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A STM study on compared chemical reactivities of different Si(111) surfaces: copper growth and ferrocene adsorption

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Résumé. — Comme illustration de nos activités dans le domaine de la microscopie de champ proche, nous présentons une étude comparative de l'adsorption du cuivre et du ferrocène sur différentes surfaces de Si(111): B-Si(111) $\sqrt{3} \times \sqrt{3}$ R(30°) de concentration en bore variable et Si(111) 7 × 7. Nous montrons que la phase $\sqrt{3}$ de la surface dopée au bore est chimiquement relativement inerte. Nous corrélons la réactivité de surface à la densité de liaisons pendantes à la surface du silicium.

Abstract. — As an illustration of our activities in the domain of near field microscopies, we present a comparative STM study on Cu and ferrocene adsorption on different Si(111) surfaces: B-Si(111) $\sqrt{3} \times \sqrt{3}$ R(30°) with various concentration of boron and a Si(111) 7 × 7. We show that $\sqrt{3}$ phases of boron doped surfaces are relatively chemical inert. We thus correlate the surface reactivity with the density of outer Si dangling bonds.

1. Introduction.

In the very early stages of its developement, STM turned out to be a powerful physical tool for surface science investigations. It has progressively enriched our understanding of structural and electronic surface properties at the nanometric or atomic scale. As many other groups participating to this meeting on near field microscopies, we have developed in the past few years a special effort to characterization of surface properties at the nanometric scale. Various fields like surface microroughness quantization [1] or photon emission mapping derived from STM [2] have thus been investigated in our group. Parallelly, our activity has long been focused more specifically on the structural and electronic properties of clean or adsorbate covered semiconductor surfaces processed in UHV conditions. As a brief illustration of these activities we present here STM data on compared reactivities of Si(111) 7 × 7 and boron doped Si(111) surfaces submitted to copper deposition or exposed to a ferrocene vapor.

Along the development of applied surface science, the correlation between structural electronic and chemical properties of metal semiconductor interfaces and their influence on the growth mode mechanisms have been stressed on. Recent experimental studies using local probes like STM and TEM have shown that the atomic ordering of the initial substrate might condition the chemical reactivity or adsorbate wetting of the substrate [3-4]. The purpose of this paper is to give atomic scale informations on the structural properties of (111) surfaces of boron highly doped Si samples which present a reconstruction B-Si(111) $\sqrt{3} \times \sqrt{3}$R(30°) hereafter abbreviated B$\sqrt{3}$ [5] and to compare the early stages of Cu growth on such substrates with the growth on Si(111) 7 × 7 surfaces. This provides a local scale characterization which confirms earlier conclusions obtained on the basis of surface sensitive techniques investigations. We had indeed suggested [6] that Cu wetting and Cu- Si interactions were strongly reduced at the surface in comparison with a 7 × 7 surface. Finally we present data on lithography experiments using decomposition of ferrocene molecules by a STM tip on the $\sqrt{3}$ ordered phase or 7 × 7 as a substrate. A detailed report on this study will be published elsewhere, so that we only mention the main characteristics of this work at the end of our paper.

One major characteristic of the boron $\sqrt{3}$ structure is that B atoms do not occupy a T4 adatom site as other group III elements [7-9], but sits in the 2nd layer of Si in a so-called S5 site [10-13] as shown in figure 1. This is a favourable situation for creating a δ doped layer which might play an important role in atomic layer doping technology [14-15]. The important charge transfer from the Si adatom to the underlying B atom confers different electronic and chemical properties of the surface as compared to those of the Si(111) substrate. At this stage, it is important to point out that these substrates are made of Si atoms in the two first layers. It is thus worth noting that boron substitution of Si atoms take place in the third layer only. Before describing and commenting on the results of Cu growth, we first describe our experimental procedure and then recall the structural properties of the B$\sqrt{3}$ phases obtained at different annealing temperatures.

2. Experimental procedures and substrate preparations.

All our measurements were carried out in a dual UHV chamber $\left(P \sim 5 \times 10^{-11} \text{ Torr}\right)$ containing surface analysis facilities (AES, EELS, LEED) and an OMICRON Scanning Tunneling Microscope (STM). A Cu-source heated by a power regulated system and calibrated using a quartz oscillator has been used for Cu growth experiments.

The tips are prepared from a W wire electrochemically etched in a 3M NaOH solution and cleaned by annealing above 1000 °C in UHV. The Si(111)7 × 7 surfaces are prepared from n-doped silicon wafers (0.1Ω.cm) by usual thermal cleaning. Boron-doped Si(111) wafers ($4 < \rho < 6$ mΩ.cm) were used for preparing $\sqrt{3}$ substrates; the samples were cleaned by rapid annealing at 1150 °C and subsequent heating at lower temperatures gave rise to $\sqrt{3} \times \sqrt{3}$ R(30°) reconstruction. All our STM results showed that boron surface segregation was sensitive to the annealing temperature. We have thus characterized samples obtained using different temperatures heating, ranging from 750 °C to 1000 °C. The steady-state regime is controlled from statistical analysis of STM images at different stages of the preparation. Calculations based on boron diffusion are in agreement with the experimental equilibrium times.

Since, depending on the annealing conditions, different equilibrium boron surface concentrations are obtained [16], we have studied the Cu growth on two different kinds of B$\sqrt{3}$ phases. They have been prepared at annealing temperature of 750 °C and 920 °C chosen in order to get respectively a large and a small concentration of surface B atoms. Figures 2a and 3a show representative images of such initial $\sqrt{3}$ structures; the bright spots observed on these figures correspond to Si adatoms in a normal T4 configuration without underlying B atom (larger electronic density at such a dangling bond), whereas the dark spots (smaller electronic density) correspond to Si adatom with a underlying B in a S5 configuration [12]. The surface concentrations of bright

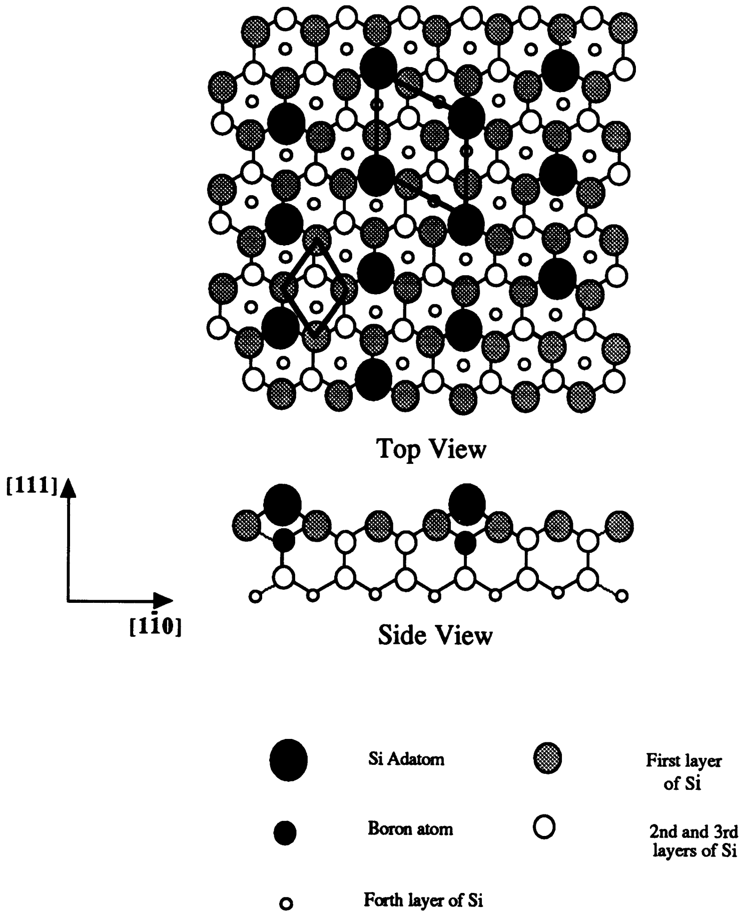

Fig. 1. — Structural model of the B-Si$\sqrt{3}$ surface. The adatoms are Si atoms placed in T4 sites.

spots referred to the number of surface Si adatoms are respectively around 1% and 30% and it was easy to compare Si(111) substrates with different outer dangling bond densities namely the B$\sqrt{3}$ (1%), B$\sqrt{3}$ (30%) and the 7 × 7 reconstructed surface.

3. Room temperature copper deposition on B$\sqrt{3}$ Si substrates.

A room temperature deposition of 2ML of copper on these $\sqrt{3}$ substrates leads to small 3D crystallites. Figure 2b and figure 3b correspond to substrate obtained at 750 °C and 920 °C respectively. Those STM micrographs show irregularly shaped crystallites. Alignement of their edges to the ⟨1-1 0⟩ like direction of the (111) plane can be observed. However, this characteristic is less pronounced at high crystallite density (Fig. 3b). The areas between crystallites are uncovered and show the $\sqrt{3} \times \sqrt{3}$ R(30°) reconstruction characteristic of the initial substrate.

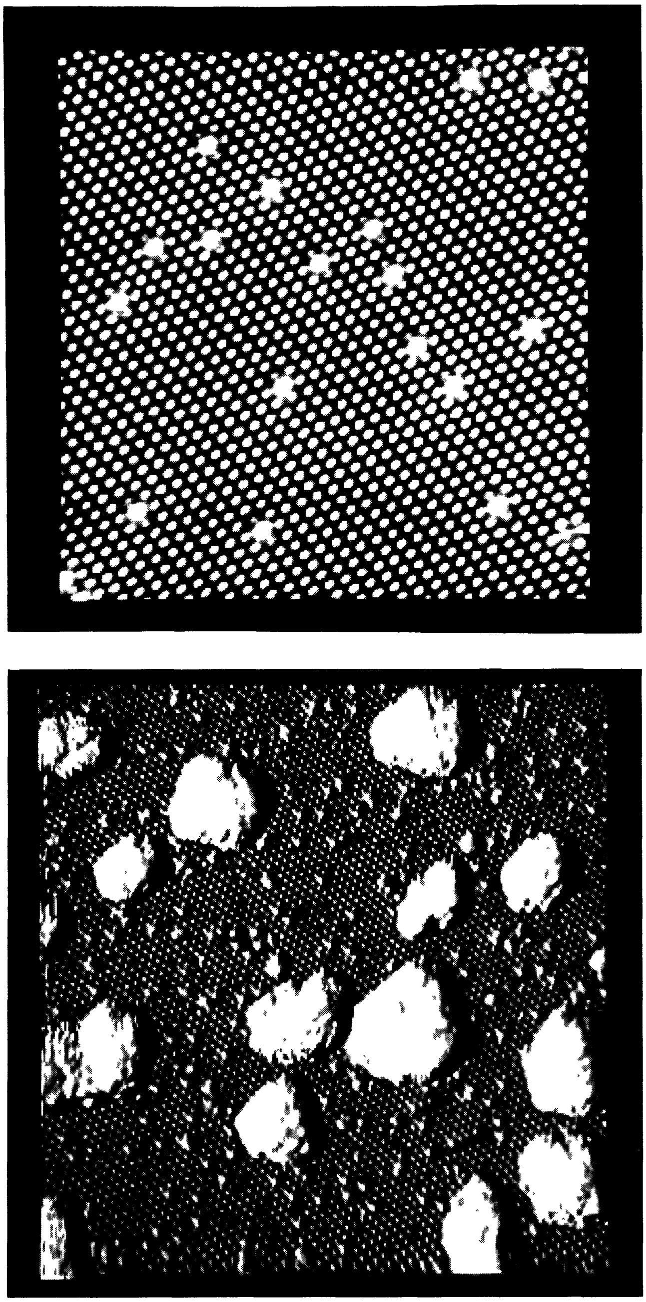

Fig. 2. — (a) 256 Å×256 Å tunneling image showing $\sqrt{3}\times\sqrt{3}$ R30° structure after boron surface segregation at 750 °C. Sample bias = 1.6 V, 1 nA. The bright features are related to the absence of boron underneath the Si adatoms and are thus a signature of a outer Si dangling bond. (b) STM topograph (512 Å×512 Å) of the surface B-Si$\sqrt{3}$ (obtained at 750 °C) after the growth of 2ML of Cu at room temperature (1ML = 7.84×10^{14} at.cm^{-2}).

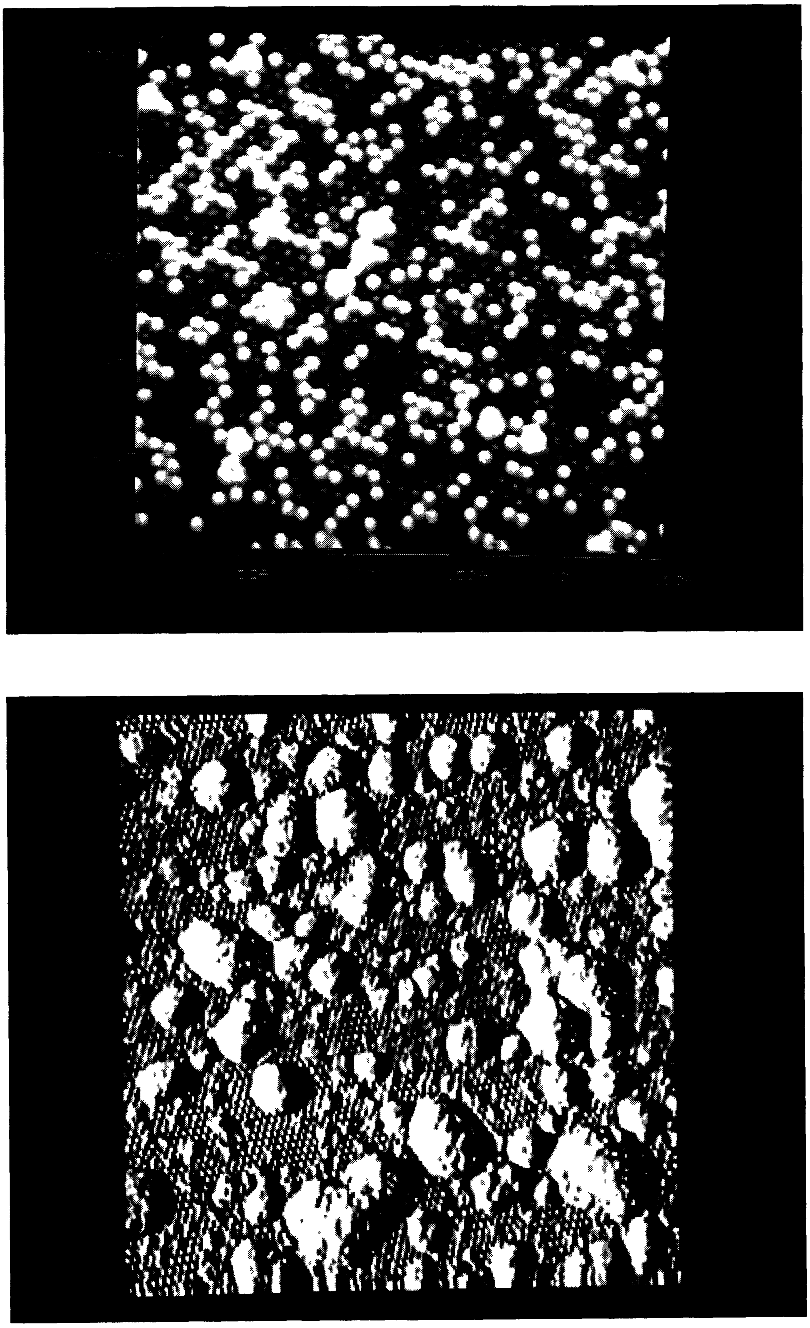

Fig. 3. — Image of a $\sqrt{3}$ substrate prepared at 920 °C. Same size and imaging conditions as in figure 2. The same amount of Cu as in figure 2b. (i.e. 2ML) is deposited (b).

4. Annealing of a RT Cu deposit on B$\sqrt{3}$ Si substrates.

Regular shaped crystallites with a truncated-triangular base and a rather plate top grow after subsequent annealing at 300 °C.

Figure 4 shows an example of one of these crystallites 90 Å height and 150 Å large obtained after annealing of a substrate.These large crystallites have different sizes and are separated by thousands of Å in most cases. One notes that irregular 2D islands subsist and that their density corresponds to the density of the initial crystallites obtained at RT. A zoom made on the uncovered substrate still indicates a B$\sqrt{3}$ reconstruction.

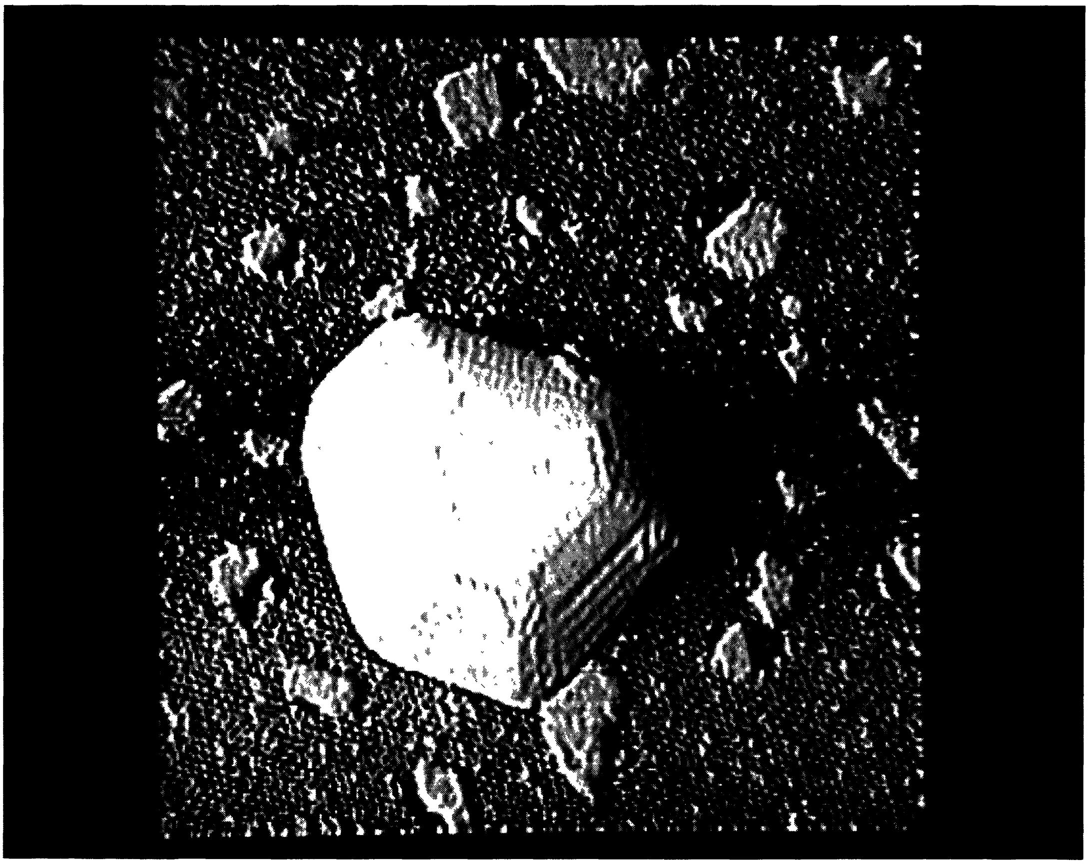

Fig. 4. — 512 Å×512 Å STM image of the surface covered with 2ML of copper after annealing at 300 °C. The height measurement does not allow us to precise the origin of the strips along the facets (for instance, multisteps of Cu(111)).

Higher annealing (650 °C) leads to a disappearance of the irregular 2D islands and large 3D crystallites a few thousands Å apart.

Growth on an annealed substrate, which temperature is maintained around 650 °C, gives the same kind of images with large uncovered parts of the B$\sqrt{3}$ phase in most of the 100 nm×100 nm scale; this confirms that Cu does not wet the the B$\sqrt{3}$ structure [6]. Large 3D clusters decorating steps could only be seen in large scan (5 μm × 5 μm) AFM images not presented here.

5. Ferrocene reactivity on B$\sqrt{3}$ Si substrates.

A preliminary study of ferrocene adsorption on different boron $\sqrt{3}$ substrates, while the STM tip is retracted have shown that up to 50000 Langmuir exposure: no visible modification of the STM images was perceptible.

In contrast, we have found tunneling conditions (summarized hereafter) which induce controllable and persistent local modifications of the substrate under the tip. They are obtained at negative sample voltages with a threshold value at − 1,7 V. The efficiency of the process (number of modifications of the substrate per unit of time during scanning) increases with the ferrocene pressure (in the ferrocene pressure range from 10^{-7} to 10^{-4} mbar) and is roughly independent of the tunneling current (from 40 pA to 4 nA).

We present elsewhere a detailed study of this work [17] where we suggest that the involved mechanism might process as follows. First, ionization of ferrocene molecules in the electric field between tip and surface with a maximum of ionization probability under the tip apex. Then, once the molecule is ionized it can react with the substrate and the dissociation occurs, leading to the formation of an amorphous alloy (likely FeSi composition as explained in [17]) while the volatile parts move off. Current experiments to assert this conclusion and characterize the deposited material are undertaken.

By switching from negative to positive voltage, it is easy to enable or disable our nanopen and thus draw a wished pattern by continuously moving the tip along this pattern. We present in Figure 5 the image of the initials of our laboratory. Magnifying of the resulting image, not shown here, allows us to estimate the sharpness of the pen. We have obtained letters with a linewidth of 3 nm and the $\sqrt{3}$ atomic ordering is clearly distinguished on the non-written part of the substrate [17].

6. Ferrocene reactivity on 7 × 7 Si substrates.

In contrast to what occurs on a B$\sqrt{3}$ Si substrate, ferrocene exposure to a 7 × 7 reconstructed surface induces sensible effects proportional to exposure. Figure 6 shows these modifications where one part of the 7 × 7 cell (unfaulted part) is majoritarly affected. Nano writing is also possible but, due to the uniform spontaneous adsorption on the surface, the contrast of the pattern is severely affected.

7. Discussion.

These results show the influence of the substrate structure on further chemical reactivity. Let us first discuss the case of Cu growth.

In a preceding paper [6], we have already mentioned that the early stages of Cu growth either on a 7×7 Si (111) substrate or on the B$\sqrt{3}$ phase are characterized by complete different behaviours. In particular, we observe that annealing of a RT deposit of Cu on a Boron $\sqrt{3}$ phase never produces the "5×5" buffer layer observed by depositing Cu on a 7 × 7 substrate [18].

From the present study, we obtain more detailed informations since our data clearly correlate the densities of Cu islands with the densities of bright spots of the initial $\sqrt{3}$ substrate. These

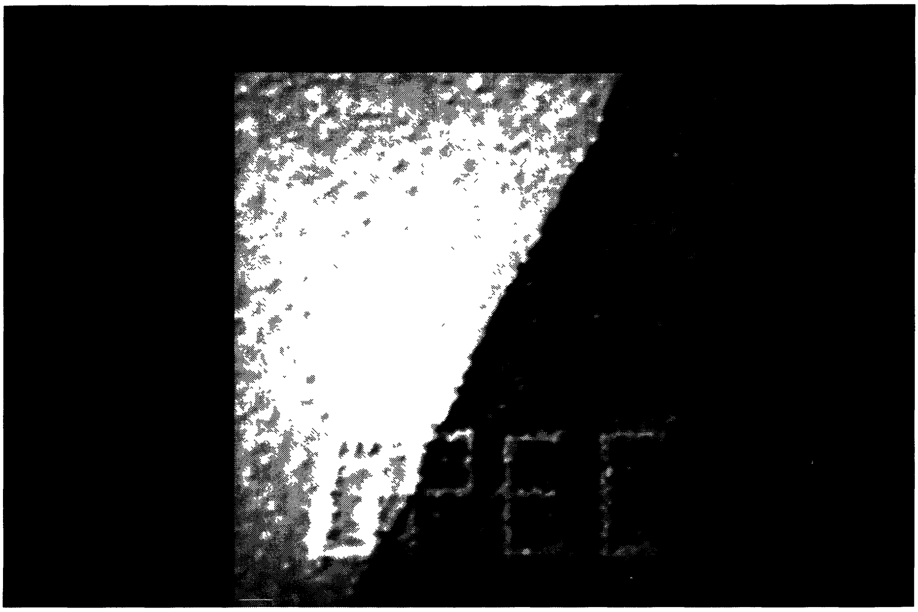

Fig. 5. — An example of lithography using ferrocene onto the B-Si$\sqrt{3}$. No spontaneous adsorption is observed. The size of the letters is 30 nm × 15 nm and the linewidth is around 3 nm.

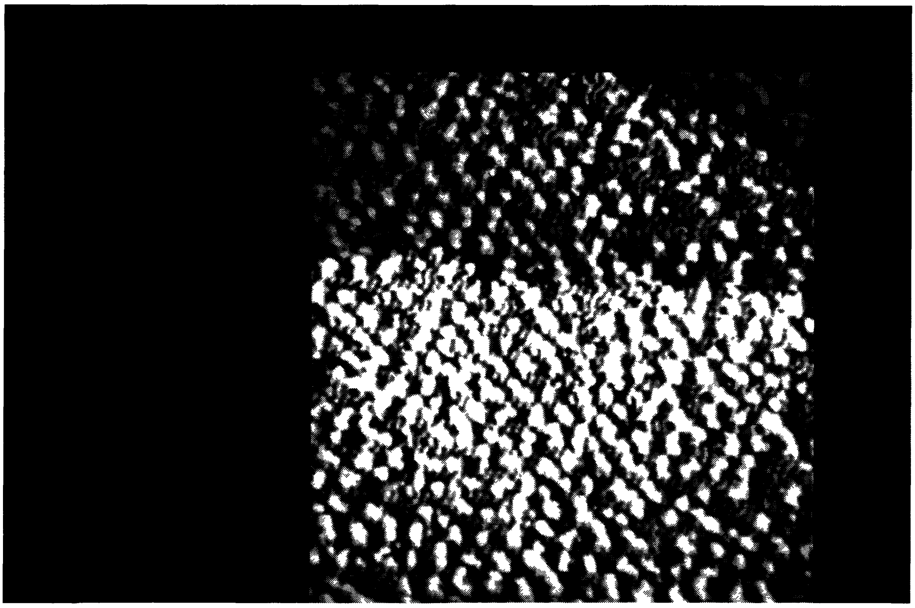

Fig. 6. — On the Si(111) 7 × 7, after an exposure to ferrocene (10 Langmuir), a spontaneous preferential adsorption on the faulted half of the cell is observed. The image presented is a 512 Å×512 Å surface.

bright spots might be viewed as defects of the B$\sqrt{3}$ phase since at this place an underlying boron atom is replaced by a Si atom; this suggests that at RT Cu islands nucleate on those defects of the $\sqrt{3}$ where the electronic density is larger. The inward charge transfer from the Si surface to the boron atoms thus confers to the surface a weaker chemical reactivity. This result is similar to that obtained for the case of H passivation on the $\sqrt{3}$ structure as compared to the case of H adsorption on a 7 × 7 surface [19].

Regarding the composition of the clusters, the two steps process observed in the disappearance of the 3D clusters suggest that their basis consists in a 2D alloyed part which remains at higher temperatures, around 300 °C, before complete removal at 650 °C.

Data concerning the ferrocene adsorption also illustrates the lowering of chemical reactivity induced by the underlying boron at the Si surface.

In conclusion, we have used STM characterization to get an atomic vision of Cu growth confirming conclusions based on averaging sensitive techniques. Our work indicates that the B$\sqrt{3}$ phase constitutes a diffusion barrier which lowers the kinetics of Cu-Si compound formation. In contrast to what is observed in Cu growth on a 7 × 7 surface, where high temperature deposition proceeds along a Stranski-Krastanov growth, we always observe in boron doped samples, a Volmer-Weber growth mode of 3D islands which nucleate at defects of the $\sqrt{3}$ phase where missing underlying B atoms are replaced by Si atoms. Finally, we have also observed different chemical reactivity in the case of exposure to ferrocene vapours and have produced sharp resolved pattern using ferrocene molecule decomposition by the STM tip on the otherwise inert substrate constituted by the $\sqrt{3}$ phase of B-Si(111) surface.

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