

ATOMIC STRUCTURE OF ION BOMBARDED TiO₂(110)

Irene Palacio, Beatriz Martínez, Arantzazu Mascaraque, Oscar Rodríguez de la Fuente
Departamento de Física de Materiales, Universidad Complutense
Madrid 28040, SPAIN

Pilar Ferrer-Escorihuela, Germán Castro
SpLine Beamline, ESRF, 38000 Grenoble, FRANCE

Low energy ion bombardment is commonly used in materials science and engineering. In surface science, it is a common routine to clean surfaces in UHV conditions, usually followed by high temperature annealing to recover the required surface flatness. In the coating industry, surfaces are usually bombarded prior to growing the film by PVD techniques to ensure a proper coating. Focused Ion Beam (FIB) is an increasingly demanded tool to sculpt nanostructures with complex shapes.

But low energy ion bombardment, more than a routine tool, is also a technique to controllably modify surfaces. In the range of high fluxes and doses, self-organization processes may, under certain circumstances, open the possibility to create an ordered array of nanostructures. This fact has been exploited in metal surfaces, some of which show interesting physical and chemical properties. In some semiconductors, the obtained nanostructured surfaces show a remarkable translational and orientational order when bombarded under the proper conditions.

Oxides have not been so thoroughly studied in this context. They do not show facile surface nanostructuring at room temperature and they are intrinsically more complex than other materials. There are many types of defects induced by an ion colliding against the surface of an oxide. Apart from structural defects, it must be taken into account that important chemical changes are inducted as well, induced by the different sputtering yield of the metal cations compared to the oxygen atoms: oxides of transition metals show, in general, a chemical reduction during ion bombardment. The resulting bombarded surface of an oxide, after high ion doses and summing up all the effects from individual events, can thus be very complex. Among the different potential processes, amorphization (i.e. the loss of short range order) must be considered. It is, in fact, a common result during low energy ion bombardment in semiconductors.

TiO₂ is a very interesting oxide, which shows a variety of physico-chemical properties of deep interest with respect to technical applications: whitening pigment, photocatalyst, hydrophobic coatings, catalyst support, medical implants, etc... The (110) orientation of TiO₂ in the rutile structure is probably the most studied surface of an oxide, because of the wide fauna of useful properties above mentioned and because the (110) is the most stable orientation.

The experiments (25-02-727) took place in May 2011 between Thursday 5th and Monday 9th, at the BM25B beamline in SpLine at the ESRF.

We used two different $\text{TiO}_2(110)$ crystals, called B2 and P1, which were ion-bombarded and flat, respectively. Atomically flat surfaces were produced by immersion in aqueous HF and high temperature annealing in air. Figure 1 shows an AFM image, in non-contact mode, of sample P1 (left). The image shows atomically flat wide terraces separated by monoatomic steps. Figure 1 also shows the surface of sample B2 (right). After ion bombardment, flat terraces disappear and a rough surface is present instead. No signs of nanometric order are evidenced.

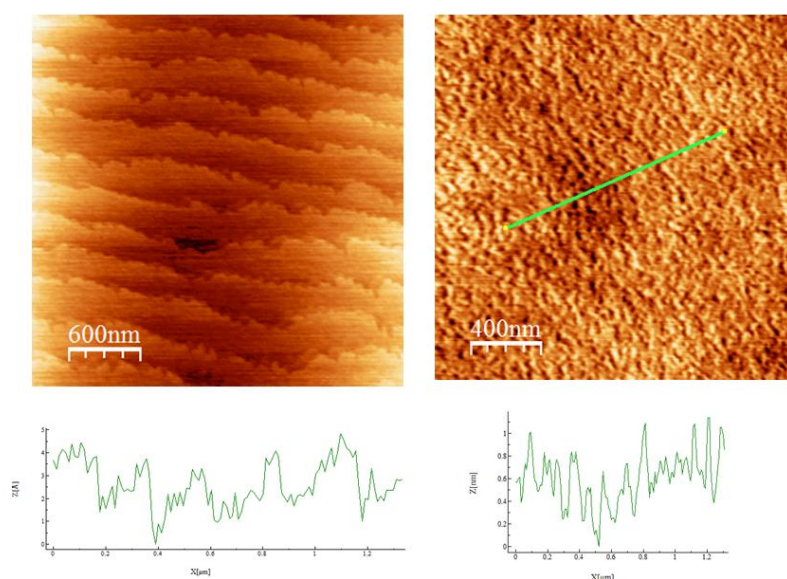


Figure 1: AFM images of samples P1 (left) and B2 (right), the ones analyzed during the beamtime. Sample P1 has large atomically flat terraces separated by monoatomic steps. Sample B2 shows, after ion bombardment, a rough topography.

Several experiments in different configurations were performed. We carried out most of the experiments in grazing incidence to better unveil the surface signal. In this respect we measured X Ray Reflectivity (XRR) curves, Crystal Truncation Rods (CTR's), etc...

CTR's (not shown in this report) are somewhat modified in the bombarded surface. Most of main features among the Bragg reflections remain constant, but a few new smaller features emerge. A detailed analysis of the CTR's obtained during the beamtime is not useful since we cannot provide a structural model to be refined. However, from these measurements we can probably discard the possibility of having created an amorphous surface during ion bombardment. Rather, we can confidently expect to have modified the surface crystal structure. This is the first relevant result obtained during the beamtime.

X Ray reflectivity curves for the two surfaces are different, as shown in Figure 2. Both reflectivity curves have share the same critical angle, but differ in their overall shapes. The smooth oscillations in both curves suggest the existence of a shallow overlayer with a different refractive index to that of bulk TiO₂. For the case of the bombarded surface, the shorter periodicity would in turn indicate that the modified overlayer has a larger depth than for the case of the flat surface. This is clearer when viewing the two shallow oscillations appearing below 1 degree for the bombarded surface, which are not present in the flat surface.

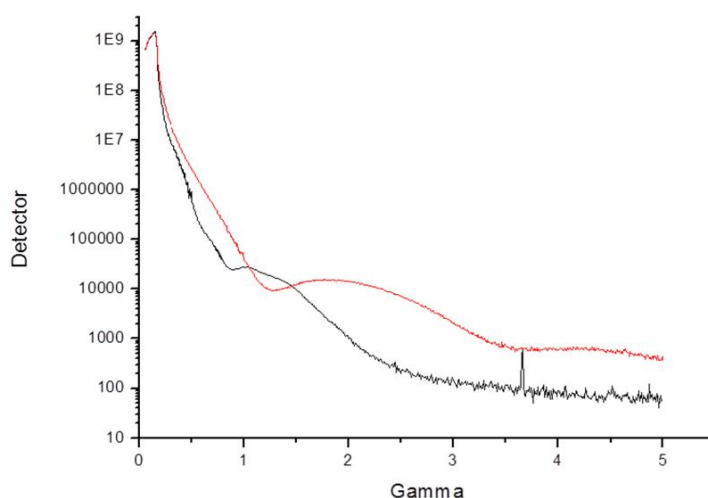


Figure 2: X Ray reflectivity curves for samples P1 (red) and B2 (black). The oscillations, indicative of a modified overlayer, have a shorter periodicity and are more evident for the bombarded surface, specially below 1 degree.

Figure 3 shows a HK reciprocal space map around the (2 1) reflection, with $L=0.3$, both for the flat and for the bombarded surfaces. The reciprocal space map for the flat surface shows a very sharp spot centered exactly at (2 1), as expected. In sharp contrast, the HK map of the bombarded surface shows a rather diminished (2 1) spot and an additional very broad reflection around (2.2 1), rather displaced from the position of the (2 1) reflection of the pristine crystal, and in a non-integer value of H.

The exploration of the reciprocal space carried out during the beamtime is quite limited, due to time constraints. A broader exploration, exploring a larger number of reflections, is necessary. However, the emergence of the additional reflection in the HK scans strongly suggests that a new structure is present at the modified surface. All the present data strongly the performance of additional experiments, specially focusing on the exploration of the reciprocal space to obtain broader information of the type displayed in Figure 3.

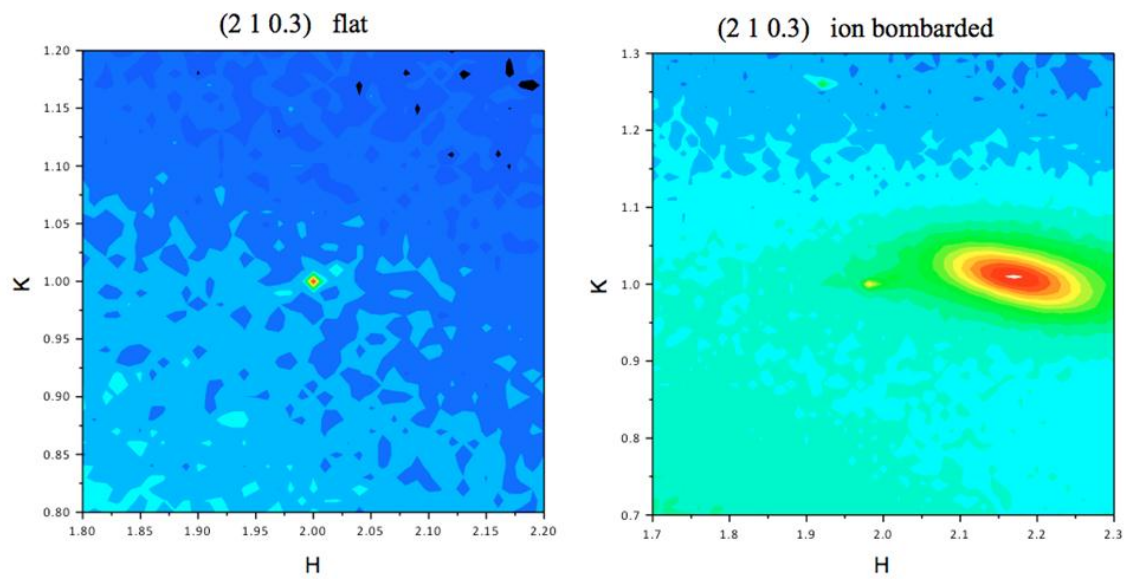


Figure 3: Reciprocal space HK maps around the (2, 1, 0.3) reflection of the rutile $\text{TiO}_2(110)$ before (left) and after (right) ion bombardment. The reflection is very sharp in the flat surface (left) and, most interestingly, a new reflection appears for the defective one (right). This new reflection, very broad and diffuse, is rather displaced from the (2,1) condition and strongly suggests the existence of a new defective crystalline structure or orientation.