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Submonolayer- and monolayer-coverage structures of K/Si(100)

A. Brodde, Th. Bertrams, and H. Neddermeyer
Institut für Experimentalphysik der Ruhr-Universität Bochum, D-4630 Bochum, Germany

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Using scanning tunneling microscopy we have measured K on Si(100)2×1 from low coverages (0.1-monolayer K) up to saturation coverage (1-monolayer K) deposited at room temperature. In the low-coverage range we have observed a structure with local order, where the atomic features are arranged in mostly threefold periodicity of the Si lattice along the rows of Si dimers. Upon increase of the coverage the surface develops a 2×3 reconstruction, where the initial dimer structure of the substrate is preserved. At saturation the surface is covered with a two-dimensional K layer. The possibility of tunneling with sample bias voltages in the mV range indicates the presence of states at the Fermi level and the metallic character of the K surface layer.

I. INTRODUCTION

While a large number of publications exists for the system K/Si(100)2×1 at saturation coverage Θ_s,[1] not much work has been devoted to the low- and medium-coverage range. In particular, the *atomic* structure of K/Si(100) is not known precisely for small and medium coverages Θ. The behavior of the *electronic* structure in this range has already been explored theoretically[2–8] and experimentally.[9–11] In the latter studies, the work function Φ has been measured,[9–11] electron-energy-loss spectroscopy (EELS) has been employed,[12] as well as angle-resolved uv photoemission (ARUPS),[13–16] inverse photoemission (IPES),[17,18] and thermal desorption spectroscopy (TDS).[19] The work function shows a strong decrease with increasing coverage and asymptotically approaches a value near 2.3 eV at saturation coverage. A crucial point in the work-function measurements is whether a minimum is present in the low-coverage range or not. Such a minimum is frequently seen for the deposition of alkali metals on metal substrates,[20] but on the basis of the theoretical work of Ishida and Terakura,[3] and of Morikawa *et al.*,[8] not expected for K/Si(100). A minimum of the work function would indicate a continuous occupation of adsorption sites, where from a certain coverage on, due to increasing overlap between the 4*s* wave function of neighboring K atoms, a considerable depolarization of the K atoms or a redistribution of the electronic charges leads to an increase of the work function. The formation of one-dimensional (1D) metallic K chains would be characteristic of such a transition.

In Fig. 1, we show the initial adsorption sites for K atoms on Si(100)2×1, assuming symmetric dimerization of the substrate, which are currently discussed in the theoretical work.[2–8] The hollow site was first proposed by Levine,[21] and for many years was considered to be the most probable adsorption site. As a consequence, a saturation coverage of $\Theta_s = 0.5$ [referred to the number of Si atoms on the bulk-truncated (100) face] has been assumed for a long time, until Abukawa and Kono analyzed their photoelectron diffraction data in terms of a K "double layer" with $\Theta_s = 1$,[22] which has been definitely confirmed by medium-energy ion scattering.[23] For saturation coverage, additional K adsorption on valley bridge sites (Fig. 1) has been proposed,[22] and recently supported by theoretical work.[8] In Ref. 8, the valley bridge site is also obtained as the most favorable site for initial adsorption, although in the calculations of Ling, Freeman, and Delley[4] and Ramîrez[6] the long bridge site was found to be more stable than the valley bridge site. In the case of saturation coverage at $\Theta_s = 1$, Batra did not find conclusive evidence either for combination of adsorption on hollow and valley bridge sites or on hollow and long bridge sites.[2] The dimer bridge site for K has been ruled out theoretically.[2,8]

Direct information on the atomic structure in the low-coverage range has been obtained by scanning tunneling microscopy (STM).[24–26] Hasegawa *et al.* found unexpected adsorption sites for the K atoms on top of the dimer forming Si atoms of the 2×1 reconstructed surface.[24] They also observed a lateral ordering perpendicular to the dimer rows, which they assigned to a 2×5 structure.

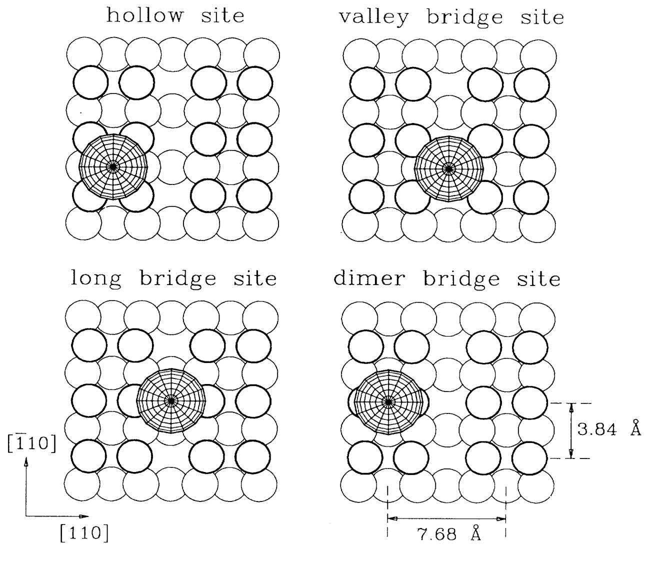

FIG. 1. K adsorption sites on Si(100)2×1, assuming symmetric Si dimers.

In a later work, Hashizume *et al.* described another initial adsorption site for K, which has previously not been considered: they located the K atom between the rows of dimers in an asymmetric valley bridge position (see Fig. 1), i.e., tilted toward one of the dimer rows.[25] They also found that the K atoms in these positions give rise to a buckling in the neighboring rows of dimers, which is also unexpected, since in the theoretical work of Morikawa *et al.* a relaxation from asymmetric dimers toward more symmetric ones has been predicted upon K adsorption.[8] The second group working on K/Si(100) with STM interpreted their STM images at about $\Theta=0.5\,\Theta_s$ with a disordered structure, which should exhibit a disorder-order transition upon reaching saturation coverage.[26] It should be mentioned that the latter authors assumed $\Theta_s=0.5$ and described their STM images at Θ_s in terms of 1D K chains.

TSD results in the low-coverage range were interpreted by K adsorption in the long bridge sites,[19] which is in contrast to the Auger electron diffraction work of Asensio *et al.*, who interpreted their measurements by initial occupation of valley bridge sites.[27] A regular structure in the low-coverage range of K/Si(100) was mentioned by Enta *et el.*, who observed a weak 2×3 low-energy electron-diffraction (LEED) pattern.[13] This structure has recently been discussed theoretically by Batra.[2] It should be mentioned that a 2×3 LEED structure has been observed earlier on other alkaline metal/Si(100) systems [Cs/Si(100) (Ref. 28) and Na/Si(100) (Ref. 29)].

In the present work, we report on STM results from K/Si(100) in the submonolayer coverage range up to saturation. We concentrate on those surface structures, which show a lateral ordering. Results for the initial regime of K condensation, where single atomic structures without much next-neighbor interaction are identified will be described elsewhere.[30] We describe one surface structure with local order, which on a scale of about 100 Å appears to be rather irregular, but very often exhibits locally a threefold periodicity in both directions of the dimerized Si(100) surface. Upon slightly increasing the coverage, this structure experiences a phase transition to a 2×3 reconstruction with drastic differences in the lateral order. Two kinds of unit cells are observed, which differ in the K occupation. They probably contain one and two K atoms per six Si atoms, respectively, in the bulk-truncated ideal lattice ($\Theta=\frac{1}{6}$ and $\frac{1}{3}$, respectively). A surprising observation was that the 2×3 structure follows two-dimensional island growth mode. The uncovered substrate could be identified in the form of holes in the 2×3 domains by the presence of the characteristic dimer chains of the clean substrate. Features that could be ascribed to 1D metallic chains of K atoms on the hollow sites of the dimer rows could not be identified. Another important issue of our work is the measurement of surfaces with saturation coverage obtained for K deposition on room-temperature substrates. Our results demonstrate that the surface is covered by a two-dimensional (2D) K layer with a clear indication of metallicity. This could not only be deduced from the general growth mode showing again small uncovered parts of the substrate, but also from the possibility of measuring the surface at sample bias voltages U in the mV range at both polarities, which indicates the presence of occupied and unoccupied states directly at the Fermi level E_F. The existence of such states had previously been ruled out theoretically[2,3] and by photoemission,[16] but not in the recent IPES work of Johansson and Reihl, where the experimental results indicate the presence of a free-electron-like unoccupied surface-state band running through E_F.[18]

It is obvious that a number of discrepancies exist in our present knowledge of the electronic and atomic structure of K/Si(100). In particular, the questions of adsorption sites in the initial coverage range, of ordering with increase of the coverage, and of the nature of K/Si(100) at saturation should be addressed by STM, and these problems will be the main issues of our work. In Sec. II, we briefly describe details of the experiment. We continue with the presentation of STM images, and finally discuss the results in terms of the current literature.

II. EXPERIMENT

The measurements have been performed by using experimental equipment which has been described previously in more detail.[31] The apparatus consists of a main chamber containing the STM and other surface physical equipment and a sample transfer stage, which can also be used for surface preparation. The structure and chemical nature of the samples can be controlled by LEED and Auger electron spectroscopy (AES), respectively. For the latter method, a spherical energy analyzer has been employed with constant relative energy resolution ($\Delta E/E=$const).

As substrates, B-doped (8-Ω cm) Si wafers have been used, which were cleaned *ex situ* in methanol and prepared in the STM chamber by slowly degassing and flashing to about 1200°C until LEED showed a sharp 2×1 pattern and the contamination was below the detection limit of AES. K was deposited at a working pressure of 5×10^{-11} mbar from SAES getter sources, which were carefully degassed prior to the deposition experiments. The pressure increase during operation of the K sources at a constant current was 10^{-12} mbar or less. The K coverage could qualitatively be estimated from the K(248 eV)/Si(92 eV) AES intensity ratio, which in the present experiments was 2–4 for saturation coverage. It has to be mentioned, however, that below saturation coverage the local surface concentration of K may show drastic differences, as could be deduced from the simultaneous presence of various surface structures on neighboring parts of the surface. The formation of 2D island structures turned out to be an unexpected property of K/Si(100). The AES intensity ratio therefore provides only an average value for the local surface concentration of K.

The question of contamination is very important for this system, since coadsorbed species give rise to considerable local changes of the Si(100)2×1 substrate, and in the low-coverage range the effects of K adsorption may be obscured by the defect structures always present on Si(100)2×1. Since we used highly oriented Si wafers, the number of steps on the sample was small, and we always recorded them when they accidentally appeared in the measured area. They allowed a rather exact calibration of the *xy* system, which normally was not completely free of drift effects and creeping. Another problem of this system is the apparent difficulty in obtaining stable tunneling conditions and a satisfactory resolution. We ascribe this behavior to a transfer of K atoms to the tip, to the high reactivity of K, and to a possible small diffusion of adsorbed K atoms during scanning. For example, on the more irregular surfaces at a small coverage (a few 0.01 Θ), specific features had sometimes moved around between subsequent measurements on a typical scale of 1–2 lattice parameters. On the other hand, the more ordered surfaces as the 2×3 structure were found to be fully reproducible. Instabilities and lack of resolution were particularly strong for positive sample bias voltages. This may be understood by the work of van Gorkom *et al.*, who investigated the influence of electric fields on the diffusion of alkaline metal (Cs) atoms on a Si surface.[32] At a sample temperature of 180 °C, considerable electromigration effects were already found in a field of 4×10^6 V/m from positive to negative potential, which is by several orders of magnitude smaller than the field in the tunneling region. Because of these instabilities, we could not measure well-resolved I/U characteristics. Instead, we have to identify electronic effects from measurements of constant current topographies (CCT's), where sample bias voltages in both polarities have been applied. The CCT's presented here are as usually displayed in the form of gray-tone images.

III. RESULTS

We first describe results which are obtained on surfaces with a K/Si AES intensity ratio of $\approx \frac{1}{3}$. Because of the above-mentioned reasons, a precise value of the absolute coverage on the measured area cannot be given. However, since for the saturation structure described below, a K/Si AES intensity of nearly 2 was obtained, we estimate an average value of $\Theta \approx \frac{1}{6}$ for the low-coverage structure. Typical CCT's measured with negative and positive sample bias U (corresponding to imaging with the filled and the empty states of the sample, respectively) are reproduced in Fig. 2. The dimer structure of the substrate is still roughly visible in the form of a line structure along the rows of dimers. In addition, the typical missing dimer defects of "clean" Si(100)2×1 are present. Inside these missing dimer defects, some isolated dimers may also be recognized on the graphic display (hardly visible on a photographic reproduction of the data); they are oriented normally to the rows of dimers, as expected. The density and size of the missing dimer defects appear to be rather high for an initially clean surface; a similar distribution was sometimes also observed prior to K deposition and possibly indicates the presence of some residual contamination. An extensive use of the sample might also have increased the number of defects on the surface.

A first inspection of the CCT does not reveal distinct features, which may be attributed to isolated K atoms. In Fig. 2(a), the maximum height of the additional protruding features is only ≈ 1 Å above the average. Most of the structures are only raised on the order of a few 0.1 Å compared to the undistorted parts of Si(100), which are probably not yet covered with K atoms.

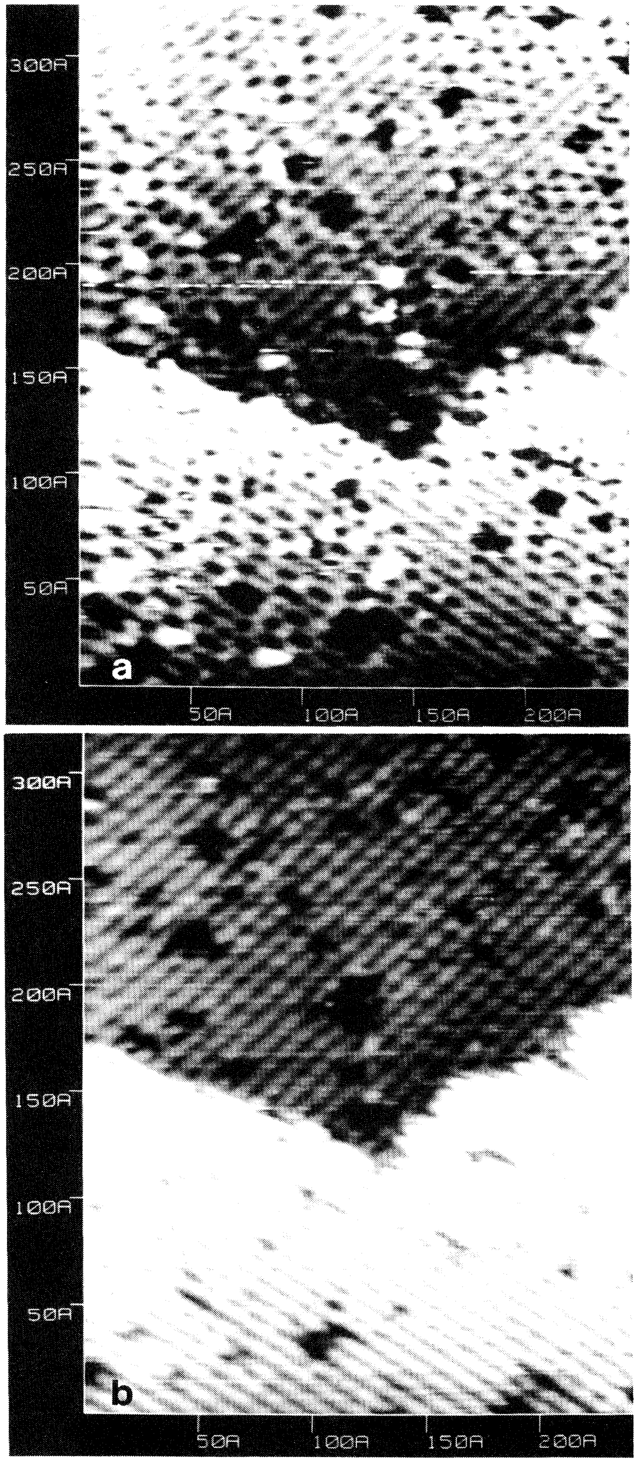

FIG. 2. CCT from K/Si(100) obtained at a sample bias voltage $U=-1.4$ V and a tunneling current $I=2$ nA (a) and at $U=1.4$ V and $I=2$ nA (b). The coverage was $\Theta \approx \frac{1}{6}$.

A closer inspection of the differences between a clean and a K-covered Si(100) substrate shows that, at U near -2 V, the K-induced effects appear as a formation of bridges between the dimer rows. In many cases, these bridges enclose small depressions, which sometimes form an ordered pattern along the [110]-like direction extending over several (typically five) units in a distance of $3a_{\mathrm{Si}}$ ($a_{\mathrm{Si}}=3.84$ Å). In neighboring rows, the pattern is generally shifted by a multiple of a_{Si}. This means that the depressions and bridges, respectively, do not form chains perpendicular to the rows of dimers. The lateral order is not very well developed; however, the similarity to a regular centered structure is obvious.

Our interpretation of the observed structure [Fig. 2(a)] is that K atoms in this coverage range are essentially adsorbed on trough positions of the dimerized surface [i.e., on valley bridge and long bridge positions). This explains the lack of many protruding features, which would be expected for adsorption on hollow sites.

The measurement at $U=1.4$ V [Fig. 2(b)] reveals even less distinct structures. In particular, the locally ordered arrangement of holes seen at $U=-1.4$ V cannot be identified here. On the other hand, we do see a small modulation of the surface, producing a line pattern perpendicular to the rows of dimers with a periodicity of $3a_{\mathrm{Si}}$. This line pattern is weakly visible on the lower terrace of the CCT.

In Fig. 3, we have reproduced a small part of a different measurement ($U=-2$ V), where the organization of the surface in this range of coverage may be demonstrated more clearly. In order to identify the registry of the local features, we have included a system of lines in a distance of the Si lattice parameter a_{Si}. It becomes quite obvious that the periodicity of structures very often is equal to $3a_{\mathrm{Si}}$, e.g., at 1. In neighboring dimer rows, these structures are always shifted by the above-mentioned multiples of a_{Si} (e.g., at 2). Sometimes, however, the observed structures are no longer in registry with the lines but shifted by $\frac{1}{2}a_{\mathrm{Si}}$ (e.g., at 3). This fact clearly indicates that valley bridge and long bridge sites are occupied at the same time. The bridges resemble nearly rectangular structures whose heights differ somewhat. Their registry with the substrate lattice cannot be determined precisely, since the resolution on uncovered parts of the Si dimers was not sufficiently good. However, the absence of structures in hollow sites on top of the dimer rows is apparent.

When the coverage was increased by a factor of 2 (corresponding to a K/Si AES intensity ratio of $\frac{2}{3}$) we found a completely different surface structure (Fig. 4). The CCT shows linear arrangements of protrusions in a distance of $2a_{\mathrm{Si}}$, which form chains with a separation of mostly $3a_{\mathrm{Si}}$. The observed regular structure obviously follows a 2×3 periodicity. The orientation of these chains with respect to the Si substrate is of crucial importance for a determination of their atomic structure. In Fig. 5, we have reproduced a CCT which is somewhat noisy, but unambiguously shows the presence of the uncovered and 2×1-reconstructed Si(100) substrate at the same time [as can be deduced from the separation of the lines of ≈ 8 Å ($2a_{\mathrm{Si}}$) (see area below A)]. According to these results the "2×3" chains are oriented perpendicular to the rows of dimers. This rules out any atomic model where the K-induced chains are located along the rows of dimers, as has previously been proposed in a model of 2×3-reconstructed Na/Si(100).[29] The directions of these chains do not follow exactly one system of lines (see again Fig. 4), which is a natural consequence of an apparent domain structure. Two domains are marked with 1 and 2, respectively. The chains in different domains are shifted laterally by a_{Si}. However, small local displacements of the individual protrusions from the ideal position cannot be ruled out completely, since the chains do not always

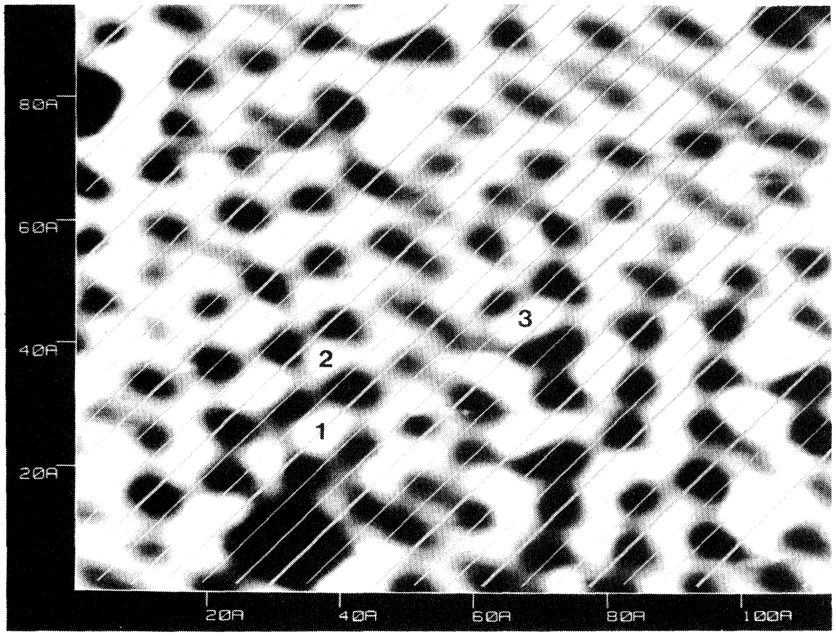

FIG. 3. CCT from K/Si(100) obtained at $U=-2$ V and $I=1$ nA. The coverage was estimated to be $\Theta\approx0.1$. The rows of Si dimers of the substrate run from the bottom right to the top left corner.

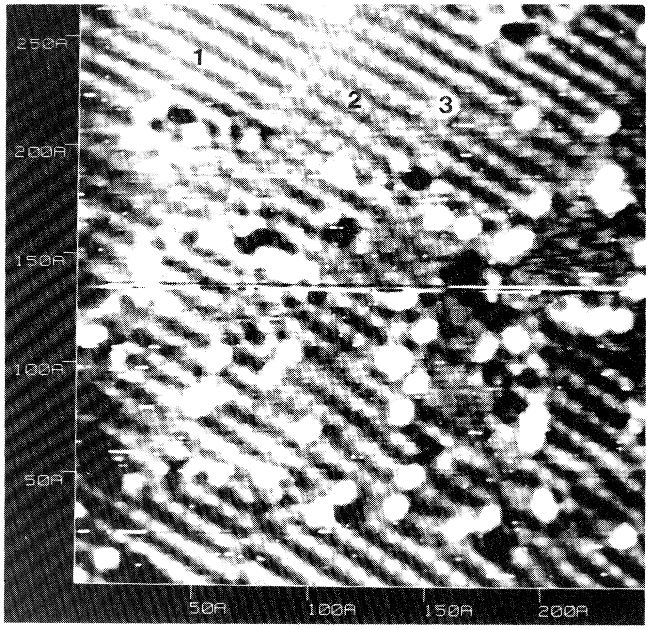

FIG. 4. CCT from K/Si(100) showing the 2×3 reconstruction obtained at $U=-2$ V and $I=10$ nA. The coverage was $\Theta=\frac{1}{6}-\frac{1}{4}$.

follow straight lines. The latter observation is in contrast to the direction normal to the chains, where the protrusions are precisely aligned on a lattice with $2a_{\mathrm{Si}}$ as the lattice parameter. Because of this order, and of the possibility of recognizing the Si-dimer structure in holes below the level of the chains, we conclude that the dimer structure of Si(100) remains essentially intact upon K adsorption.

In the following, the main properties of the observed 2×3 surface structure as deduced from the CCT's shown in Figs. 4 and 5 are summarized. (i) The twofold periodicity of the Si(100) substrate is transferred to the 2×3 reconstruction. The protrusions are perfectly oriented normal to the chains even if they belong to different domains. (ii) The coverage with K atoms must be larger than in the "distorted" low-coverage structure shown in Figs. 2 and 3. This may not be concluded only from the AES intensity ratio but indirectly also from the observed height of ≈1.5 Å above the uncovered substrate (see Fig. 5), which is larger than for the K-induced less regular structures reproduced in Figs. 2 and 3. (iii) The lateral interaction in the 2×3 unit cells looks drastically different compared to that in the "distorted" low-coverage structure. This may be concluded from the fact that the CCT's reproduced in Figs. 2 and 3 and others (not shown here) do not provide as much evidence for chain formation as the 2×3 structure. (iv) The 2×3 surface structure shows island growth mode. This follows immediately from Fig. 5, and also becomes obvious from the striking observation that the characteristic "2×3" chain structures have been found on the same sample showing the "distorted" low-coverage structure, and even close to an area where the surface seemed to be nearly uncovered with K. (v) The chains are very often terminated by protrusions with a height of nearly 1 Å. These features (e.g., at 3) are always shifted somewhat against the chains and often are located on domain boundaries. We tentatively assign them to atomic K on hollow sites. (vi) In some of the domains (e.g., domain 2 in Fig. 4), the protrusions appear as a double structure.

For saturation coverage (the K/Si AES intensity ratio was nearly 2) the CCT's from K/Si(100) again show drastic differences compared to the previous ones. In Fig. 6, an overview image is displayed which has been obtained at $U=-2$ V, corresponding to the usual sample voltage

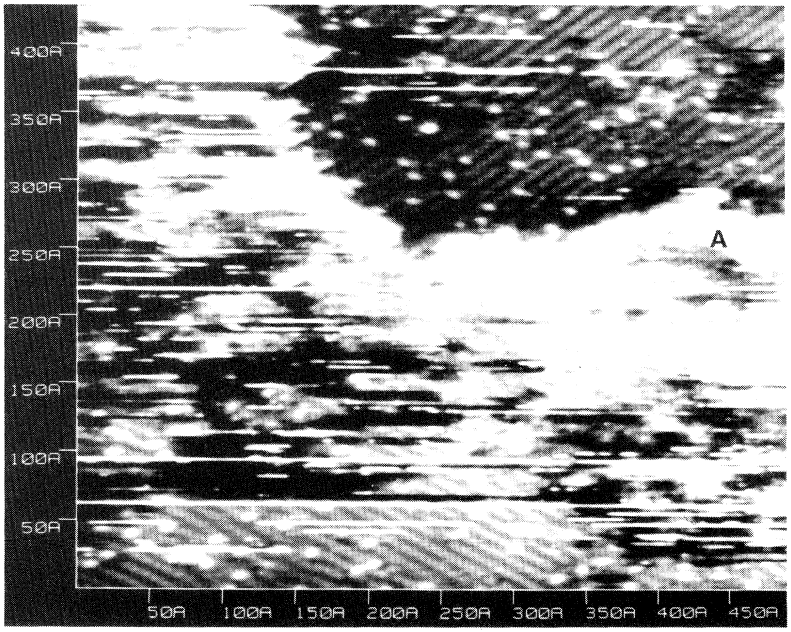

FIG. 5. CCT from K/Si(100) showing the 2D island structure of the 2×3 reconstruction. $U=-2$ V and $I=10$ nA.

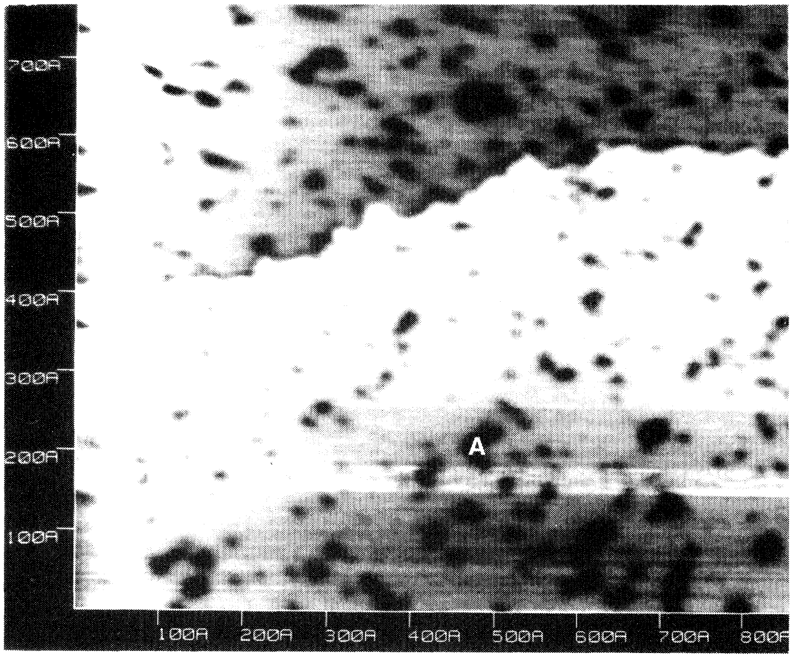

FIG. 6. CCT from K/Si(100) at the saturation coverage and at $U=-2$ V and $I=1$ nA.

for a Si surface. The CCT shows a fairly uniform surface (the noise is 0.1–0.2 Å) with a number of distinct holes with a typical lateral extension of 20 Å. Their depth was found to be 1.5–2.5 Å, which would be consistent with the formation of a K-surface layer not yet covering the substrate completely. In some cases, the edges of the holes approximately follow [110]-like directions (e.g., at *A*). Note that on the lower terrace (the top part of the image) a narrow uncovered region extends along the step edge. Single protrusions as those in Fig. 5 cannot be recognized. Qualitatively, the surface looks quite similar to that of a system where a metallic monolayer has been formed on a surface (see, e.g., Ref. 33).

To obtain atomically resolved images from K/Si(100) at saturation coverage, various sample bias voltages U and tunneling conditions have been employed. Only by the use of voltages in the mV range could an atomically resolved structure finally be obtained at both polarities. We observed a row structure (Fig. 7) in the Si dimer distance with a corrugation between 0.6 and 0.7 Å, the noise being 0.1–0.2 Å. It must be mentioned that for clean Si(100)2×1 the tunneling current cannot be stabilized with such small values of U. The results clearly show that for saturation coverage the surface has developed metallic states near the Fermi level E_F. The corrugation is consistent with the theoretical value of 1.11 Å for simultaneous adsorption on hollow sites and valley bridge sites.[8]

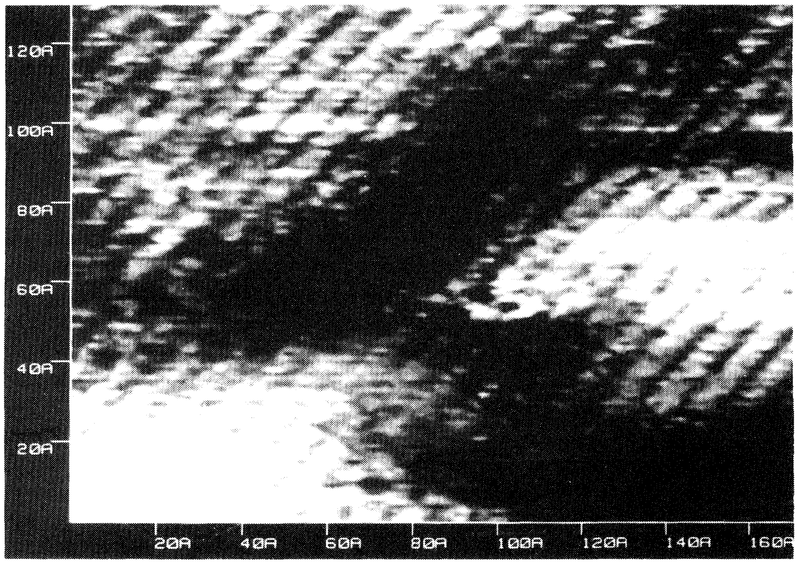

FIG. 7. CCT from K/Si(100) at the saturation coverage and at $U=2$ mV and $I=0.5$ nA.

IV. DISCUSSION

Before we discuss our results in the light of the existing literature, we must describe those results in terms of plausible atomic models. We have already mentioned that in the low-coverage regime the adsorption of species on top of a dimer row cannot be recognized. Therefore, only valley bridge and long bridge sites can be occupied at this stage. In Fig. 8(a), typical atomic patterns are shown which could give rise to the CCT's as shown in Figs. 2 and 3. In the upper part of Fig. 8(a), mainly valley bridge sites and some long bridge sites have been used for K adsorption. The periodicity is not strictly threefold and therefore the adsorbed K atoms give rise to a somewhat irregular surface pattern. A regular arrangement such as that shown in the lower part of Fig. 8(a) is sometimes also seen. This is the pattern which resembles a centered structure, although, as a matter of fact, it does not correspond to the $c(4\times2)$ symmetry. The local surface concentration of K is $\Theta=\frac{1}{6}$.

The 2×3 structure is found upon a slight increase of the coverage. Two possible atomic configurations for the 2×3 structure are displayed in Figs. 8(b) and 8(c) for $\Theta=\frac{1}{6}$ and $\frac{1}{3}$. As may be deduced from the twofold periodicity and the exact alignment of the protrusions along the original dimer rows, no essential rearrangement in the substrate lattice is necessary to form the 2×3 reconstruction. That the dimer structure of the substrate is still preserved may also be directly seen in the holes of the surface (Fig. 5), where the 2×3 structure has not yet covered the substrate. Whether the K atoms occupy valley bridge or long bridge positions cannot be decided since the resolution of the CCT shown in Fig. 5 is not sufficient. Domain 2 in Fig. 4 may indeed consist of K dimers since the protrusions have doublet character, which was found reproducible in subsequent measurements. An interesting feature of the 2×3 structure is that it appears to be due to a kind of disorder-order transition which is not necessarily connected to an increase of the coverage, although in the case of K dimer formation it may accommodate K atoms up to $\Theta=\frac{1}{3}$.

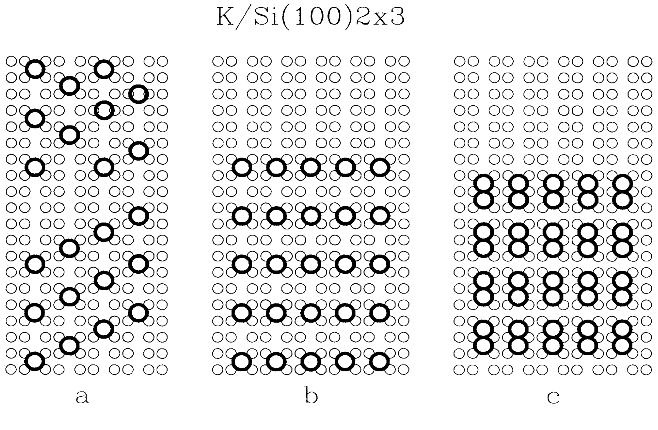

FIG. 8. Atomic models of low-coverage structures on K/Si(100) (a) and of two domains of 2×3 reconstruction on K/Si(100) [(a) and (b)].

For the fully developed K/Si(100) surface, a system of rows could be identified in the Si-dimer distance. The most interesting aspect of the measurement is certainly the metallic character of the surface at saturation coverage, which is deduced from the fact that tunneling is possible with sample bias voltages in the mV range, i.e., by the contribution of states close to the Fermi level. The fact that under no experimental conditions could isolated 1D metallic K chains such as those observed by Whitman *et al.* for Cs on Cs/GaAs(110) (Ref. 34) be seen on the images is consistent with the simultaneous occupation of hollow and valley bridge or long bridge positions, where the K/K interaction is comparable in both directions along and normal to the row of dimers. The compact shape of the holes in the not-yet-completed monoatomic K layer not showing any noticeable elongation (Fig. 6) is also an indication for rather isotropic K/K interaction.

Regarding the previous STM measurements on this system, we should mention that the results of Hashizume *et al.* in the low-coverage range, where the initial adsorption sites are located on "asymmetric" valley bridge positions, are consistent with our analysis. We did not find K adsorption in "on-top" positions (above one of the dimer-forming Si atoms), as was reported in Ref. 24. Comparing our work with that of Ref. 26, we find differences in the data (particularly in the medium-coverage range) and arrive at different conclusions. As has already been emphasized, with a sample bias in the order of 1–2 V (which has been used for the measurements reported in Ref. 26), we were unable to resolve atomic features in the Si-dimer distance. Only by applying a voltage in the mV range could we identify a row structure, which we assigned to a 2D metallic K layer. We note that some of the data of Ref. 26 also shows a row structure which was assigned to 1D K chains. These features measured in Ref. 26 with $U=\pm1.2$ V could actually be the same as those seen in our data.

Our observation of a saturation surface structure for room-temperature deposition with metallic behavior is in conflict with a number of previous results, where both theoretically[1,2] and experimentally a semiconducting surface was obtained by using photoemission.[13–16] It is, on the other hand, in agreement with the recent IPES study reported by Johansson and Reihl.[18] Absence of a metallic edge at the Fermi level in the results of Refs. 13–16 can be explained, in our opinion, by a small cross section for photoionization of K atoms which might exclude the detection of K 4*s* photoemission transitions in the monoatomic 2D metallic overlayer.[35] We cannot explain the discrepancies between our experimental findings and the theoretically predicted surface-state band structures of Refs. 2 and 3, where a metallic K 4*s*-derived surface-state band is absent. One has to ask, however, whether or not the K-derived surface-state band labeled S_3 in Ref. 3 could explain the presence of states near E_F if it would be shifted downwards by about 0.5 eV. Intuitively, the STM verification of a metallic surface at saturation coverage, including the apparent structural similarity with other monoatomic metal layers (on a metal substrate[33]), provides evidence for a stronger K/K interaction (referred to as the K/Si interaction), as theoretically expected. Consequently, the electronic charge transfer to the Si substrate cannot be large, which is actually expected theoretically.[3]

Concerning the theoretical description of low-coverage adsorption sites, it varies between the extreme situations of practically complete charge transfer to the dangling-bond surface states[1] and of no charge transfer at all.[2] In the latter case, one would expect the presence of distinct spherical protrusions in the case of K adsorption on hollow sites. Such structures are indeed observed as isolated features on those surfaces, which have developed a 2×3 reconstruction. They tend to be located on the edges of 2×3 domains. On the other hand, the protruding features defining the 2×3 pattern are elongated and can hardly be ascribed to individual K atoms. Their similarity to the dimer bond states of clean Si(100)2×1 indicates that the K atoms are bound in this structure at least by two (or even four) Si atoms, which is consistent with adsorption in long bridge or valley bridge sites.

For K/Si(100), a 2×3 structure has already been mentioned by Enta *et al.*[13] It seems plausible that the 2×3 structures reported by some authors for other alkaline metal/Si(100) systems have to be described by similar atomic models. The 2×3 reconstruction observed by Hashizume *et al.*[25] on Cs/Si(100) by using STM exhibits a better long-range order than our measurement on K/Si(100); a domain structure and additional protrusions are not seen in the image reproduced in Ref. 25.

Glander and Webb have carefully investigated Na/Si(100) (Ref. 29) and proposed a model for the 2×3- (actually the 3×2-) reconstructed surface, where the threefold periodicity occurred perpendicular to the direction of the dimer rows. Such a structure is not consistent with our STM observation, since the dimer structure of the substrate is reproduced along the "2×3" chains by the regular arrangement of oblong protrusions (defining the 2×3 pattern), which would be not the case for the model of Ref. 29. Moreover, we do not see indications of the necessary mass transfer of Si atoms proposed in Ref. 29 for the formation of the 2×3 structure, since the presence of steps did apparently not affect the 2×3 structure.

V. CONCLUSION

Our STM measurements of K/Si(100) in the coverage range from submonolayers up to saturation (deposition at room temperature) have nominally for $\Theta=\frac{1}{6}$ revealed two low-coverage surface structures, which upon increase of the coverage experience a kind of disorder-order transition to a 2×3-reconstructed surface. Already the more irregular low-coverage structure shows local ordering with mostly threefold periodicity along the rows of dimers. The dimerization of the substrate is preserved in both low-coverage surface structures. We found remarkable differences in the local K coverage of a sample. The 2×3-reconstructed surface region shows a 2D island growth mode, i.e., the uncovered Si substrate showing the normal arrangement of dimers was visible in the form of 2D holes within the 2×3 reconstructed areas. This allowed us to orient the 2×3 unit cells with regard to the underlying Si dimer structure. At low coverages, both valley bridge and long bridge sites between the rows of dimers are occupied by K atoms. In the case of the 2×3 reconstruction, additional protruding features are identified, which we tentatively assigned to K atoms in hollow sites on top of the row of dimers. The 2×3 reconstruction occurs in three domains; in some cases the domains exhibited atomic features which could be explained by the formation of K dimers leading to a maximum nominal coverage of $\Theta=\frac{1}{3}$. At saturation, the surface was covered with a 2D K layer, which showed qualitative similarities to a metallic overlayer on a metal substrate. By using sample bias voltages in the mV range, an atomic corrugation in the Si dimer distance was found. Our observations at saturation coverage are consistent with the existence of a 2D metallic K layer with a coverage of $\Theta_s=1$.

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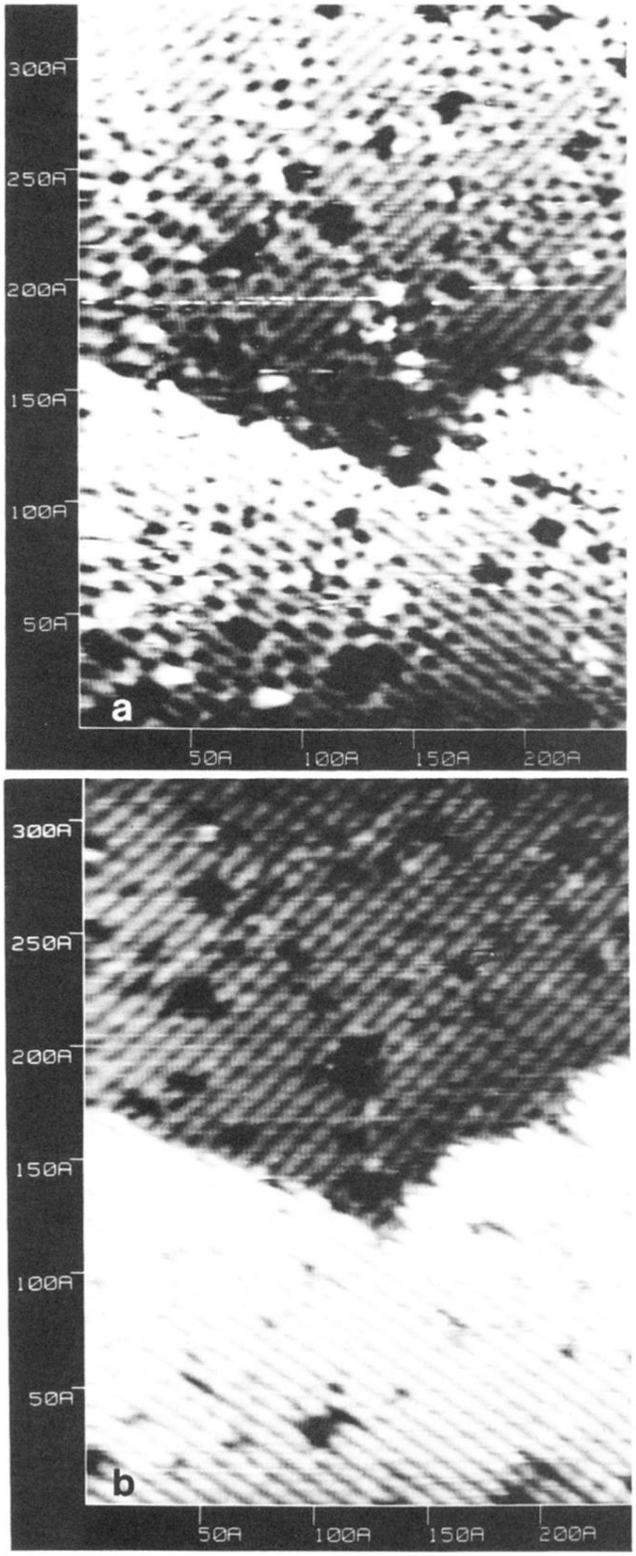

FIG. 2. CCT from K/Si(100) obtained at a sample bias voltage $U=-1.4$ V and a tunneling current $I=2$ nA (a) and at $U=1.4$ V and $I=2$ nA (b). The coverage was $\Theta \approx \frac{1}{6}$.

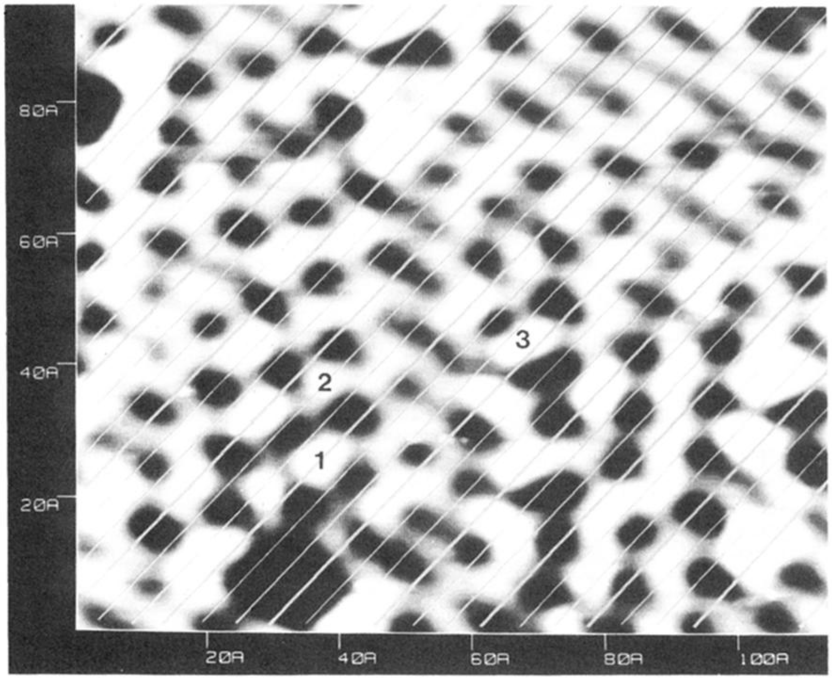

FIG. 3. CCT from K/Si(100) obtained at $U = -2$ V and $I = 1$ nA. The coverage was estimated to be $\Theta \approx 0.1$. The rows of Si dimers of the substrate run from the bottom right to the top left corner.

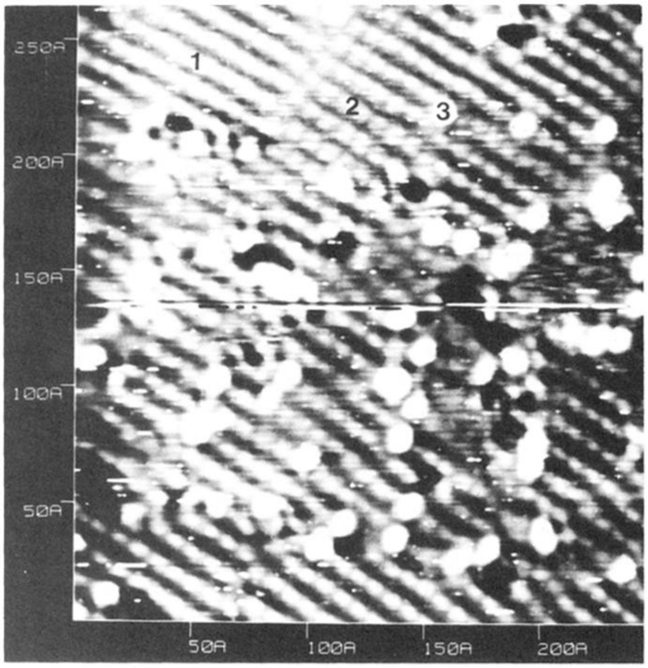

FIG. 4. CCT from K/Si(100) showing the 2×3 reconstruction obtained at $U=-2$ V and $I=10$ nA. The coverage was $\Theta=\frac{1}{6}-\frac{1}{4}$.

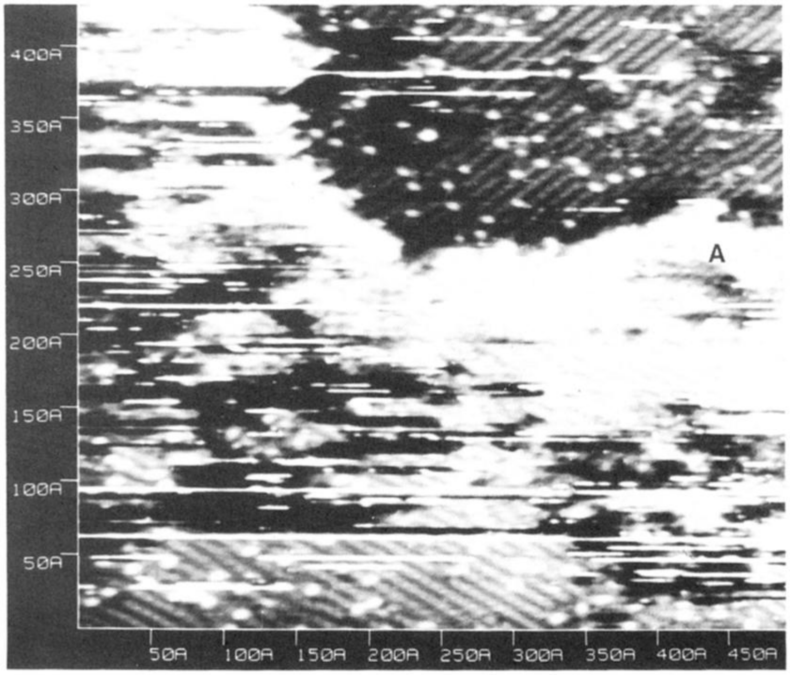

FIG. 5. CCT from K/Si(100) showing the 2D island structure of the 2×3 reconstruction. $U=-2$ V and $I=10$ nA.

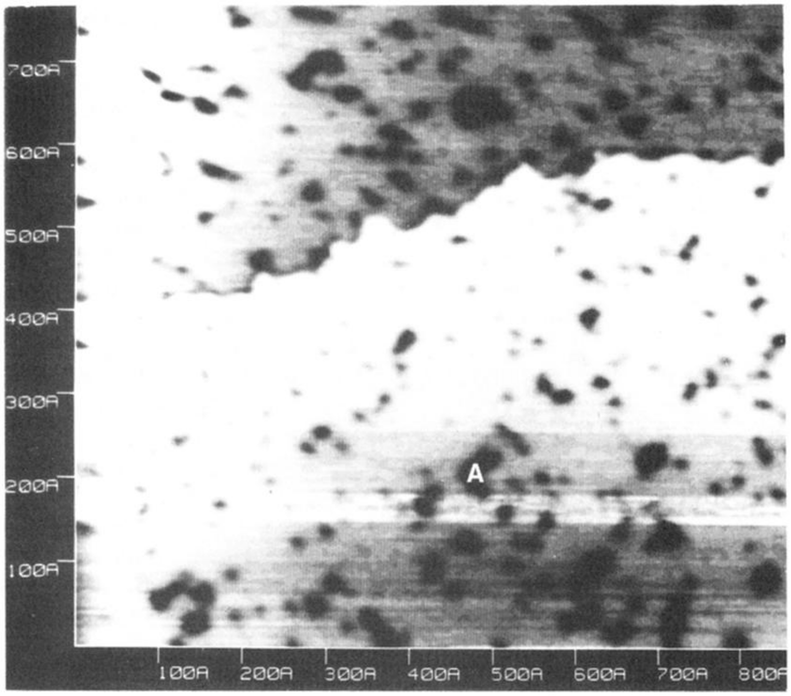

FIG. 6. CCT from K/Si(100) at the saturation coverage and at $U=-2$ V and $I=1$ nA.

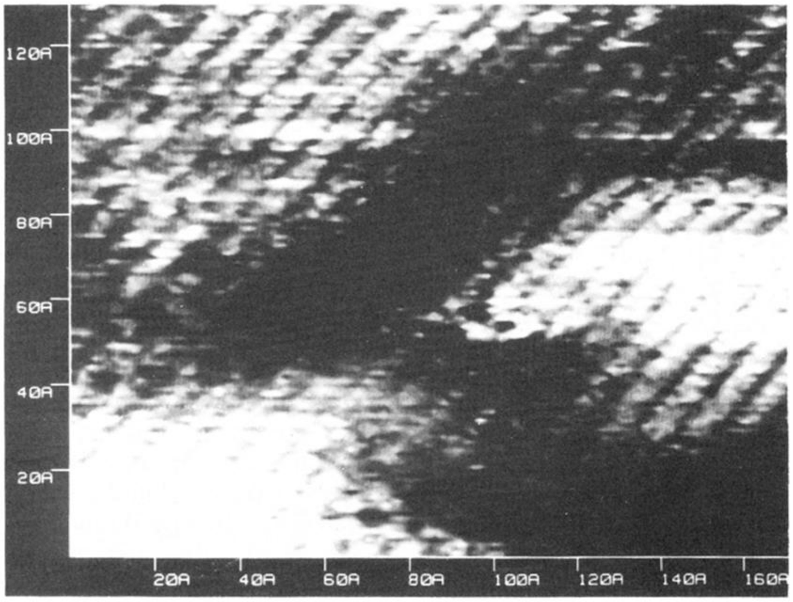

FIG. 7. CCT from K/Si(100) at the saturation coverage and at $U = 2$ mV and $I = 0.5$ nA.