

Scanning tunneling microscopy of the UO_2 (111) surface

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Scanning tunneling microscope (STM) studies of UO_2 surfaces have previously not been performed due to insufficient conductivity at room temperature. In order to increase the sample conductivity we have carried out imaging at elevated temperatures in a JEOL 4500XT ultrahigh vacuum STM. With this instrument we can routinely image atomic terraces of the UO_2 (111) surface and under exceptional circumstances also resolve atomic structure within the terraces. We have used low-energy electron diffraction and Auger electron spectroscopy to study the surface order and purity and correlated these results with our STM data. © 1996 American Vacuum Society.

I. INTRODUCTION

UO_2 has a high melting point (2840 °C) and crystallizes into the face centered cubic (fcc) fluorite structure with a lattice parameter of 5.470 Å.¹ Limited oxidation of UO_2 leads to the formation of a single phase UO_{2+x} with $0 < x < 0.25$. During such oxidation the crystal density increases showing that the extra oxygen atoms are accommodated interstitially. The p - d band gap, as determined in the studies by Baer and Schoenes² and Arko *et al.*,³ is approximately 5 eV. The filled oxygen $2p$ band tails off at around -4 eV relative to E_F and within the gap are uranium $5f$ states which lie at approximately -1.5 eV. Above E_F the onset of the density of states occurs at ~ 1 eV due to a uranium $6d$ band. Conductivity at room temperature is approximately $4 \times 10^{-3} (\Omega \text{ cm})^{-1}$ (Ref. 4) which rises by an order of magnitude at 200 °C.

The (111) surface is the natural cleavage plane of the fluorite-type structure. Examination of the stacking sequence indicates that cleavage of the UO_2 crystal between two oxygen planes is likely to be energetically favorable. The outermost layer of a cleaved (111) surface should therefore consist of oxygen atoms.

Tasker⁵ presents a calculation of the surface energy, tension, and structure of the (111) surface using an ionic model of the crystal which assumes that the bulk potentials are transferable to the surface. The calculated surface geometries show small but significant distortions from the bulk structure, the most significant of which is a substantial inwards relaxation of the oxygen ions in the outermost layer of about 0.14 Å.

Ellis and Taylor^{6,7} have studied UO_2 (111) surfaces by means of low-energy He^+ ion scattering spectroscopy (ISS). In combination with low-energy electron diffraction (LEED) observations, angular dependent ISS appears to be particularly useful in characterizing atomic positions in the outermost layer. A way of determining O positions relative to U positions is to direct a collimated beam of 500 eV He^+ ions onto the surface, and measure the He^+/U signal as a function of polar angle of incidence β and of azimuthal angle ϕ . The

results are adequate to allow postulates on qualitative surface atomic arrangements. The He^+/ISS data confirm that the outermost surface layer is composed of oxygen atoms that occupy to a first approximation the positions expected from a simple termination of the bulk lattice. The measurements may also indicate a few percent contraction of the oxygen layer toward the bulk, but in the absence of a well defined scattering potential qualitative statements concerning the U–O interlayer spacing cannot be made with certainty.

As demonstrated by Thompson *et al.*,⁸ Rutherford backscattering (RBS) is an appropriate method for precise determination of surface crystallography. With knowledge of the two-dimensional surface structure of UO_2 (111) RBS can be used to obtain additional information on surface relaxation. Hence the expansion or contraction of the topmost surface layers for both oxygen and uranium can be determined. Using the surface peak-versus-energy curve for the surface peak of uranium together with Monte Carlo simulations, an outward relaxation of $0.19 \text{ Å} \pm 0.01 \text{ Å}$ normal to the surface was determined for uranium.

The structure of the UO_2 (111) surface has been extensively studied by LEED, where Ellis *et al.*^{9,10} have observed different surface reconstructions according to the type of surface preparation that was used. Crisp and clear (1×1) LEED patterns have been obtained by preparing the surface with Ar^+ ion bombardment and a vacuum anneal at 800–900 °C for about 1 h.

The motivation for this scanning tunneling microscope (STM) study of urania surfaces is to gain structural information on the atomic scale. This is the first step in a project directed at using STM to gain a deeper understanding of the nature of gas–surface interactions.

II. EXPERIMENT

UO_2 single crystals were grown at BNFL, Springfields. The process involves growing a polycrystal and then separating the grains, with the result that the crystal faces are of

unknown orientation. The individual crystals vary in size, but a significant proportion are suitable for experimental investigation.

It should be noted that none of the authors referred to above examined the (111) cleavage surface by LEED but only used cut and polished surfaces. In those studies the mechanically damaged surface layer was exposed to HF(g) to form layers of UF₄ which were removed in 0.2 M HNO₃. The RBS experiments on surface damage in UO₂ due to mechanical polishing and ion bombardment by Matzke *et al.*¹¹ show that cleaved (111) samples display order in the surface region that is very close to that of the bulk. The samples used in the study presented here were cleaved in air to expose (111) surfaces and then introduced into the ultrahigh vacuum (UHV) chamber. The surface was then sputtered with Ar⁺ ions at 200 eV for 30 min and annealed at 600 °C for 30 min at an O₂ partial pressure of 3×10^{-5} Pa.

A four-grid VG Microtech rear view LEED/Auger electron spectroscopy (AES) system was used to determine the condition of the surface prior to STM observation which was carried out in a JEOL 4500XT high-temperature STM. The base pressure in the vacuum system is $\sim 10^{-8}$ Pa. Etched tungsten tips were used. The sample was allowed to reach thermal equilibrium at approximately 300 °C before STM imaging was attempted.

III. RESULTS AND DISCUSSION

Figure 1 shows typical crisp LEED patterns of the UO₂ (111) cleavage surface taken at incident electron energies of 41, 55, and 121 eV. Ellis⁹ presents very similar results on samples prepared by another treatment and states that they are patterns from clean stoichiometric (111) surfaces. Our additional AES data shown in Fig. 2 is consistent with a clean surface as only uranium and oxygen peaks are present.

A typical STM image of terraces on the (111) surface can be seen in Fig. 3. The abrupt changes in a gray level are terrace steps of approximately 3 Å height compared to the 3.2 Å literature value. The threefold symmetry of the surface can be observed through triangular regions. Imaging conditions of the 200 nm×200 nm area were -2.0 V sample bias and 0.26 nA tunneling current, however it was found that a wide variety of biases (-2 V to +2 V) and tunneling currents (0.2–1.2 nA) were suitable for terrace imaging.

An image of a 100 nm×100 nm region from another (111) sample is shown in Fig. 4. Here the terraces can also be seen but more disorder is visible within the terraces of this image compared with Fig. 3. This variance could be due to slight differences in sample preparation, imaging conditions ($V_{\text{sample}} = -2$ V, $I_t = 0.6$ nA), or possibly a different tip configuration.

The terraces of Fig. 5 appear completely flat apart from adsorbates of unknown origin which show up as bright dots. Imaging conditions of the 57 nm×42 nm area were $V_{\text{sample}} = -2$ V and $I_t = 1.1$ nA. The edges of the terraces also appear slightly brighter than the terraces themselves and it is interesting to note that the adsorbates seem to have a tendency to adhere to the step edges. While taking this image it

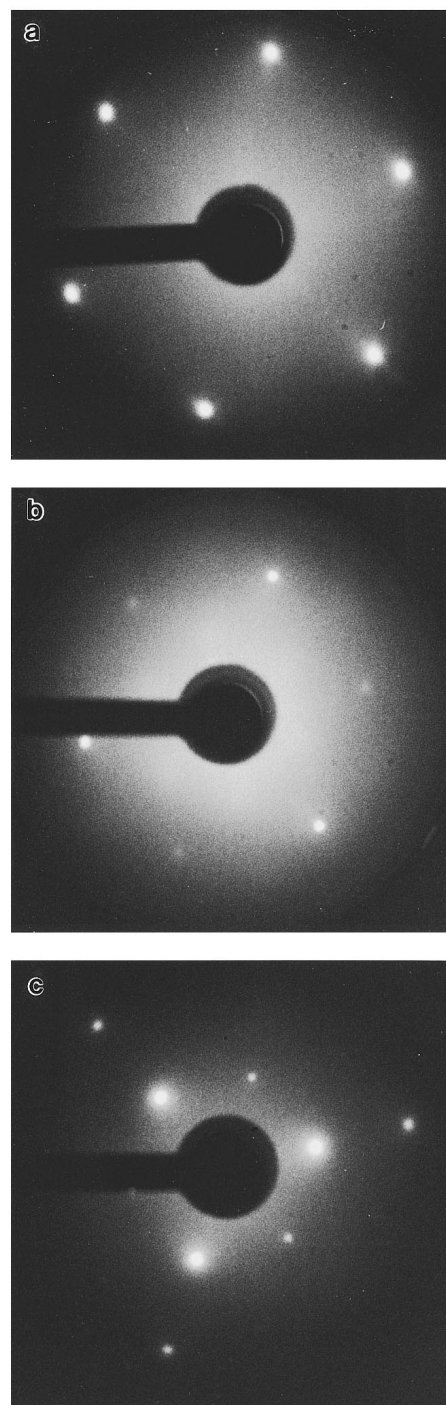


Fig. 1. (1×1) LEED patterns of the UO₂ (111) surface. Incident electron energies of patterns, a, b, and c are 41, 55, and 121 eV, respectively.

was not possible to achieve atomic resolution and it is thought that the conditions for achieving this are mainly tip dependent.

At high magnification atomic resolution images are sometimes observed such as the one shown in Fig. 6, which is

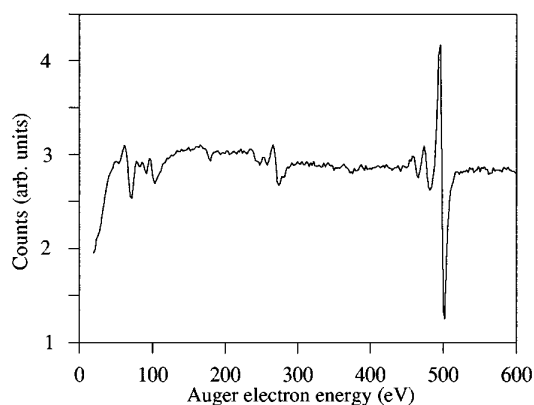


FIG. 2. Auger electron energy spectrum of a clean UO_2 surface. The uranium peak lies at 280 eV and the oxygen peak at 510 eV.

from a $20 \text{ nm} \times 15 \text{ nm}$ area. The (1×1) surface and atomic periodicities can be seen as well as a step edge running diagonally across the left-hand side of the image. In Fig. 6 the atomic corrugation height is approximately 0.5 \AA and the periodicity along the three zone axes is approximately 4.2 \AA . For the (111) surface the periodicity of either oxygen or uranium atoms is 3.9 \AA , which is close to the measured value. The bright area is due to contamination and the abrupt horizontal stripes are imaging artifacts due to tip changes during scanning. The area was scanned from top to bottom and a tip change was necessary to allow atomic structure to be imaged, whereas another tip change had the opposite effect as the scan progressed. It is still not clear what conditions are necessary to allow images containing atomic structure to be taken routinely.

The imaging conditions for Fig. 6 were -2 V sample bias and 1.16 nA tunneling current. With these settings one would

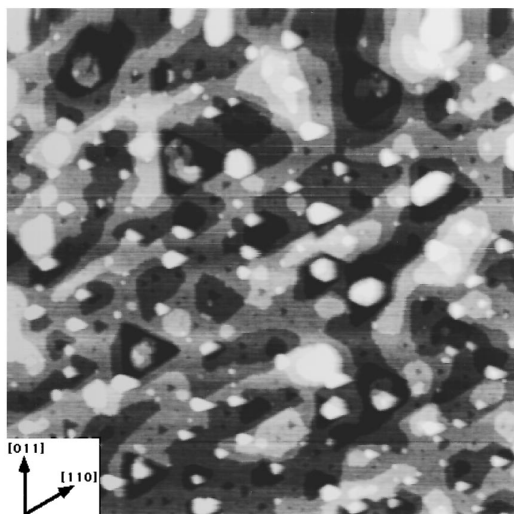


FIG. 3. Typical $200 \text{ nm} \times 200 \text{ nm}$ terrace image of the (111) surface.

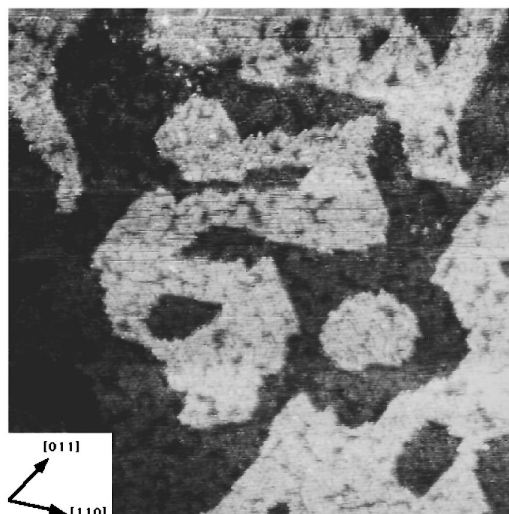


FIG. 4. $100 \text{ nm} \times 100 \text{ nm}$ terrace image with a high defect density within the terraces.

expect to probe the filled $5f$ states of the uranium atoms and hence one might conclude that the image shows uranium atom sites. However, the structure is almost certainly oxygen terminated as determined by Ellis and Taylor^{6,7} in previous ISS studies, so there will be a layer of oxygen atoms that lies $\sim 0.8 \text{ \AA}$ closer to the tip than the uranium atoms. It is unclear whether the tunneling image is dominated by the proximity of the oxygen atoms to the tip or due to the advantageous states of the uranium atoms.

IV. CONCLUSIONS

We have shown the first STM images of the UO_2 (111) surface. Atomic terrace images can be routinely obtained which can be either predominantly flat or show irregular structure. Atomic structure images cannot generally be ob-

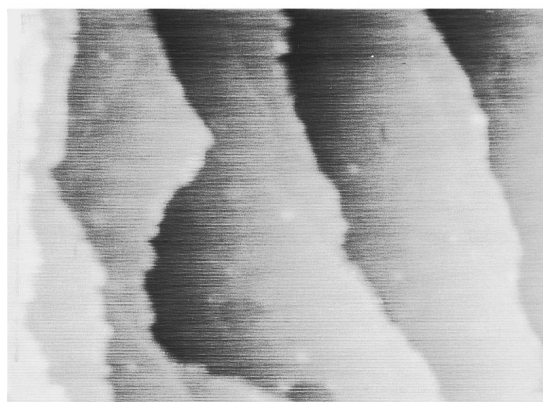


FIG. 5. STM image of a $57 \text{ nm} \times 42 \text{ nm}$ area of a cleaved (111) surface. Terraces and adsorbates are visible.

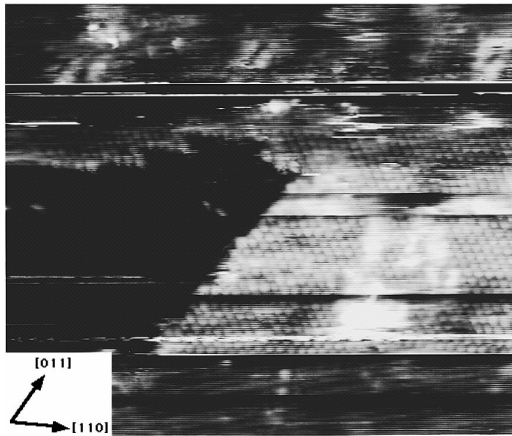


FIG. 6. STM image of a $20 \text{ nm} \times 15 \text{ nm}$ area of a cleaved (111) surface where the (1×1) arrangement and atomic periodicities can be seen. A certain tip configuration is required to obtain atomic structure images.

tained unless the tip adopts a favorable configuration and even then it is not clear what atomic species is dominating the tunneling images.

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