Use of Scanning Tunnelling Microscopy for Atomic Manipulation on Semiconductors

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BIOGRAPHY

Arie van Houselt earned MSc degrees in physics and chemistry at the University of Utrecht, The Netherlands, in 2004. Currently he is employed as a PhD researcher in the Physical Aspects of Nanoelectronics & Solid State Physics groups headed by Prof. Zandvliet and Prof. Poelsema at the University of Twente. His research project involves the preparation and characterization of quantum structures using scanning tunnelling microscopy and spectroscopy. His PhD work resulted in a number of articles that appeared in Physical Review Letters, Nanoletters, Nanotechnology, Angewandte Chemie and Physical Review B.

ABSTRACT

The scanning tunnelling microscope (STM) can be used as a tool for assembling nanostructures at the atomic level. In this article we briefly review several pathways for controlled manipulation of atoms and molecules on semiconductor surfaces at room temperature. As an illustrative example we discuss the controlled manipulation of atomic platinum chains. We were able to carry the constituting dimers of the atomic Pt chains from point to point with atomic precision at room temperature. Besides the ultimate control of the surface structure we also show that the manipulated Pt dimer can be attached to the apex of the STM tip in various stable configurations.

KEYWORDS

scanning tunnelling microscopy, atomic manipulation, semiconductors, nanotechnology, low dimensional systems, surface science

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INTRODUCTION

The introduction of the scanning tunnelling microscope (STM) in the early 1980s by Binnig and Rohrer [1] enabled the imaging of surfaces down to the atomic scale [2]. The imaging mode of the STM has now become a standard technique in almost every materials science research laboratory.

The power of STM, however, goes beyond the imaging mode. The STM has unique capabilities for local spectroscopy and manipulation experiments as well. In 1990 Eigler and Schweizer demonstrated in a breathtaking experiment the lateral manipulation of adsorbed xenon atoms on a metal surface [3]. During the last two decades many other examples of atomic manipulation on metal surfaces have been published. Most of these experiments, however, are performed at low temperatures (typically 5-20 K), and the created structures are often unstable at room temperature. The latter is a real drawback if one aims at technological applications. From a technological point of view it is required that the nanostructures are stable at room temperature. Hence it is worthwhile to study controlled atomic manipulation on semiconductor surfaces, since these surfaces are thermodynamically rather stable due to the covalent nature of their chemical bonds.

In this brief review article we focus on the manipulation of adsorbed atoms and molecules, as well as the manipulation of surface atoms on semiconductor surfaces at room temperature.

The very first reports of atomic room-temperature manipulations of surface atoms with the STM were published in the late 1980s. Becker, Golovchenko and Swartzentruber demonstrated in their pioneering work the possibility to create atomic-scale 'bits' on a Ge(111) surface [4]. To deposit the 'bit', they increased the bias between tip and sample for a short time interval. The results were explained in terms of a field ion-emission process. However, their attempts to modify the closely related Si(111) surface with biases up to 20 V failed. Lyo and Avouris [5] reported the successful manipulation of Si(111) surfaces by reducing the STM tip to surface distance to a few ångströms and subsequently increasing the sample bias with 1 V. They demonstrated the possibility to extract and deposit single atoms of a Si(111) 7×7 surface. These authors interpreted their manipulation experiments in terms of a chemically assisted field evaporation process.

A few years later, Ugida, Hang, Grey and Aono showed that the central adatoms of the Si(111) 7×7 surface are more easily 'removed' than the corner adatoms [6]. The latter is explained by a difference in the binding energy of the centre and corner adatoms. On a Si(001) surface Salling and Lagally showed the removal of segments of individual dimer rows by applying a voltage pulse at decreased
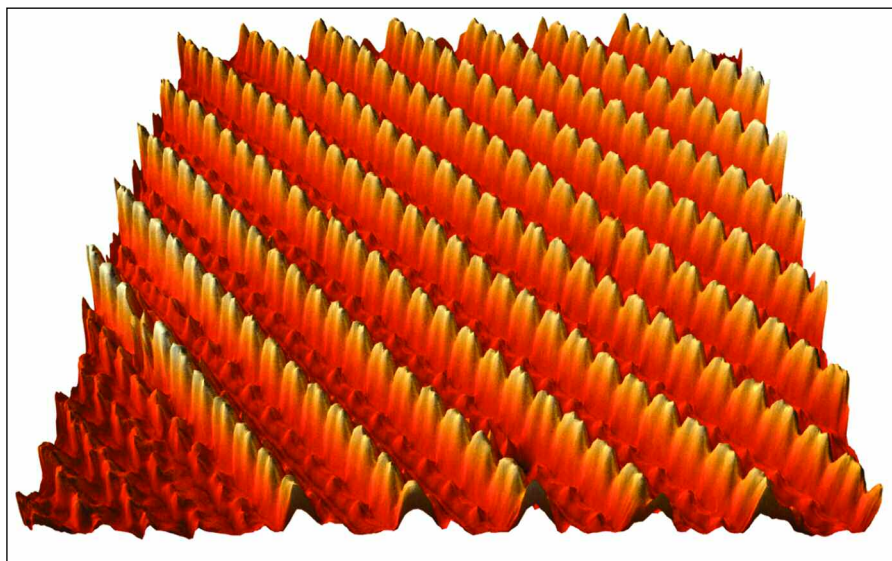

Figure 1:
Three-dimensional representation of a scanning tunnelling microscope image of a surface covered with atomic platinum chains. The image size is 15.0 x 15.0 nm², the bias voltage was -1.45 V and the tunnelling current was 0.50 nA.
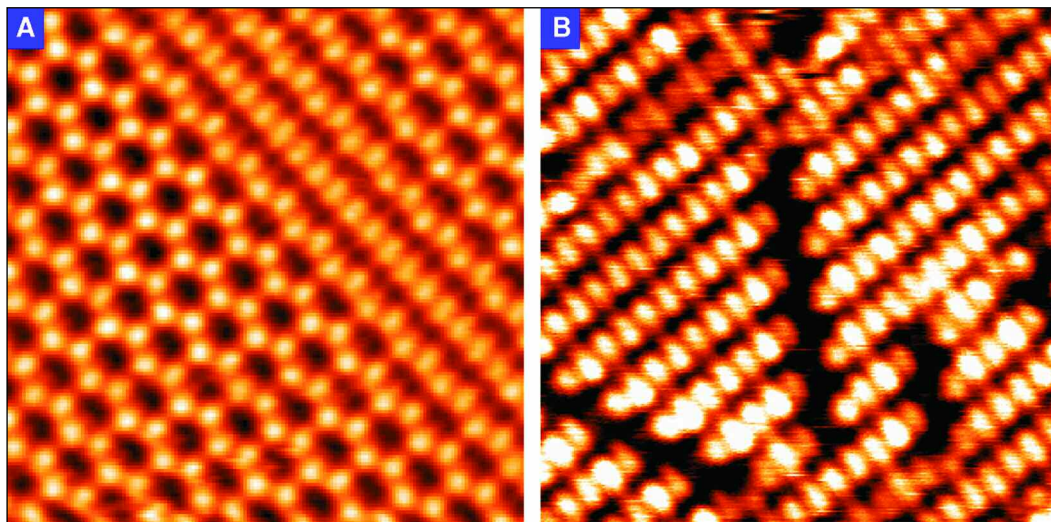
tip to sample separations [7].

The manipulation of adsorbed atoms on surfaces undoubtedly obtained the greatest boost by the manipulation experiments of individual xenon atoms on a Ni(110) surface by Eigler and Schweizer in 1990 [3]. Soon it was realized that atomic engineering of metal adatoms on semiconductor surfaces at room-temperature would, at least from a technological point of view, be very advantageous. Whitman, Stroscio, Dragoset and Celotta used field-induced diffusion to align Cs atoms into atomic zigzag structures on the (110) surfaces of GaAs and InSb [8]. Precise control over the

position of the Cs atoms was, however, not achieved in their experiments.

In this article we will discuss an example from our own laboratory, in which we selectively picked-up and subsequently deposited individual platinum atom dimers on a Pt modified Ge(001) surface [9]. In addition, we will also show that the Pt dimers can attach to the apex of the STM tip in different stable configurations. In most cases the Pt dimer attached to one of the facets of the tip apex, however, in some cases the Pt dimer adhered to the tip in a horizontal configuration. The latter configuration was easily recognized in the exper-

iment, since upon subsequent imaging it produced a double tip image.

MATERIALS AND METHODS
Experiments were performed at room temperature with a commercial available Omicron STM-1 in an ultrahigh vacuum (UHV) system.

The Ge(001) sample was prepared as described elsewhere [10]. When the sample was atomically clean, a well ordered $(2 \times 1) / c(4 \times 2)$ domain pattern developed. Subsequently Pt was deposited by resistively heating a W wire wrapped with high purity Pt (99.995%). After deposition of the Pt the sample was
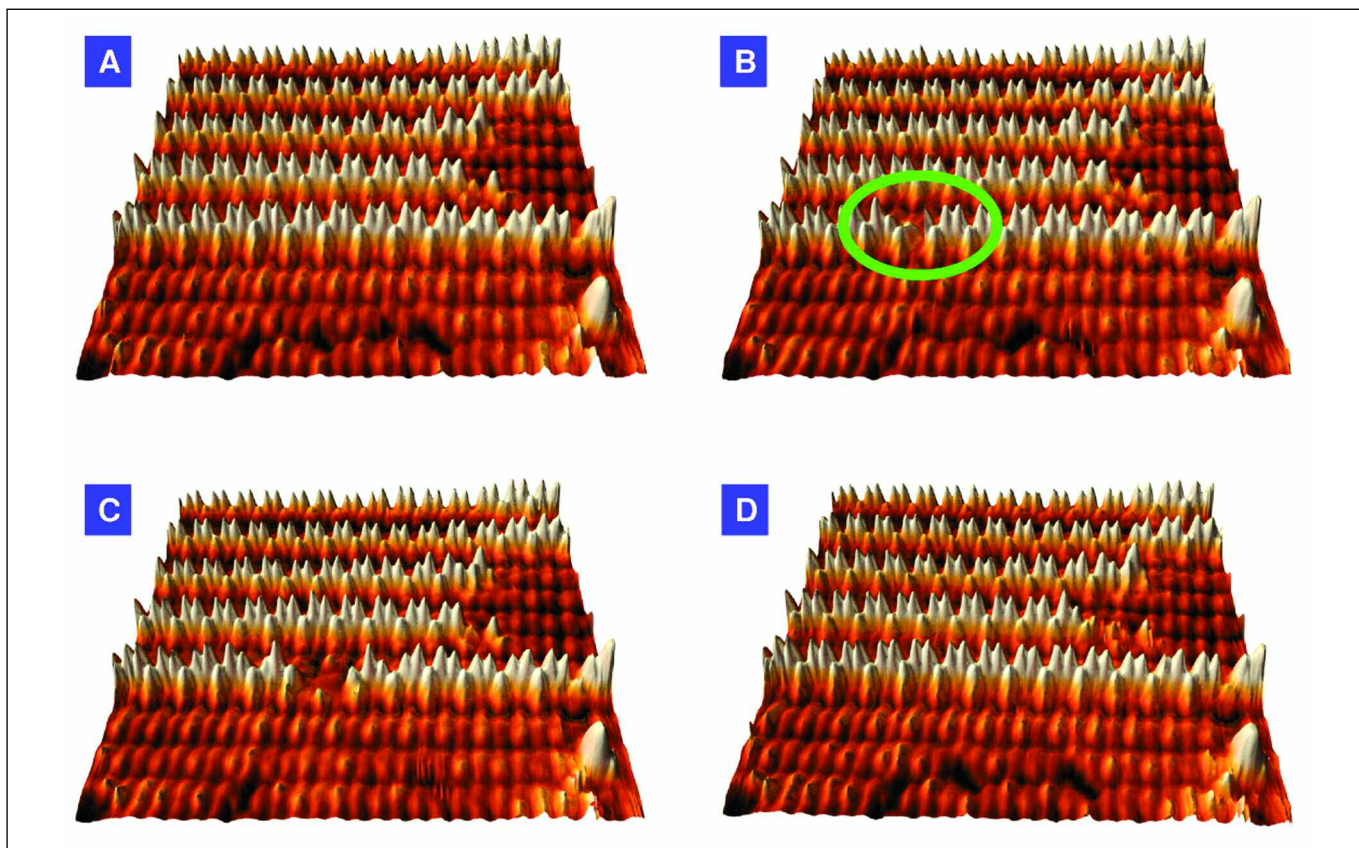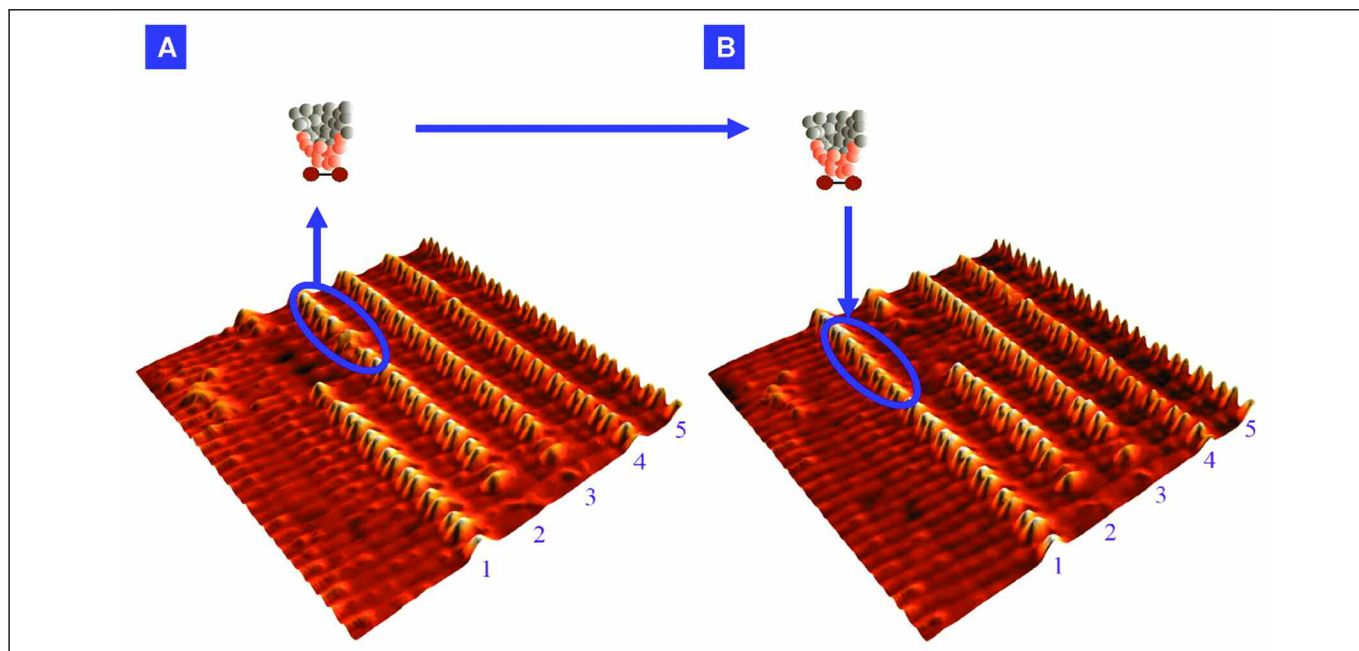
Figure 4:
An array of five atomic Pt chains (sample bias 20 mV, tunnelling current 0.4 nA). The size of the images is 10 x 10 nm². Chain 1 contains a large defect, comprising several missing dimer defects (A). This defect is repaired in (B) by picking up individual Pt dimers from chain 2 and putting them in the defect region of chain 1.

annealed at elevated temperature as described in detail in [11].

RESULTS AND DISCUSSION

After annealing at 1100 K for several minutes we observed the formation of one-dimensional, literally defect- and kink-free atomic Pt chains. These Pt chains had a cross section of only one atom and had lengths up to hundreds of nanometers [12, 13]. An example of a patch with Pt chains is shown in Figure 1. The Pt atoms within a chain dimerized. Interestingly, although the underlying terrace was dimerized and looked quite similar to a normal Ge(001) terrace, it turned out that this terrace contained a significant fraction of embedded Pt atoms [12]. The latter was confirmed by spectroscopic measurements, which revealed that the local density of states of the Pt modified terraces deviated significantly from a regular Ge(001) terrace.

In Figure 2 we show STM images of the bare Ge(001) surface (Figure 2a) and the Pt modified terrace (Figure 2b) on which the atomic Pt chains can be found. On the bare Ge(001) surfaces two types of dimer rows were noticed: (a) zigzag dimer rows, and (b) symmetric dimer rows. Detailed information about these two types of dimer rows can be found in [10]. The Pt modified surface in Figure 2b shows only symmetric dimer rows. Moreover, dimer vacancy lines running along the <130> and <-110> directions are present on this surface. This type of dimer vacancy lines has never been observed on a bare Ge(001) surface [13]. In summary, the underlying terrace of regions that contain atomic Pt chains, is clearly different from the bare Ge(001) surface.

Within the dimers of the atomic Pt chains (see Figure 1), the individual atoms were still observable. The Pt chains occurred in patches and the spacing between nearest neighbour

Pt chains was only 1.6 nm. Occasionally nearest neighbour spacings of 2.4 nm or 3.2 nm were found [11].

We will now demonstrate the manipulation of a single Pt dimer of a Pt chain. The procedure which we used for the controlled manipulation was as follows:

1. First a conventional STM image (tunnelling current 0.5 nA, sample bias -0.020 V) was recorded of the surface that contained regions with Pt chains (see Figure 3a).

2. During a second scan of the surface (same parameters, see Figure 3b) the STM tip was placed on a pre-designated point over the Pt dimer we had selected for manipulation (marked with the green ellipse in Figure 3b). At this position the tunnelling current was increased to 20 nA and the voltage was decreased to -0.002 V for ~1 ms, and subsequently set back to -0.020 V. Finally, the tunnelling current was decreased to its standard set point (0.5 nA), and the scanning process was continued. The result of the manipulation experiment is already visible in Figure 3b; the left part of the selected dimer (within the green ellipse) was not observable after the manipulation experiment (the scanning direction was from right to left in these images). Note that during the whole procedure the feedback-loop remained closed.

3. The third scan of the same area (same parameters, Figure 3c) revealed that indeed one Pt dimer was missing, exactly at the location where the manipulation experiment was performed.

During the second step the tunnelling resistance between tip and Pt-dimer was reduced to only 100 kΩ, a value for which a jump-to-contact may occur, see for example [14]. We anticipate that a chemical bond has been formed between the (most likely Pt-coated) W tip and the Pt dimer.

A repetition of the second step, at exactly the same location, revealed that it was possible to place the previously removed Pt dimer back in its original position (see Figure 3d). Obviously the Pt dimer had been picked up from the surface and it remained at the apex of the tip during the scanning process before we placed it back in its original position.

In a next experiment we moved several Pt dimers from one atomic Pt chain to another, in a one-by-one fashion. Figure 4 shows a patch of atomic Pt chains. In chain 1 of Figure 4a, several Pt dimers are missing. By subsequently picking up Pt dimers from the almost perfect chain 2, the large defect in chain 1 was repaired, at the expense of the production of a similar appearing defect in chain 2 (Figure 4b). Due to the high thermal stability of the atomic Pt chains, the manipulated chains remained stable even at room temperature. Using this procedure the length as well as the quality of the Pt chains, in terms of the amount and size of the defects, can be tailored down to the atomic scale. This enables a systematic study of the influence of defects on the physical properties of the Pt chains.

Another manipulation procedure which we successfully applied to the Pt chains was a chemically assisted field-evaporation process as proposed by Lyo and Avouris for the manipulation of Si(111) [4]. At a pre-defined location above a Pt dimer, the feedback loop was opened, the tip approached the Pt dimer (typically 3-5 Å closer than in tunnelling conditions) and a voltage pulse (-3.0 V) was applied. Subsequently the tip-sample distance was brought back to tunnelling conditions, the feedback was closed and the scanning was continued.

The differences from the earlier described method are: (a) in this case the feedback loop was open while the actual manipulation took
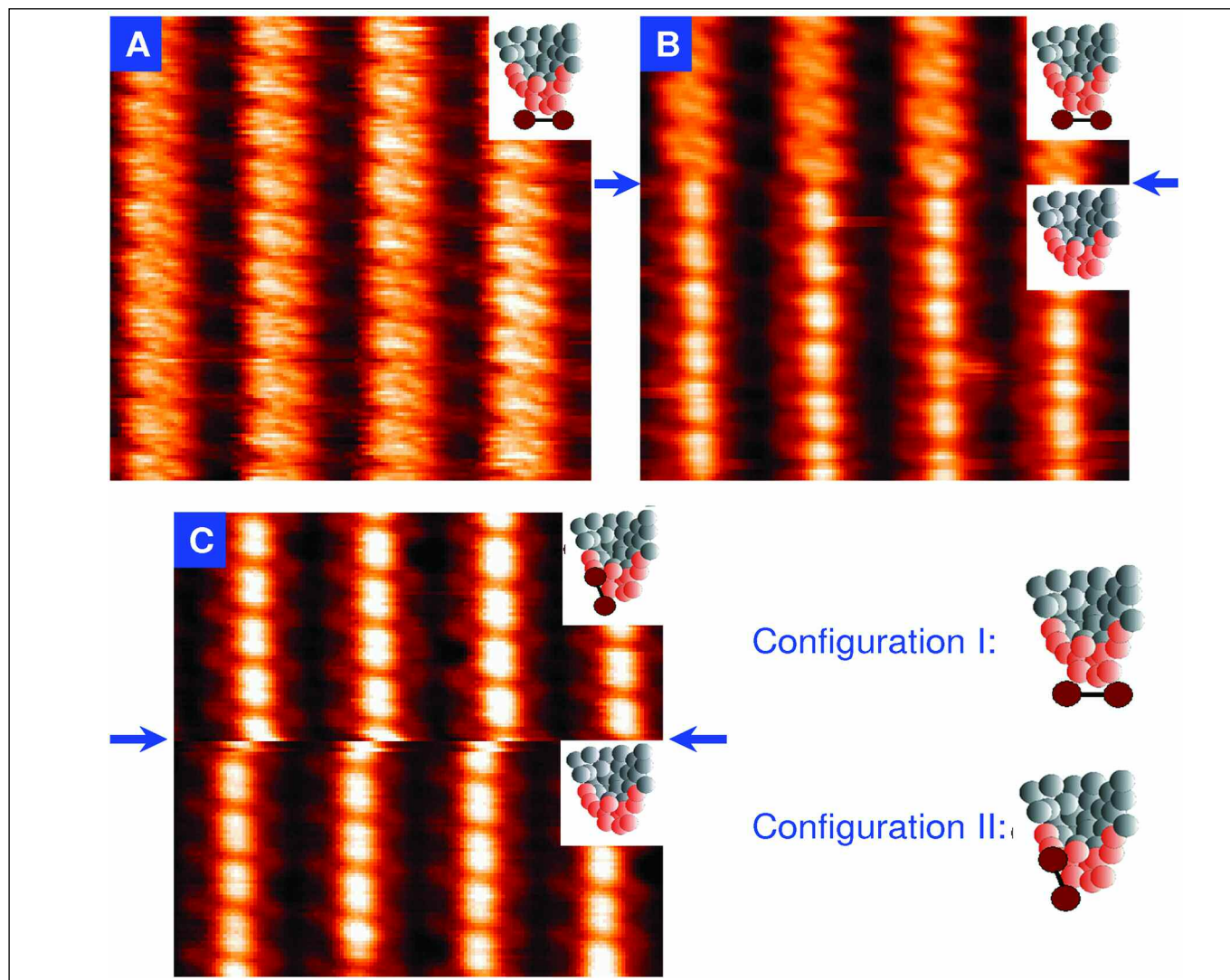
Figure 5:

(A-C) STM images of array of atomic platinum chains: -10 mV, 0.4 nA, scan areas 6.0 x 6.0 nm². (A) Image taken just after a single dimer pick-up event, resulting in a double tip image (configuration I). (B) A Pt dimer is picked up from the Pt chain halfway down the image. The lower part of the image is scanned with an atomically sharp tip. Halfway down the image, at the scan line indicated with the blue arrows, a single dimer is picked up from a Pt chain. The upper half of the image, imaged with the picked-up dimer attached to the apex of the STM tip, clearly shows a double tip (dimer attached to the tip in configuration I). (C) In the middle of the image a single dimer is picked up from one of the Pt chains (the change at the apex of the STM tip is indicated by the blue arrows). After the pick-up event the resolution of the image remains atomically sharp (the Pt dimer is attached to the apex of the tip in configuration II).

place and (b) the actual distance between the STM tip and the Pt dimer could be somewhat larger than in the earlier described method.

We believe that during a pick-up event the Pt dimer can be attached to the apex of the STM tip in two different configurations, which we label as configurations I and II. Upon picking up a Pt dimer, we often observed double tip images. In this case the STM images are formed by two (mini)tips, both contributing to the tunnelling current instead of one single tip. We believe that in this case the Pt dimer is attached to the apex of the tip in a horizontal position (configuration I, see Figure 5a).

In Figure 5b we picked up a dimer from an atomic Pt chain during imaging. The lower part of the image was scanned with an atomically sharp tip. Halfway down the sample (scanning from bottom to top) we picked up a Pt dimer from the Pt chain (the tip change is indicated with the blue arrows). The upper half of the image, scanned with the Pt dimer attached to the apex of the STM tip, is clearly a double tip image. We believe that in this case the dimer was attached to the STM tip in a hor-izontal configuration (configuration I).

Figure 5c shows an image in which a Pt dimer was picked up halfway through the scan (the tip change is indicated with the blue arrows) from one of the Pt chains (again scanning from bottom to top). The resolution of the STM image remains essentially unaltered. We believe that in this case the Pt dimer was attached to the side of the tip-apex, resulting in well-defined atomically resolved images.

CONCLUSIONS

In summary, we have briefly reviewed several atomic manipulation experiments on semiconductor surfaces using the scanning tunnelling microscope. Due to the relatively high thermal stability and the covalent character of the bonds of the semiconductor crystal, it is possible to perform these kinds of manipulations experiments at temperatures as high as room temperature. In addition, beside the ultimate control of the surface structures, we have also shown that the manipulated molecule can be attached to the apex of the STM tip in various stable configurations.

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