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Observation of domain-wall dynamics in rare-gas monolayers at $T = 5$ K

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Abstract

We have investigated the system Xe on graphite in the submonolayer coverage regime using scanning tunneling microscopy (STM) at $T = 5$ K. The Xe adlayer forms hexagonal domains in a honeycomblike superstructure. Dynamic properties of the domain-walls could be studied for the first time by a series of STM images, revealing a time-dependent overlayer structure with the spontaneous creation and disappearance of the dislocations. In addition the influence of Xe island step edges on the local structure of the domain-walls of the Xe adlayer is discussed.

Keywords: Graphite; Noble gases; Physical adsorption; Scanning tunneling microscopy; Surface structure, morphology, roughness, and topography; Surface thermodynamics (including phase transitions)

1. Introduction

Rare gases are prototype systems in surface science due to their spherical symmetry and closed-shell electronic structure. In view of the geometric properties, physisorbed rare-gas monolayers provide ideal testing grounds for two-dimensional adsorbate phases and phase transitions, as they may exhibit — depending on the substrate used — a large variety of different adsorbate phases.

The advent of scanning tunneling microscopy (STM) and its application at low temperatures has now opened the possibility of real-space atomic-scale studies. Local information in a static as well as a dynamic sense on, for example, domain boundaries becomes accessible which are either inaccessible to diffraction methods due to their non-periodic nature or, for periodic features, beyond the intensity limits of such experiments.

Here, we will focus on the system Xe on graphite, which has attracted great attention in the past [1]. The lateral interaction of the rare gas atoms is of the same order of magnitude as the graphite surface potential [2], giving rise to a wealth of different adsorbate phases in the monolayer coverage regime. The Xe monolayer forms a commensurate $(\sqrt{3}\times\sqrt{3})R30^\circ$ phase on graphite at temperatures below $T = 60$ K [3]. As this $(\sqrt{3}\times\sqrt{3})R30^\circ$ lattice constant is ca. 2% smaller than the Xe bulk lattice constant, Xe forms an incommensurate phase in the submonolayer regime (or for the monolayer at $T > 70$ K [3]), because compressive strain is needed for the formation of the commensurate phase. This incommensurate phase exhibits a domain structure of commensurate domains separated by incommensurate domain-wall regions, which form a honeycomblike array [3,4]. The incommensurate Xe adlayer may

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be rotated for energetic reasons [3,5] in agreement with the theory of Novaco and McTague [6]. In a recent STM study [7], we found evidence for tilted domain-walls with respect to the atomic rows of the Xe layer, which have been discussed previously in theoretical work [8–11] but could not be observed by diffraction techniques [3] due to the lack of intensity.

In this paper, we will report on additional local and dynamic properties of domain walls as revealed by STM. The large body of theoretical work on physisorbed rare-gas systems on graphite comprises predictions on the dynamical properties [12–14] of these systems, which are now experimentally accessible by low-temperature STM.

2. Experimental

The experiments were performed in an ultrahigh vacuum (UHV) two-chamber surface-science facility, which has been described elsewhere [15]. It consists of a preparation chamber equipped with a high-resolution hemispherical energy analyzer for ultraviolet photoelectron spectroscopy (UPS) and an analysis chamber containing a low-temperature STM operating at $T=5$ K [16]. The air-cleaved highly oriented pyrolytic graphite (HOPG) substrate was heated in UHV for 1 h at $T=870$ K prior to the experiments. We checked its cleanliness by ultraviolet photoemission.

The sample was mounted on a manipulator and cooled to below $T=50$ K by means of a liquid-helium flow cryostat. This manipulator allows cold sample transfer between the two chambers of the surface-science facility [15]. A submonolayer of Xe was dosed onto the sample by controlling the partial pressure with a leak valve. The Xe coverage was cross-checked by the Xe 5p photoemission signal during the adsorption process [17]. After adsorption the sample was transferred into the STM, which was cooled to 5 K. The cool-down process of the sample takes several minutes. The timescale for reaching thermal equilibrium at $T=$ 5 K can be much longer, but the sample will be close to the low temperature ground state after the cool-down process. However, differences in the adsorption temperature as the starting point of this process may influence the final structure of the Xe adlayer. The coverage could be re-checked by photoemission after the STM experiments had been performed.

3. Results and discussion

Fig. 1 shows a series of three atomically resolved STM images each displaying a surface area of 14×14 nm^2 with a nearest-neighbor distance inside a domain of 0.45 nm with an estimated error of ±0.05 nm. This is close to the expected $(\sqrt{3}\times\sqrt{3})$R30° value and rules out the possibility that the atomic structure is due to the graphite substrate. The Xe atoms form irregular hexagonal patches of typical diameters between 5 and 10 nm and are separated by domain walls, which appear in the constant current STM signal as a smooth contrast several atomic rows in width. Xe atoms forming domain walls are slightly darker in the image than the surrounding Xe domains. The origin of this contrast has been discussed previously [7]. The STM images of Fig. 1 were scanned at a tunneling current of 0.1 nA and a tip bias of $+3.2$ V with respect to the sample. The topographs have been measured consecutively from the same surface area as proven by the bright adsorbate spot in the upper left part of each image. Recording one image took 10 min.

As can be seen from Fig. 1a the Xe adlayer forms irregular domains. In Fig. 1b the adlayer structure has significantly changed and a dislocation was formed in the lower right part of the image. The dislocation has completely disappeared in Fig. 1c and all visible domains have resumed a more hexagonal shape. We have observed numerous similar events in a long series of 23 images. We were surprised to observe these dynamics at a temperature as low as $T=5$ K.

Theoretical studies [12–14] have discussed the formation of dislocations for an incommensurate two-dimensional solid phase exhibiting a periodic domain wall structure. Coppersmith et al. [12,13] predicted that these incommensurate phases may be unstable to the spontaneous creation of dislocations independent of temperature and consequently

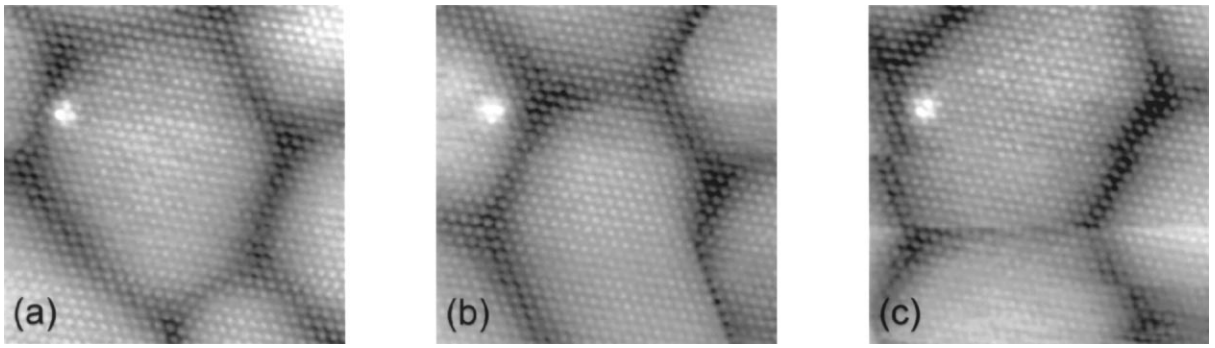

Fig. 1. A series of three subsequent STM images showing the same surface area. The Xe adlayer forms distorted hexagonal domains changing from one frame to the next. In (b) a dislocation is formed. Image parameters: scan area, $14 \times 14\ \mathrm{nm}^2$; tip bias, 3.2 V; current, 0.1 nA.

these phases are liquids at all temperatures. A crucial parameter for the stability of incommensurate phases is the number of different commensurate domains p. In the particular case of honeycomblike arrays of domain walls Coppersmith et al. [12,13] finds stable structures only for $p \geq 7.5 \pm 1.5$ and one would therefore expect instability for the system Xe on graphite displaying $p = 3$ possible commensurate domains for the $(\sqrt{3} \times \sqrt{3})\mathrm{R}30^\circ$ adlayer structure. The second requirement for the spontaneous creation of dislocations in the adsorbate layer is the weakly incommensurate nature of the adlayer. In other words, the adlayer must be in the vicinity of the commensurate–incommensurate transition.

The compressive strain needed for approaching the commensurate structure originates in this experiment from an adsorbate contaminated surface, as the submonolayer coverage was obtained by UPS controlled adsorption. Contrary to the regular hexagonal Xe domains observed if the same coverage was adsorbed without UPS on a clean graphite surface, this results in a distorted domain structure, which has been discussed before [7]. The adsorbates create distortions of the regular honeycomblike domain walls as the presence of adsorbates creates a local preference for one certain domain leading to distortions of the wall structure. The contamination-induced strain leads to a pinning of the distorted domain structure, which then locally comes close to the commensurate phase. Though we cannot completely rule out the influence of the STM tip while recording the images, it seems unlikely to be a measurement-induced effect, as we did not observe such spontaneous creation of dislocations for regular adlayer structures in long series of STM images. This clearly shows the instability of the distorted domain structure, which may exist even at $T = 5$ K as described above. In addition to the thermal contribution energy might be transferred into the system, for example, by inelastic tunneling processes.

Additional aspects of local properties of the domain-wall structure can be derived from its behavior at an island step edge of a large close-packed Xe island. The preparation procedure described above yields typical island sizes of the order of some micrometers in diameter. The STM image of Fig. 2a displays a surface area of $65 \times 100\ \mathrm{nm}^2$ with a step edge of a close-packed Xe island. The images of Fig. 2 were recorded at a tunneling current of 0.1 nA and a gap voltage of $+3.2$ V with respect to the sample. Simultaneous imaging of the Xe domain structure and a Xe island step edge in large area scans is a demanding task as on the one hand, scanning of the Xe area requires a high stability of the tip perpendicular to the surface, and on the other hand the Xe step edge has to be imaged.

The honeycomblike structure of the Xe domains exhibits no major distortions at the step edge. The island edge runs along close-packed directions of the Xe atomic rows, which can be verified by

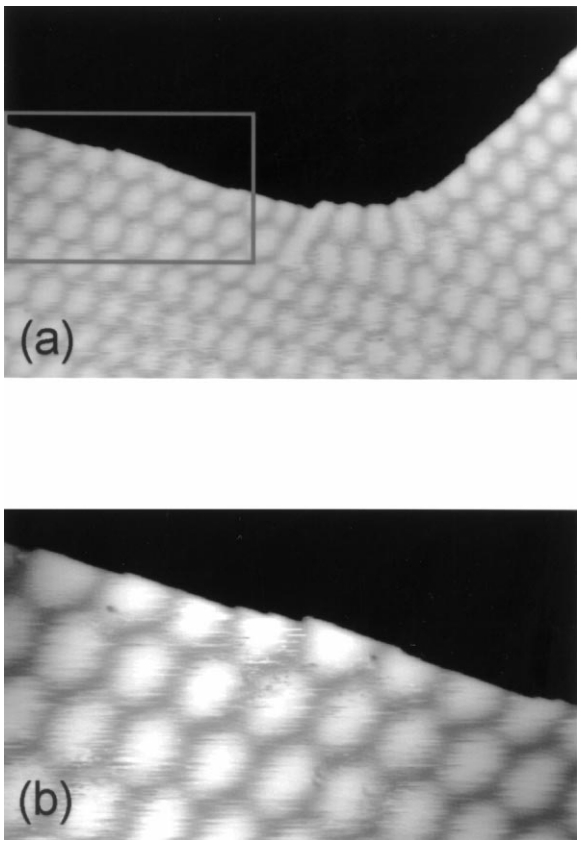

Fig. 2. (a) STM image of step edge of a close-packed Xe island. The honeycomblike domain-wall structure shows no major distortions in the vicinity of the step edge. Domain-walls have a perpendicular orientation with respect to the step edge. Image parameters: scan area, $65 \times 100\ nm^2$; tip bias, 3.2 V; current, 0.1 nA. (b) Near-atomic resolution STM image of the marked area in (a). Kinks along the close-packed step are preferentially adsorbed in domain-wall regions of the Xe adlayer. Image parameters: scan area, $25 \times 45\ nm^2$; tip bias, 3.2 V; current, 0.1 nA.

the change in orientation of the step edge from the left part to the right part of Fig. 2a by an angle of 120°. The micrograph of Fig. 2b displays the marked area of $25 \times 45\ nm^2$ in Fig. 2a with atomic resolution of the steps. Kinks in the Xe step edge are clearly visible, which often are located in domain wall regions. This indicates an energetic preference for the adsorption of Xe atoms within the commensurate Xe domains as has been found previously [18].

We note that the domain walls of the Xe adlayer are perpendicular to the close-packed step edge of the Xe island, which implies a tilt of the domain walls by 30° with respect to the Xe atomic rows. This is different from the tilt angle of 10–15°, which we found inside the Xe islands far away from step edges for undistorted areas as large as $50 \times 50\ nm^2$ [7]. The step edge cuts through the hexagonal domains at their largest diameter. This maximizes the number of Xe atoms adsorbed in commensurate adsorption sites within the domain structure at the step edge and again reflects the energetic preference of these adsorption sites [18].

In the vicinity of the change in orientation of the step edge the Xe domains are somewhat distorted, but the domain walls still run perpendicular to the island step edge. Long straight Xe island step edges and an undistorted honeycomblike domain pattern as well as the orientation and position of the step edge relative to the domains indicate a Xe structure being close to its equilibrium state.

4. Conclusion

We have studied submonolayers of Xe on HOPG using low-temperature STM. Xe forms an incommensurate adlayer with a honeycomblike pattern of domain walls in this coverage regime. In the present paper we focussed on local details of these domain walls. As a new experimental result, dynamic properties of the Xe overlayer could be revealed at temperatures as low as $T = 5$ K confirming the theoretically predicted spontaneous creation of dislocations in the Xe structure. Static properties of the honeycomblike domain-wall structure in the vicinity of Xe island step edges have been obtained and could be related to earlier studies.

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