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STM investigation of the island growth of gold on WS_2 and WSe_2

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Abstract

We have investigated the island growth of Au on the van der Waals surfaces of WS_2 and WSe_2 by STM. We show how the STM can be used to image as well as to manipulate nm-sized crystallites on these atomically smooth non-reactive substrates. The islands on the van der Waals planes are triangular in shape and are well aligned with the substrate lattice. Statistical analysis of our data yield subtle differences in the growth of Au on WS_2 compared to WSe_2.

Keywords: Chalcogenides; Clusters; Gold; Growth; Scanning tunneling microscopy; Sulphides; Surface morphology

1. Introduction

STM investigations of clusters and small islands on atomically smooth non-reactive substrates have received increasing attention over the past several years [1–5]. STM allows for directly mapping physical properties on an atomic scale, and therefore it is well suited to the investigation of single clusters, grown or deposited on a surface. Quite often, however, these investigations are rendered impossible because the islands are displaced by the tip [5–7]. In this context, we have studied the growth of gold on the van der Waals surfaces of the layered semiconductors WSe_2 and WS_2, which provide ideal chemically passive semiconductor surfaces. Evaporation of submonolayer amounts of gold on to cleaved surfaces leads to the formation of nm-sized gold islands. We find that, depending on the tip configuration and tunneling parameters, the STM can be used to image as well as to manipulate the islands on these weakly interacting substrates. The analysis of our data yields information about the growth on the van der Waals surfaces as well as on crystal defects such as cleavage steps.

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2. Experimental

For the investigations to be described, we used p-type WSe_2 and WS_2 single crystals with typical doping densities of $10^{17}\,cm^{-3}$, which were produced by chemical vapor phase transport. Fresh surfaces were prepared by cleaving in UHV, which produces atomically flat areas of several μm^2. Occasionally, defects such as monolayer steps can be observed.

After cleavage, Au was evaporated from a resistively heated tungsten boat with rates of

0.05–0.5 Å s^{-1} to obtain a mean coverage of 0.5–5 Å. During evaporation, the substrate temperature (300–580 K) was kept constant. Then, the samples were transferred to the STM (home-built variable temperature STM [8]) under UHV conditions. We used electrochemically etched W tips, additionally cleaned and sharpened by field emission prior to the measurements.

3. Results and discussion

In preliminary experiments, which were performed under ambient conditions as well as in a high vacuum, we found that it was very difficult and often impossible to obtain images of Au islands on these weakly interacting surfaces. The islands were manipulated by the tip and pushed out of the imaging area during prolonged scanning. This is consistent with observations of several other groups, which tried to image small metal clusters and islands on HOPG or MoS_2 [5–7]. Only occasionally were we able to obtain stable images for very high tunneling resistances (20–100 GΩ, depending on tip configuration). We ascribe this observation to contamination of the tip or sample, which can lead to remarkable forces in scanning tunneling microscopy. For instance, force effects can result in unnaturally high atomic corrugations measured on graphite and other layered structure materials [9] and are also presumed to be responsible for the low barrier heights usually measured with STM under ambient conditions [9,10].

Due to these experimental difficulties, all subsequent studies have been performed in UHV. Great care was taken to obtain clean and sharp tunneling tips. After cleaning the tip via field emission on a tantalum counter electrode, the distance characteristic of the tunneling current was measured until a typical barrier height of several eV was obtained. Usually, the Au islands could then be imaged on in-situ prepared samples, but occasionally, single Au islands were manipulated by the tunneling tip. Fig. 1a and b display two STM images of Au islands on WS_2 (1 Å mean coverage), taken at the same area of the sample. In Fig. 1a, two triangular Au islands are imaged undisturbed, whereas a

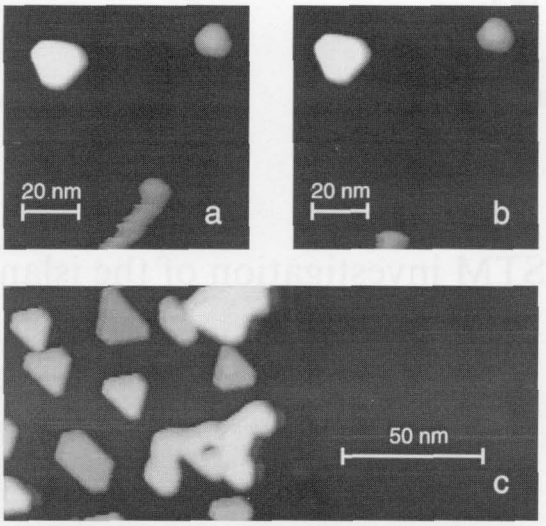

Fig. 1. Gray-scale STM images (4-nm height difference, black to white) of (a),(b) Au islands on WS_2. $I_t = 1$ nA, $U_{sample} = 1$ V. (c) Au on WSe_2. $I_t = 150$ pA, $U_{sample} = 1.4$ V. The right half of the image area was scanned with a lower tunneling resistance ($I_t = 2$ nA, $U_{sample} = 1$ V) prior to measurement.

third one is manipulated by the tip. The island is pulled by the tunneling tip and repeatedly imaged, leading to the observed stripe in the STM image. In Fig. 1b, which was taken immediately after Fig. 1a, the manipulated island can be observed at the bottom of the scanning area. Apparently, there is an attractive interaction between the tunneling tip and the gold island, which leads to the observed phenomenon. Similar observations were recently reported by Li et al., who investigated the tip-induced diffusion of single Ag atoms on Ag(110) at low temperature [11].

To gain further insight into this behavior, we systematically varied the tunneling parameters. The tunneling current and sample voltage were varied from 50 pA to 10 nA and from 0.8 V to 2 V. Due to the diode type I–V characteristic, tunneling is only possible for voltages higher than about +0.7 V on p-type samples. We found a systematic variation of the manipulation probability with the tunneling resistance, irrespective of whether the voltage or current was varied. Typically, stable imaging is possible for $R_t > 5$ GΩ, whereas small tunneling resistances ($R_t < 500$ MΩ) lead to the manipulation of nearly

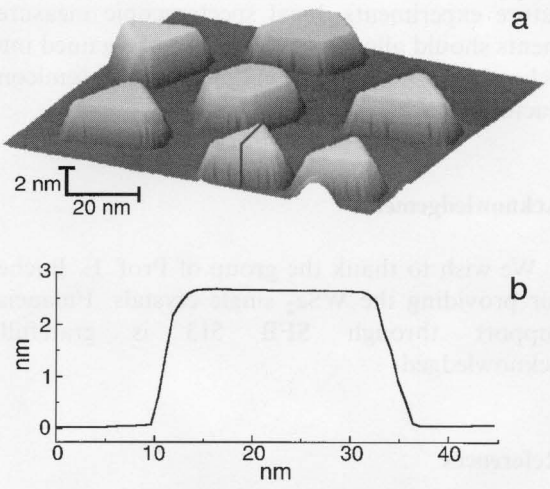

Fig. 2. (a) STM image of Au islands on WSe_2 (3-D representation). (b) Line profile of an Au-island as indicated in (a).

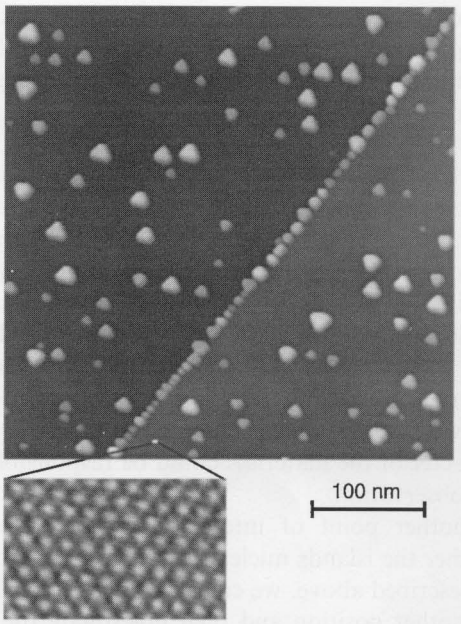

Fig. 3. Gray-scale STM image obtained on WS_2 for an Au coverage of 1 Å (4.5-nm height difference) and atomically resolved sulfur lattice.

all islands. However, tip changes can dramatically change the parameters given above for imaging and manipulation. The manipulation probability does not vary with the applied voltage as long as the tip–sample distance is kept constant. Therefore, we can exclude field migration of Au, which is often discussed in terms of nanostructuring with the STM on Au surfaces [12]. Since the tip–sample distance is the criterion for stable imaging or manipulation under UHV conditions, we suppose that attractive forces between the metallic tunneling tip and the islands are the dominant process [13]. However, under non-UHV conditions, as well as with contaminated tips, we also observe repulsive forces, which we attribute to a tip-induced deformation of the substrate [9].

Fig. 1c shows Au islands on WSe_2 (3.5 Å mean coverage). The right part of the image was swept clean by repeatedly scanning with a low tunneling resistance (500 MΩ). It can be seen that a coagulation process takes place when islands are pushed together by the tip.

Fig. 2a displays a 3-D representation of several Au islands on WSe_2. Individual crystal facets as the (111)-plane on top of the islands are clearly resolved. Fig. 2b represents a typical line profile of an Au-island. The island is about 25 nm in diameter and 3 nm in height. As can be seen, the radius of the tunneling tip has to be extraordinarily small in order to obtain such an excellent lateral resolution. Comparable sharp tips can be obtained reproducably via field emission. Therefore, STM can be used to obtain information on the growth and equilibrium shape of crystals as well as deformation of deposited clusters.

To learn more about the growth, several samples were prepared, varying the growth parameters over the range mentioned in the experimental section. Fig. 3 shows a typical STM image obtained on WS_2 for an Au coverage of 1 Å (evaporation rate, 0.1 Å s^{-1}; substrate temperature, 250°C). A monolayer step – 6.2 Å in height – crosses the image and is decorated by individual gold islands. The islands grown on the van der Waals planes are all triangular and well aligned with the substrate lattice (inset of Fig. 3). Furthermore, the crystallites point in two opposite directions. This phenomenon is known as double positioning and is typical for the growth of fcc metals on hexagonal substrates [14]. The 2H-molybdenite structure of WS_2, however, is not hexagonal but trigonal. This asymmetry is brought in by the atomic plane of W which is shifted against the sulfur layers.

Therefore, the two different directions should not be equivalent [15], and indeed, we always find that one direction is observed more often for a given van der Waals plane. From the analysis of more than 1000 islands, we find a ratio of 1.6 ± 0.2 for WS_2 and 2.9 ± 0.3 for WSe_2, independent of the growth parameters. The size distribution of the crystallites is quite inhomogeneous on WS_2 as can be seen from Fig. 3, whereas a much sharper distribution is found for WSe_2. As in the case of the double positioning, there is a significant difference in the growth of Au on these very similar materials. Subtle differences in lattice mismatch of the two systems under study or the different ionic character of the materials could be responsible for this observation.

Another point of interest is the question of whether the islands nucleate at surface defects. As we described above, we can pull individual islands to another position and then investigate the substrate lattice at the former position of the island. The atomic lattice was always found to be undisturbed and defect-free on an atomic scale. Therefore, we can conclude that the nucleation on the van der Waals planes is not significantly influenced by surface defects.

A detailed study of the nucleation and growth of gold on these van der Waals surfaces will be presented in a forthcoming publication.

4. Conclusions

In summary, we have shown how to image and to manipulate nm-sized gold islands on the layered structure semiconductors WSe_2 and WS_2. Our investigations reveal interesting details on the growth of Au on the van der Waals surfaces as well as at defects such as monolayer steps. In future experiments, local spectroscopic measurements should allow a new insight to be gained into Schottky barrier formation on these ideal semiconductor surfaces.

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