Unusual diffusivity and clustering of alkali metals on the Si(111)-7x7 surface

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Abstract

In this paper I review our recent experimental and theoretical works on the behaviors of submonolayer alkali metals (Li, Na, K, Cs) on the Si(111)-7x7 surface. The important aspects in the experimental preparation are discussed. While Li forms clusters even at the initial coverage, all other alkali metals (Na, K, Cs) form two-dimensional (2D) gases at room temperature and low coverage, due to their unusual high diffusivity on the surface. At higher coverage, cluster formation is observed, but with very different behaviors for Na, K, and Cs. Issues relative to the phase transition with increasing coverage are discussed: (1) the mechanism for the 2D gas formation; (2) the effect of 2D gas formation on STM observations; (3) The effect of structure on the charge transfer from alkali metals to the surface; (4) the exchange of alkali metal atoms with the Si adatoms during the cluster formation.

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1. Introduction

The Si(111)-7x7 surface is the first surface studied by the scanning tunneling microscopy (STM) when it was invented 20 years ago. The large unit cell, 2.7 nm in size, makes it a promising candidate for use as the substrate for self-assembling various adsorbates, from metals to organic molecules [1,2]. Alkali metals (AM) adsorption has received considerable attention since they possess simple hydrogen-like electronic structures and are regarded as prototypical systems [3–12]. 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. For examples, the effects of charge transfer from AM to the Si substrates and the surface metallization have been well understood based on photoelectron emission spectroscopy (PES) [3,4] and work function (WF) studies [5,6]. However, surprisingly, the basic adsorption geometry of AM on Si surfaces, particularly at the sub-monolayer (ML) coverage, have not been well understood, though some results have been published on direct observations of AM adsorption by STM [7–10]. In this paper, I review our recent experimental and theoretical works on the adsorption of submonolayer AMs on the Si(111)-7x7 surface, with emphasis on the dynamics and charge transfer at the initial coverage, and the formation of magic clusters at higher coverages.

2. Experimental aspects

Because of the high reactivity of AM to the residual gases in vacuum, and the sensitivity of STM to surface contaminations, extremely high vacuum (XHV, \textless 1 \times 10^{-11} \text{Torr}) is necessary for the study of AM adsorption by STM. For example, Soukiassian et al. showed that a small amount of contamination can effectively change the growth mode of K on the Si(100) surface [11]. We suggest that unintentional contaminations, either from the residual gas in the vacuum chamber or from the AM source itself, may be the origin of the uncertainties and controversies in the previous STM observation at low AM coverage.
In addition to an extremely high vacuum, great care has to be taken to avoid the contamination from the AM doser itself and from the heated doser stage during deposition. For the commercial doser we used (SAES Dispensers, Italy), a prolong degassing and pre-evaporation of a considerable amount of AM is needed to clean the doser. The pressure rise during evaporation was normally kept below $3 \times 10^{-11}$ Torr in our experiment.

The calibration of the AM coverage is another major issue. AM adsorption induces significant surface WF change, which has been widely used for calibrating the relative AM coverage \cite{5,6}. The WF can be measured by the secondary electron cut-off energy in PES or Auger spectroscopy. The accuracy of which is limited by the energy resolution of the photon (PES) or electron (Auger) beam. To improve the accuracy of our WF measurement, we used a combined STM-high resolution electron energy loss (HREELS) system. The WF measurement can be as accurate as 20 meV, due to the high-energy resolution of the system. The calibration of absolute AM coverage is, however, very difficult. The idea of counting the number of AM atoms in the STM images was found unsuccessful because of the invisibility of AM atoms in the STM images due to their unexpected mobility \cite{12}. However, in the particular case of Na/Si(111)-7x7, we succeeded to calibrate the absolute Na coverage by using the well-known Si(100)-4x1-Na surface \cite{12}.

### 3. 2D gas phase

Because of the hydrogen-like electronic structure of AM, it had been assumed that AM atoms simply adsorb on top of the Si adatoms, similar like the case of atomic hydrogen on the Si(111)-7x7 \cite{3–10}. This appears to be true for Li. Hasegawa et al. reported individual Li atoms can be observed in STM by three brighter Si adatoms in a half 7x7 unit cell \cite{7}. We also observe such adsorption sites, but we suggest they might be more likely Li clusters. The density of the Li clusters increases linearly with increasing Li coverage from the beginning, indicating no invisible Li atoms in the STM images \cite{13}. We therefore exclude Li in the following discussion.

However, as has been pointed out by Cho and Kaxiras, AM atoms on the Si(111)-7x7 surface do not actually adsorb ‘on top’ of the Si adatoms, but rather on several high-coordination sites surrounding the Si rest-atoms. These sites define a valley in the potential energy surface, i.e. the so-called ‘basin’ \cite{14}, as indicated in Fig. 1 \cite{12}. There are three basins in each faulted half unit cell (FHUC) or unfauluted half unit cell (UHUC). AM atoms can diffuse along the potential valley by overcoming the corresponding energy barrier.

For Na, although the binding energy is high (~2.2 eV), the diffusion barrier is relatively quite small. The energy barrier for a Na atom to hop inside the ‘basin’ is 0.14 eV, allowing for about $7 \times 10^{10}$ hopping/s at 300 K. The diffusion barrier is 0.36 eV ($1 \times 10^{6}$ hopping/s at 300 K) for a Na atom to move among different basins in the same unit cell and 0.42 eV ($1 \times 10^{5}$ hopping/s at 300 K) for moving across the unit cell boundaries. As a result, Na atoms can move freely on the Si(111)-7x7 surface at room temperature (RT) and low coverage, forming a 2D adatom gas system \cite{12}.

It was also found that with the increase of atomic size from Na to Cs, the diffusivity of AMs on the Si(111)-7x7 surface increases. As a result, all alkali metals (except Li) form 2D gas at RT and low coverage. For example, the diffusion barrier for a K atom to move around the ‘basin’ is 30 meV, allowing a fast hopping of $10^{13}$ hops/s at RT (compare to the 140 meV of Na, which allows $10^{6}$ hops/s at RT) \cite{15}.

In STM images at RT, no adsorption sites can be observed, though we know unambiguously that AM atoms are presented on the surface from the significant WF change. Instead, two features can be observed: (1) A change of the image contrast as compared to the clean Si(111)-7x7 surface. It can be demonstrated more clearly by subtracting the clean 7x7 background, which results in well-defined triangle and lobe-like patterns depending on the AM coverage, as shown in Fig. 2. Such contrast modulations are induced by selective charge transfer from moving AM atoms to the Si adatoms, making them brighter in the filled state STM images as an average effect. (2) The presence of noisy features in the case of Na, which is absent in the cases of K or Cs. Such noise is indicative of moving atoms on a surface probed by the STM tip. The absence of the noise in the case of K and Cs indicates higher mobility of K and Cs atoms than Na, making the STM completely unable to chase the motion of K and Cs atoms.

The dynamics of Na atoms on the Si(111)-7x7 surface can be revealed by temperature-dependent STM measurements. While the surface is cooled to 160 K (Fig. 3(a)), Na...
atoms become visible as fuzzy features confined in the triangular FHUCs, indicative of moving Na atoms confined in the FHUCs. When the surface is further cooled to 80 K, localized bright spots located at one of the three Si corner adatom sites (Fig. 3(b)) in the FHUCs are observed. The total density of the spots agrees exactly with the Na coverage, therefore, each spot should correspond to one Na atom inside the corresponding basin [16].

4. Clustering of AM

Li magic cluster, consisting of 6 or 9 Li atoms per cluster, was reported by Hasegawa et al. [7]. The K magic cluster was reported by Watanabe et al., but little structural information has been given [6]. We observed the formation of Na magic clusters, each consisting of 6 Na atoms, at the coverage >0.08 ML. The Na clusters have identical threefold symmetric appearance, and they can adsorb in either the FHUCs or the UHUCs. The density of Na magic clusters increases linearly with the Na coverage up to 0.22 ML. For coverage higher than 0.22 ML, the surface becomes disordered. Thus there are three adsorption stages: (I) 2D 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. 4. Note, that the slope of the curve in section II corresponds to the number of Na atom per cluster, which is derived to be six.

In response to the structural change, the corresponding WF curve shown in Fig. 4 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 WF change is related to lifting of the surface Fermi level due to charge transfer from Na to the Si surface, the result nicely demonstrates three charge transfer regimes corresponding to different surface structures. 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). This finding can well explain the previous reported work-function observations for the same system [5,6].

First-principles calculation on the atomic structure of the Na cluster gives the most stable Na cluster structure ($E_R = 2.13$ eV/atom) illustrated in Fig. 5. This structure
involves significant displacement of the Si adatoms. Three Si center-adatoms move inward to form a trimer with a bond length of 2.44 Å, and the six Na atoms form a triangle centered at this trimer. One of the corner Na atoms is pushed outwards, resulting in a triply-degenerate mirror symmetric structure (one can obtain the other two states by 120° rotations). The STM images are characteristic of the Si 3 trimer dangling bonds modified by the decorating Na atoms and hence are more extended outwards.

The reason for the site exchange between the Na and Si atoms in the cluster formation is unclear yet. However, it seems to be supported by our experimental observations. The Na magic cluster is very stable once forms on the Si(111)-7x7 surface. It never decomposes or moves from one unit cell to another, in contrast to many other cases such as the Pb [17] and Tl [18] 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. 6. This fact strongly supports a site-exchange between the Na and Si atoms, which makes the formation of Na clusters irreversible.

The clustering behavior of K is very different from Na, though their behaviors in the 2D-gas regime are similar. K clusters only form on the FHUC, leaving the UHUC completely empty (Fig. 7) [15]. We reported two different types of K clusters. The first type (A) is asymmetric, with two different chiralities. The other type (B) is mirror-symmetric, consisting of two bright spots sitting along the mirror line of the triangular 7x7 unit cell (it may correspond to the dimmer-like cluster...
reported by Watanabe et al. [11]). Thus, there are totally nine possible configurations of K clusters, including six A type clusters (three equivalent rotational directions with two different chiralities) and three B type clusters (three rotational directions). Interestingly, at room temperature a K magic cluster is continuous jumping inside the half 7x7 unit cell, among the 9 different configurations [15].

Similar to the Na case, we observed 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 [15].

We have also found the deposition and removal of the K magic cluster on the Si(111)-7x7 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. When a K cluster is removed from the surface by the tip scanning, the Si(111)-7x7 unit cell is completely recovered, indicative of no intermixing between the K and the Si atoms [15].

Cs has similar behavior like Na and K in the 2D gas regime. At higher coverage, Cs also forms clusters, which are, however, irregular and no magic clusters are observed. In conclusion, it seems that more and more complicated clustering behaviors are observed in AMs with the increasing atomic size from Li to Cs.

5. Summary

The adsorption dynamics of submonolayer alkali metal (Li, Na, K, Cs) on the Si(111)-7x7 surface are reviewed. While Li shows atomic hydrogen-like adsorption behavior, other AMs (Na, K, Cs) all form 2D gas phase at RT and initial coverage. The diffusivity of AM atoms increases from Li to Cs with the increasing atomic size. At coverage >0.08 ML, both Na and K form magic clusters consisting six Na (K) atoms, which suppresses the charge transfer from Na (K) atoms to the Si surface. Though the 2D gas formation in Na, K and Cs is very similar, their clustering behaviors are very different, being more and more complicated with the increasing atomic size.

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