

## Superlattice structure of an Ar monolayer on Ag(111) observed by low-temperature scanning tunneling microscopy

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Scanning tunneling microscope (STM) images of a carefully prepared monolayer of Ar on Ag(111) reveal patterns of bright spots, which exhibit perfect ordering over large areas. The dimensions of the slightly oblique unit cell are  $1137 \times 2507$  pm<sup>2</sup>, where the short side is aligned along the  $[-110]$  high-symmetry direction of the substrate, and the long side shows a regular division into two parts. In total six domains are observed. Analysis of this pattern, taking into account the tendency of noble gas overlayers to form hexagonal structures, which might be slightly stretched or compressed, leads to a structure for the Ar overlayer, which reproduces all the observed features. Surprisingly, it turns out that the bright STM spots correspond to Ag atoms which are not directly covered by Ar but surrounded by three Ar atoms from the adsorbate layer. A possible electronic origin for this unusual appearance is discussed.

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Understanding of adsorption on surfaces has been pursued for many years and is still intensively investigated, especially with respect to elucidating of basic processes in heterogeneous catalysis, as well as for developing templates for regular nanostructures.<sup>1,2</sup> For the purpose of investigating fundamental physical adsorption processes, the study of noble gas adsorbates is particularly informative due to their closed-shell electronic structure and correlated chemical inertness.<sup>3</sup> Nevertheless, the number of studies concerning adsorption of light noble gases on solid surfaces is still relatively small. The low-energy electron diffraction (LEED) measurements of Ar monolayers (ML) on graphite by Shaw *et al.*<sup>4</sup> constituted first evidence of the validity of the theory of Novaco and McTague,<sup>5</sup> which predicted that transversal deformations of elastic overlayers on a rigid surface can occur. Detailed structural and thermodynamic studies based on LEED measurements of Xe, Ar, and Kr on Ag(111) were presented by Cohen *et al.*<sup>6</sup> and Unguris *et al.*<sup>7</sup> The scanning tunneling microscope (STM) (Ref. 8) in combination with cryogenic techniques also allows investigations of these physisorbed species in real space, whereas up until now, mainly the relatively strongly bound heavy Xe has been investigated.<sup>9-11</sup>

In this Rapid Communication we present STM investigations of Ar adsorbed on Ag(111). A carefully prepared Ar ML shows a puzzling appearance in STM images, and we postulate that the dominant features can be attributed to the convolution of electronic contributions in the STM images with the geometric Ar structure. The model for the geometric structure takes into account the well-known tendency of noble gas overlayers<sup>3</sup> to form hexagonal structures, together with the possibility of small elastic deformations within the layer.<sup>5</sup>

The measurements were performed with a custom built STM operated at liquid helium temperatures in ultrahigh vacuum (UHV). A detailed description of the microscope and the sensor can be found elsewhere.<sup>12,13</sup> The microscope is situated inside a superinsulated bath cryostat in an ultrahigh vacuum environment, which is thermally coupled to a liquid helium bath. This ensures that the microscope and its surroundings are cooled down to 5 K.

The argon overlayer on the Ag(111) surface was prepared in a special manner. With the Ag(111) sample situated in a room temperature area of the UHV chamber, the microscope and its surrounding chamber were predosed with a pressure of  $2.0 \times 10^{-5}$  mbar of Ar for 85 min. Note that this pressure is measured in the room temperature area of the UHV chamber and not in the cold area, where the microscope is located. The Ar adsorbs to the microscope and surrounding cold chamber walls. After cleaning the Ag(111) sample by several cycles of Ar sputtering (beam voltage=800 V, ion current = 10  $\mu$ A, Ar backfill pressure =  $1.6 \times 10^{-5}$  mbar) and annealing at  $T=783$  K, it was transferred to the microscope. Because the sample and the manipulator were at room temperature, Ar desorbed from the walls and parts of the microscope, establishing a partial pressure of Ar. While the Ag(111) crystal in the microscope slowly cooled down it eventually reached a temperature at which Ar started to adsorb on the Ag(111) surface.<sup>7</sup> During the entire procedure the walls of the microscope surrounding the sample were always colder than the sample. We think that this quite complex desorption and adsorption procedure leads to perfect equilibration and is, thus, responsible for the buildup of the ML Ar structure on the Ag(111) sample, which we observed reproducibility using this procedure.

Our STM measurements of Ar on Ag(111) reveal highly ordered structures with rows of bright spots as shown in Figs. 1(a)–1(c). These row structures extend over huge terraces of the Ag(111) surface, where a terrace is always covered by just one orientation [see Fig. 1(c)] with no domain boundaries. On some terraces disordered structures are found, which sometimes coexist with the ordered structure on the terrace. Typical stable imaging conditions were  $V_S=50$  mV and  $I_T=50$  pA for the sample voltage and tunnel current, respectively. For voltages larger than  $V_S=2000$  mV we observed a tip-induced disordered structure.

The unit cell of the row structure [Figs. 1(a)–1(c)] has the dimensions  $d_1=1137$  pm and  $d_2=2507$  pm. A crucial structural element is the angle  $\alpha=84.3^\circ$  between  $d_1$  and  $d_2$ . Due to this angle two possible unit cells for each of the three

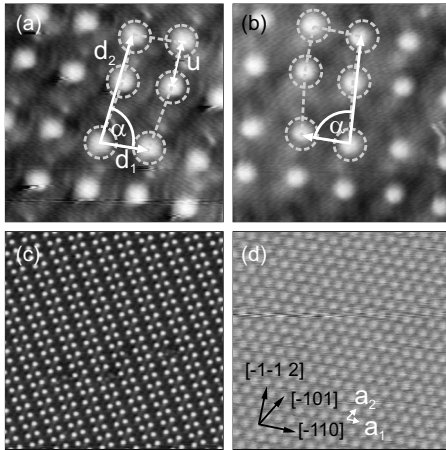


FIG. 1. (a)–(c) STM images of Ar monolayer on Ag(111) at 5 K. The Ar superstructure unit cells of the observed bright spot row structure are indicated. The short side  $d_1$  of the unit cell is aligned along a high-symmetry  $[-110]$  axis of the Ag(111) surface; experimental values:  $d_1=1137$  pm,  $d_2=2507$  pm, and  $u=1039$  pm. (a), (b)  $5 \times 5$  nm<sup>2</sup>,  $V_S=50$  mV,  $I_T=50$  pA. (a) Notice the slight misorientation of the large unit-cell side  $d_2$  of the Ar superstructure against the  $[-1-12]$  direction yielding  $\alpha_{\text{exper}} \approx 84^\circ$ . (b) A domain (reflection domain) symmetric with respect to  $[-1-12]$  as compared to (a). (c) Large area image of the row structure showing another domain rotated by  $60^\circ$  against the domain in (a),  $25 \times 25$  nm<sup>2</sup>,  $V_S=50$  mV,  $I_T=10$  pA. No domain boundaries have been found on terraces. Image (d) shows an atomically resolved  $5 \times 5$  nm<sup>2</sup> area of the clean Ag(111) surface ( $V_S=20$  mV,  $I_T=1$  nA), which could be used to determine the exact orientation of the Ar unit cell against the substrate. Relevant crystallographic directions as well as the substrate unit cell are indicated.

high-symmetry directions of the Ag(111) surface are found [Figs. 1(a) and 1(b)], resulting in a total of six possible domains for the superstructure. All of them have been imaged.

As indicated in Figs. 1(a) and 1(b) the long side  $d_2$  is divided into two parts, whereby  $u=1039$  pm. An image of the atomically resolved clean Ag(111) surface can be seen in Fig. 1(d). From this image the row alignment of the Ar structure relative to the substrate can be derived: Side  $d_1$  of the unit cell is aligned along the closed packed direction  $[-110]$  of the Ag(111). Side  $d_2$  deviates from the orthogonal  $[-1-12]$  direction by  $\pm 5.7^\circ$ , and side  $u$  is closely aligned along  $[-1-12]$ .

Bearing in mind that rare gas atoms tend to adsorb on surfaces in hexagonal structures (whereby even on hexagonal substrates slight distortions are possible<sup>5</sup>), we tried to develop a geometric model, which basically consists of two hexagonal structures, one above the other. One of the key experimental findings that supports our model for the surface structure of the monolayer of Ar is that STM images from  $V_S=-500$  mV up to 1500 mV reveal the same features. As reported by Hüfner *et al.*<sup>14</sup> the surface state of 1 ML of Ar on Ag(111) shifts close to or even slightly above the Fermi level. Thus the bright spot structure seems to be unrelated to the Ag(111) surface state. Nevertheless, the adsorption processes might be influenced by the surface state as has been shown for other systems.<sup>15,16</sup> Furthermore adsorption of just 1 ML Ar is proved by a temperature experiment: The sample

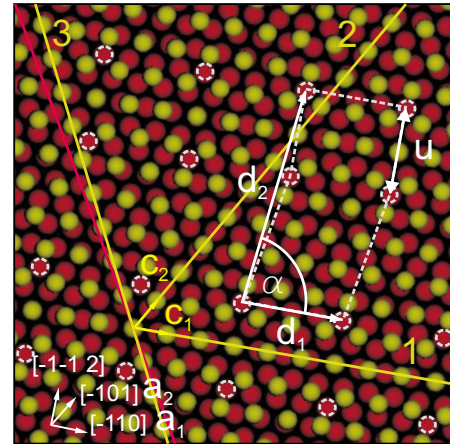


FIG. 2. (Color online) Model of the adsorbed Ar monolayer (yellow/light gray) on Ag(111) (red/gray). The dashed circles indicate Ag atoms that are uncovered but surrounded by three Ar atoms. The Ag layer (red/gray) is a perfect hexagonal structure with a lattice constant of 289 pm and angles of  $60^\circ$ . For the modeled Ar monolayer a stretching by a few percent of the nearest-neighbor distances as compared to the bulk value is found:  $c_1=385.3$  pm and  $c_2=412.9$  pm. The angle between directions 1 and 2 is  $60^\circ$ , and between 1 and 3 is  $116.6^\circ$ . Thus, the directions 1 and 2 of the Ar monolayer are coincident with the closed packed directions of the Ag lattice beneath. Direction 3 is rotated by  $\sim 3.4^\circ$  with respect to the Ag lattice. Angle  $\alpha_{\text{model}}=83.4^\circ$  (see text).

was heated up and the structure stayed stable up to 37 K. Multilayers would have desorbed at this temperature.<sup>7</sup>

In order to model the substrate lattice, the lattice parameters  $a_1=a_2=289$  pm for the Ag(111) structure were kept constant while—in the spirit of Ref. 5—the analogous parameters  $c_1$  and  $c_2$  of the argon lattice on Ag(111) were allowed to vary to yield slightly stretched or compressed structures (for bulk argon  $b_1=b_2=371$  pm). Moreover, the rotational angle between the lattices was also allowed to vary. The previously reported bonding of Ar and other rare gases on the Ag(111) surface in the low-coordination top site has been used as an initial starting point for our calculations.<sup>17,18</sup>

Figure 2 shows a sphere model of the Ar monolayer (yellow/light gray) on top of the Ag(111) lattice (red/gray) that matches the geometry and lengths of the experimental data for the following distances between the Ar atoms (see Fig. 2):  $c_1=385.3$  pm,  $c_2=412.9$  pm, with an angle between  $c_1$  and  $c_2$  of  $60^\circ$ ; consequently the angle between  $c_1$  and direction 3 in Fig. 2 is  $116.6^\circ$ . The dashed circles in Fig. 2 match very well with the geometry and the spacings of the experimentally found bright spot structure (a detailed comparison is given in Table I). Surprisingly the bright spots belong to Ag atoms which are not directly covered by an Ar atom, but are surrounded by three Ar atoms of the Ar monolayer. Notice that these very special positions appear in the regular pattern observed in the experiment. Consequently, we have to conclude that the STM images highlight these unique Ag positions.

The Ar atom positions repeat after 4 and 10 Ag lattice spacings along the high-symmetry directions 1 and 2 shown in Fig. 2, respectively. The Ar superlattice can, therefore, be expressed in the matrix notation as

TABLE I. Comparison of experimental distance and angle values of the Ar ML on Ag(111) (see Fig. 1) with the values derived from the model shown in Fig. 2. The uncertainties are the standard deviations.

	$d_1$ [pm]	$d_2$ [pm]	$u$ [pm]	$\alpha$
Experimental values	$1137 \pm 36$	$2507 \pm 54$	$1039 \pm 31$	$84.3^\circ \pm 1.8^\circ$
Model values	1156	2519	1001	$83.4^\circ$
Deviation relative to model	-1.6%	3.8%	-0.5%	

$$\begin{pmatrix} d_1 \\ d_2 \end{pmatrix} = \begin{pmatrix} 4 & 0 \\ -4 & 10 \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \end{pmatrix}$$

with  $a_{1,2}$  and  $d_{1,2}$  denoting the lattice vectors of the Ag surface and the Ar superlattice, respectively. One surprising feature of this structure is that direction 3 in Fig. 2 of the Ar superlattice is not in registry with the Ag high-symmetry direction. This direction is shifted by  $\pm 3.4^\circ$ , leading to six domains overall as a consequence. Therefore, the angle  $\alpha = 83.4^\circ$  (compare Fig. 2) is a consequence of this shift.

It is interesting to note that with our model the LEED images of Ar adsorbed on Ag(111) reported by Diehl *et al.*<sup>17</sup> might be explained. The LEED patterns show Ar superspots smeared out by an angle of about  $\pm 5^\circ$ , which is close to the mismatch angle of direction 3 (see Fig. 2). Considering a random distribution of the six domains of the row structures aligned with side  $d_1$  along one of the three  $[-110]$  symmetry directions of the Ag(111) substrate, one would expect LEED spots aligned with the Ag symmetry axes and additional spots broadened by angles plus or minus the mismatch angle of direction 3.

Since STM images yield the spatial variation of the local density of electronic states (LDOS), we have to establish a relationship between the geometric structure and the LDOS. The question that arises is why the local density of states at the dash-marked Ag positions in Fig. 2 is so much higher than on others so that these positions give rise to the bright spots in the STM images. Guided by the fact that the Ag seems to determine the adsorption structure of the Ar (directions 1 and 2 are in registry), we conclude that the Ar-Ag interaction might be strong enough to repel electrons of the Ag surface according to Pauli repulsion arising from the Ar electron orbitals. Thus, the substrate electrons will shift to favorable energy states to minimize the effect of repulsion.

Since the dash-marked Ag positions in Fig. 2 are almost uncovered by Ar, the repulsion might be minimized here, resulting in a favorable place for the electrons. Thus the Ar monolayer changes the image contrast in an indirect way since it is not directly visible, and the observed STM images are dominated by electronic effects.

In summary, we have presented STM measurements of an Ar monolayer adsorbed on Ag(111). We found large terraces with row structures of bright spots with the smaller unit side of the supercell aligned along the  $[-110]$  symmetry directions of the Ag(111) substrate. The geometry of the observed STM patterns can be explained by superimposing a slightly distorted hexagonal Ar lattice on the undistorted hexagonal lattice of the Ag substrate with the lattice constants presented in Figs. 1 and 2. The adsorbed Ar modulates the local density of states in a special manner depending on the location and arrangement of the Ar atoms relative to the underlying Ag atoms. The Ar atoms are not directly seen with STM, and according to our analysis Ag atoms directly sitting under hollow positions of the adsorbed Ar monolayer seem to dominate the imaging contrast. The presented model matches very well the experimental findings as can be seen from Table I. The comparably high deviation of the distance  $u$  within the supercell (Figs. 1 and 2) is due to the fact that this value can only be measured for each single bright spot unit cell and not over several as in the case of  $d_1$  and  $d_2$ . In the present work the Ar atoms are not directly seen with STM. This is in line with STM investigations of a Xe film on Ag(111) by Hövel *et al.*,<sup>10</sup> where a Xe monolayer had been detected indirectly by  $dI/dV$  curves. However, Horch *et al.*<sup>19</sup> reported atomically resolved STM images of a full ML of the heavier Xe on Pt(111). Therefore, further experimental studies of noble gas adsorption on different metal substrates are highly desirable to fully understand the STM imaging of rare gas adsorption structures. It appears necessary that in future theoretical studies of the formation of noble gas monolayers on metal substrates for the noble-gas/noble-gas and noble-gas/metal interactions are extended. The extension should cover van der Waals and dipolar forces, but also many body noncentral forces, and even vibrational effects should be taken into account. Also the peculiar appearance of the Ar structure as seen with STM constitutes a challenge for theory.

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