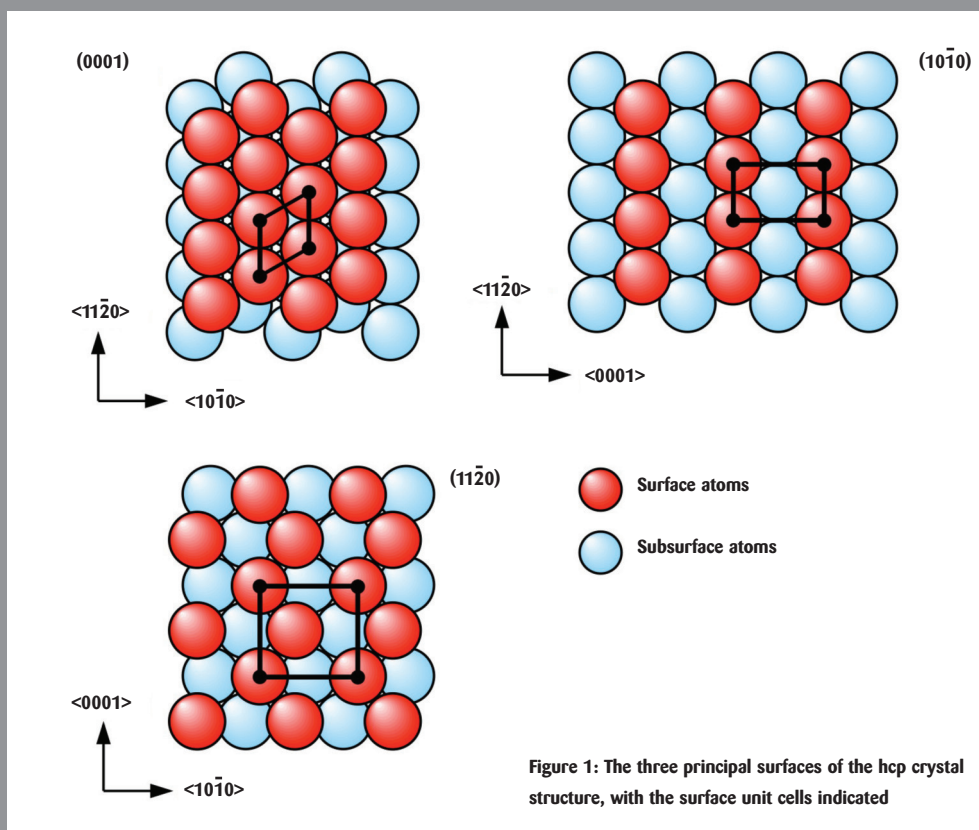


Figure 1: The three principal surfaces of the hcp crystal structure, with the surface unit cells indicated

Note that whereas the (0001) and $(10\bar{1}0)$ surfaces have unit cells with a basis of one atom per unit cell, the $(11\bar{2}0)$ surface structure cannot be represented by a choice of a unit cell with a single-atom basis – the primitive surface unit cell contains two atoms, just like the primitive unit cell of the hcp structure itself. The (0001) surfaces of the double-hcp and Sm-type crystal structures appear the same as that of the hcp, but the $(11\bar{2}0)$ and $(10\bar{1}0)$ surfaces are rather different. There have been relatively few studies attempted of these surfaces, presumably because of the problems associated with preparing these surfaces from bulk single crystals and the difficulties associated with growing them as epitaxial thin films.

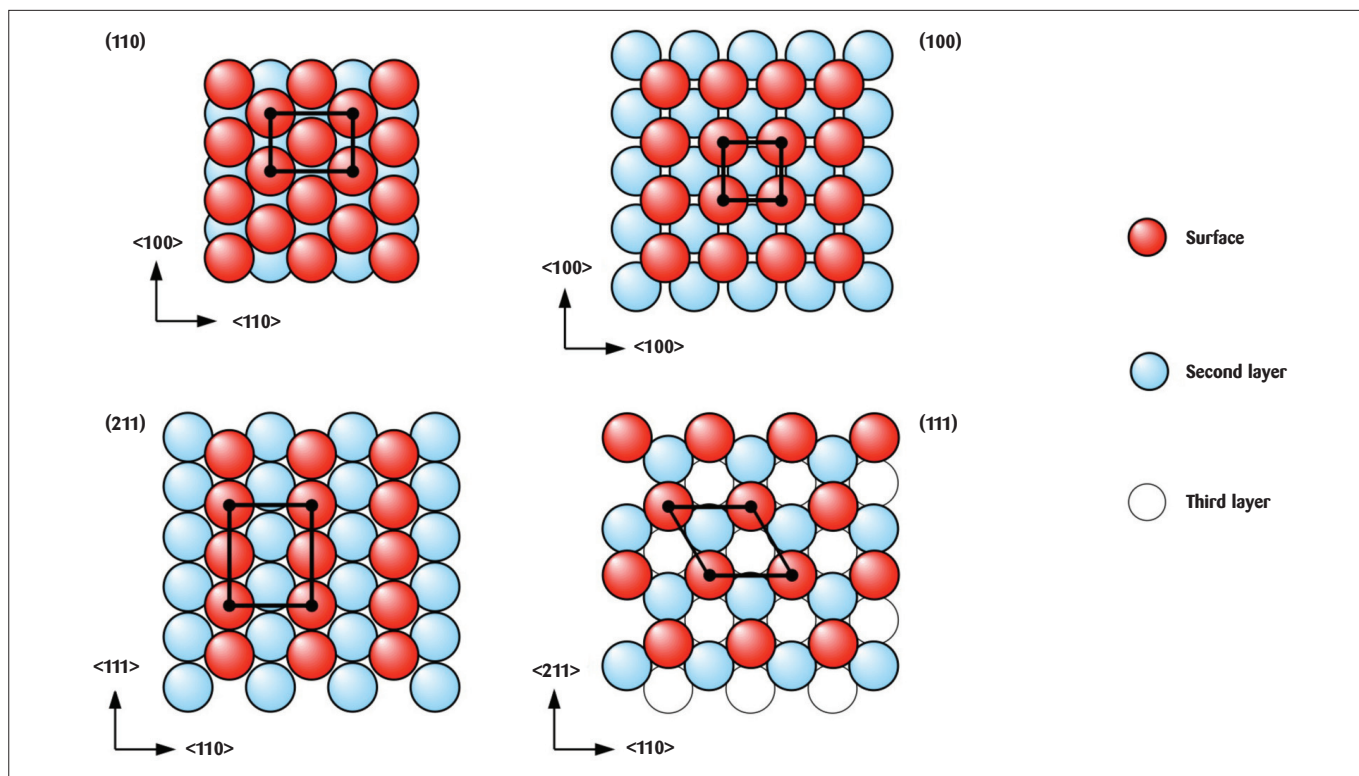


Figure 2: Principal surfaces of the body-centred cubic crystal structure, with the surface unit cells indicated

followed, but were hampered by problems with surface preparation.

Interest in the surfaces of rare earth metals went through a renaissance around the turn of the millennium, principally due to the discovery of novel magnetic properties of the elemental metal surfaces. Before this, surface studies could be categorised as more chemistry than physics. Until the 1980s, most rare earth surface studies focused on the chemical properties of the metals and their compounds. These included studies of the adsorption of molecules onto metallic and oxide surfaces, with emphasis on their chemical reactivity and catalytic properties.

Many studies involved semiconductor substrates, and in particular the formation of rare earth silicides. However, this article focuses on studies of the clean surfaces of rare earth metals. The surfaces of rare earth metals have been examined since the elements themselves were discovered. Much of the research was not necessarily intended for surface study, but was the result of the probing depth of the techniques employed. For instance, attempts to study the electronic structure of a bulk material using UV photoelectron spectroscopy will, due to the limited mean-free path of the photoelectrons, probe only the top atomic layers of the material. Early studies of rare earth metal surfaces used polycrystalline samples because of the difficulties involved with the preparation of single-crystal surfaces of such reactive metals.

Sample preparation

The methods used to create clean and well-ordered

surfaces from such crystals vary between research groups, but often follow this sequence of *ex-situ* and *in-situ* procedures:

- Laue diffraction to determine crystallographic orientation
- Spark machining to the desired orientation and geometry
- Mechanical polishing using a number of grades of diamond paste down to a particle size of $0.25\mu\text{m}$ (or electropolishing)
- Insertion into an ultra-high vacuum system

In-situ cleaning comprises cycles of argon ion bombardment and annealing at a temperature between $500\text{--}700^\circ\text{C}$, depending on the element and the orientation of the surface, for a period of about 30 minutes. These cycles are repeated until the surface contamination, determined from Auger spectroscopy or X-ray photoelectron spectroscopy is acceptably low. For the surfaces of bulk single crystal samples, that is typically a few per cent of carbon and oxygen.

Epitaxial thin films

For rare earth metal surfaces prepared by growth of epitaxial thin films, rather than cut from bulk single crystals, the refractory metals tungsten, molybdenum and niobium have been found to be most suitable as substrates. They adopt the body-centred cubic (bcc) structure, which has four atomic planes of interest. Substrates whose surfaces are parallel to these planes have been used for the growth of rare earth thin films, and the surface crystallography of these are shown in Figure 2. The relatively high surface energies

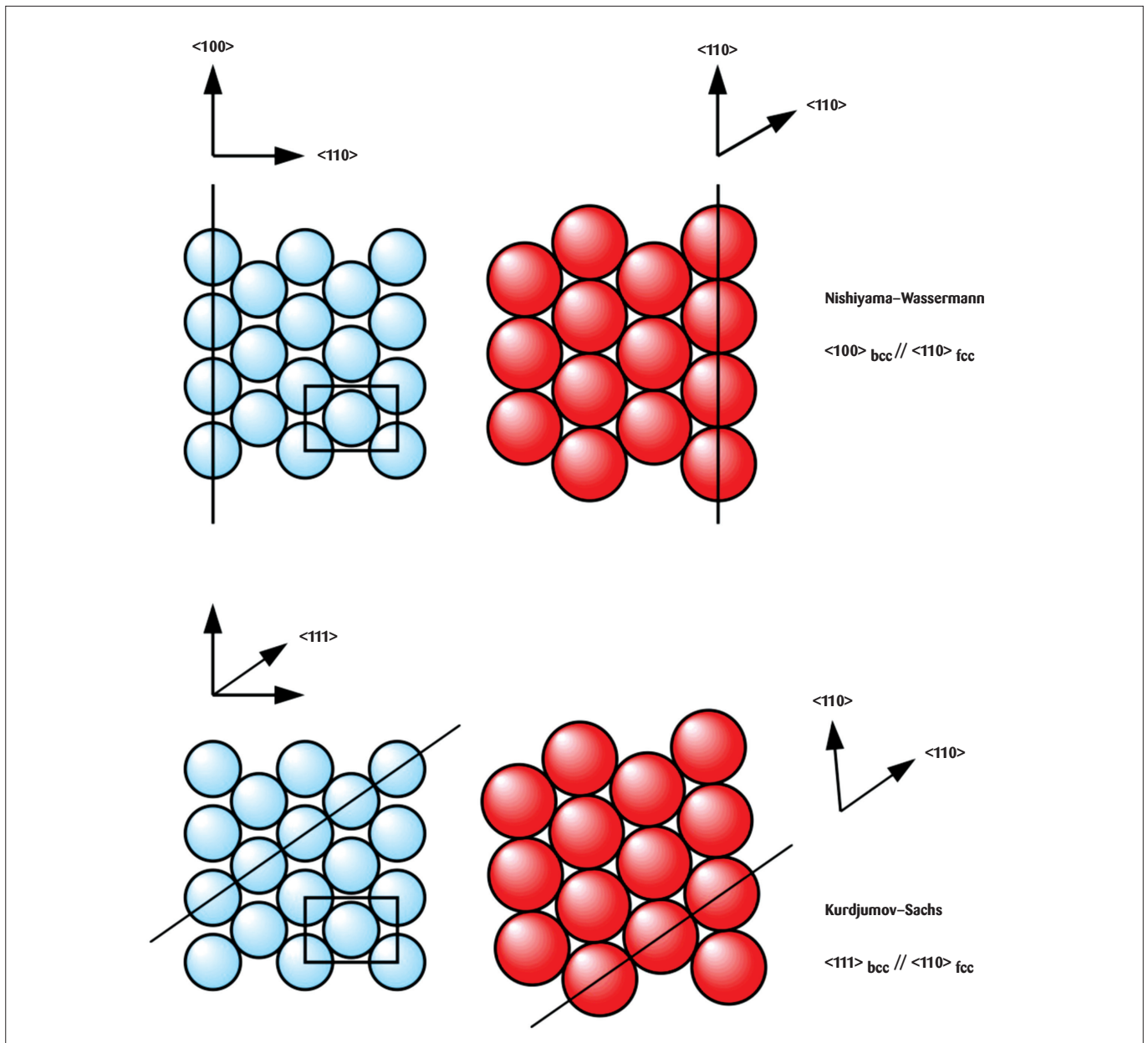


Figure 3: The Nishiyama-Wassermann (NW) and Kurdjumov-Sachs (KS) orientation relationships for a close-packed face-centred cubic (fcc) or hcp overlayer (right) on a bcc (110) surface (left). The Miller indices of the directions in the overlayer are those appropriate for an fcc structure

of the (110) surfaces means that they are not susceptible to adsorbate-induced reconstruction or relaxation, and so can be considered to be rigid foundations on which rare earth metal films can be constructed.

Although the (110) surface is the most common substrate for the growth of epitaxial rare earth metal films, the other surfaces have been used in a number of studies. The (100) surfaces are more open than the (110) surfaces, with a relative packing density of 71%, and hence are more heavily corrugated. The growth of rare earth metals on the (100) surface is epitaxial, but occurs in two orthogonal domains due to the four fold rotational symmetry of the (100) surface. The (211) surface has been chosen as a substrate to produce thin films that exhibit considerable anisotropy in the degree of strain and the density of dislocations.

For metals that adopt the face-centred cubic (fcc) or hexagonal close-packed (hcp) crystal structure in the bulk phase, two preferred orientation relationships exist for the growth of overlayers on bcc (110) surfaces at monolayer and multilayer coverages. They are referred to as the Nishiyama-Wassermann (NW) and Kurdjumov-Sachs (KS) structures and are illustrated in Figure 3. The NW orientation aligns the close-packed $\langle 110 \rangle$ rows of the fcc overlayer (or, equivalently, the $\langle 1120 \rangle$ with the hyphen over the 2 rows of the hcp overlayer) to the $\langle 100 \rangle$ rows of the bcc substrate. The KS orientation aligns the same overlayer rows to the $\langle 111 \rangle$ rows of the bcc substrate.

The KS orientation is actually a pair of orientations, as the $\langle 110 \rangle$ rows of the fcc overlayer can be aligned to either of the two row directions in the $\langle 111 \rangle$ set of the bcc (110) substrate. As these are equivalent

by symmetry, a superlattice that adopts the KS orientation at the interfaces will have a random azimuthal misorientation from one layer to the next but one layer, producing a layered, rather than a crystalline, superlattice. The relative orientations of NW and KS differ by only five degrees and a relatively small variation in the growth conditions (such as the flux of adsorbing atoms, or the temperature of the substrate) can switch the preferred orientation from one to the other.

A number of non-refractory metal substrates have been used in the study of rare earth metal adsorption or thin-film growth, most notably aluminium, iron, nickel and copper, and to a lesser extent also magnesium, cobalt, ruthenium, rhodium, palladium, silver, rhenium, iridium and platinum. For these systems the substrates cannot be considered to be the inert, rigid foundations that the refractory metals provide. The formation of intermetallic compounds is common, and in some cases is the purpose of the study, and so the resulting structures will be dependent on the atomic species involved and their temperature treatment. As a result, generalised comments on the structures are of limited use, and care must be taken before drawing conclusions about the structure of rare earth metal surfaces grown on these substrates.

Structure studies

Examinations of the geometric structure (using electron diffraction, X-ray diffraction and scanning tunnelling microscopy), electronic structure (using UV and X-ray photoelectron spectroscopy) and magnetic structure (using many techniques) of rare earth metal surfaces, both bulk single crystals and epitaxial thin films, number in the thousands.

The first published image of a rare earth metal surface imaged with a scanning tunnelling microscope is shown in Figure 4 (and in Figure 5 as a 3D representation of the surface). The topography of the (0001) surface of scandium shows atom-high steps separating flat terraces. The terrace edges tend to align with the close-packed directions of the (0001) surface, though there are signs of distortion in the vicinity of, for example, screw dislocations emerging from the bulk. The protrusions, which tend to occur at kinks in the terrace edges, are oxygen atoms or clusters of oxygen atoms. Their apparent size is exaggerated as the tunnelling current is a function not simply of the surface topography, but also of the electron density at the surface.

The surfaces of rare earth metals continue to be a source of considerable interest due to their magnetic properties and the potential for technological applications. The use of local probes, for example scanning tunnelling spectroscopy, allows the intimate connection between electronic structure and magnetic structure to be explored. Such techniques will no doubt play an important role in future studies of these in-demand metals.

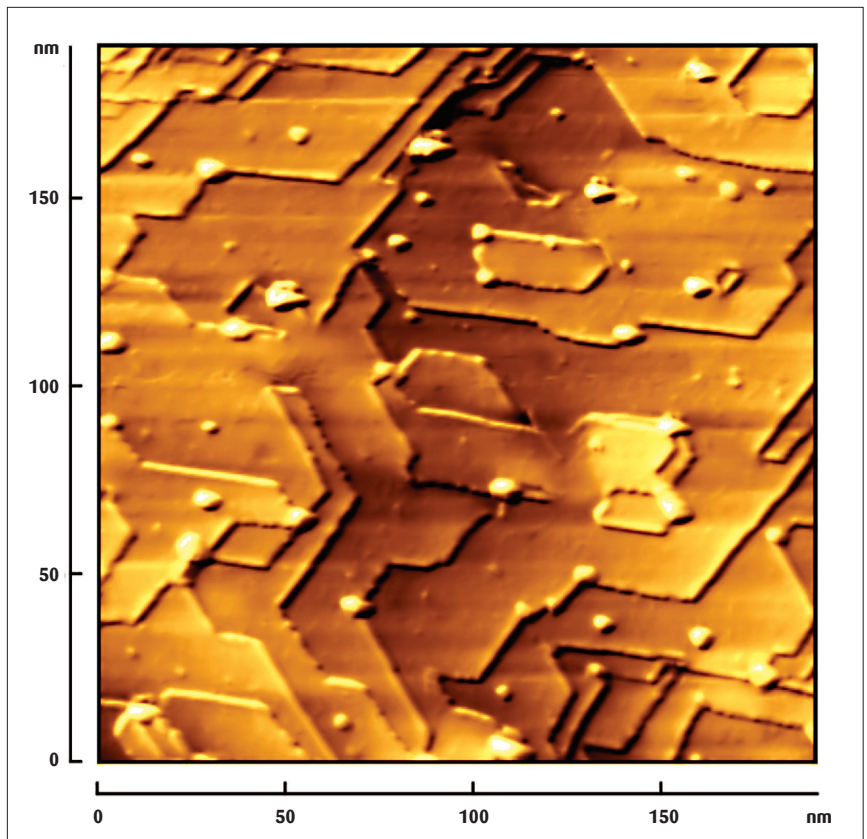


Figure 4: STM image of the surface of Sc(0001) taken in topographic, or constant current, mode. The image has been differentiated to give a better impression of the surface topography

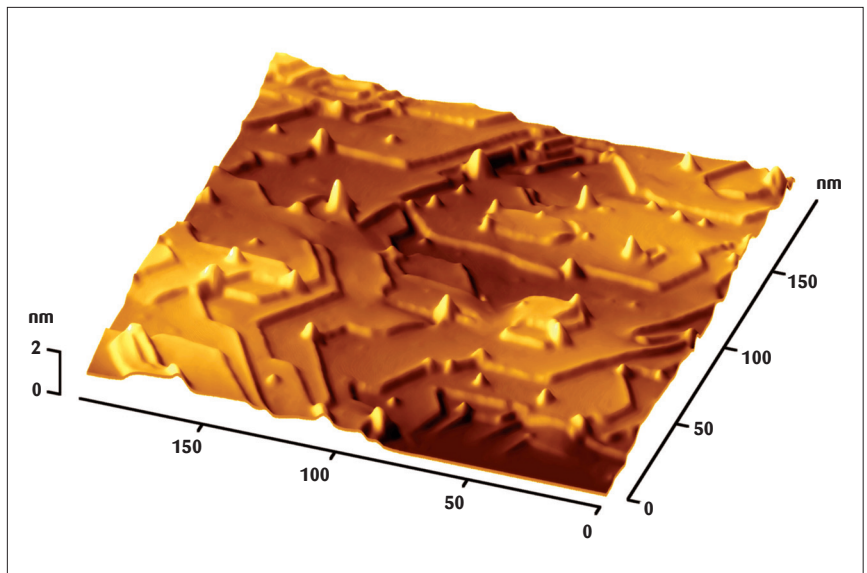


Figure 5: STM image of Sc(0001) displayed as a 3D surface

Further information

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