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Sr adatoms on As bridge positions on $SrFe_2As_2$ observed by scanning tunneling microscopy at 4.2 K

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Abstract

We used a scanning tunneling microscope to image the surface of $SrFe_2As_2$ single crystals at 4.2 K. We found, besides the commonly reported row structures and some disordered areas, also maze-like regions. Atomically resolved images of the maze show that the atoms on the surface sit on As bridge positions of the underlying Fe_2As_2 layer. Examination of the corner positions within the maze-like reconstruction reveals the presence of adatoms rather than As dimers. Hence, the surface atoms on these samples are most likely to be Sr atoms.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

$SrFe_2As_2$ is the parent compound of one of the recently discovered pnictide superconductors [1]. On virtually all members of the pnictide family several surface structures have been observed in scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) studies, from a $\sqrt{2} \times \sqrt{2}$-R45° reconstruction to 2×1 row- or maze-like structures as well as disordered areas. Most of the studies have been performed on $BaFe_2As_2$ derived compounds [2–7] but $SrFe_2As_2$ based samples show similar results [8, 9] (see also [10]). The difference of creating a $\sqrt{2}\times\sqrt{2}$-R45° or a 2×1 reconstruction appears to be the cleaving temperature with a preference for the $\sqrt{2}\times\sqrt{2}$-R45° structure at low temperatures. The disordered regions are likely inclusions of material from the sintering process. There is some speculation about the nature of, especially, the 2×1 row structure: whether it consists of adatoms or As dimers. In this paper we use atomically resolved images of 2×1 maze structures to investigate the location and nature of the surface structures.

2. Measurements

The measurements were performed using a 4.2 K STM system with ultra-high vacuum (UHV) sample preparation capabilities [11]. We used etched tungsten wires as tips. The tips were cleaned by field emission on a gold single crystal. Subsequently, $I(V)$ and $I(s)$ curves were measured to verify that the tip shows a straight $I(V)$ curve and a tunneling barrier height of at least $\Phi = 2$ eV. The samples were 3 mm in diameter and 750 μm thick single crystals of $SrFe_2As_2$ [12]. The crystals were glued to the sample holder with conductive epoxy (Epo-Tek H72). A post was glued to the top of the sample to facilitate cleaving when inserting the sample into the UHV system via the load lock. The pressure at that time was typically of the order of $P \sim 10^{-8}$ mbar. After closing the gate valve to the load lock the pressure dropped back to $P < 10^{-10}$ mbar within seconds. The success of the cleave was verified optically on the sample as well as the remaining part on the post after retrieving it from the load lock. The sample was then placed in the STM at 4.2 K and measured.

2.1. Surface structures

Several surface structures were observed in the STM scans as shown in figure 1. Besides the typical rows with a spacing of $d \sim 8$ Å, we found a maze-like structure where the rows run in two directions at an angle of 90° with respect to each other. As can be seen from the top image in figure 1 the maze and row structure coexist with no discernible boundary.

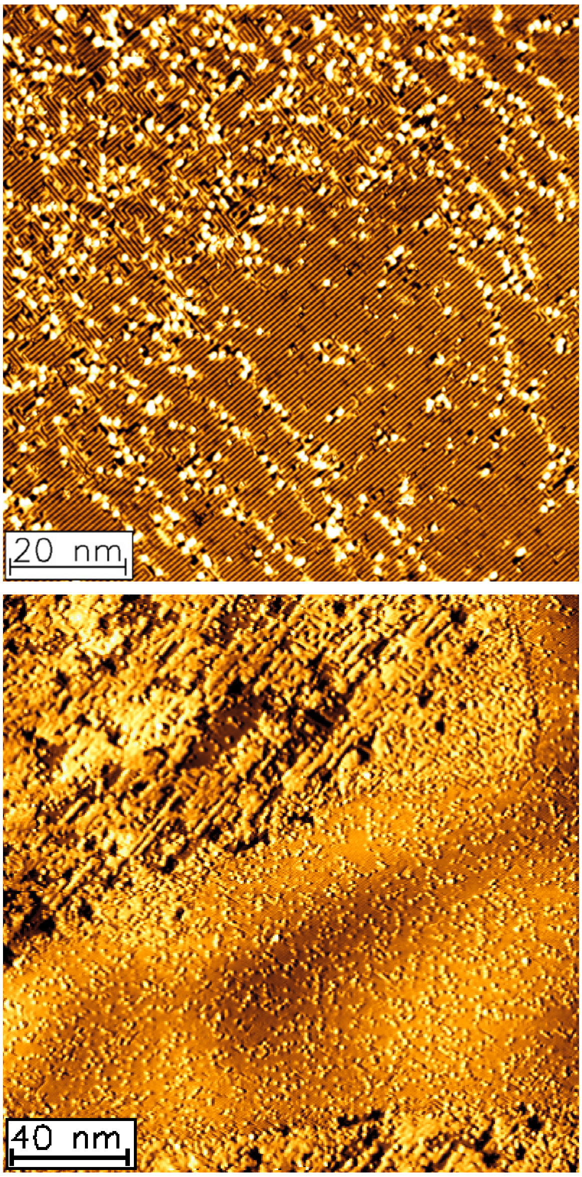

Figure 1. Variety of surface structures on $SrFe_2As_2$. Typical row structure next to maze structure (top), maze structure next to disordered region (bottom). ($V_{\mathrm{bias}} = -100$ mV, $I_0 = 200$ pA, $\Delta z = 5.3$ Å; $V_{\mathrm{bias}} = 800$ mV, $I_0 = 100$ pA, $\Delta z = 2.1$ nm.)

Overall, the image shows a well ordered structure with some defects in the rows as well as adatoms. Within the row structures these defects tend to line up roughly perpendicular to the row direction. Some areas had a somewhat disordered or contaminated appearance as shown in the bottom image. Still, the areas show rectangular shapes aligned with the overall crystallographic direction. Hence, they likely consist of non-stoichiometric residue from the sintering process. We never observed a $\sqrt{2} \times \sqrt{2}$-R45° phase on the crystals.

2.2. *Position of Sr adatoms*

Atomically resolved images of the maze structure offer a unique opportunity to identify the position of the adatoms. An example is shown in figure 2 alongside a model of possible adatom positions (figures 2(a)–(d)). Within the model red spheres indicate Fe, yellow spheres represent As and blue spheres Sr. The model shows the FeAs surface with possible positions for the Sr adatoms. The observed 2×1 superstructure obviously eliminates possibility (a) (bulk positions) and (b) ($\sqrt{2} \times \sqrt{2}$-R45°) which are both square lattices with a lattice constant of 3.9 Å and 5.6 Å, respectively. The two row structures (c) and (d) represent the atoms sitting in hollow sites, as in the bulk, and at As bridge position, respectively. These two possibilities can be distinguished by examining the relative atomic positions between the two directional domains of the rows.

Figure 3 shows an enlarged area of figure 2 alongside a model for Sr adatoms located in hollow sites as well as at As bridge position for two adjacent directional domains. Notice that for the hollow sites the atomic positions across domains always line up. This would also be the case if the adatoms were positioned on top of the As atoms. In contrast, for the bridge position the rows in one domain are aligned with gaps in the other. The latter case is clearly what is observed in the image.

3. Discussion

Given that the surface atoms are sitting on As bridge positions, the remaining question is whether we observe adatoms or As dimers since the latter would also reside in bridge positions. Figure 4 shows a close up of several corners where the two row directions meet alongside a model of the atomic surface positions. Most lines avoid each other by leaving a vacancy rather than forming a trimer. However at corners, two bumps are positioned close together and are thus forced to share an As atom on the inside corner. This configuration seems harder to obtain by forming a dimer than an ionically bound surface atom. Note also that the corner atoms appear higher than the ones in the rows. This would be expected if the electrostatic repulsion pushes the atoms out of position. In contrast, for a dimer bond one might expect a weakened appearance since three atoms rather than four contribute to two bonds. This makes the presence of adatoms far more likely although density functional theory (DFT) calculations would be needed to confirm this. A recent photoemission study on $BaFe_2As_2$ [13] also concluded that Ba remained on the surface, supporting this view.

Apparently, the surface atoms get repositioned during cleaving or by thermal activation thereafter. Since the bond is ionic in nature [14] the (nominally) Sr^{2+} ions are free to choose a position closer to the As^{3-} and farther away from Fe^{2+} ions. In an alternative scenario cleaving would expose a clean—and thus charged—Fe_2As_2 surface which then becomes contaminated. Water is the only contaminant available in sufficient abundance inside the UHV system, especially after cleaving the sample at $P \sim 10^{-8}$ mbar. The exposure time of about 20 s together with the transfer time of 300 s at $P \sim 10^{-10}$ mbar would be sufficient to form about 0.25 ML of water on the surface—assuming a sticking coefficient of 1. The geometry would also work out: putting H_2O at the apex of an isosceles triangle with a base of $c = 3.9$ Å and a length

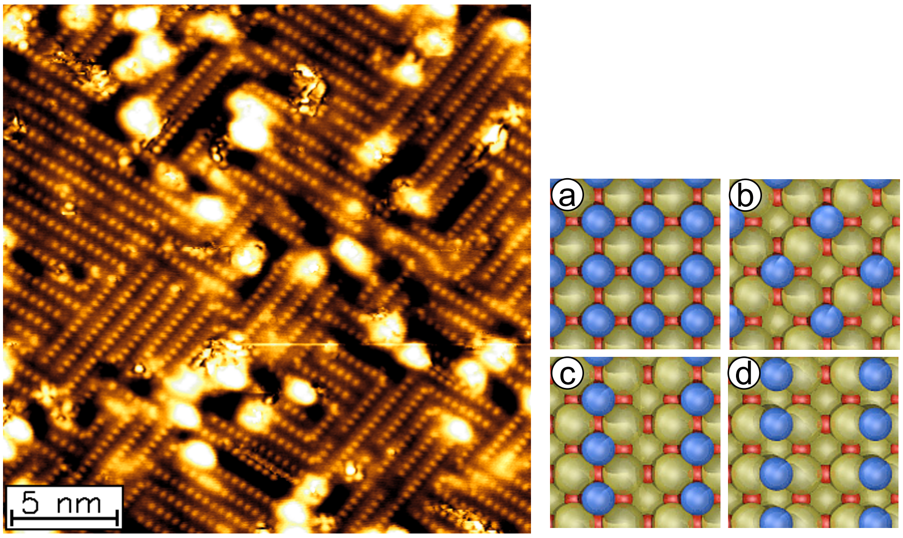

Figure 2. Atomically resolved maze structure showing a 2 × 1 surface reconstruction ($V_{\text{bias}} = -25$ mV, $I_0 = 400$ pA, $\Delta z = 4.4$ Å) and possible atomic positions for Sr: (a) bulk positions, (b) half, square lattice, (c) row structure, hollow sites (bulk), and (d) row structure, As bridge positions.

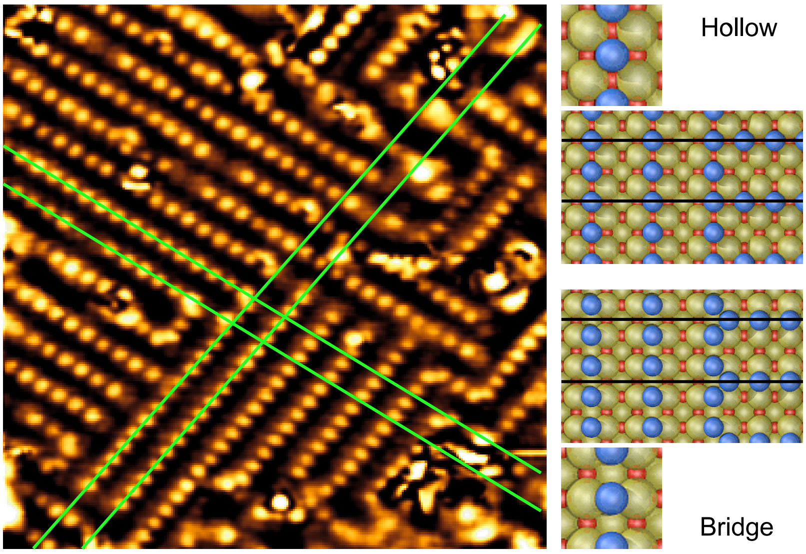

Figure 3. Atomically resolved maze structure (12×12 nm^2, $V_{\text{bias}} = -25$ mV, $I_0 = 400$ pA, $\Delta z = 2.6$ Å) compared to model of surface atoms of perpendicular rows sitting in hollow and bridge positions. The image has been high pass filtered to suppress the background. Green lines highlights the atomic alignment in adjacent domains. With atoms in the hollow sites, the atoms line up, in the bridge position they do not. The latter is clearly the case shown in the STM image.

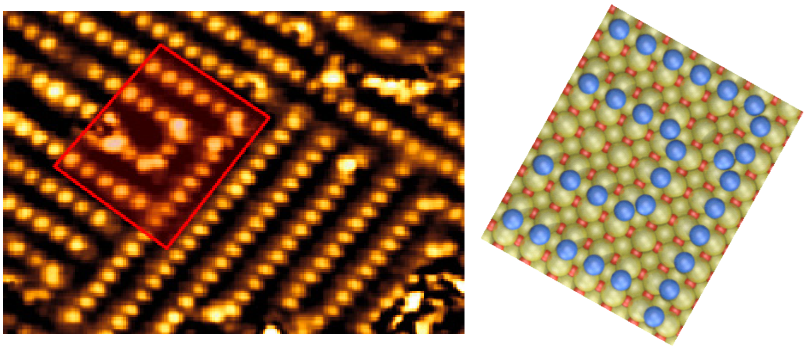

Figure 4. Model of a particular region with several corners of the atomically resolved $SrFe_2As_2$ surface compared to a model. The corner positions share one surface As atom to support bumps in two row directions. The corners also appear brighter and thus higher than the rows themselves.

of the sides of $a = 0.95$ Å + 1.5 Å = 2.45 Å (sum of the H bond length of water and arsine), the apex angle becomes $\gamma = 105.5°$. This is close to the bond angle of H_2O of 104.5°. However, the partial charge per H of $q = 0.34e$ would lead to a weaker ionic bond than Sr^{2+} resulting in an overall increase in energy. Barring other processes, this makes a substitution of Sr by H_2O highly unlikely.

Finally, from the smooth transition between the row and the maze structure as shown in figure 1 we can deduce that the surface atoms always sit in bridge positions—at least in the case of $SrFe_2As_2$.

4. Conclusion

We showed that for our $SrFe_2As_2$ samples, cleaved at room temperature and measured at 4.2 K, we observe Sr adatoms sitting on As bridge positions. This is true for the maze structure where it can be verified by atomically resolved images as well as for the 2 × 1 row reconstruction.

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