

UHV microscopy of surfaces

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Results are reported using UHV electron microscopy to determine the role of background gases in influencing surface damage experiments and on the gold (001) surface prepared by ion-beam cleaning/thinning and annealing. In maximum valence oxides the end product is a higher-symmetry oxide or metal in UHV, but in a non-UHV environment secondary reactions take place. No evidence is found for electronic damage of non-maximal valence oxides, only sputtering and electron-stimulated reactions. For the gold (001) surface we have reproduced conventional surface-science preparations using ion-beam cleaning and annealing to produce the known reconstructed hexagonal monolayer on the surface.

1. Introduction

Despite the demonstrations some years ago that electron microscopy techniques can be applied to surfaces (see, e.g., refs. [1–19]) to date electron microscopy has only yielded results for a very limited number of materials and surfaces. The reasons for this are two-fold: the problem of attaining a sufficiently good vacuum level in the microscope and the problem of preparing a clean, well annealed surface. It is appropriate to briefly review the importance of these two. Assuming a unitary sticking coefficient, i.e., that every molecule striking a surface adsorbs, at a pressure of 10^{-6} Torr a monolayer adsorbs on the surface every three seconds [20,21]. Therefore in any standard microscope the surface is contaminated, not just by diffusion pump oils which creep along surfaces within the microscope, but also by the residual hydrocarbons from the rotary pump, water vapor, carbon monoxide and nitrogen, to name some of the main vacuum contaminants. A prerequisite for any controlled surface work is therefore pressure in the low 10^{-10} or 10^{-11} Torr

range, although even at such pressure one only has working times of a few hours assuming a unitary sticking coefficient.

Given that a sufficiently good vacuum level can be obtained, something which is now possible with either commercial or custom-built microscopes [22–28], there remains the problem of removing intrinsic contaminants. For instance, the typical 99.999% purity level of commercial metals only corresponds to the metallic impurity levels, not the level of dissolved hydrogen, carbon or other species. These need to be removed, and at present the most obvious approach is some combination of reduction/oxidation/ion-beam sputtering/annealing similar to what is routinely done in surface-science experiments. For electron microscopy where simultaneously one wants a thin, flat substrate-free region there are experimental problems. (Stress transferal from the substrate may alter any surface reconstructions and the substrate is also a source of impurities.) There are additional problems; for instance, one has to avoid ion-beam sputtering of the cartridge and coarsening of the thin regions during an anneal.

The combination of these various problems has meant that, to date at least, only materials with low intrinsic sticking coefficients such as gold [29,30], which can be prepared by evaporation, and silicon, which self-cleans on heating (see for instance ref. [31]), have been studied, and even in these cases restricted to certain surfaces such as the (111) gold surface which can be produced epitaxially (see, e.g., refs. [8,10,32]). Although many results have been published using the profile imaging technique (see e.g., refs. [6–8,11,12,17,18, 33,34]) one should be aware of the dangers; for instance, there is still substantial controversy concerning the measurement of an expansion for the Au(110) surface from HREM [6,34] since it is not clear whether impurities such as alkali metals were present (since these can drive a reconstruction [35,36]); and other techniques have reported both expansions [37–39] and contractions [40] for the same surface, in general with quite poor agreement between the experimental results and theoretical simulations. To be completely honest, to date there has been no experimental transmission or reflection electron microscopy where surface contaminants or segregants can be completely ruled out. On the other hand, it is unclear just how flat and homogeneous many of the surfaces used in conventional surface science are, and how free they are of defects such as subsurface dislocations.

In this paper we will focus on two particular aspects of UHV electron microscopy which illustrate both the above problems and our progress in overcoming them, namely the role of an uncontrolled microscope vacuum on surface radiation damage experiments and the microstructure evolution of gold during an ion-beam sputtering/annealing cycle.

2. Experimental methods

In this paper results are described for a number of different materials. All the oxides were prepared by crushing high-purity material, and the powder was either dry or suspended in acetone dispersed on holey carbon (for standard microscopy) or holey SiO (for UHV microscopy). In general, the UHV microscopy samples were baked

for 1–2 days in the microscope transfer chamber (see below) prior to analysis in the microscope. The gold specimens were 99.999% pure (001)-oriented single crystals cut using an E.D.M. to 3 mm disks and then gently mechanically polished with 15 to 0.1 μm diamond paste (attempting to minimize mechanical damage) down to about 80 μm . These samples were then dimpled slightly and ion-milled in a commercial Gatan system to about 16 μm and transferred to the microscope. After a 3-day bake (to completely remove any hydrocarbons from the walls, not simply to achieve UHV) the sample was ion-beam thinned with Xe in the transfer chamber at normal incidence (see later for more details). We should mention that it was critical to keep the hydrocarbon levels during ion-beam thinning down in the 10^{-10} Torr range to avoid contaminating the surface with carbon, the reason for the long bake.

All the UHV experiments were performed in a UHV H-9000 HREM which has a base pressure of 6×10^{-11} Torr and a stable operating pressure (stable for months) of $2\text{--}3 \times 10^{-10}$ Torr with the beam on. A schematic of the microscope is shown in fig. 1. For the results described herein the most significant features are a LEED system which was used as a low-energy electron damage source, a triple-source ion gun operable in the range 100 eV to 4 kV which yields ion currents at the specimen of the order of 4 μA at 2 kV, a Gatan parallel EELS interfaced to an Apollo computer [41] and an optical annealing source. We should note that the annealing temperatures quoted in the text correspond to thermocouple measurements which represent lower bounds to the true annealing temperature.

3. Comparison of surface damage in UHV and non-UHV

It has been known for many years that ionizing radiation of almost any type can damage materials by electronic excitations (radiolysis), particularly maximum valence (empty d-shell) oxides (see e.g., ref. [42]) The earliest mechanisms proposed to explain these were the MGR [43,44] (a local bonding-antibonding transition) and the Knotek–

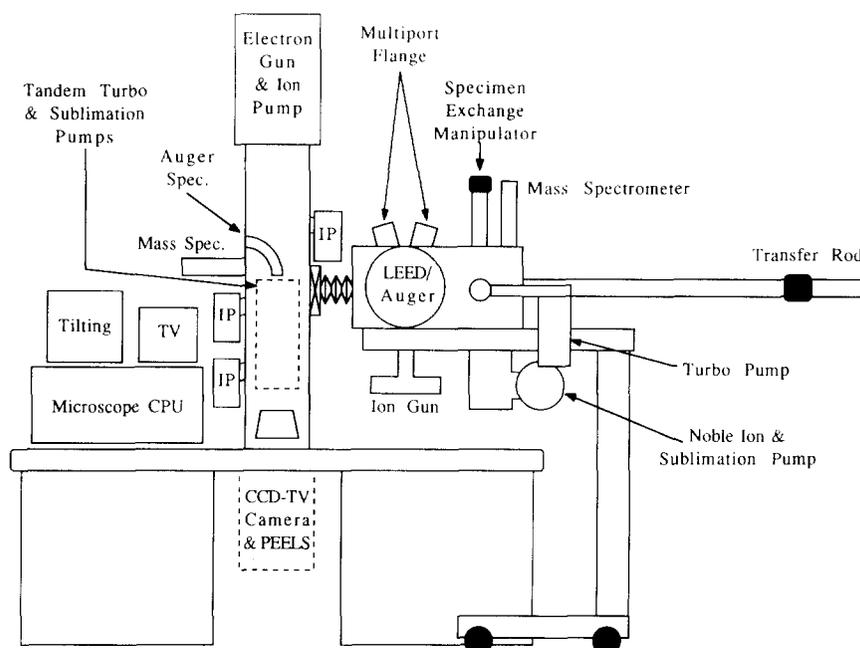


Fig. 1. Schematic diagram of the UHV microscope showing the column and transfer chamber. The Auger spectrometer in the microscope is still being developed; the optical annealing source faces the LEED/Auger optics, and the attachments on the side chamber change frequently.

Feibelman [45–47] (interatomic Auger) mechanisms, although many more have appeared in the literature since (see, e.g., refs. [48,49]). In the maximum valent (empty d-shell) transition metal oxides the major processes are thought to involve desorption of ions with thresholds typically around the onset energy for excitation of the metal p-shells, although at higher (incident electron or photon) energies there is good evidence for desorption driven by higher-energy core excitations. It should be stressed that it is still very unclear which mechanisms are responsible for damage in maximum valent oxides. For instance, whereas the Knotek–Feibelman mechanism explains well ion emission by a double Auger mechanism, one would expect neutral emission from a single Auger process to be 100–1000 times more likely, and there the evidence for neutral desorption is very indirect and unclear except for covalently bonded systems [44,46,50–52]. It should also be stressed that it is well established in the surface-science literature that electronic excitations do not appear to damage

non-maximum valence oxides, although there is ballistic damage for high-energy ions.

In electron microscopy such processes are distinct from ballistic damage which can be readily demonstrated by monitoring the damage as a function of beam energy. As an alternative confirmation, fig. 2a shows the results of irradiating V_2O_5 with 3 kV electrons in the microscope side chamber at a flux of $7 \times 10^{-4} \text{ A/cm}^2$ for a period of 15 min and fig. 2b XPS results under comparable conditions showing the expected shift of the vanadium $2p_{3/2}$ levels upon reduction [53]. It should be noted that such damage is readily visible to the eye by a color change from yellow to black. Of course, at higher electron voltages, knock-on damage will accompany electronic damage.

The structural evolution as oxygen desorbs from these materials has previously been shown [54] to be an ascent of symmetry path with the products being higher-point-and-space-group lower oxides or metals. Particularly when the final product is a

metal the residual vacuum has a very major effect since the clean metal surfaces are highly reactive. One clear example is tungsten trioxide where in UHV (see figs. 3a and 3b) the product is clearly metallic tungsten whereas in the non-UHV environment the tungsten reacts to produce W_3C [55] (figs. 3c and 3d). (A high-pressure WO phase has also been reported [56,57], the difference being presumably due to different uncontrolled residual gases.)

With non-maximal valence oxides such as CoO [58], MnO [58], FeO [58] and NiO [59] the effects

of the residual gases in the microscope are just as apparent. In all of these systems there is very good evidence that no electronic processes occur in UHV [55] and the only damage is isotropic sputtering. For instance, in NiO there is general isotropic sputtering with a threshold of 105 ± 5 kV [59,60]. As just one example, fig. 4 compares CoO in UHV and when the sample was exposed to a leak of about 10^{-8} Torr; with the leak the sample oxidizes (as evidenced by a volume increase) to the spinel Co_3O_4 at the surface [58]. The evidence indicates that reports of Knotek-Feibel-

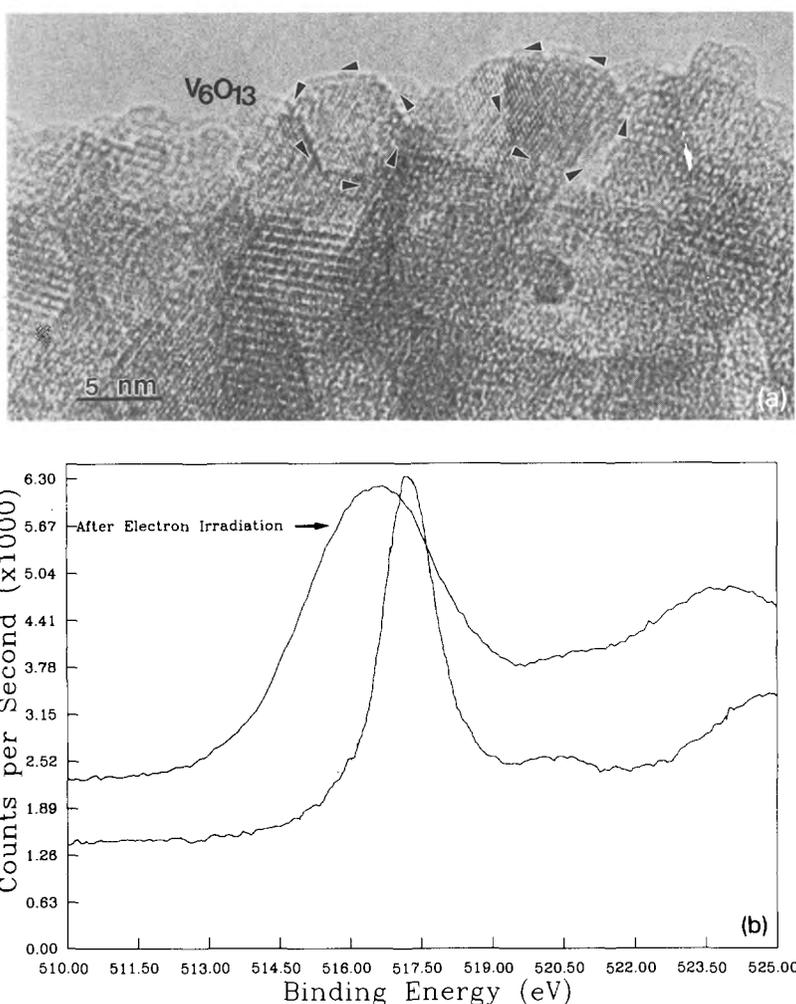


Fig. 2. (a) High-resolution image of V_2O_5 after irradiation at 3 kV showing the formation of V_6O_{13} at the surface. (b) XPS spectra before and after showing shift in the $2p_{3/2}$ core edge.

mann oxygen desorption from these systems are, instead, electron-beam-stimulated reactions with the residual gases in the microscope.

To summarize these results, there are two types of surface damage which occur in the electron

microscope (in addition to ballistic sputtering which is always present at higher voltages). Oxygen desorption from electronic excitations occurs in empty d-shell oxides, but the end product will be influenced by secondary reactions. In partially

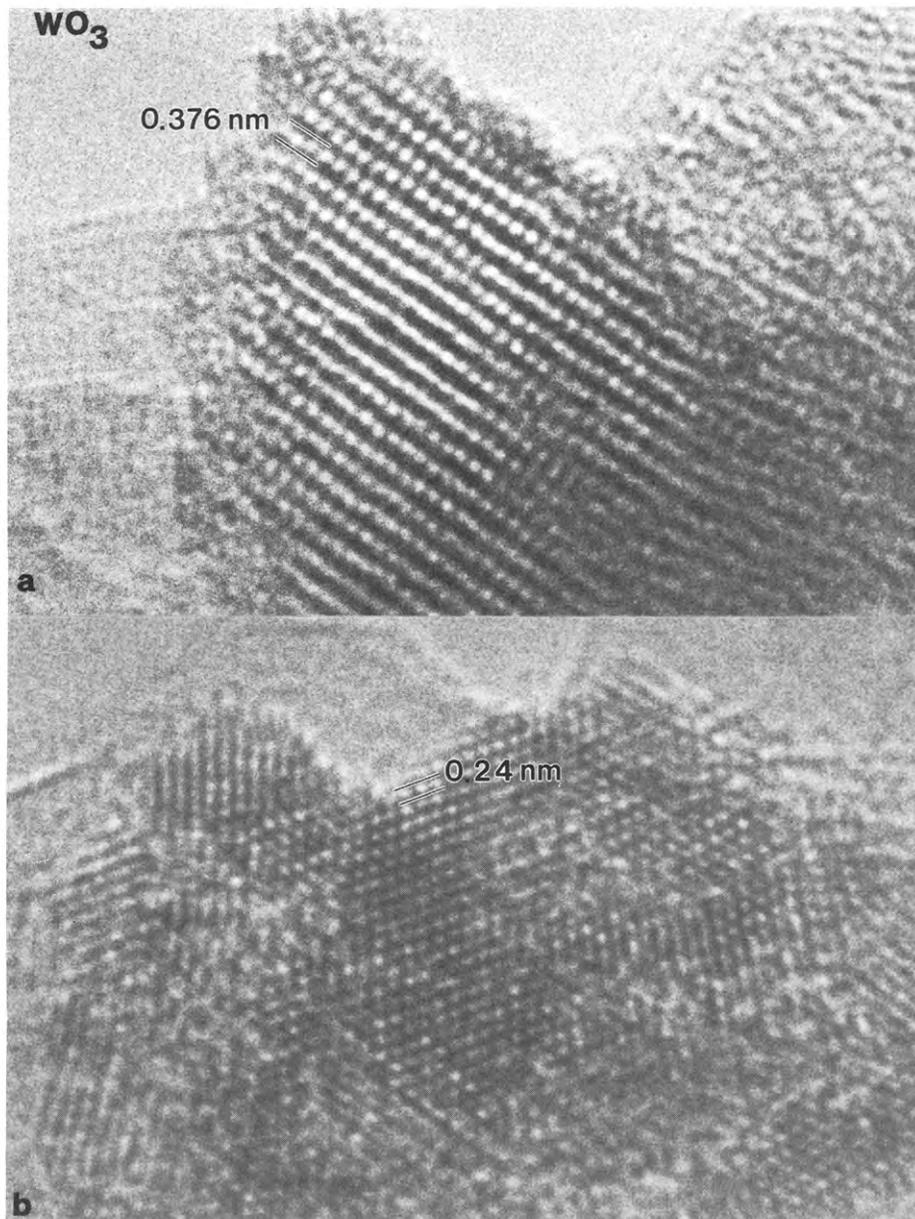


Fig. 3. A comparison of damage to WO₃: (a, b) damage in a normal microscope where some metallic W and W₃C is formed where (a) is the initial state and (b) the damaged material; (c, d) formation in UHV of metallic tungsten with selected-area diffraction pattern inset in (d). Note that secondary reactions confuse the issue in non-UHV.

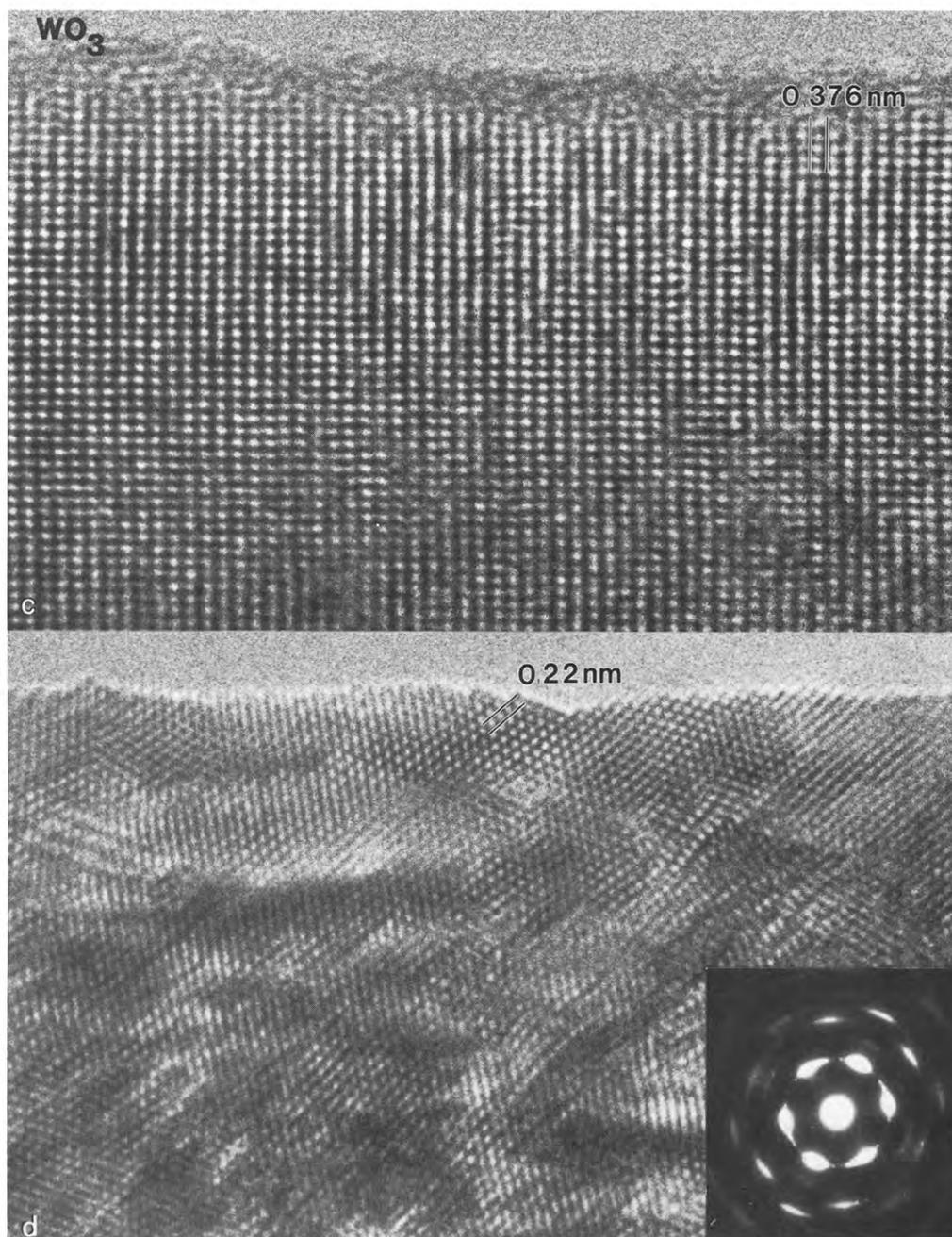


Fig. 3 (continued).

filled d-shell materials and non-transition metal oxides the damage mechanisms are reaction with the ambient vacuum and sputtering. For completeness, it should be mentioned that the damage

propagation mechanism into the bulk is diffusion controlled [61–63] with a diffusion constant which appears to be a function of the beam flux [62], and that encapsulating the surface protects it from

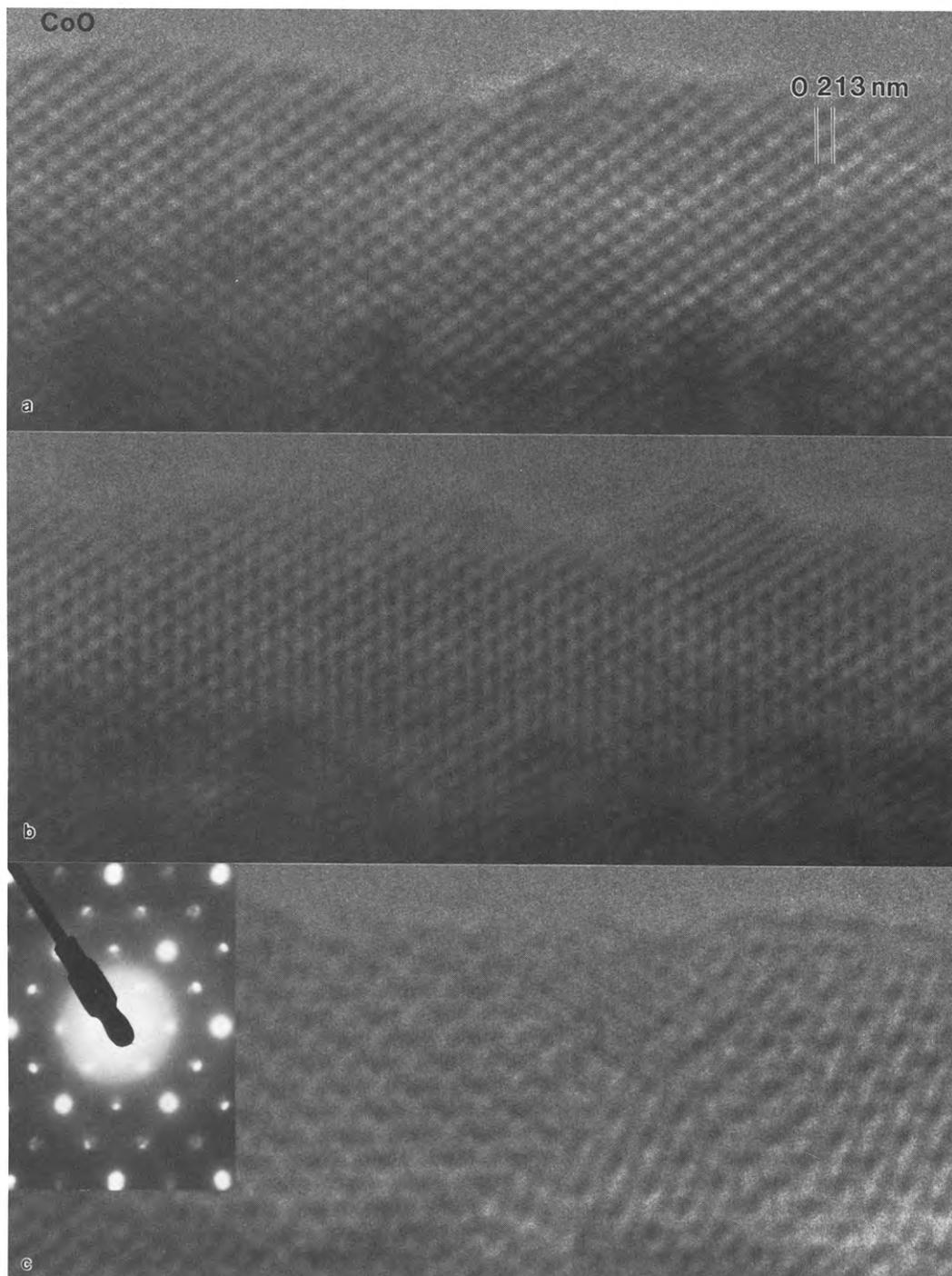


Fig. 4. Images of CoO: (a) initial state, (b) after damage in UHV where a little isotropic mass loss occurred, (c) after exposure to a leak where there was both a surface volume increase and structure change. The inset diffraction pattern in (c) shows the formation of the spinel Co_3O_4 by oxidation of the CoO at the surface.

Table 1
Comparison of damage in UHV and non-UHV environments for a number of metal oxides

Material	Non-UHV	UHV	Notes
CoO	ESR/sputtering	Sputtering	ESR to spinel
FeO	ESR/sputtering	Sputtering	ESR to spinel
MnO	ESR/sputtering	Sputtering	ESR to spinel
MoO ₃	O loss	O loss	Metal reacts in non-UHV
Nb ₂ O ₅	O loss	O loss	Metal reacts in non-UHV
NiO	ESR/sputtering	Sputtering	Sputtering anisotropic in non-UHV; isotropic in UHV
Ta ₂ O ₅	Unclear	O loss	Metal formed in UHV
TiO ₂	Slow O loss	Fast O loss	Reoxidation in non-UHV
V ₂ O ₅	O loss	O loss	Rates different
WO ₃	O loss	O loss	Metal reacts in non-UHV
ZrO ₂	No change	No change	

In CoO, FeO, MnO and NiO only electron-stimulated reactions (ESR) occur to the spinel phase (or reactions with carbon coatings) and sputtering; with the other oxides except ZrO₂ there is oxygen loss by low-energy electronic excitations, secondary reactions and sputtering.

damage [64]. The data for a number of systems are summarised in table 1.

4. Microstructure evolution in Au(001)

As mentioned in the introduction, a standard method of producing specimens for general surface observation is ion-beam cleaning followed by annealing. We have recently performed a number of experiments to reproduce this, ideally to produce a LEED pattern to match the electron diffraction patterns and images, although to date with no success with the LEED. These experiments have been with gold, which is a good choice in terms of having a number of well documented but quite poorly understood reconstructions [65–72]; it is established that the top layer is a slightly compressed hexagonal monolayer [65] but the depth of the reconstruction, the issue of long-range misfit strains and the nature of any longer-range superstructures or incommensurations is very unclear. Gold also has an exceedingly low sticking coefficient for almost all gases [29,30]. Unfortunately, it is a poor specimen from the viewpoint of mechanical polishing and ordering due to its very ductile nature. We will describe here some of the main features of the sputtering/annealing cycle, and a more detailed report is in preparation [73].

Fig. 5 shows a gold specimen following thinning at 4 kV with Xe at 90° incidence for six hours. (In order to avoid sputtering the holder onto the specimen and producing Cu–Au alloys we are restricted in the range of energies and angles with the current specimen holder design.) One feature to note is the appearance of large spacing fringes in the specimen and superstructure in the diffraction spots; EELS spectra indicate that substantial Xe has been implanted in the gold. The superstructure is linked to the observation of the Xe, and is probably some form of metastable solid solution. With annealing to 150°C or higher the Xe disappears, and when the sample is dosed with 2 kV Xe no implantation was observed although there was substantial damage as shown in fig. 6a, both point defects, dislocations and almost a mosaic structure. With further annealing the damage drops, see the sequence 6b–6d, although we did observe some carbon appearing after the annealing. This was due to small diamond particles which had become embedded in the gold during the polishing and could be readily identified as such by diffraction and EELS. With continued sputtering/annealing cycles and annealing at higher temperatures (> 300°C) the damage density dropped and the hexagonal reconstruction [65–72] could be seen both in the diffraction pattern and dark field images, see fig. 7.

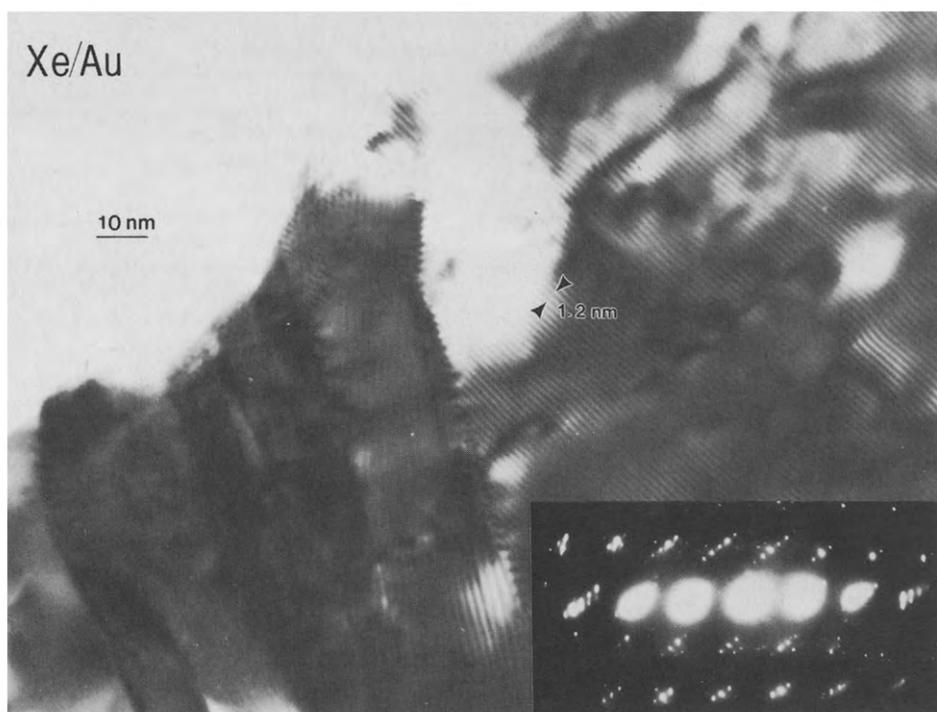


Fig. 5. Low-resolution image with a representative diffraction pattern inset showing a Xe-implantation-induced phase in gold, most clearly evident by fairly large (about 1 nm) fringes.

The reconstruction is quite complicated, and for reasons of space we will not go into many details here. However, a few points should be made.

(a) From the diffraction pattern, we can confirm the existence of a hexagonal surface layer as seen in previous TEM diffraction patterns [74] and by STM [71]. We should note, however, that the diffraction pattern does not appear to be kinematical as suggested previously [74]; one has to include double diffraction effects.

(b) Provided that the sample is sufficiently well annealed, the reconstruction occurs everywhere, and in dark field images the dominant five-fold period is evident with a domain structure. (We have repeated the ion-beam disordering of the surface and annealing experiments.) Presumably, earlier reports [74] which only show limited regions were due to too low an annealing temperature or poor samples; these samples were prepared by depositing Au on Ag which Palmberg and Rhodin [66] showed led to a LEED pattern com-

parable with that of straight gold if more than three monolayers were deposited. There is very little evidence for a longer period normal to the five-fold period, but some very complicated local domains and modulations along the five-fold direction, which is consistent with both the STM [71] and He diffraction data [70].

(c) There is clear evidence for small bulk defects, particularly small voids, coexisting with the reconstruction.

More details will be published elsewhere [73].

5. Discussion

Although we can claim substantial progress in UHV microscopy, for instance clarifications of the critical role of background gases and being able to match a surface-science surface preparation, it would be incorrect to say that far more progress is not needed. Clearly far more development work needs to be done, for instance we need to redesign

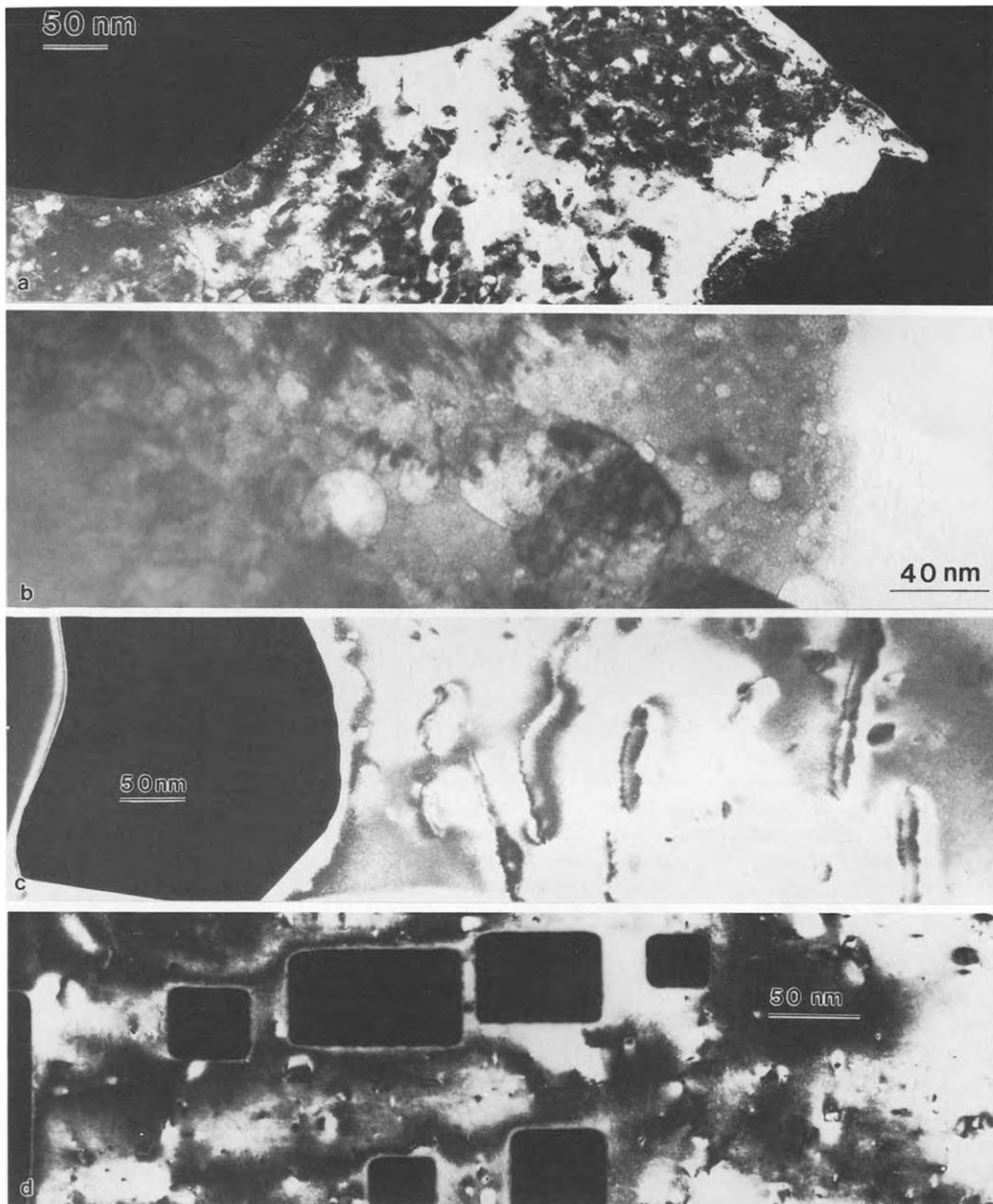


Fig. 6. Sequence of dark field images, showing different stages in the annealing/cleaning process: (a) after bombardment with Xe at 2 kV, (b) after annealing to about 150°C, (c) after annealing to about 230°C, [001] zone, (d) after annealing above 300°C, [001] zone. Point defects and small voids apparent in (a–c) have vanished in (d), and the dislocation density has dropped as expected, and in (d) the surface is reconstructed although it is not apparent at the magnification of the micrograph.

our cartridge to accommodate lower sputtering energies, lower incident angles and larger specimens, e.g. 5 mm specimens. It would also be

incorrect to say that we are satisfied with the vacuum levels attainable; at 2×10^{-10} Torr the working time is too short for reactive materials

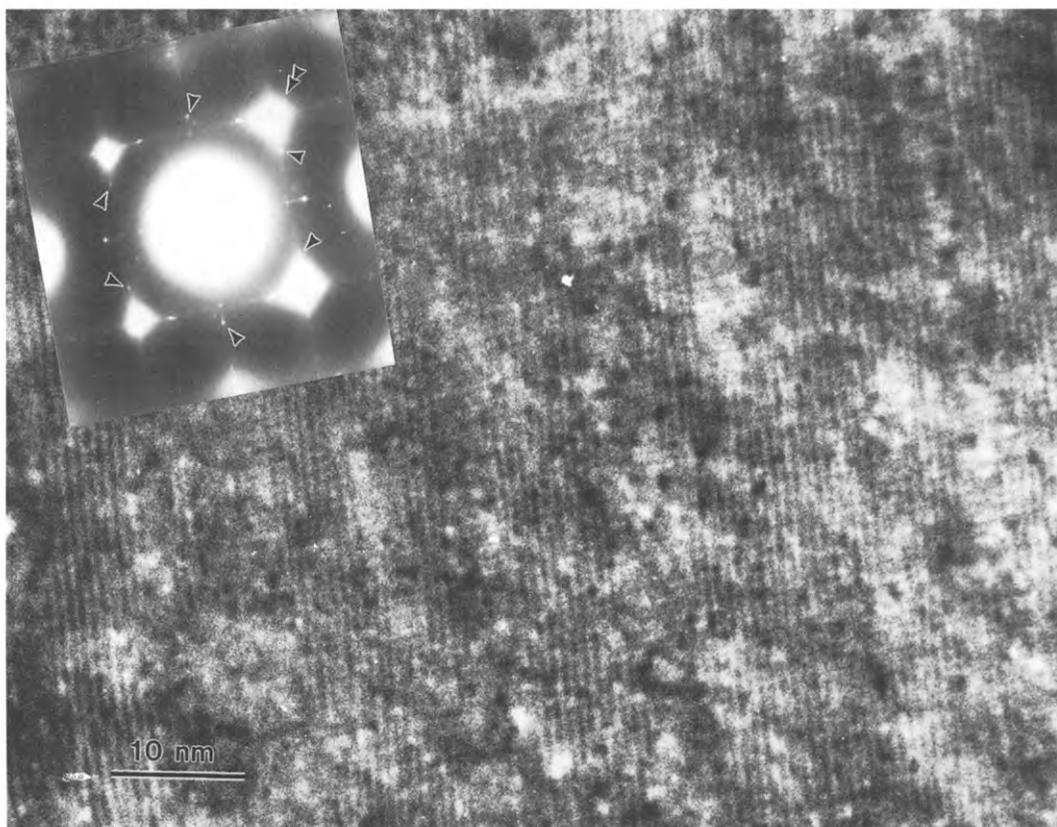


Fig. 7. Dark field image of the reconstructed gold (001) surface using a (200) bulk spot with diffraction pattern inset. The relative orientation of the two is approximately correct with the (200) bulk spot double-arrowed used for the dark field. One set of the surface spots is (single) arrowed. There are many complicated features in both the image and diffraction patterns, for instance the surface diffuse intensity along bulk [110] directions and a long-range periodicity along the same direction in the images, which will be discussed in more detail elsewhere [73].

and the low 10^{-11} Torr range is really required. Work is in progress to repeat the gold experiments with more reactive materials to calibrate in more detail the true vacuum levels at the specimen and, if necessary, to improve the pumping in parts of the microscope down to the 10^{-11} Torr regime. In addition, the observation of the unexpected structure due to Xe implantation means that chemical characterization is as necessary for surface microscopy as it is for bulk microscopy: Auger spectroscopy plus electron energy-loss spectroscopy of bulk contaminants should, it is hoped, solve this problem. We believe that UHV electron mi-

croscopy of surfaces will only come of age when it is possible to show LEED, Auger, electron energy-loss, transmission electron diffraction and transmission electron microscopy results all from the same surface.

Such problems aside, there does appear to be a good future for UHV electron microscopy. Obviously, for UHV electron microscopy to be viable it must be able to yield information which STM cannot. From our results to date there would appear to be a lot of information which falls into this category, for instance monitoring the penetration of surface damage and reactions into the bulk

and investigations of the effects of strain fields on surface reconstructions. However, we have only scratched the surface.

6. Conclusions

To perform surface science within an electron microscope, in addition to controlling the vacuum it is necessary to be able to control the specimen. In the absence of good control of these two aspects, results of investigations of surface structure and surface modifications due to ionizing radiation are suspect. The ideal electron microscope for surface studies is one which combines both conventional microscopy imaging and spectroscopic tools with surface-sensitive surface-science tools, all of which can be used on the same surface.

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