Dynamics and nano-clustering of alkali metals (Na, K) on the Si(1 1 1)-(7 × 7) surface

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Abstract

We report scanning tunneling microscopy and work function measurement studies on Na (K) adsorption on the Si(1 1 1)-(7 × 7) surface at room temperature and sub-monolayer coverage. A systematic comparison is reported on their dynamics and clustering behaviors to reveal the atomic size effect. We find that both Na and K form two-dimensional gases at room temperature and coverage < 0.08 ML. K shows faster diffusion speed and stronger charge transfer to the Si substrate as compared to Na. At coverage > 0.08 ML, both Na and K form magic clusters consisting of six Na(K) atoms. However, the clustering behaviors of Na and K are very different. In the K case, there is no intermixing between K and Si atoms, and the K clusters are very mobile inside the half (7 × 7) unit cell, whereas Na clusters are unmovable due to the site-exchange between Na atoms and the Si adatoms.

Keywords: Alkali metals; Scanning tunneling microscopy; Clustering; Dynamics

1. Introduction

Alkali metal (AM) adsorption on semiconductor surfaces is one of the classical problems in surface science because of the prototypical nature of alkali metals and the important applications such as surface metallization, catalytic reaction and work function reduction. The intensive investigations in the past decades have brought much insight to the interface structure, electronic property and the nature of the chemical bonds for various AM/semiconductor interfaces. However, compared with ordered AM overlayers formed near monolayer coverage, such as the Si(1 1 1)-(3 × 1)-Na [1,2], the adsorption configuration and dynamics of AM atoms at the initial coverage, which may be fundamentally more important, has been much less understood. For example, sub-monolayer AM (Na, K, Cs) adsorption on the Si(1 1 1)-(7 × 7) surface has been studied by Magnusson et al. [3], Reihl et al. [4] and Weitering et al. [5] using photoelectron emission spectroscopy.
(PES), and charge transfer from AM atoms to the Si adatoms at the initial coverage has been reported. However, the atomic configuration and dynamics of AM on the Si(111)-(7×7) surface is only poorly understood. Due to the hydrogen-like electron structure of AM, it had been assumed that AM atoms simply adsorb on top of the Si adatoms [3–10], similar to the case of atomic hydrogen on the Si(111)-(7×7). On the other hand, Watanabe et al. [11] reported triangular patterns in the empty state scanning tunneling microscopy (STM) images of K adsorption on the Si(111)-(7×7) at the initial coverage, and suggested that K atoms are adsorbed around the Si rest-atoms. However, Gorelik et al. [7] observed that K atoms picked up by the STM tip could significantly modify the tip state and induce triangular pattern in the empty state images. In their theoretical work, Cho and Kaxiras [12] suggested that individual K atoms should move rapidly on the Si(111)-(7×7) surface at room temperature (RT), thus being invisible to the STM tip. In our recent work, we employed variable temperature STM, work function measurement and first-principles calculations and clarified that Na adsorption on the Si(111)-(7×7) surface is a two-stage process, from two-dimensional gas to nano-cluster array depending on the Na coverage [13,14].

Because of the extreme sensitivity of AM to contaminations, an extremely-high vacuum (XHV, <1×10^{-11} Torr) is necessary for the study of AM adsorption. Soukiassian et al. [15] showed that a small amount of contamination can effectively change the growth mode of K on the Si(100) surface. We suggest that unintentional contaminations, either from the residual gas in the vacuum chamber or from the AM source due to insufficient outgassing, may be the origin of the uncertainties and controversies in the previous STM observation at low AM coverage.

In this paper, we report a systematic study of the dynamics and clustering of Na and K on the Si(111)-(7×7) surface at room temperature and low coverage, by using STM, work function measurement and first-principles calculations. The behaviors of Na and K are compared in order to reveal the atomic size effect. We find that both Na and K form a two-dimensional gas at coverages <0.08 ML. K atoms diffuse faster than Na atoms at room temperature and induce larger charge transfer to the substrate. At a coverage >0.08 ML, both Na and K form magic clusters consisting of six Na (K) atoms. However, the dynamics of Na and K clusters are very different; K clusters show weaker interaction with the substrate and higher mobility as compared with Na.

2. Experiment

The experiments were carried out in an XHV (<1×10^{-11} Torr) STM in a specially processed stainless-steel chamber (NKK “clean-Z”) to minimize contaminations. The system was equipped with a high-resolution electron energy loss spectroscopy (HREELS) setup, which we have employed to measure the surface work function change (Δϕ) with an accuracy of 20 meV [16]. Phosphor-doped (0.3 Ω cm) Si(111) wafer was used as the substrate, which was cleaned supersonically in acetone, ethanol and deionized water prior to loading into the vacuum. The Si(111)-(7×7) surface was prepared by standard flashing to 1100°C. Na (K) was evaporated from well-outgassed commercial dispensers (SAES Getters, Italy) to the Si surfaces held at RT, keeping the pressure rise during evaporation below 3×10^{-11} Torr. For STM investigations, electrochemically etched single-crystal tungsten tips were used. All images were obtained in constant current mode, with sample bias and the tunneling current of 20 pA.

To calibrate the absolute Na coverage, we first measured the Na flux by using the well-known Si(100)-(4×1)-Na surface. It has been reported that the Si(100)-(4×1)-Na surface forms upon the deposition of 1/4 ML (here 1 ML refers to the atomic density on the Si(100) plane, i.e., 6.8×10^{14} cm^{-2}) Na on the clean Si(100)-(2×1) surface at RT, with a work function reduction of −1.5 eV [17,18]. We have confirmed by STM that the surface is indeed fully converted to perfect (4×1) reconstruction at Δϕ = −1.5 eV, in good agreement with the previous reports. The flux of our Na source is calibrated by recording the evaporation time for preparing the Si(100)-(4×1)-Na
surface. The Na coverage on the Si(111)-(7×7) surface can then be calculated by the evaporation time under the same Na flux (the sticking coefficients of Na on both Si(111) and Si(100) are assumed to be 1, which is reasonable for small coverage at RT \[17,18\]). To ensure a stable Na flux, we frequently check the \(\Delta\phi\) value under the standard evaporation dose. We believe that the accuracy of our coverage determination should be within 5%.

For K, STM observations combined with work function measurements are also performed for each K coverage. However, the absolute K coverage is more difficult to calibrate, as K does not form a phase with distinctive coverage on either the Si(100) or the Si(111) surface. However, as we will report in this paper, the behaviors of K and Na are very similar in the 2D gas phase (judged from the contrast modulations). Thus in our study, we assume that K has the same critical coverage for clustering as Na (0.08 ML), and this is used for the calibration of the flux and absolute coverage of K (hereafter 1 ML refers to the atomic density on the Si(111) plane, i.e., \(7.84 \times 10^{14} \text{ cm}^{-2}\)).

3. Results and discussion

3.1. Na adsorption

In Fig. 1 we show the coverage-dependent filled-state STM images of the Si(111)-(7×7) surface with increasing Na coverage up to 0.10 ML. We observe two main features in these images: (1) a change of the image contrast in Figs. 1(b)–1(f) as compared with the clean Si(111)-(7×7) surface in 1(a). The change of the surface can be demonstrated more clearly by subtracting the clean (7×7) image (1(a)) from these images (1(b)–1(f)), as shown in Figs. 1(h)–1(l). Well-defined triangle and lobe-like patterns can be observed in 1(i) and 1(k), respectively. (2) The presence of noisy features in Fig. 1(b)–1(f)—such noise is intrinsic to the Na-adsorbed surface at low coverage, independent of the STM tip conditions. In fact, at room temperature and coverage <0.08 ML, the Na atoms are moving fast over the (7×7) surface to form a two-dimensional gas \[13,14\], and charge transfer from the moving Na atoms to the Si surface results in contrast modulation patterns in STM images as a time-averaged effect.

At coverage >0.08 ML, Na magic clusters appear in STM images. The Na clusters have identical three-fold symmetric appearance with three protrusions and they can adsorb in either the faulted half unit cells (FHUC) or the unfaulted half unit cells (UHUC). The density of Na magic clusters increases linearly with the Na coverage up to 0.22 ML (Fig. 2). For coverage higher than 0.22 ML, we observed a decay of the Na magic clusters. The number of the magic clusters decreases and irregular spots emerge, indicating...
that the magic clusters have been converted to irregular clusters to involve excess Na atoms. Upon the formation of the irregular clusters, the surface becomes disordered. If one counts only the number of the magic clusters, its density decreases above the coverage of 0.22 ML. Thus there are three adsorption stages: (I) a gas phase (< 0.08 ML); (II) formation of Na magic clusters (0.08–0.22 ML); (III) decay of Na magic clusters (> 0.22 ML). A statistical counting of the number density of Na clusters as a function of the Na coverage is plotted in Fig. 3. Note that the slope of the curve in Section 2 corresponds to the number of Na atoms per cluster, which is derived to be six.

In response to the structural change, the corresponding work function curve shown in Fig 3(b) also indicates three regions, and two inflection points can be observed at 0.08 and 0.22 ML, which correspond to the starting of Na magic cluster formation and the maximum density of Na magic clusters, respectively. As the work function change is related to lifting of the surface Fermi level due to charge transfer from Na to the Si surface, our results nicely demonstrate a change of the charge transfer from the Na atoms to the Si substrate, driven by the structural change on the surface. Upon the formation of Na magic clusters, the charge transfer is suppressed (a reduced slope in the \( \Delta \phi \) curve), while it increases with the disordering of the surface at coverage > 0.22 ML (an increase of the slope). Our results can well explain the previous reported work function observations for the same system [11,19,20].

In Fig. 3 we also separately plot the distribution of Na magic clusters in the FHUC and UHUC, respectively. As seen at the early stage of Na magic cluster formation, the clusters prefer to adsorb on the FHUCs than the UHUCs. However, interestingly, this tendency is reversed at the coverage around 0.16 ML. More Na magic clusters

Fig. 2. (a) and (b) The formation of Na magic clusters at 0.10 and 0.22 ML, respectively. In the image (b), the decay of Na magic clusters starts, as marked by an arrow. (c) The decay of Na magic clusters at 0.26 ML.

Fig. 3. (a) Surface work function change (\( \Delta \phi \)) as a function of the Na coverage. (b) Corresponding number densities of Na magic clusters in FHUC and UHUC, and the total number density of Na magic clusters.
appear in the UHUCs than the FHUCs. This phenomenon can be explained by two effects: (1) as the Na coverage increases, the chemical potential of Na also increases and smears out the energy difference between the FHUC and UHUC; (2) a decay of the Na clusters takes place before the full occupation of the surface (which is believed to be due to the insufficient diffusion at high coverage)—more Na clusters decay in the FHUCs as compared with the UHUCs.

The Na magic cluster is very stable once it forms on the surface. It never decomposes or moves from one unit cell to another, in contrast to many other cases such as the Pb [19] and Tl [21] where the cluster mobility is commonly observed. If one tries to move a Na cluster by the scanning tip, one simply destroys the cluster and creates a hole-like feature, as shown in Fig. 4. This fact strongly suggests that a certain irreversible process takes place during the formation of Na magic clusters, which results in a tight bonding of the cluster to the substrate. This is exactly supported by our first-principles calculations, where the most stable structure model of the Na magic cluster involves a site-exchange between Na atoms and the Si center adatoms: the three Si center adatoms are displaced by three Na atoms and moved to the center of the half unit cell to form a trimer there [13].

3.2. K adsorption

K shows very similar behavior in the low coverage range (<0.08 ML). In Fig. 5 we show the filled state STM images of a K-adsorbed surface with increasing K coverage up to 0.08 ML. We see similar contrast change in these images as compared with the Na case. Initially the FHUC gets brighter and the UHUC becomes relatively darker, and at higher coverages the UHUC also becomes brighter. If we subtract the image of the clean (7×7) surface from these images, we obtain triangular patterns at the lower coverage (Figs 5(g)–(j)) and lobe-like patterns at higher coverages (Figs 5(k) and (l)). However, we also notice differences in these images compared with the Na case. Firstly, the contrast change is significantly stronger, and the patterns much clearer than the Na case. This can be understood by a stronger charge transfer from K atoms to the surface compared with Na atoms, as is consistent with previous studies of AM adsorption on either the Si(100) or the Si(111) surfaces [3–5,22]. Secondly, K-adsorbed surfaces are noise-free, indicating that K atoms are diffusing faster on the surface than Na atoms, and the STM tip is completely unable to trace the motion of K atoms.

To understand the mobility of K atoms on the Si(1 1 1)-(7×7) surface, we have performed...
first-principles calculations. The detail of our calculation method is the same as the Na case [13]. We find that the diffusion barrier for a K atom to move around the “attraction basin” centered on the Si rest-atom is 30 meV, agreeing with Cho’s value of 50 meV as calculated by using a $2 \times 2$ unit cell [12]. Such a small diffusion barrier allows a fast hopping of $10^{13}$ hops/s at room temperature inside the basin. For comparison, the corresponding diffusion barrier for Na is 140 meV, which allows a hopping frequency of only $10^6$ hops/s at room temperature. Thus our calculation agrees with our experiment very well.

At higher coverage (>0.08 ML), K also forms magic clusters, as shown in Fig. 6, but its clustering behavior is very different from Na. We find that K clusters only form on the FHUC, leaving the UHUC completely empty, consistent with the observation by Watanabe et al. [11]. However, in contrast to their report of only a dimer-like K cluster, we observe two different types of K clusters. The first type (A) is asymmetric, and roughly consists of three parts in the filled state STM images: (1) a “bar” in the corner, (2) a “spot” in the opposite lateral side of the “bar” and (3) a blur feature in another corner (see Fig. 6(b) for details). Depending on the relationship between (1) and (3), the cluster can have different chiralities. The other type (B) is mirror-symmetric (Fig. 6(c)), which consists of two bright spots sitting along the mirror line of the triangular $(7 \times 7)$ unit cell (it may correspond to the dimer-like cluster reported by Watanabe et al. [11]). Thus, there are totally nine possible configurations of K clusters, including six A-type cluster (three equivalent rotational directions with two different chiralities) and three B-type clusters (three rotational directions).

The interesting observation in our experiment is that, at room temperature a K magic cluster is jumping inside the half $(7 \times 7)$ unit cell, among the nine different configurations. For examples, in Fig. 7, we show a series of image frames during a continuous STM scanning. The interval between two frames is 13 s. For clarity, we deleted duplicated frames (which means no change of the cluster between two scans). We observe the rotation of the B-type cluster among the three equivalent directions, the flipping of the chirality of the A-type cluster, as well as the exchange between A-type and B-type clusters. Interestingly, several rules are strictly obeyed in our observation of thousands of jumping events: (1) when an A-type cluster changes its chirality, the “bar” is flipped from one corner to another, while the “blur feature” is kept in the original corner—a different process (i.e., flipping the blur feature while keeping the bar intact) never takes place; (2) when an A-type cluster exchanges with a B-type cluster, the corner part of the B-type cluster and the “blur
feature” of the A type cluster remain in the same corner; (3) the A-type cluster cannot rotate to change its direction, unless mediated by the B-type cluster. Based on these strict rules, a K cluster can jump among the nine different configurations only along strict routes as shown in Fig. 7(j).

In Fig. 8 we plot the number density of the K clusters as well as the corresponding work function change of the surface, as a function of the K coverage. We observe a larger work function change as compared with the Na case. For example, at 0.08 ML, the work function change is –1.2 eV for K and –0.8 eV for Na. This difference agrees well with our STM observation of a stronger contrast modulation, which also suggests a stronger charge transfer in K than Na. In addition, similar to the Na case, we observe a clear relationship between the structure and surface work function change. The slope of the work function curve decreases upon the formation of K magic clusters, indicating that the charge transfer from K atoms to the surface is suppressed by the formation of magic clusters. This can be understood because magic clusters normally have closed shell electronic structures, thus being more stable and reluctant to donate its charge to the surface.

We have also derived the number of K clusters in each magic cluster from the slope of the curve in Fig. 8. We note that although there are two (A, B) different types of K clusters; fortunately, they must consist of the same number of K atoms in order to be exchangeable. Interestingly, the calculation shows that each K cluster also contains six K atoms, same as the Na magic cluster. However, the real structure model of the K magic cluster and the origin of its dynamic behavior are still unknown due to the complex structure of K clusters. In fact, as implied by the high mobility of the K clusters, it is likely that the STM image itself also reflects a time-averaged picture of moving K atoms composing the cluster. For example, the blur feature in the A-type cluster can be a diffusing K atom around the corner, similar to the blur feature formed by one Pb atom in a half-(7 × 7) unit cell [19]. More experiment and theoretical efforts are called for for understanding the K clustering and dynamics.

An experimental fact which is helpful to understand the structure of the K cluster is the
deposition and removal of the K magic cluster on the Si(1 1 1)-(7/7) surface by the STM tip. Unlike the Na magic cluster which is unmovable once formed, the K magic cluster as a unit can be deposited to or removed from the surface, as shown in Fig. 9. When a K cluster is removed from the surface by tip scanning, the Si(1 1 1)-(7/7) unit cell is completely recovered. This fact indicates no intermixing between the K and Si atoms.

4. Summary

To summarize our paper, we have performed systematic STM and work function measurement studies on Na (K) adsorption on the Si(1 1 1)-(7/7) surface at room temperature and low coverage. We find that both Na and K form two-dimensional gases at coverage \( \theta > 0.08 \) ML. K has a smaller diffusion barrier on the surface compared with Na, so they diffuse faster than Na atoms. K adsorbed Si(1 1 1)-(7/7) surface is noise-free, in contrast to the Na case where the surface is intrinsically noisy. In addition, we observed stronger charge transfer from K atoms to the Si substrate. At coverage \( \theta > 0.08 \) ML, both Na and K form magic clusters consisting of six Na (K) atoms, which suppresses the charge transfer from Na (K) atoms to the Si surface. Very
different clustering behaviors are observed for Na and K. Na clusters are identical and three-fold symmetric, whereas K clusters can take two types: totally, nine different configurations. Moreover, the Na cluster is unmovable due to the site-exchange between Na and Si atoms, the formation of K cluster does not include such intermixing, and K clusters can jump among nine different configurations (following several strict rules), and they can be deposited on or removed from the surface as a unit. These observations reveal the atomic size effect on the AM adsorption, i.e., larger atoms have higher diffusivity and weaker interaction with the substrate.

References


