Local structures and processes on surfaces studied by scanning tunnelling microscopy

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Abstract. The applicability and power of scanning tunnelling microscopy studies on the mechanism of various surface processes, ranging from surface diffusion/ordering via structural transformations to corrosive reactions with the surface, and on the nature and distribution of surface defects is demonstrated on the basis of several case studies. These studies underline the importance of local probes for the mechanistic understanding of surface processes.

Most surface processes proceed on a very local scale and local structures play an important role. These processes include physical ones such as surface diffusion or ordering, as well as a variety of 'chemical' surface reactions which transform the surface phase. Adsorbate-induced structural transformations, decomposition reactions, surface oxidation and corrosion belong to the latter category. Well-prepared single-crystalline surfaces are dominated by the periodic lattice structure. Often, however, structural defects act as active centres for many surface processes and, on the other hand, these processes often result in local deviations in the formerly periodic structure, i.e. in new surface defects. Therefore the structural characterization of these defect structures is important for the mechanistic understanding of the respective processes. In addition, the shape, distribution and correlation of surface defects also contain information on the stability of different structural elements and hence on the energetics of the surface itself. In all of these cases local information is crucial. This is demonstrated in the present paper on the basis of different scanning tunnelling microscopy (STM) case studies which have been performed in our laboratory. It also serves to demonstrate the information that can be derived from STM studies in these areas. This paper is intended to give a brief overview; complete reports of these studies including pertinent references were published recently [1–8]. In the subsequent section results relating to the defect structure of a clean reconstructed metal surface are discussed. This is followed by studies on different surface processes, including surface diffusion, ordering, structural transformations and surface corrosion. More examples are found in recent reviews on STM investigations into the structure of metal surfaces and on the interaction of metal surfaces with various adsorbates [9–11].

We have investigated in detail the nature, density and distribution of surface defects on the (1×2) missing-row reconstructed surfaces of Pt(110) and Au(110) [1]. As mentioned before, correlations between different types of defects may also exist and

on these reconstructed surfaces certain defects may be stabilized by the presence of the reconstruction. We found these surfaces to exhibit large domains of perfect (1×2) structure, separated by monatomic steps or by individual (1×3) structural units with a $[1\bar{1}0]$ string of atoms also missing in the second layer. Steps along $[1\bar{1}0]$ have a very low kink density and can proceed linearly over many hundred angstroms. This was associated with the formation of very stable (111) microfacets. Steps with an over-all orientation along [001], in contrast, are highly kinked, indicative of a rather low stability of the (100) microfacets exposed along these steps. It was also shown that higher order (1×3), (1×5) or (1×7) reconstructions, which are frequently observed on surfaces in the presence of trace impurities, result from ordered sequences of (1×2) and (1×3) structural units. These data gave a coherent picture of a class of surface reconstructions which had been under debate for a long time.

Surface diffusion involves different atomic processes all of which contribute to the macroscopically measurable diffusion constant. Hence it is difficult and usually impossible to differentiate between these processes in macroscopic diffusion measurements. However, direct observation by STM allows access to some of these individual processes. Only a few examples of STM measurements on surface diffusion exist so far [9, 11, 12]. One involves the coverage-dependent mobility within O adlayers on Ru(0001) [2]. STM images demonstrate that at very low coverages individual adatoms are quite mobile, on a timescale of seconds, at room temperature. Adatoms are still resolved in the images, but change their position from image to image and often between subsequent scan lines. Small clusters of $p(2 \times 2)$ structure, which represents the ordered adlayer phase at higher coverages, are continuously formed and dissolved. At coverages $\theta > 0.13$, islands of $p(2 \times 2)$ were found to co-exist with a dilute two-dimensional (2D) gas phase, which at coverages > 0.20 cover the entire surface. The perimeters of these islands also undergo continuous changes by 2D evaporation of adatoms into the 2D gas phase and by condensation of adatoms from that phase. The islands themselves exhibit advacancies which can equally migrate over the surface. Their mobility, however, is much lower and site changes occur only every 50 to 100 s on average. Making use of the Einstein relation a diffusion coefficient of about 10^{-17} cm^2 s^{-1} was derived [2].

The formation of ordered surface phases is mostly followed by diffraction techniques. Nevertheless, STM observations can provide useful information, in particular at the very early stages of ordering which are hardly accessible by the above techniques because of the low intensities. Quantitative evaluation of the adatom distribution and of the structure and size of ordered clusters allow conclusions on the interactions between adatoms to be drawn. This was demonstrated recently for O/Ni(100) where two ordered adlayer phases, a $p(2 \times 2)$ and a $c(2 \times 2)$, with ideal coverages of $\theta = 0.25$ and $\theta = 0.5$ are formed. In addition to repulsive interactions between adatoms on nearest and next-nearest neighbour sites, attractive interactions to third-nearest neighbour sites could also be derived from this work [3].

Structural transformations of metal substrates where, upon interaction with an adsorbate, the substrate transforms from one phase into another, are often related to a change in the density of surface substrate atoms. Hence they require substantial mass transport. Since in many cases they have been observed at temperatures where surface self-diffusion was determined to be negligible, their mechanism has long been a matter of debate. In a number of transformations this question could be resolved in recent STM investigations, which in several cases have also led to new mechanistic concepts. In fact very different reaction paths were found for apparently similar processes such as

the formation/removal of the missing-row reconstruction on various FCC(110) surfaces [4–6, 13–15]. For the CO-induced $(1 \times 2) \rightarrow (1 \times 1)$ transformation on Pt(110), it was shown that at room temperature this proceeds on a very local scale, where substrate atoms have to move only by a few sites and form local (1×1) patches on two adjoining terrace levels [4]. The formation of the 'missing-row' reconstructed (2×1) phase on Cu(110) was shown to actually follow an 'added-row' mechanism, where O and Cu adatoms condense in –O–Cu–O–Cu–O– strings [5, 13]. These grow on the surface from a dilute adlayer, i.e. this reaction represents a two-dimensional analogy to the precipitation of a solid from a dilute fluid phase [5]. Continuous 2D desorption from and condensation at step edges lead to a (very low) equilibrium concentration of Cu adatoms on the flat terraces, in good agreement with the observed high mobility of these step edges [14, 15]. Finally, the alkali-induced (1×3) and (1×2) reconstructions of Cu(110) were found to involve local exchange processes, where individual K atoms replace short strings of the 2–3 topmost layer metal atoms, thereby creating a local missing-row reconstruction [6]. The Cu atoms then migrate over the flat terraces until they are condensed at step edges.

Chemical reactions between substrate and adsorbate, which include a variety of oxidation and corrosion processes, were investigated in similar ways to provide insight into their mechanism. This was demonstrated in a study on the wet chemical etching of Si(111) surfaces by NH_4F-buffered HF solutions [7, 8]. Pronounced effects of the acidity of the etching solution were found. After etching in neutral or slightly alkaline solutions large, atomically flat terraces and rather few steps with preferential orientation along [1$\bar{1}$0] were observed, indicative of a strongly anisotropic etch process. These flat terraces consist of an unreconstructed (1×1) surface, where the dangling bonds of the Si surface atoms are terminated by hydrogen atoms. Their formation was explained in a very simple mechanistic model in which the etching rate is highest for (trihydride-terminated) Si adatoms, smaller for (dihydride-terminated) Si atoms at step edges and lowest for (monohydride-terminated) Si atoms on flat terraces or at [1$\bar{1}$0] steps with (111) microfacets exposed. In more acidic solutions, the etch rates become increasingly lower and in pure HF solutions, at pH = 1, the Si surface is basically inert against etching. It was shown that under these conditions only the oxide cover layer is removed and the former Si/SiO_2 interface is exposed as the new surface. Despite of the overall very flat topography of these wafers, this interface is relatively rough on an atomic scale.

In conclusion it was demonstrated for various different surface processes, ranging from surface diffusion/ordering via structural transformations to corrosive reactions with the surface, that STM observations can give an atomic scale picture of these processes, revealing details of the reaction mechanism. The local information gained by STM, in combination with data from integrating techniques for surface characterization, opens up new possibilities for the mechanistic understanding of surface processes.

Acknowledgments

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