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STM imaging of electrically floating islands

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Abstract

Appearances and disappearances of Gd islands grown on top of a W(1 1 0) substrate were observed in time scales of hours after exposing the surface to a few Langmuirs of hydrogen. The phenomenon is presented and explained in terms of (temporary) creation of electrically floating islands, due to electrical decoupling of the island and substrate by the hydrogen that diffuses into the island/substrate interface. The disappearance of such an island is explained by forming a double barrier junction consisting of two tunneling barriers in series, causing, by charging, the potential of the island to become equal to that of the tip. The island then becomes "invisible" and the tip follows the corrugation of the surface under the substrate. The reappearance follows hydrogen mobility that retains the electrical conductivity of the island–substrate interface.

Keywords: Scanning tunneling microscopy; Interface dipole; Surface electronic phenomena; Lanthanides; Hydrogen; Hydrides

1. Introduction

The invention of the scanning tunneling microscope (STM) initiated a revolution in the field of nanoscience and nanotechnology. The STM is also an ultimate tool for surface science, since it is capable of imaging surfaces of a wide variety of conducting surfaces (metal and semiconductor alike) with atomic resolution. The atomically resolved information which is available from STM measurements is very broad – examples are studies of the electronic structure of surfaces, magnetic structure, elastic deformation of surfaces, studies of molecular and atomic adsorbates and vibrational spectra using inelastic tunneling spectrum of a single molecule.

Unlike other surface science techniques, STM is traditionally considered as a genuine surface science technique, namely, it is sensitive only to the upper layer of atoms. This is due to the rapid decay of the electronic wave function, which means that the layers underneath the surface gives a negligible contribution to the local density of states (LDOS) imaged by the STM.

Nevertheless, it was soon realized that this simplified picture cannot explain many experimental observations that clearly point to the ability of the STM to image subsurface layers. The main reason for this ability is the fact that the three dimensional barrier formed between the tip and the sample is a very strong directional filter. Namely, that the tunneling probability reduces rapidly if the tunneling electrons propagate in nonorthogonal (to the surface) directions. Therefore, the tunneling current filament which has a width of atomic scale on the surface, remains highly focused also in a depth of several nanometers (and in some cases tens of nanometers) in the sample.

The most well known example of using this property of the tunneling electrons is ballistic electron emission microscopy BEEM [1]. In BEEM, the subsurface Schottky barrier formed when a metal thin film is deposited on a semiconductor surface is examined. This constitutes a three

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terminal devise: The tunneling tip, the metal base and the semiconductor collector. The base collector current is measured separately. Electrons that enter into the base propagate ballistically until they arrive to the collector. Once the tip sample bias voltage exceeds the internal Schottky barrier height, the base–collector current increases significantly. Thus the BEEM can follow both the spatial variation of the subsurface Schottky barrier, as well as its electronic structure. BEEM is now an established technique and a complete review is beyond the scope of this paper.

However, subsurface information was revealed also in regular STM experiments. A famous example is the subsurface restatoms seen in the images of the Si(1 1 1) 7×7 surface [2] at the relevant bias voltage. Another example is the imaging of subsurface lattice mismatch dislocations in an alloy surface [3], Imaging of subsurface Cu islands under a Pb(1 1 1) surface [4], Ir atoms and chains buried below noble-metal surfaces [5], or palladium surfaces [6], the observation of subsurface diffusion [7] and subsurface buried noble gas bubbles [8].

2. The model

In this paper, we discuss another form of subsurface imaging, in which a metallic island is separated by a thin insulating barrier from the substrate. This is an electrically floating island. As will be shown here, the description of such a system is in terms of a double barrier junction consisting of two tunneling barriers in series. One of the junctions is between the tip and the island and the second junction is between the island and the substrate through the insulating barrier.

Systems of double barrier junction were intensively studied with STM, in particular at low temperatures for studying phenomena which are connected to the small capacitance of isolated islands. Such islands are formed by deposition on a substrate, with an insulating thin film between them. Examples for such phenomena are Coulomb blockade and staircase [9,10]. According to the theoretical analysis [11], two such tunneling junctions form a voltage divider according to:

$$V_1 = V[C_2/(C_1 + C_2)] - Ne/(C_1 + C_2) - V_p \quad \text{and}$$
$$V_2 = V[C_1/(C_1 + C_2)] + Ne/(C_1 + C_2) + V_p \qquad (1)$$

where V is the total voltage on the two junctions, C_1 and C_2 are the capacitance of the first (tip–island) and second (island–substrate) tunneling junctions, respectively. N is the number of excess electrons in the island, e is the electron charge and V_p is a voltage due to Fermi level misalignment. Thus the voltage on the junctions is divided to two voltages, V_1 and V_2 on the first and the second junctions, respectively.

As shown in Fig. 1, since the capacitance of the first junction is smaller, in the voltage divider that is formed,

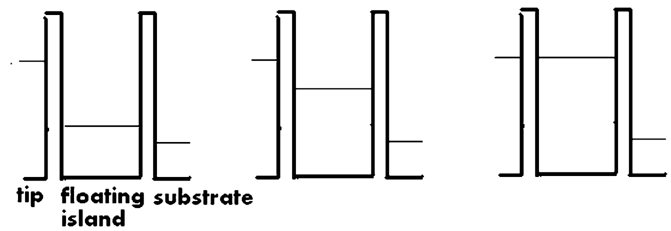

Fig. 1. Level scheme of the electrically floating islands, before charging (left); In the middle of the process of charging (middle); The charging process was progressed to a level that the island is invisible to STM imaging. The surface underneath is imaged.

the voltage drop across the first junction will be larger. Our experiments were done with positive sample bias. Thus as the tunneling proceeds the potential of the negatively charged island increases till it is equal to the Fermi level of the tip (Fig. 1 left and right). If the insulating layer is without leaks, the island will charge as a result of injection of electrons from the STM tip, until the accumulated negative charge will totally inhibit the successful STM operation. In the other extreme case if there are sufficient leaks in the insulating barriers, the charge will be sufficiently dissipated and the island will appear as usual. Some of the islands are in the situation in between, whereby there is charge dissipation, but it is insufficient. As a result, the floating island will be sufficient amount of time at the Fermi level of the tip. Consequently, the island will be at zero bias and the measured tunneling current will be from the second junction only. In this case the STM will follow the corrugations of the interface between the island and the substrate underneath, in the same way (perhaps with a bit worse resolution) as usual scanning of the upper surface. The island then will become "invisible", unless the insulating layer will be unstable and convert into a conducting layer. For such a periodically insulating–conducting underlayer, the island will appear and disappear in consequent STM images following the changes in the interface layer.

3. Experimental and discussion

In our experiments we have studied different Gd islands on top of W(1 1 0), exposed to different amounts of H_2. The experiment was performed in a UHV system (base pressure: 5×10^{-10} mbar). Gadolinium was epitaxially grown on a clean W(1 1 0) substrate: 14 ML of Gd were deposited on the substrate at room temperature using an electron gun. Afterwards, the sample was annealed by either an AC current (40 A) or similar DC currents to a temperature of 650 °C. In all the steps of this process the sample was characterized by AES to verify that the sample was clean before the deposition and to characterize quantitatively the deposition process. About 0.5% of oxygen and a similar amount of carbon are present. After annealing the oxygen (and carbon) amount increases to ~6%. Finally, using an in situ STM, the surface of the sample was imaged in constant current mode. It was observed that after annealing, 0.01–1 μm islands were formed with heights in the range of 18–50 ML.

It should be emphasized that before exposure to hydrogen, consecutive STM images taken during periods of a few hours displayed the same island patterns with no noticeable time dependent changes.

Hydrogen exposures were performed on the islands covered surfaces by exposing these surfaces to a given dose of H_2 (under H_2 pressure of 8.3×10^{-9} mbar). Then pumping the hydrogen until the base pressure was attained and taking series of consecutive STM images to follow possible dynamic structural changes induced by the hydrogen exposure.

Fig. 2 displays 10 consecutive STM images of a W(110) surface covered by some Gd islands, which underwent an 1.5 L exposure to H_2. STM images were performed with a bias voltage of 0.8 V and a current of 1.5 nA. In the center of the figure a large and a very clear island of a scale of more than 0.5 μm is clearly seen. The time elapsed between consecutive STM images, was roughly 30 min. The island consists of ∼14 ML of Gd with H_2 dissolved inside (α phase). On top of the island there are much smaller islands that are Gd hydride in the β phase (presumably GdH_2). In

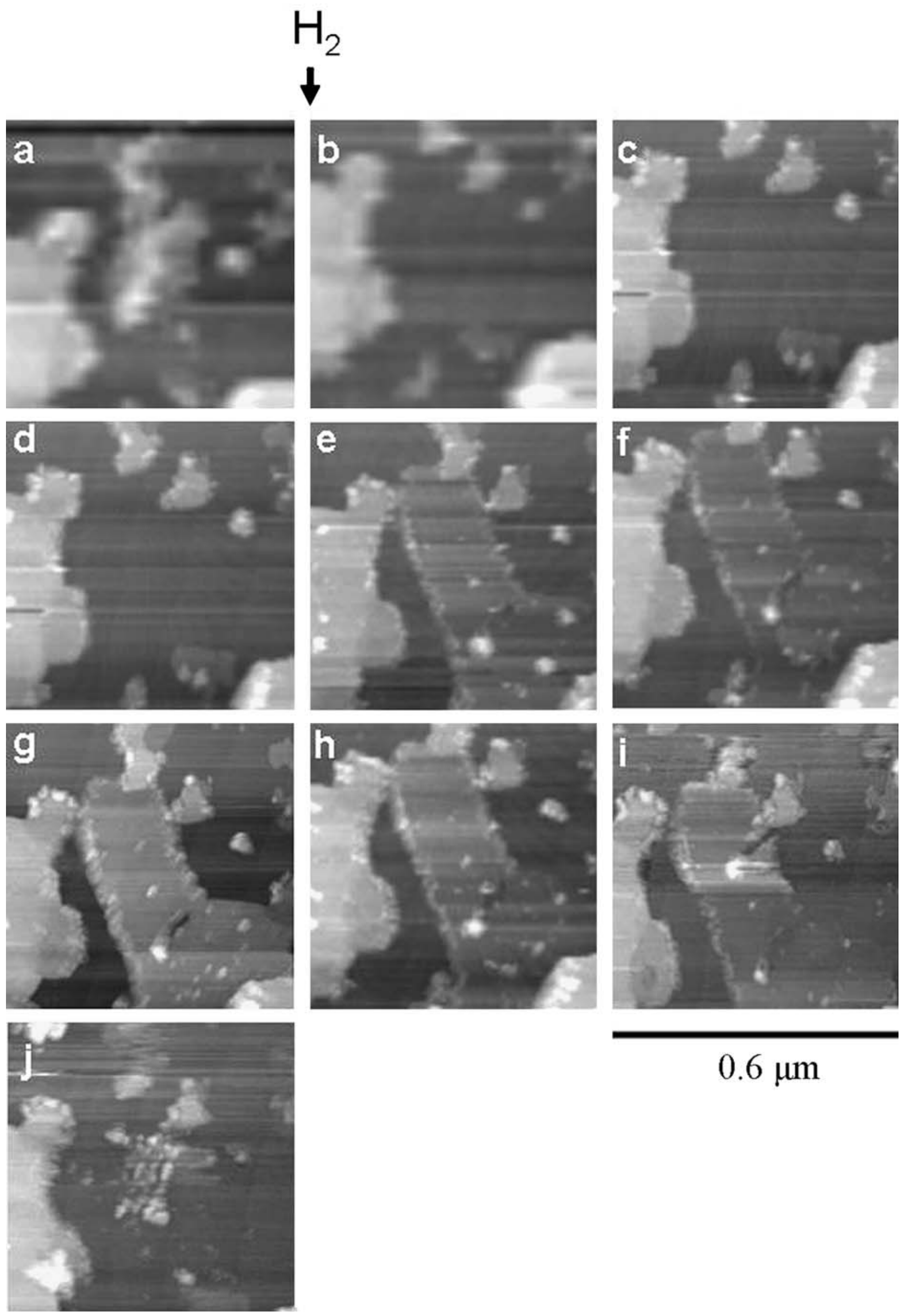

Fig. 2. Ten consecutive STM images, of W(110) covered with Gd after exposure to hydrogen. The time between consecutive images is about 30 min. The height of the appearing/disappearing island is about 6 nm.

some of the later images, it is possible to see that this island is fading, it appears lower and parts of it become invisible. For the sequence of appearance (e–g) and disappearance (h–j), the island's boundary looks exactly the same, hence we conclude that there was no diffusion of Gd away from the island, but the island became partially transparent to the STM imaging process. In some of the images, this process is completed and the island had vanished completely. Instead we see several residual much smaller amorphous islands that are probably GdH_2 that were contained in the large Gd island. The hydride was probably produced by the hydrogen accumulated in the island substrate interface, as will be discussed later.

It is evident that the "disappearance" of the island is not real, but it is attributed to the STM imaging process, when the interface between the Gd and the W(1 1 0) is being imaged. The island which was seen in the previous images although it is completely transparent is still there, as can be seen from the deterioration of the image quality in the region where this island exists. The island appears and disappears periodically. This behavior is observed in other experiments too. A more detailed analysis of hydrogen dynamics on the surface, governing the appearance–disappearance effect and the formation of hydride islands, will be presented in a separate publication.

The view that these appearance–disappearance phenomena are caused by charging effects is supported also by the bias voltage dependence of the images. Fig. 3 presents four consecutive STM images which were taken with intervals of half an hour between them. The surface was prepared by deposition of 2.4 ML of Gd on W(1 1 0) Annealing at 650 °C and exposure to 1.06 L of H_2. The images were taken at different tunneling conditions. Going from the top down, the tunneling conditions are 0.8 V, 1.4 nA, 0.8 V, 1.4 nA, 2.7 V, 0.5 nA and −0.3 V, 0.3 nA, respectively. It is easy to see, that although the third image was taken at smaller currents (namely the tip is a bit further from the surface) still, since the image was taken at a bias of 2.7 V it is possible to see two circular islands in this image, which are not (or hardly) visible in the other images of the same area. Again, this behavior is seen in other islands. This is consistent with the explanation of the electrically floating islands. The island is invisible at 0.8 V when its potential is the same as the tip. It becomes visible when the tip voltage increases to 2.7 V.

The problem of a thin metal film (turning into islands) grown on a substrate on which a gas layer exists were investigated quite intensively for the specific case of W(1 1 0) and hydrogen [12–15]. These and other studies from the same group have shown that even very thin layers of O, N and H chemisorbed on W(1 1 0) are very effective in decoupling the deposited metal film from the substrate. In addition, these works showed very clearly that upon adsorption of H_2 on top of a thin metal film deposited on W(1 1 0) a substantial amount of H_2 reaches the interface between the metal layer and the substrate.

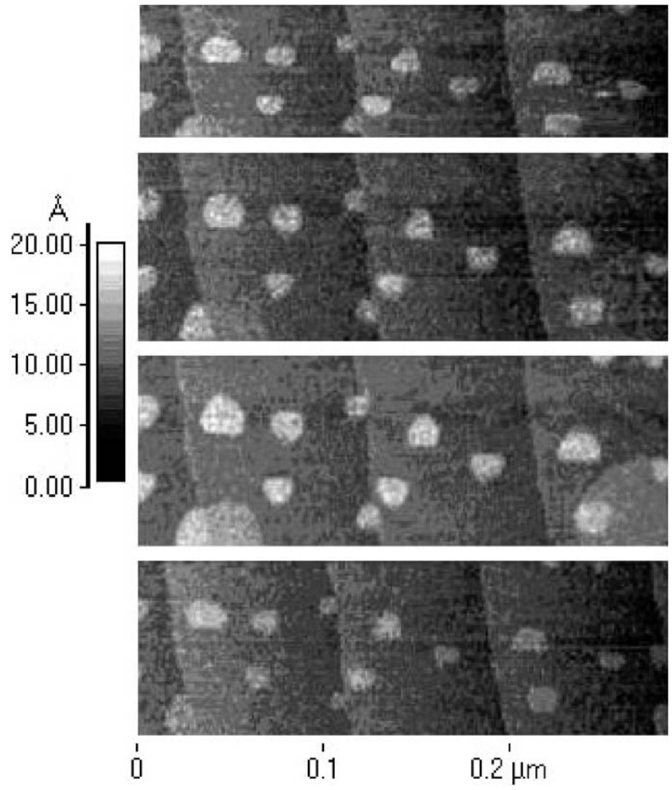

Fig. 3. Four consecutive STM images of the same area in different tip–sample bias voltage and different tunneling currents as described in the text. They show that an island invisible at low voltage become visible at higher ones.

In our STM experiments we observe islands that initially are invisible but appear following an H_2 exposure and then gradually disappear. Two alternative explanations are suggested: (1) The island may reside on an oxide film that was there when the Gd was evaporated on the W(1 1 0) (as shown by AES), making the island invisible in the first place, and then it is reduced by the hydrogen atoms reaching the Gd/W interface [16], causing the reduced oxide to be more conductive, thus the island appears. Mobility of the hydrogen, leaving the interface, may cause a reverse in the conductivity and disappearance again; (2) disappearance can be caused also by the interface of hydrogen atoms that reached the Gd/W interface after exposure [12–15]. By itself, this hydrogen layer is probably not enough of a dielectric layer to make the island electrically floating. However, if this layer is capable of trapping electrons, then a drastic increase of N (Eq. (1)) may cause the charging that will make the island float electrically and it should gradually disappear. Again, reappearance will be due to hydrogen mobility.

Such a dynamics in a double barrier junction is expected to lead to strong Coulomb blockade in a scanning tunneling spectroscopy spectrum. Probably it will be detectable also in room temperature, and we plan such measurements. In this paper, however, we focus on the subsurface STM imaging.

Although it is possible to see some deterioration of the STM resolution in the region where the island is, it is somewhat surprising that islands several nanometers thick can be present without spoiling the STM tip. Although the exact value of the tip–sample distance is debatable, still it is clear that it is less than the thickness of the "invisible" island. Initially we have observed some scans for which crushing into the surface was evident. It is suggested that in one or two such crushes into "invisible" islands, surface material (probably Gd) was collected on the end of the tip, forming flexible whiskers that in the scans following this encounters, enable such measurements of several nm high islands without a significant damage caused to either the island or the tip. Examples of the existence of such flexible tips are well known in the literature [17–19].

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