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UHV microscopy of surfaces

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A brief overview is given of the procedures for preparing clean, well ordered surfaces of thin specimens suitable for UHV surface science with an electron microscope. Examples are presented of results from the gold (001) 5×20 reconstruction and the boron-doped Si(111)$\sqrt{3}\times\sqrt{3}$R30° reconstruction. Results from the electron-beam-induced reduction of NiO in a controlled pressure of 1×10^{-7} Torr of CO are described which illustrate the critical role of background gases in electron microscopy.

1. Introduction

For many years now there has been a strong interest among electron microscopists in studying surfaces. Although there are now many different techniques available, see, e.g., refs. [1–24], the issue of how to prepare general surfaces which are both clean and well ordered has been an area of some difficulty. For instance, in a normal microscope one only has about 1 s to look at a clean surface (if it existed), and even at lower pressures such as the 10^{-9} Torr high-vacuum range only very inert materials can be studied; one has to have a pressure in the low 10^{-10} Torr or better.

Over the last few years we have been moving towards understanding the technical challenge of using a true ultrahigh-vacuum electron microscope to prepare and examine clean surfaces. The intention of this note is to describe some of our progress, both instrumental and in understanding UHV microscopy, which has put us in the position to routinely perform such experimental work. In particular, we will discuss some of the features of the microscope, the critical role of residual gases as exemplified by the effects of CO under controlled conditions on NO, and some of the issues in specimen preparation for UHV and characterization of surface reconstructions.

2. Experimental equipment

The microscope is a UHV-H9000 electron microscope, which is a conventional H-9000 microscope modified both in the objective region and above and below it so that the operating pressure (with the beam on) is about 2×10^{-10} Torr. The objective region is bakeable to about 200°C by internal halogen lamps and external flange heaters; the regions above and below to about 100°C. The intrinsic differential pumping of a microscope column is exploited with a 400 ℓ/s tandem-turbomolecular pump with a home-built Ti sublimation pump for the specimen region, and three 20 ℓ/s diode ion pumps above and below. On the side of the microscope is a separate transfer chamber which was designed to accommodate surface science hardware, see fig. 1. This transfer chamber is pumped by a 60 ℓ/s ion pump assisted by a home-built Ti sublimation pump and a small turbomolecular pump for roughing and exhaust pumping during bakeout. Specimens can be loaded into the transfer chamber by a load-lock mechanism, baked there either by external heating, an internal halogen lamp or a combination of the two. The base pressure in the transfer chamber is in the low 10^{-10} or high 10^{-11} Torr range, somewhat dependent upon the length of the bake.

As an idea of the turnaround time with the microscope, to bring the column down to UHV from air takes a bake of 2–3 days maximum; to bring the transfer chamber down a bake of similar length although if the load-lock mechanism is used a halogen bake overnight is sufficient. We should make the very important point that background pressure alone is not a guarantee of a clean vacuum; there may still be hydrocarbons adsorbed on the walls which do not desorb at room temperature but will desorb, for instance, when the transfer chamber is backfilled with inert gas for ion beam cleaning. We have found it necessary to bake until the hydrocarbon levels are low even when the chamber is backfilled. It should also be mentioned that the pressure levels quoted above are stable for periods of months; we do not observe any pressure rise when the electron beam is turned on, when the camera is loaded with new film or over a period of days. Any of these would be indicative of problems with the differential pumping or leaks. (Just after baking the clean walls act as pumps and can give an artificially low pressure which will decay progressively if there is a leak.) The primary residual gas at the specimen appears to be water vapor coming from below the specimen region where the pumping is conduction-limited; improvements to the differential pumping would probably result in operating pressures in the 10^{-11} Torr range.

The primary use of the transfer chamber is cleaning and conventional surface science characterization of specimens. The specimen can be moved both forwards and rotated 360° to face any particular piece of equipment. The most important of these, at least for this work, are a triple-source differentially pumped ion gun with a useable range from 500 eV to 4 keV, a large window with a lens to focus the light from a broad-band optical annealing source onto the specimen, and an electron gun which can deliver up to 3 mA at a variable voltage of up to 10 kV. The ion gun is used to thin/clean samples with either optical or electron beam heating to anneal the samples. Other equipment such as a LEED/Auger system and a laser focussed on the specimen will be used in other experiments.

3. Specimen preparation

The most successful approach that we have found for samples is to use self-supporting 3 mm

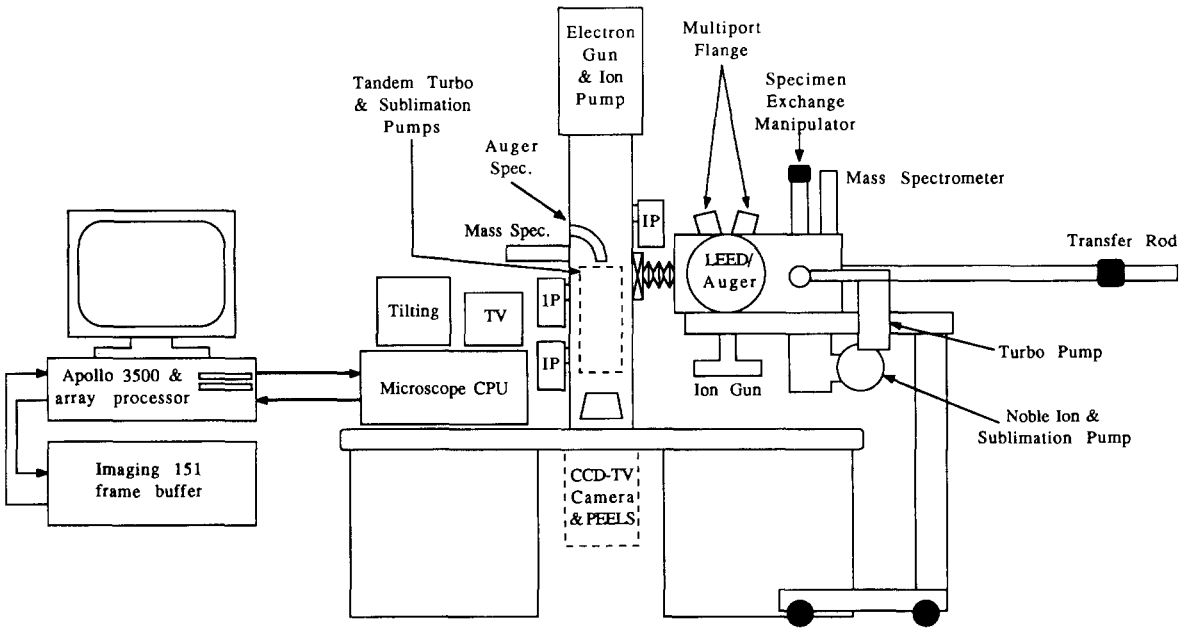

Fig. 1. Schematic diagram of the UHV-H9000 microscope.

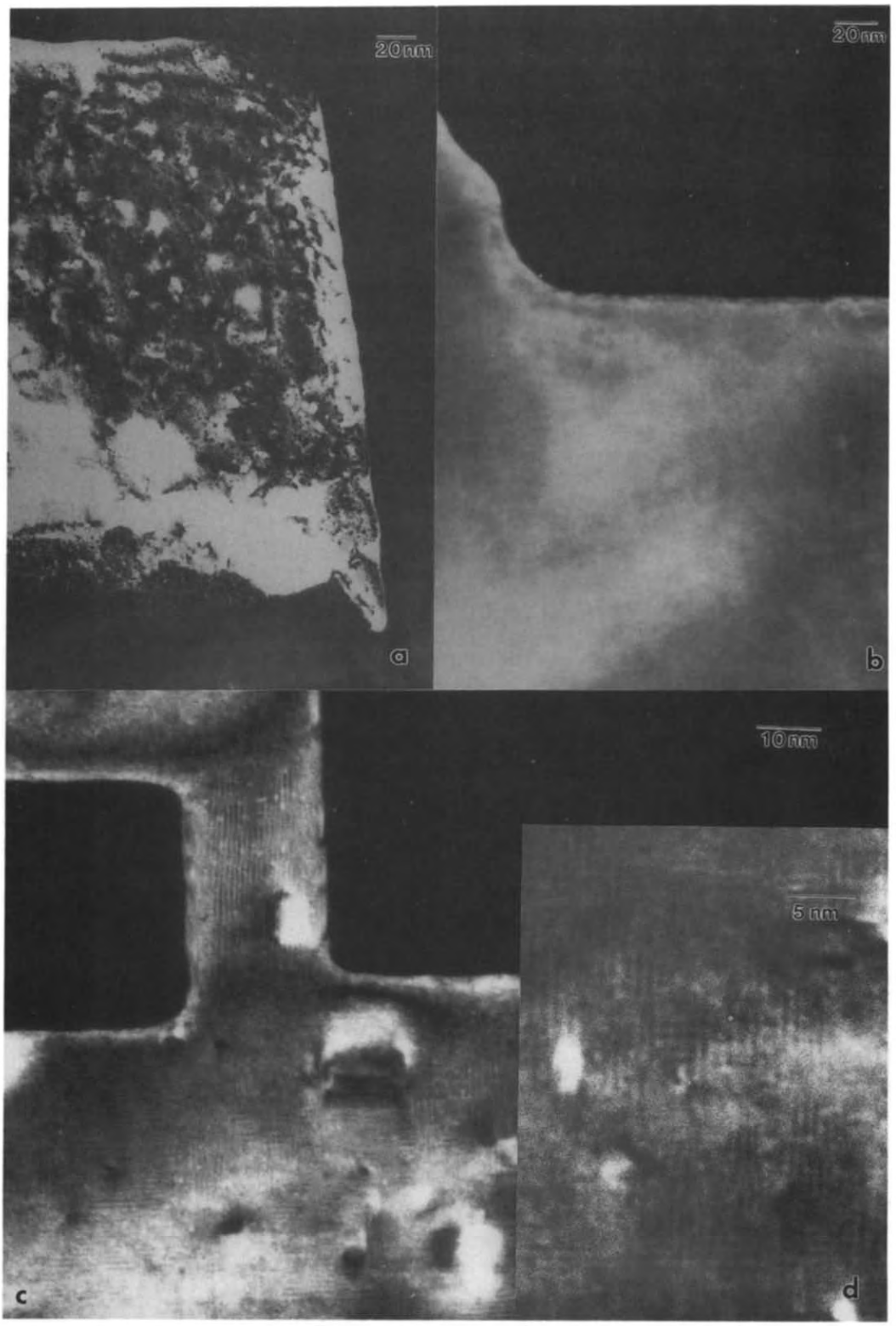

Fig. 2. Montage of images from the gold (001) surface: (a) dark-field image of a specimen after thinning/cleaning with 2 kV Xe ions; (b) dark-field image after annealing at 300°C for 30 minutes which removed most of the damage; (c) dark-field image after annealing at about 400°C when the surface reconstructs; (d) higher magnification image of (c) showing the "5" component of the 5×20 reconstruction.

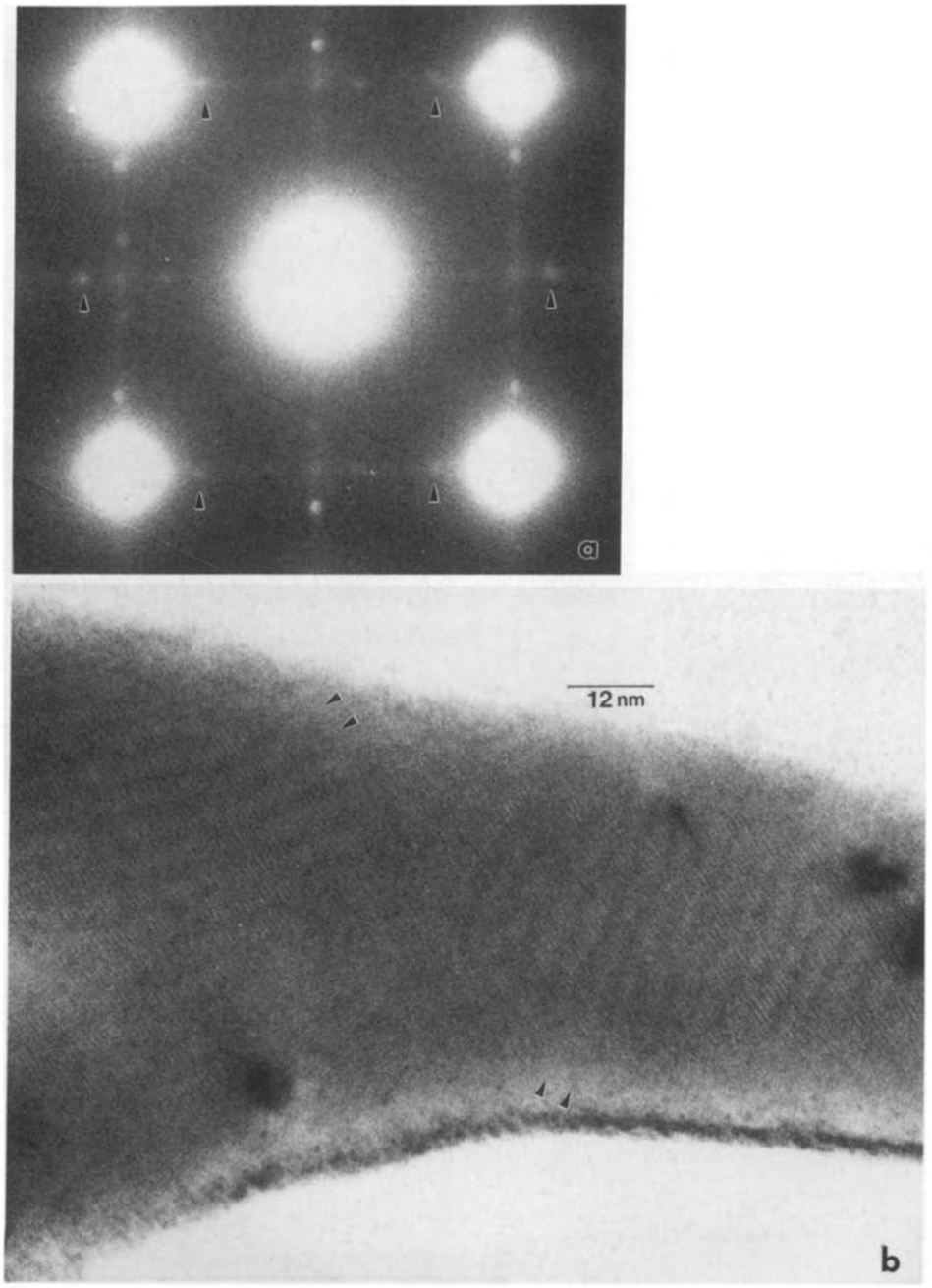

Fig. 3. Diffraction pattern (a), and bright-field image in (b) of the 5×20 reconstruction. One set of six spots from the surface monolayer is arrowed in (a). In the bright-field image the finer fringes are the "5" component of the reconstruction; the wider fringes (arrowed) are due to the relatively soft registry along the common [110] direction. The domain size is larger than that in fig. 2c due to additional annealing.

discs, thinned external to the microscope to perforation; sufficiently thin regions can be retained by skimming the surface with an ion beam to clean it and annealing. Grids are not useful because of the problem of specimen contamination by sputtering of the grid material onto the specimen. As mentioned briefly above, it is not sufficient to have a low background pressure to produce clean surfaces. During ion-beam cleaning and any annealing the walls of the chamber will degas, and one has to ensure that the pressure of contaminants at all times stays in the low 10^{-10} Torr range. As an example of this, during some low-energy-electron damage experiments on V_2O_5 [25] in a commercial ESCA/SIMS lab with a base pressure of 2×10^{-11} Torr, we have encountered severe problems due to electron-beam-stimulated desorption of hydrocarbons from the chamber walls. Following the cleaning, the surfaces need to be re-ordered by annealing. It is important to avoid overheating the sample since this leads to coarsening. We have found that temperatures which activate surface diffusion appear to lead to good surfaces, although at such temperatures the bulk defects induced by ion-beam cleaning do not always anneal out.

We will here describe some results on two simple surfaces which illustrate the sample preparation. Fig. 2 is a montage of images for a gold (001) crystal which illustrate the changes in the microstructure as the sample is cleaned and annealed (optically). Initially there is substantial damage, but as the sample is annealed this clears up and a microdomain 5×20 reconstruction develops [24,26–34]; with longer annealing times the domain size increases. Fig. 3 shows a diffraction

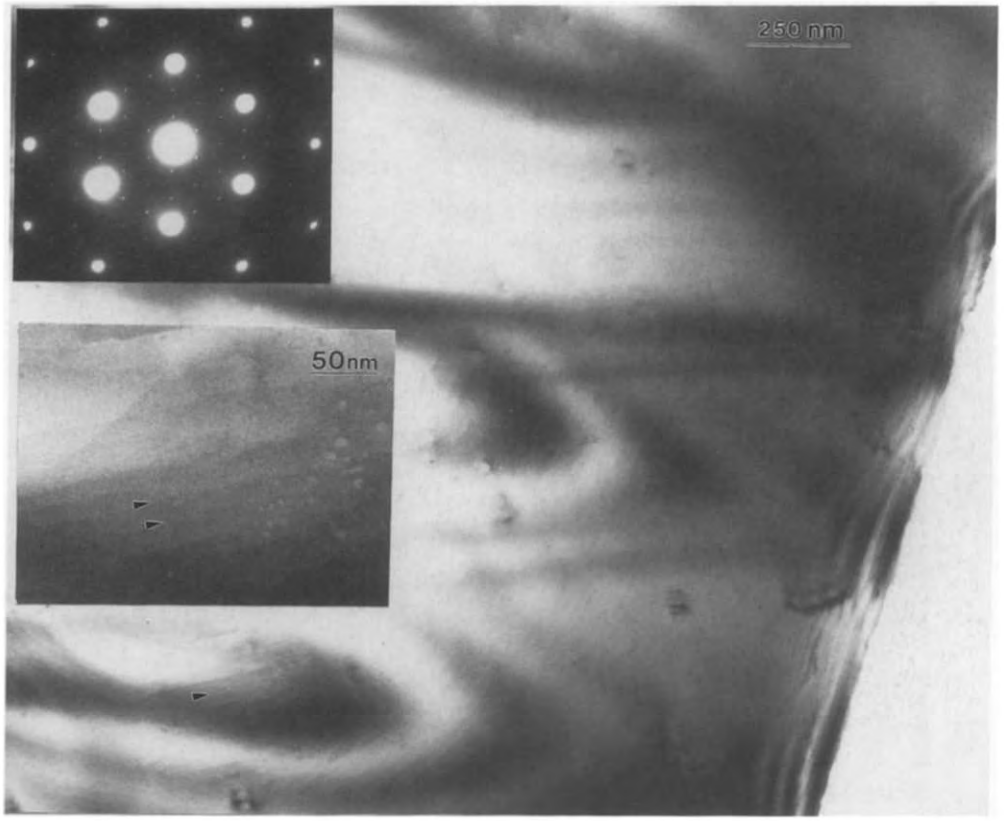

Fig. 4. Image with diffraction pattern inset showing the boron-doped Si(111)$\sqrt{3} \times \sqrt{3}$R30° reconstruction. Surface steps are indicated by the arrows with a higher-magnification image inset.

pattern and image which shows the moiré fringes between the bulk and the surface hexagonal layer. A more detailed analysis [35] of the surface indicates that there is a single (111) plane, contracted relative to the bulk and very slightly sheared into two domains, with two 90° rotational sets of these domains. There is a strong registry of the surface monolayer and bulk along one direction, and a very soft registry along the nearly co-incident [220] direction. This will be published in more detail elsewhere [35].

The second example which we will show here is the B-doped Si (111) surface. Following ion beam cleaning with 2 kV Xe, the surface region

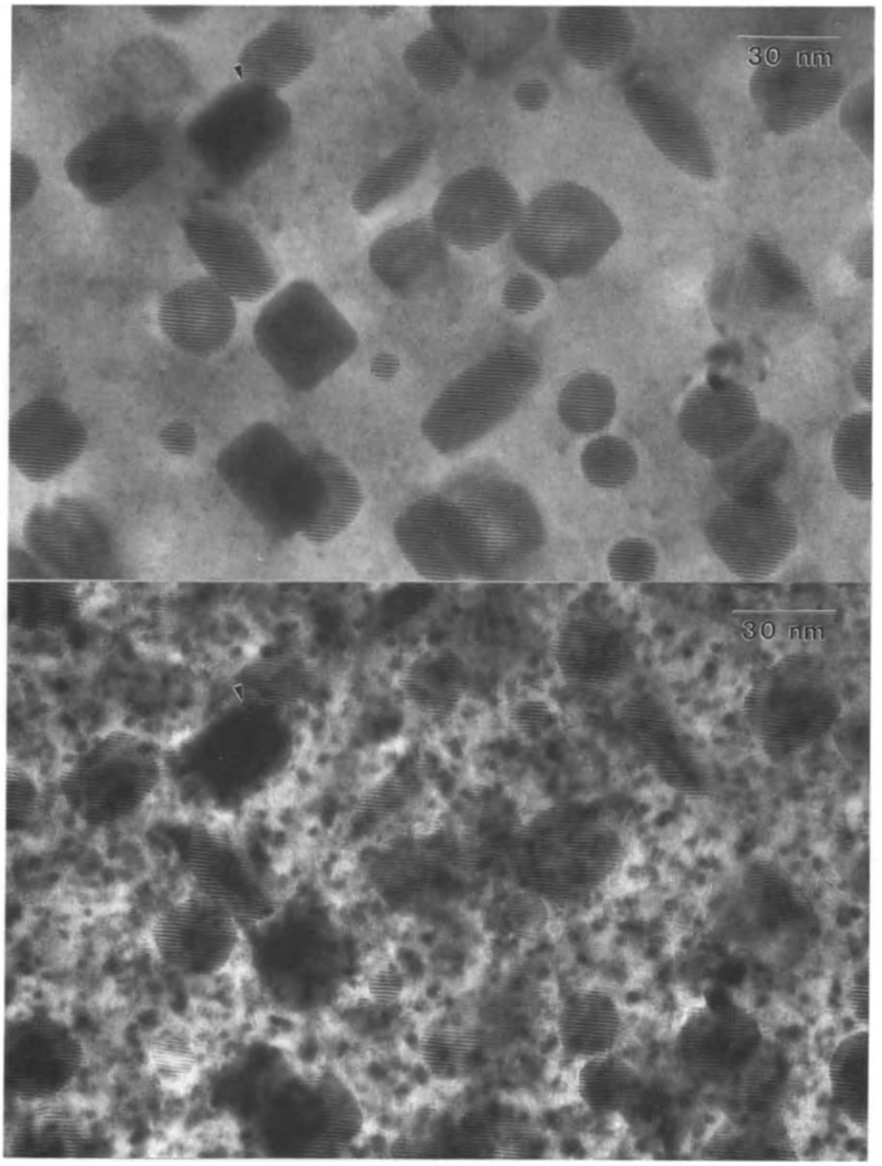

Fig. 5. Images of (a) a NiO surface with islands of Ni observed in UHV, and (b) growth of Ni on the surface due to electron-beam-induced reduction at a pressure of 1×10^{-7} Torr of CO. The large fringes are moiré's due to the cube-cube epitaxy with the substrate, and the arrow marks the same particle in both cases.

amorphizes, and on annealing to about 600°C the amorphous regions recrystallize leading to a flat surface with a $\sqrt{3} \times \sqrt{3}$ R30 reconstruction [36–39], see Fig. 4. We should mention that with inadequate cleaning SiC was formed on the surface; this could be removed by ion beam sputtering. The surface is sufficiently flat that surface steps can be readily seen by phase contrast at relatively high defoci as shown in the figure. Further work is in progress on this surface.

4. Effect of CO on NiO

The results described above cover the general approach to producing bulk, clean surfaces. It is well known in electron microscopy that hydrocarbons can have a significant effect upon surfaces, but it is perhaps not so well appreciated that other gases can have just as disastrous an effect. As an example of this, we show here some results on the effect of a pressure of 1×10^{-7} Torr of CO on the surface of NiO, admitted via a leak valve attached to the transfer chamber. The NiO samples were prepared as 3 mm discs which were chemically and ion-beam polished, and then cleaned briefly with 2.1 kV Xe ions. These samples were then optically annealed in an oxygen atmosphere of 10^{-6} Torr (via a leak valve) at about 300°C. The ion-beam milling left the material nickel-rich (due to differential sputtering) and during the anneal this led to small nickel islands with a cube–cube epitaxy embedded in the material – see fig. 5a. On deliberate exposure to a controlled atmosphere of 1×10^{-7} Torr of CO, in the electron microscope beam the NiO was rapidly reduced, producing many small islands of Ni – see fig. 5b. Presumably the electron beam is catalyzing the reduction of the NiO by introducing excited states either in the adsorbed CO or in the NiO.

5. Discussion

The results which have been described herein indicate that it is realistic to prepare clean, thin samples with good surfaces by a combination of ion-beam cleaning and annealing. Of course, for any particular surface the appropriate combination of ion energy/mass and annealing temperature and environment will vary; for instance, a higher pressure of oxygen appears to be required during annealing of the NiO to completely reoxidize the nickel. Whilst we have not emphasized the point so much in this paper, an important issue is the cleanliness of the surface and detection of surface contaminants. We have found that EELS is useful for this, although it does not appear to have monolayer sensitivity; we have not been able to detect amorphous carbon patches which are clearly visible in high-resolution images. A combination of high-resolution bright-field/dark-field, selected-area diffraction and EELS appears to be the most sensitive conventional approach. In the near future we will be testing an Auger spectrometer in the microscope, which may prove to be a more sensitive approach.

We should mention what appears to be the most significant technical problem that we have encountered working in UHV with clean surfaces, namely astigmatism correction. Normally one has regions of amorphous carbon which can be used to correct the astigmatism, but with a clean surface these are absent. In order to routinely perform high-resolution electron microscopy, some new approach to this and coma-free tilt correction for UHV will need to be developed.

6. Conclusions

It is possible to produce clean, bulk-like surfaces for UHV study by a combination of ion-beam cleaning and annealing, for instance the gold (001) 5×20 reconstruction and the boron-doped Si(111) $\sqrt{3} \times \sqrt{3}$ R30° surface. To achieve this, it is critical to pay attention to the general cleanliness of the system, not just the base pressure. As an example, 1×10^{-7} Torr of CO as a background pressure leads to electron-beam-stimulated reduction of NO.

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