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Problems with the use of surface reconstructions as indicators of a well-ordered surface

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The presence of sharp surface reconstruction or diffraction spots is often taken as an indicator of a well-ordered surface. We present results obtained using transmission electron microscopy in ultra-high vacuum (UHV) which demonstrate that even if the surface is well-ordered and reconstructed, there may be very high defect concentrations just below the surface of the order of 10^{11}–10^{13} cm^{-2}. The key point is that surface ordering takes place via surface diffusion, but the temperatures where this is active are too low to anneal out the near-surface defects through bulk diffusion.

1. Introduction

In a sense, the significance of surface defects for surface science and thin film growth is well known. Particularly for electronic materials, great lengths are often gone to avoid defects, for instance, good quality epitaxial layers are grown to serve as buffer layers prior to processing. However, such lengths are rarely if ever gone to with other materials. For instance, ion beam sputter/anneal cycles are standard for cleaning metal surfaces, but we are unaware of any experiments where metal buffer layers have been grown to avoid this issue. It is well known that ion beam bombardment leads to the formation of point defects and stable defects in the surface and near-surface regions (up to 100 Å in depth) of many materials [1–4]. Although in some cases these defects can be removed by annealing, very high temperature annealing is often precluded to avoid segregation of bulk impurities. To be realistic, the presence of a sharp LEED pattern and the absence of contaminants in Auger spectra are often taken as sufficient indicators of a good surface. Almost all surface science probes are insensitive to near surface defects, and for those which in principle have such sensitive such a low energy ion scattering [3], X-ray diffraction [5], field ion microscopy [6] and Rutherford backscattering [7], the interpretation for such defects is difficult and none of these techniques has been able to yield the desired microscopic information.

The intention of this note is to demonstrate through transmission electron microscopy performed in ultra-high vacuum conditions that very high densities of subsurface defects can co-exist with apparently well-ordered surfaces. The density of these defects is so high that they could readily perturb many near-surface properties, and there would be no way with conventional surface science techniques of detecting systematic errors due to them. For different surfaces of gold, silicon and iridium, we find in all cases substantial concentrations of small defect clusters coexisting with reconstructed surfaces obtained after repeated sputtering and annealing cycles.

2. Experimental method

The first step in the specimen preparation was to produce conventional electron microscope samples. For all the materials, bulk high purity single crystals were cut into 3 mm discs, mechanically polished, dimpled and then ion-beam milled

using 5 kV argon ions to produce electron transparent samples. It is appropriate to mention that this procedure often leads to embrittlement of the samples, so the number of defects introduced by the mechanical polishings is not negligible. Ion milling also introduces significant number of point defects. These samples were then transferred into the side chamber of the ultra-high vacuum (UHV) H9000 Hitachi electron microscope [8] and baked down to UHV conditions ($< 2 \times 10^{-10}$ Torr). Surface contaminants were cleaned off by ion-beam sputtering, typically with Ar or Xe ions at 3–4 kV with a flux of about 1×10^{14} cm^{-2} and nearly normal incidence. (More details about the specimen preparation are described elsewhere [9].) Annealing of the samples was performed using either a broad-band optical source focussed onto the specimen or by the electron beam heating.

Samples were examined under UHV conditions (without any air exposure) at 300 kV by standard electron microscopy techniques including selected area diffraction (SAD), dark field and high resolution electron microscopy. The sputtering and annealing cycle was repeated until the surfaces reconstructed or sharp 1×1 spots were obtained in the SAD patterns.

3. Results

We want here to focus upon the subsurface defects that we have commonly observed in the samples that co-exist with otherwise apparently

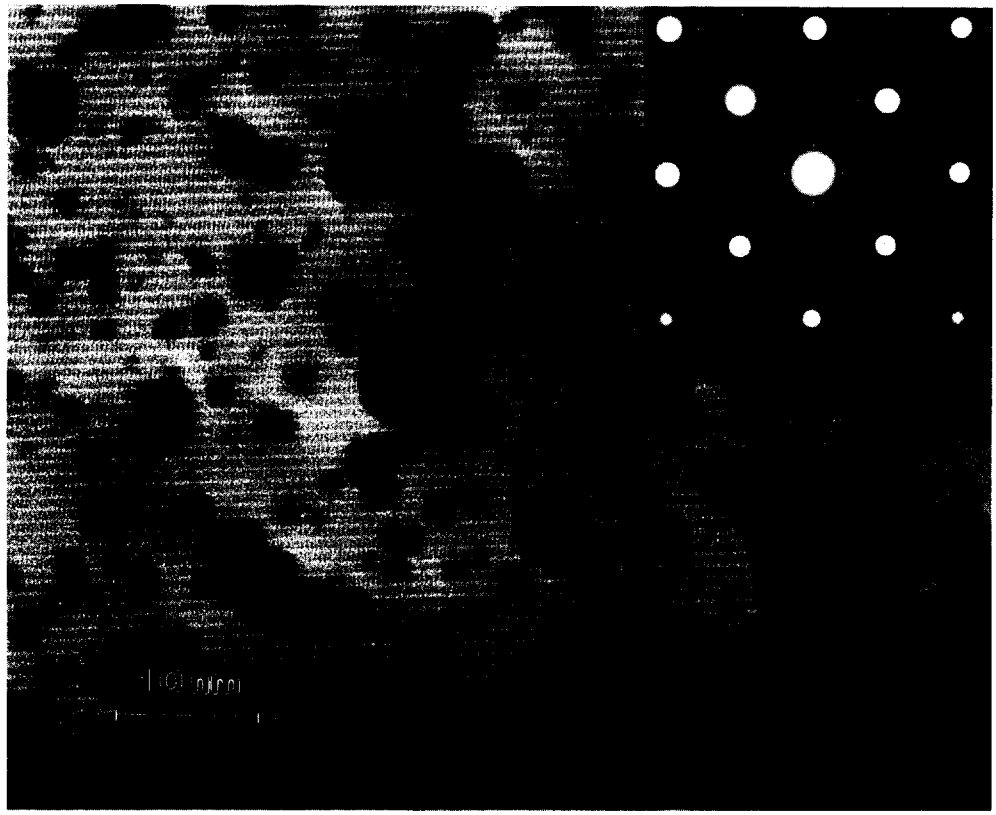

Fig. 1. Dark field micrograph showing primarily the moiré fringes (across the image) of 0.68 nm spacing from one of the two domains of the Ir(001) 5×1 reconstruction. The diffraction pattern inset shows the two perpendicular sets of domains of the reconstruction. Square shaped particles were identified as IrO_2 precipitates.

Fig. 2. Dark field micrograph of a $5 \times n$ reconstructed Au(001) specimen with moiré spacings (aross the image) varying from 4 nm to 5.5 nm representing the soft "n" dimension of the reconstruction where $15 \leq n \leq 21$. A selected area diffraction pattern of the reconstruction is shown in the inset.

well-ordered surfaces. Examples are shown in figs. 1–4. Fig. 1 is a dark field micrograph showing the iridium (001) surface with a 5×1 reconstruction [10], the repeat distance of the horizontal band being the half length along the "5" direction. Fig. 2 shows a dark field micrograph of a $5 \times n$ reconstructed Au(001) surface [11], the fringe spacing being due to the "n" ($15 \leq n \leq 21$) dimension of the reconstruction. Shown in fig. 3 is a silicon (111) surface with the 7×7 reconstruction evident from the diffraction pattern inset, although no superlattice fringes are seen in this dark field image. Fig. 4 was taken from another silicon (111) sample where a boron-induced $\sqrt{3} \times \sqrt{3}$ R30° reconstruction was observed [12]. Transmission electron diffraction patterns (inset) in all four cases showed well established surface reconstructions. All micrographs shown here were true representations of the state of the specimen, and the observed defect structures were homogeneous.

Common in all four cases is the presence of small defect or impurity clusters of 1–10 nm in size near the surface. The total thickness for all specimens is less than 50 nm, so in effect the total sample is in the near-surface region. Also seen in fig. 3 are extended defects such as stacking faults and stacking fault tetrahedra, and surface steps are also visible in fig. 4. There is a drastic difference in the appearance of the moiré fringes due to the reconstruction in fig. 1 for Ir(001) and fig. 2 for Au(001); fringes in fig. 1 were straight and seemed to be undisturbed by the presence of the defects, while the fringes bend and are affected

by the defects in fig. 2. The interaction of the subsurface defects with the surface reconstructions will be the subject of another paper [13].

4. Discussion

Whereas there does appear to be some knowledge in the literature that well-ordered surfaces may not be particularly defect free in the near surface region, the concentration of the defects that we are observing is astonishingly high. As an estimate, for all four samples these are about 10^{11}–10^{13} cm^{-2}. What we have observed consistently with these and other samples is that the surface equilibriates at temperatures below those required for substantial bulk diffusion, therefore, substantial numbers of bulk defects can remain when the surface becomes well-ordered. In fact we exploit this phenomenon with our samples, since when bulk diffusion becomes active the thin regions near the central hole in the 3 mm disc will coarsen, and if this happens the samples become too thick for optimal electron microscopy.

The implications of our results in terms of thin film growth are fairly obvious, and we will briefly mention some of them. Perhaps the most significant one is that these defects are likely to be electrically active. The second is that the presence of these defects can easily alter the strain state of the surface and affect epitaxial growth onto the surface; for instance, if they diffuse to the interface during growth there may act as nuclei for dislocation formation. Finally, such defects may be a source of undesirable chemicals in

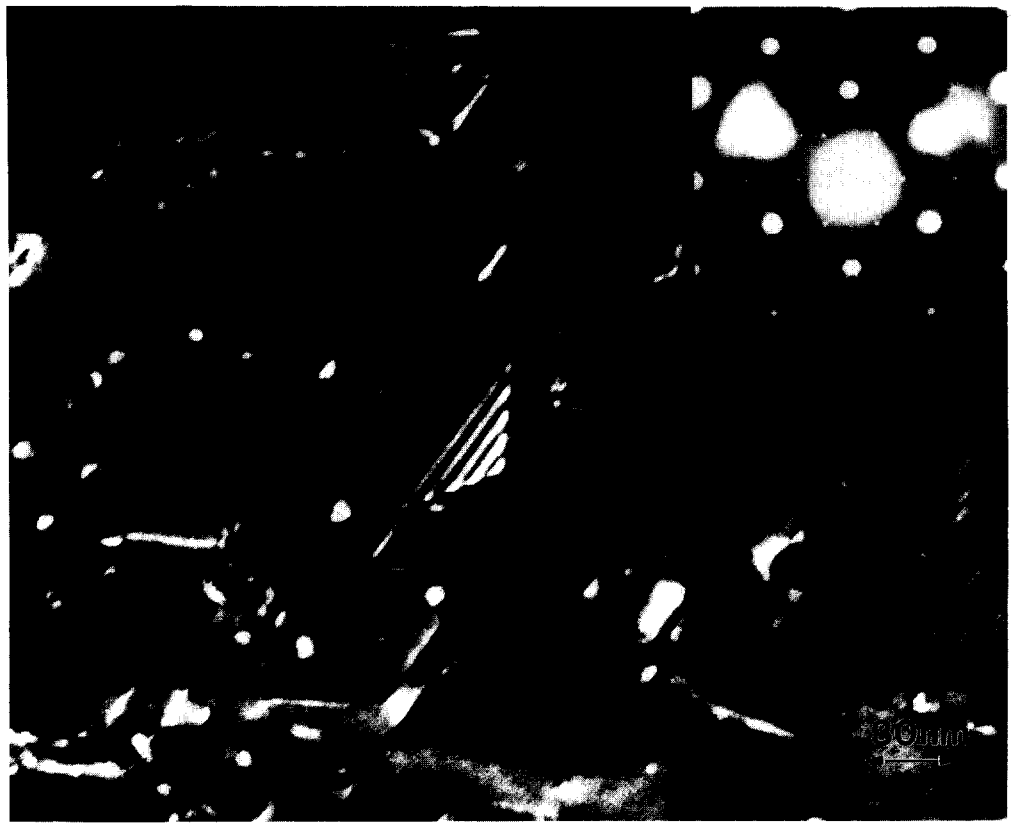

Fig. 3. Dark field image of a Si(111) specimen after the 7×7 reconstruction was established by sputtering and annealing. Stacking faults and stacking fault tetrahedra were observed in this specimen as well as in other silicon specimens with the same surface preparation procedure.

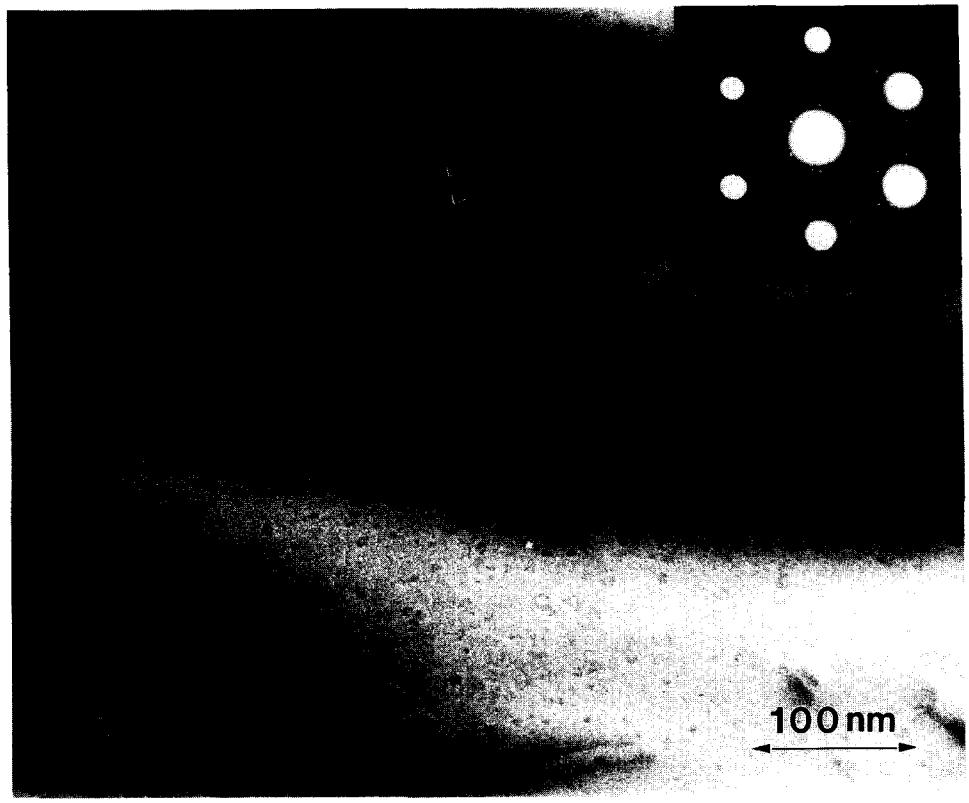

Fig. 4. Dark field image of a boron-doped Si(111) specimen with the $\sqrt{3} \times \sqrt{3}$R30° reconstruction (diffraction pattern inset). Features in the image include impurity particles of 5 nm in size and surface steps.

the near surface region, since they can trap gaseous species from the vacuum.

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