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Formation of an iodine zig-zag chain $c(2 \times 4)$ reconstruction on the Ge(111) surface

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Abstract. — Room temperature adsorption of I_2 on the Ge(111) surface is found to break the initial $c(2 \times 8)$ adatom reconstruction as iodine preferentially occupies the on top substrate site, breaks the backbonds between the adatom and the substrate and thus removes the Ge adatoms. As this process continues a $c(2 \times 4)$, and modifications thereof, reconstruction is formed consisting of chains of I_2 molecules bound in almost T_1 sites with a I-I bond length of 3.6 Å.

1. Introduction.

Chemisorption of the monovalent halogens on the (111) faces of the diamond structure semiconductors Si and Ge can in a simple bonding picture be expected to saturate the substrate dangling bonds leading to a stable, ideally terminated and inert surface. In this picture the adsorption site would be the so-called T_1 topsite directly above the substrate atom. This has indeed been verified experimentally for the Ge(111)-I system by Surface extended X-ray absorption fine structure (SEXAFS) [1] and X-ray standing wave (XSW) [2].

From a soft X-ray photoemission study of the Si(111) (7×7)-I surface [3] it was found that iodine adsorbs dissociatively, forming SiI, SiI₂ and SiI₃ entities. The adsorption was found to occur primarily on the adatom dangling bond (DB), where the presence of a DB is a necessary prerequisite for the dissociation of the molecular iodine, and thus the adsorption. The total iodine coverage is therefore limited by the number of available DBs. After additional exposures the adatom to substrate bonds, the back bond, were broken after which the adatoms were converted to SiI₂ and SiI₃ species.

In this paper we report results from a scanning tunneling microscopy (STM) investigation of the sub monolayer (ML) room temperature adsorption of molecular iodine on the Ge(111) $c(2 \times 8)$ surface. The preferential initial adsorption site at the lowest coverage is determined to be on top of the substrate atoms, to which the rest atoms are included, although examples of H_3 and T_4 sites were also observed. At higher iodine coverage a $c(2 \times 4)$ reconstruction is formed consisting of chains of iodine molecules with an I-I distance of 3.6 Å within the dimer and 3.8 Å between atoms in neighboring dimers. A modification of this structure is also observed, where every second iodine row is shifted out of phase to form a slightly larger unit cell, i.e. $c(8 \times 4)$.

2. Experimental.

The experiments were performed on a commercial Omicron UHV STM housed in a separate vacuum chamber. Connected to this chamber is a preparation chamber containing low energy electron diffraction (LEED) optics, Auger electron spectroscopy (AES), an electro chemical cell for iodine dosing, Ar^+ ion sputtering and sample heating through electron bombardment. The substrates used were cut from a Ga doped Ge(111) wafer, and cleaned in situ by repeated cycles of sputtering (500 V) and annealing (650 °C) until a sharp $c(2 \times 8)$ LEED pattern emerged. Iodine was dosed from the electro chemical cell with a rate of 10 μA .

3. Results.

3.1 LOW ENERGY ELECTRON DIFFRACTION (LEED). — In LEED the $c(2 \times 8)$ pattern gradually weakend upon room temperature deposition, the half order spots being the most persistent of the reconstruction related spots, until only a blurry (1×1) pattern was seen. When heated moderately, i.e. 400 °C, the (1×1) spots became very sharp. After further heating, from 500 °C to 800 °C, the $c(2 \times 8)$ spots became visible again, the intensity and sharpness being accentuated as the temperature was raised. No extra spots, other than (1×1) and $c(2 \times 8)$, were seen during the course of the experiment.

3.2 SCANNING TUNNELING MICROSCOPY (STM). — Room temperature deposition of molecular iodine on the Ge(111) $c(2 \times 8)$ reconstruction preserves the initially flat and homogeneous germanium surface, as shown in figure 1, throughout the whole coverage range investigated. A smaller number of larger islands randomly distributed over the surface was observed, the number

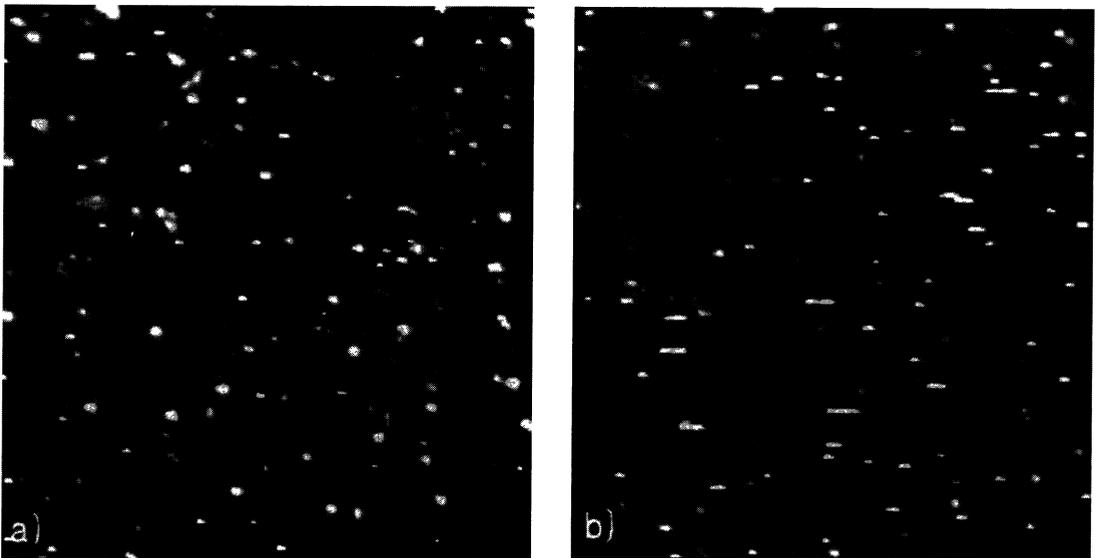


Fig. 1. — $550 \times 550 \text{ \AA}^2$ overview STM images displaying a Ge(111) surface partially covered with iodine. a) was recorded at +1.6 V and b) +1.0 V sample bias.

though not being very sensitive to the iodine exposure. A larger number of small white, i.e. higher, spots were also seen scattered over the substrate surface. As the iodine dose was increased the spot density accordingly increased, and the spots are therefore interpreted as due to iodine. Figure 1a, recorded at +1.6 V sample bias, presents an example of these white spots on the surface. Between the islands the $c(2 \times 8)$ reconstruction is still, in a large extent intact though smaller areas with a higher concentration of iodine is seen to be more disturbed. At +1.0 V bias, figure 1b, the surface produces a different image. Although the largest white spots still remain as protrusions, the majority of the smaller spots now have turned into what rather appears as missing adatoms, possibly indicating a substitution of germanium adatoms with iodine adatoms.

In figure 2a and b two simultaneously acquired STM images from the low iodine coverage surface are shown. The image in figure 2a was recorded at 2V positive sample bias, thus tunneling to the empty states of the surface located on the adatoms, which appear as on the clean Ge(111) $c(2 \times 8)$ surface. The most apparent difference from the clean surface is the increased disorder and the slightly higher preference for the $c(2 \times 4)$ unit cell as compared to the (2×2) unit.

In the 2V negative bias image in figure 2b the white spots are enhanced and appear much higher than the surrounding substrate. In addition to the larger spots also visible in figure 2a numerous smaller protrusions have emerged, which we attribute to the deposited iodine.

The filled state image displays both rest atoms and adatoms and it is thus possible to determine where the iodine adsorbs, since the germanium adatoms can be identified from the empty state image. As can be seen in figure 2a some adatoms have a lower apparent height compared to the surrounding adatoms, this situation is reversed in the filled state image where they instead appear as protrusions. Suggestively there is a replacement of Ge adatoms with I adatoms, as we mentioned above. These lower adatoms, in the +2 V image, which we attribute to iodine are not in positions equivalent to the germanium adatom T_4 site, but they are slightly shifted away from the hollow site so that they are instead located on top of a substrate germanium atoms. A ball and stick model of the outlined part in the STM images is presented in figure 2c, where the largest, hatched circles represent the Ge adatoms, the open circles represent the iodine adatoms located directly on top of the substrate germanium atoms which are denoted by the smallest, black dots.

The iodine appears in dimers with a I-I distance between 3.7 and 3.9 Å, thus a little smaller than the substrate surface lattice parameter of 4.0 Å, indicating that the molecular bond between the iodine atoms is not completely broken by the presence of the germanium substrate. As can be seen in the lower right hand corner of the model one dimer, marked with arrows, is located in a H_3-T_4 site, however this is clearly a minority situation for this adsorption process.

At slightly higher iodine doses areas with a surface reconstruction different from the $c(2 \times 8)$ structure was observed. This reconstruction is displayed in the $50 \times 55 \text{ \AA}^2$ empty state STM image in figure 3a, with a rectangular structural unit with side lengths 8 Å and 6.9 Å respectively in close similarity with the $c(2 \times 4)$ unit cell present in the $c(2 \times 8)$ structure. Contrary to the Ge(111) $c(2 \times 4)$ reconstruction, which displays only one single protrusion per surface unit cell, the present structure has a dimer like configuration, marked A and B, with a separation of about 3.6 Å within each dimer and 3.8 Å between atoms in neighboring dimers, i.e. fairly similar to what was observed for the iodine-iodine distance at lower coverage, which encourage us to propose that the dimers are iodine molecules. Furthermore the difference in distances, i.e. 3.6 vs 3.8 Å, indicates a stronger bond within the dimer than with respect to the surrounding iodine atoms thus further reflecting a diatomic molecular behaviour of the iodine. This idea is also supported by the filled state image in figure 2b where dimers, or even longer chains of what we believe is iodine are displayed. The chains show pronounced similarities with solid iodine [4] which crystallizes as molecular iodine. Occasionally this unit is shifted one position along the zig-zag chains, as can be seen in figure 3, but the basic building is still the same.

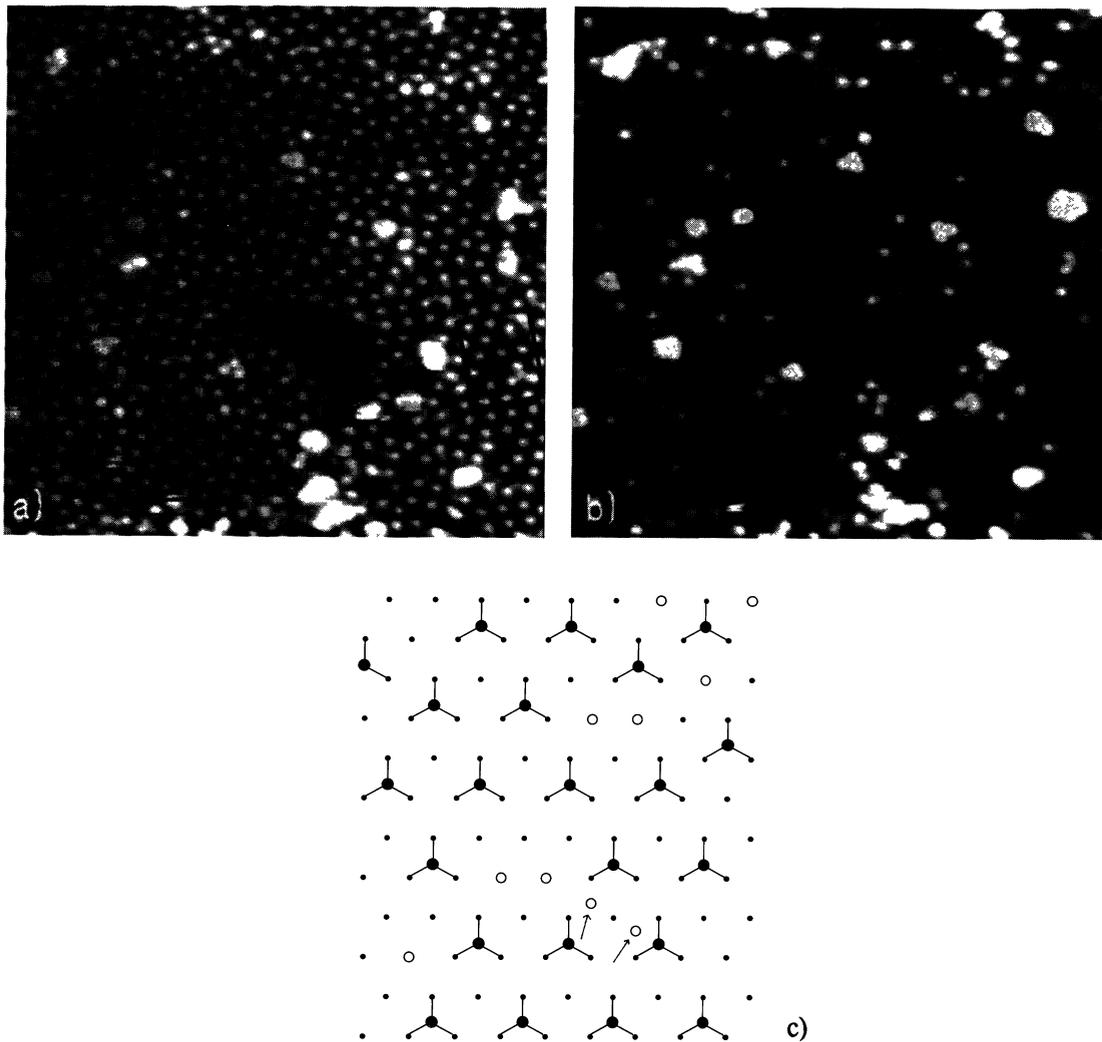


Fig. 2. — $200 \times 200 \text{ \AA}^2$ close up image showing initially adsorbed iodine on the Ge(111) $c(2 \times 8)$ surface. The tunneling voltages used were a) +2.0 V and b) -2.0 V. Figure 2c shows a ball and stick model of the outlined part of the STM images, where the iodine adsorption site is shown to be on top of the substrate atom.

A third, slightly lower protrusion, marked C in the STM image, is seen to coexist with the dimers in the empty state image. At negative sample bias, see figure 3b, the structure has changed its appearance, with one protrusion being the more dominant. This maximum coincides with the dimer atom (A) closest to the bottom of the image, and it appears as if there is a difference between the two dimer atoms. Furthermore the lower protrusion (C) in the empty state image has now, in the filled state image, disappeared and a new feature, marked D, has instead emerged in the position of the hole in the empty state image.

Recalling the adsorption of I at lower coverage, we suggest a similar T_1 bonding site also in this reconstruction. Furthermore the occurrence of iodine pairs or dimers leads us to the geometrical model presented in figure 4, consisting to 0.5 ML of iodine adsorbed in almost T_1 positions, leaving 0.5 ML of unsaturated germanium substrate dangling bonds. What we mean by almost T_1 is that,

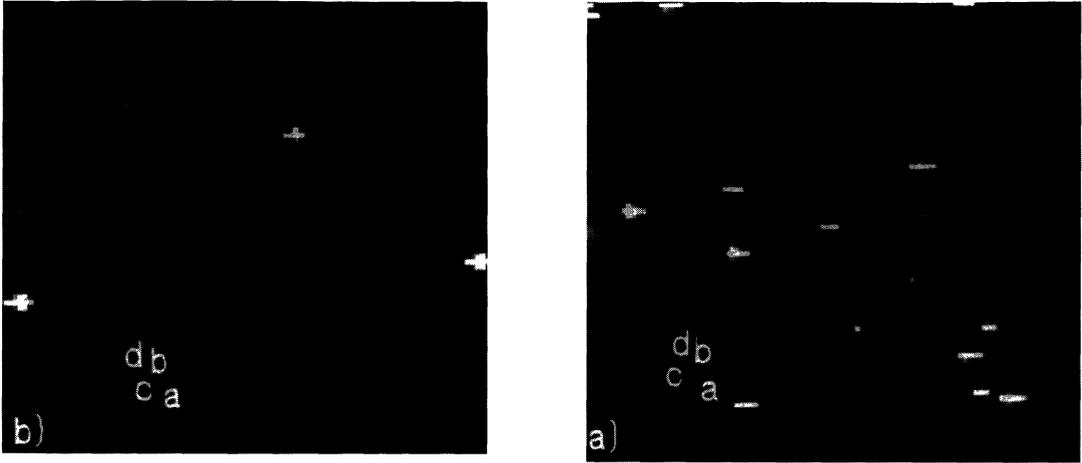


Fig. 3. — $60 \times 60 \text{ \AA}^2$ dual polarity high resolution images of the $c(2 \times 4)$ reconstruction recorded at 2 V sample bias.

to agree with the observed 3.6 \AA distance, the iodine adatoms must be shifted off from their true top site, and also rotated slightly to conform with the observed dimer direction as compared to the substrate.

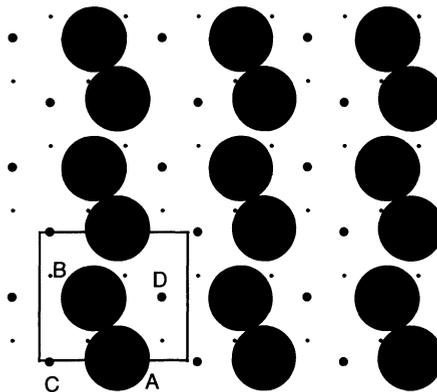


Fig. 4. — Simple model with 0.5 ML of I adsorbed in T_1 positions leaving two unpaired substrate dangling bonds. To conform with the voltage dependency in the STM images there must be a charge transfer from one Ge dangling bond to the other.

This model can explain the images fairly well if the iodine dimers correspond to the features A and B, and also the voltage dependence of the features C and D in the image if there is a charge transfer from one Ge rest atom to the other. Still there are questions that need a clarification; why is there a difference in the filled states between the two iodine atoms, and why is there a charge transfer between two apparently similar Ge dangling bonds?

Some arguments can be found in the model; the contraction and rotation of the dimers shifts atom A towards atom C, and B towards D. Still the situation is symmetric as long as the reconstruction is not disturbed. Although not shown in figure 3 an overview image of this reconstructed area displays a similar surface as the one presented in figure 1 with a substantial amount of iodine impurity islands scattered over the surface. In the vicinity of these impurities the perfect symmetry is broken which might initiate a charge transfer between the dangling bonds. And as soon as the Ge dangling bonds are no longer equivalent the equivalency of the iodine dimer atoms is also broken due to the above mentioned shifts of A towards C and B towards D.

4. Summary and conclusions.

We have used scanning tunneling microscopy (STM) to study the initial room temperature adsorption of iodine on the Ge(111) $c(2 \times 8)$ surface. The preferred adsorption site has been determined to T_1 , although examples of H_3 and T_4 were also observed. After further iodine deposition a $c(2 \times 4)$ reconstruction was formed consisting of chains of iodine molecules, among which a filled state asymmetry was observed accompanied by a charge transfer between substrate germanium dangling bonds due to impurities in the surface.

Acknowledgements.

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