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SCANNING TUNNELING MICROSCOPY STUDY OF ALKALI METAL ADSORPTION ON THE Si(001) 2x1 SURFACE

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Abstract - Li and K adsorption on the Si(001)2x1 surface has been investigated by field ion-scanning tunneling microscopy (FI-STM). The STM images have shown that at the initial stage of adsorption Li (K) atoms (1) adsorb on top of one of the dimer forming Si surface atoms and stabilize asymmetric (buckled) dimerization and (2) form linear chains, perpendicular to the substrate 2x1 dimer rows. Our observations suggest that alkali metal adsorption on the Si(001)2x1 surface may be significantly different from the conclusions of earlier reports.

The adsorption of alkali metals on the Si(001) 2x1 surface has been investigated extensively by LEED (low energy electron diffraction), AES (Auger electron spectroscopy), EELS (electron energy loss spectroscopy) and XPD (X-ray photoelectron diffraction) over the last ten years.¹⁻¹⁶ Alkali metals having rather simple electronic properties, their adsorption on the Si(001) surface should be of great interest from the view points of both experimental and theoretical consideration. Nevertheless, the nature of alkali metal-silicon bonding as well as the geometry of the adsorption sites are not well established. The degree of the saturation coverage of alkali metal atoms is in dispute. Some groups believe that $\theta = 0.5$ (half a monolayer) as a saturation coverage,^{2,4,6} while others suggest $\theta = 1.0$.^{11,13}

Formation of linear chains of alkali metal along the dimer row has been suggested by several groups.^{2,5,11} The mechanism of one-dimensional metallization of alkali metal chains was thought to be solely due to the alkali metal overlayer.^{6,7} Now this is being questioned by people who claim that it is more likely due to alkali metal-Si substrate interaction; namely the metallization of the Si(001) surface itself.⁹ The behavior and driving force of the work function change as functions of alkali metal coverage are also disputed along with the degree of charge transfer of alkali metal atoms.^{5,6,12,14}

Realizing this unsettling situation and the power of scanning tunneling microscopy,¹⁷ we have applied our newly constructed field ion-scanning tunneling microscope (FI-STM) for the Li and K adsorption on the Si(001) 2x1 surface. Our STM is equipped with a room-temperature field ion microscope (FIM) and, thus, the in-situ characterization and shaping of a STM tip can be performed, to improve the stability and reproducibility of the STM images.¹⁸ Our FI-STM can now routinely achieve atomic resolution in the STM imaging without failure, by utilizing sharpness of the <111> oriented tungsten tip. The operation and details of this instrument can be found in the review.¹⁹

A Si(001) specimen was prepared by cutting an As-doped n-type commercial Si wafer ($R=0.1$ ohm-cm) into a $4 \times 19 \text{ mm}^2$ piece. Cleaning of the specimen surface was carried out with a background pressure of 4×10^{-11} Torr by a series of heatings up to 1200°C . By this method, a high-quality 2x1 surface (defect density of less than 3%) can be obtained routinely, as is shown in Fig. 1 (a), in which the dimer rows in two terraces can be resolved together with defects. When the empty states are imaged with a higher resolution, bifurcated electron clouds (individual atoms) forming buckled dimers can be resolved.²⁰ Asymmetric (buckled) dimerization easily takes place at monoatomic steps as well as near vacancy defects while symmetric dimerization is commonly observed inside terraces.^{21,22} These observations are consistent with the calculation that buckled dimers are slightly more stable than the symmetric dimers.²³

A clean 2x1 surface was exposed to Li or K atoms at room temperature using a SAES alkali metal dispenser (S.A.E.S. Getters) and was studied by the STM as a function of metal coverage. Typical STM images of the Li coverage θ of 0.05 are shown in Fig. 1 (b) and (b'). Similar observations were also made in the case of K adsorption (Fig. 1 (c)). Several important new facts are immediately evident from these STM images:

- (1) Individual Li (K) atoms reside on top of one of the dimer forming atoms, contrary to earlier reports which favor a hollow site, bridge site or cave site. This observation is most important to positively identify the adsorption site of alkali metals.
- (2) Li (K) atoms do not preferentially adsorb on the defect sites (dimer defect or terrace edges) as reported by Oellig & Miranda.⁸
- (3) Li (K) adsorption appears to stabilize the buckled dimerization. This is in stark contrast to the earlier notion based on the LEED measurements⁵ that buckling of the surface dimers disappear upon alkali metal adsorption. Realizing the experimental observation that asymmetric dimerization takes place at steps and defects, stabilization of the asymmetric (buckled) dimers by Li adsorption is not unreasonable. Furthermore, the present STM result does not contradict the LEED observation on the behavior of the streak. Indeed, the LEED pattern of the clean 2x1 surface corresponding to the STM image of Fig. 1 (a) does exhibit streaks at non-integral spots.
- (4) The spatial range of asymmetric (buckled) dimer stabilization due to alkali metal adsorption reaches approximately 20 units ($\times 3.84 \text{ \AA}$) in the dimer direction and a few units ($\times 7.7 \text{ \AA}$), perpendicular to the dimer direction. Together with the observation of Fig. 3, this implies that a long-range adatom-substrate interaction may exist on the Si(001)2x1 surface.
- (5) Li (K) adsorption site is identical to that of atomic hydrogen, reported by Hamers et al.²⁴ This finding is reasonable, if one realizes the similarity between Li and atomic hydrogen. A big difference, however, is that alkali metals appear to stabilize the buckled dimerization of the 2x1 surface, while no such observation is found in the case of hydrogen chemisorption.²⁴
- (6) The fact that Li (K) atoms are imaged bright at a positive bias (with respect to the scanning tip) suggests that these alkali metals on the 2x1 surface are not completely ionized contrary to the earlier report.⁶ Nishigaki et al.²⁵ have recently reported that the Cs-4s state is not empty upon adsorption, agreeing with our STM data,

although our STM data are on Li and K only at present.

When the 2x1 surface was exposed to more Li (K) atoms ($\sim 0.1\text{L}$), it was found that alkali metals form linear chains perpendicular to the Si dimer rows (Fig. 2 (a) and (b) for Li and K, respectively). This observation is very much different from the case of alkali metals on a metal surface where alkali metals tend to be dispersed due to the repulsive force originating from their large dipole moment.²⁶ A slightly smaller exposure of Li occasionally resulted in a STM image with an interestingly new feature as shown in Fig. 3. Individual Li atoms on the 2x1 surface appear to extend their lobes of electronic charge density perpendicular to the substrate dimer rows over 20 to 30 Å on both sides of atoms. Realizing the fact that the STM probes the electronic structure of the surface, this observation may be taken as evidence of occurrence of a new density of states induced by the adsorption of alkali metals.

These STM images further suggest several interesting points:

- (1) The individual bright spots forming linear chains are significantly elongated along the dimer row and may consist of two or three atoms. However, a recent calculation by Ishida and Terakura shows that the electronic density of states of a single Li atom spreads over two or three substrate Si atoms along the dimer row.²⁷ We, therefore, conclude tentatively that the individual bright spots consist of single Li atoms.
- (2) The linear chain of the alkali metal may not always exactly form a straight line. Some of the atoms are shifted along the dimer row by one or two units.
- (3) The observation that Li (K) atoms form linear chains perpendicular to the dimer rows at the initial stage of adsorption appears to be contrary to the earlier experimental and theoretical results on this system, which is on the saturated coverage. We, however, note that, in recent STM investigations on Ag and Ga on Si(001)2x1, both Ag and Ga atoms are found to form initially linear chains perpendicular to the dimer rows.^{28,29} Realizing these experimental results, it is fair to suggest that the formation of linear chains of adsorbates perpendicular to the dimer rows may be the intrinsic feature of the Si(001) 2x1 substrate itself.

In the case of K (Fig. 2(b)), it appears that the linear chains of K are spaced by 5 units ($\times 3.84\text{Å}$), making up a "2x5" superstructure. We note that a similar superstructure, that is a 2x3 pattern, has been reported recently.^{11,30}

- (4) The adsorption site of alkali metals does not change from the on-top site with increasing coverage. With respect to the geometrical site of Li adsorption, no earlier work has suggested that Li (K) atoms may reside stably on the top of one of the dimer forming atoms.¹⁻¹⁶
- (5) There is some indication in the present STM study that Li (K) atoms may reside at the trough region (between two neighboring dimer rows) in addition to top of the dimer rows. This observation agrees partly with the recent result by Kono's group.^{11,13} Further study is warranted.
- (6) The quality of filled state STM images of the Si(001) 2x1 surface does not deteriorate much upon alkali metal adsorption. This is a marked contrast to the case of the Si(111)7x7 surface, where the quality of the STM image drastically reduces upon even a small amount (~ 0.01) of Li adsorption.³¹ It may be that the electronic structure of the surface experiences drastic changes at or near the Fermi level with a small amount of adsorbates. A similar phenomenon was discussed theoretically in the case of a metal surface by Feibelman and Hamann.³²

In conclusion, we have shown, using a FI-STM, that the initial stage of alkali metal (Li, K) adsorption on the Si(001)2x1 surface is strikingly different from the adsorption models based on other surface analytical methods, such as EELS, LEED, UPS and XPD. The detailed

investigation of the surface structure as a function of coverage is currently underway.

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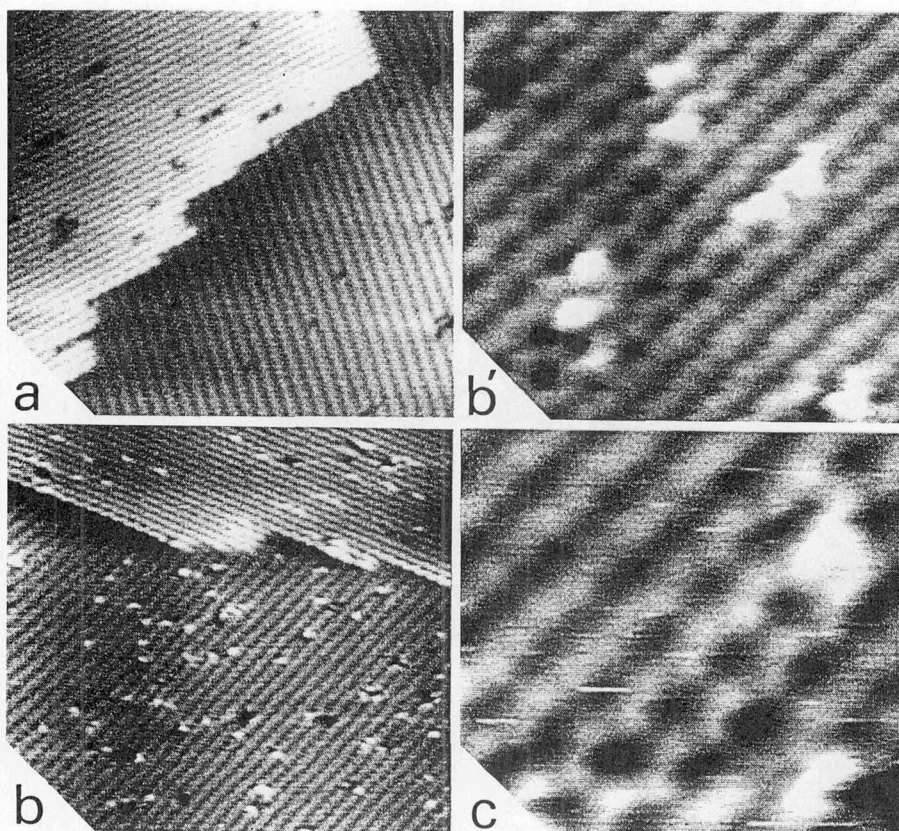


Fig. 1. STM images of (a) clean Si(001) 2x1 ($V_S = -1.2V$), (b) Li ($\sim 0.05L$) deposited ($V_S = -1.2V$), (b') enlarged segment of (b), and (c) K ($\sim 0.05L$) deposited ($V_S = -2.5V$) surfaces.

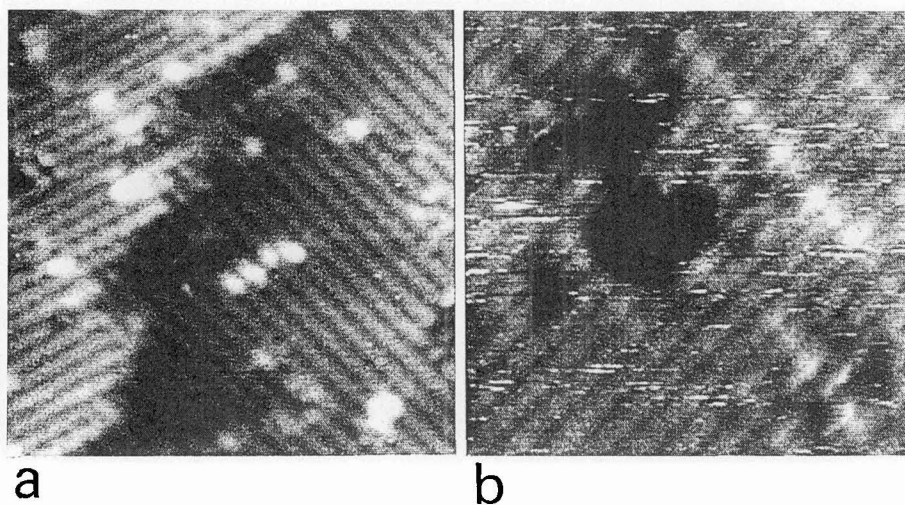


Fig. 2. STM images of (a) Li ($\sim 0.1L$) covered ($V_S = -2.2V$) and (b) K ($\sim 0.1L$) covered ($V_S = -2.2V$) Si(001) 2x1 surfaces.

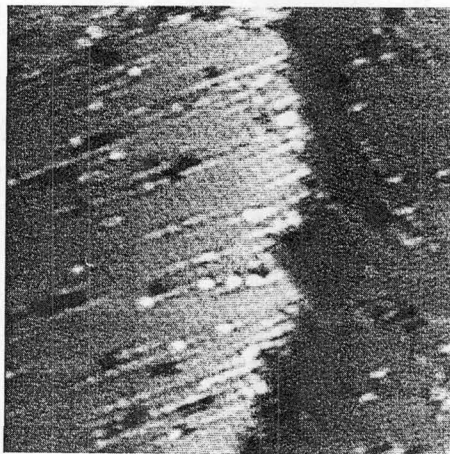


Fig. 3. STM image showing extended lobes of electron clouds from individual Li adsorbates, perpendicular to the dimer rows ($V_S = -2.2\text{V}$).