

Bonding at the K/Si(100) 2×1 interface: A surface extended x-ray-absorption fine-structure study

T. Kendelewicz

Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

P. Soukiassian*

*Department of Physics, Northern Illinois University, Dekalb, Illinois 60115
and Synchrotron Radiation Center, University of Wisconsin—Madison, Stoughton, Wisconsin 53589-3097*

R. S. List

Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

J. C. Woicik and P. Pianetta

Stanford Synchrotron Radiation Laboratory, Stanford, California 94305

I. Lindau and W. E. Spicer

Stanford Electronics Laboratories, Stanford University, Stanford, California 94305

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Using surface extended x-ray-absorption fine-structure spectroscopy we establish the K—Si bond length to be 3.14 ± 0.10 Å at the K/Si(100) 2×1 interface for $\frac{1}{2}$ -monolayer K coverage. This value corresponds to the sum of the Si and K covalent radii and suggests weak interaction of K with the substrate relative to the interaction along the K chains on the surface. This finding, while consistent with earlier studies of this system, disagrees with recent total-energy pseudopotential calculations which determine a K—Si distance of 2.59 Å.

The adsorption of alkali metals on metals or semiconductors is at the center of attention of surface science. Interest comes from the unique physical properties of these simple model interfaces which allow one to test basic ideas of chemisorption, bonding, and metallization. Two additional reasons for this interest are applications in negative-electron-affinity (NEA) devices and unique catalytic reactions mediated by alkali-metal agents. In this work we concentrate on the properties of the K/Si(100) 2×1 interface which have recently been widely studied and are a subject of controversy.^{1–4} This interface is perhaps the simplest metal-semiconductor system for theorists to model. The understanding of such a system is clearly of great importance for the development of the field. Early studies suggested that K atoms deposited on Si(100) chemisorb between the outward tilted Si dimers and that for a 0.5-monolayer (ML) coverage from one-dimensional rows of atoms along the [110] direction.⁵ This structural model was first proposed by Levine for a similar Cs/Si(100) interface.⁶ However, no attempt has been made to identify experimentally this adsorption geometry. The confirmation comes from low-energy electron diffraction (LEED) which upon K deposition does not show a pattern change but only some redistribution of the intensities of the Si(100) 2×1 reconstruction. Our LEED characterization agrees with the results of other workers.^{3,7} Qualitatively this tentative geometry seems to be consistent with all experimental data and theoretical calculations,^{1–4,6,8–11} although the quantitative value

of the K—Si bond length, which has important implications for the electronic properties, has not been determined experimentally and is a subject of a theoretical debate.^{1,2} In this configuration the distance between the K atoms along the chain of 3.84 Å is as much as 20% shorter than the K—K distance in bulk metallic K (4.52 Å) and should result in a strong overlap of the K orbitals along the row. Concomitant to this, the large distance between K atoms in adjacent rows of 7.68 Å makes the interaction of the K atoms perpendicular to the chain negligible. Under the condition that the substrate-overlayer bond is weak the considered system should provide a unique opportunity to study properties of a one-dimensional metal adsorbed on a substrate. This type of bonding was found consistent with a variety of experimental and theoretical work. The related changes in the overlayer structure have been considered by Ishida and co-workers⁸ in terms of the Mott insulator-metal transition. These results provided, despite some differences in detail,³ a consistent picture of the K/Si(100) 2×1 system. Recently, however, Ciraci and Batra¹ proposed an alternative interpretation of the data. Their work together with the work of others^{2,8,9} points out that the properties of these systems rely on the very delicate balance between the adatom-adatom and the adatom-substrate interaction. In their total-energy pseudopotential calculation they found an extremely short K—Si bond of 2.59 Å for all the alkali-metal coverages. This strong ionic bond places the K atoms so close to the surface (1.27 Å) that they are

embedded in the substrate dangling-bond states. As a result the alkali-metal electron is at all coverages donated to the dangling-bond states, making the substrate but not the overlayer metallic. This calculation required a reinterpretation of the available data. In particular the metal-insulator transition was assigned to dangling-bond-induced metallization of the substrate rather than to a Mott transition in the overlayer. Lately, the system was again theoretically reexamined by Kasowski and Tsai.² Using a pseudofunction method they found a K—Si bond length of 3.30 Å which is only slightly larger than the sum of the covalent radii of Si and K (1.11 Å + 2.03 Å = 3.14 Å). Due to the weaker adatom-substrate bond the results of this latest work support earlier models and interpretations.

It is clear that a direct experimental determination of the K—Si bond length is required to resolve the dilemma. This led us to undertake a surface extended x-ray-absorption fine-structure spectroscopy (SEXAFS) study of the K/Si(100) interface. SEXAFS is now well established as a technique particularly suitable for the surface bond length determination. The description of SEXAFS in application to the bond length and geometry studies has been described in several excellent reviews.¹² Our results give strong support to Kasowski's calculation and the conclusion of earlier work. For a $\frac{1}{2}$ -ML coverage we find a K—Si distance of 3.14 Å which corresponds to the sum of K and Si covalent radii. In our opinion the formation of a strong bond as found in the pseudopotential calculation and the properties derived from this interpretation are therefore questionable.

The experiments were performed on the Jumbo monochromator beam line at the Stanford Synchrotron Radiation Laboratory. The Si(100) surfaces were cleaned by a high-temperature flash (> 1000 °C), followed by an anneal at a slowly decreasing temperature. The wafers displayed a 2×1 LEED reconstruction and no traces of O or C contamination [as measured by Auger-electron spectroscopy (AES)] for the runs used in the SEXAFS final analysis. K was evaporated from a carefully outgassed chromate source (SAES getter). The pressure during K exposures was below 1×10^{-10} Torr and during the data acquisition was maintained at 2×10^{-11} Torr. Due to high sensitivity of the alkali-metal overlayer to contamination, the surface cleanliness was checked by Auger spectroscopy before and after each set of data was taken. The overlayer thickness was monitored by the K(252 eV)/Si(92 eV) Auger ratios using as a guide the calibration of Oellig and Miranda.³ In their work the first break in the Auger intensities plotted against evaporation time was assigned to $\frac{1}{2}$ ML coverage and corresponds to the ratio of about 22%. A full monolayer has the Auger ratio of about 65%. In this work we concentrated on the coverage of $\frac{1}{2}$ ML, which is believed to correspond to the fully developed chains in the [110] direction. Above this coverage a multisite chemisorption may exist which would smear out the SEXAFS information. However, it is established that the binding of extra K atoms is weaker and excess K atoms can be removed from the surface by low-temperature annealing. In the present experiment we annealed the interfaces to approximately 100 °C (under

this condition a small burst of pressure from desorbed K could be initially observed) for a few minutes to promote one-site chemisorption and remove extra K atoms. To completely remove K from the surface temperatures of about 600 °C were necessary. For all the 12 samples studied in this experiment the Auger ratios of about 30% which were close to Oellig's value for $\frac{1}{2}$ ML.³

The SEXAFS signal was monitored by both total and Auger electron yields. Presumably due to the very low work function of the alkali metal the total yield did not show any absorption jump and therefore was only used for the normalization to the incident photon flux. The normalization signal was also monitored by another channeltron upstream of the analysis chamber. The Auger yield was monitored with a PHI double-pass cylindrical-mirror analyzer for both *KLL* (2960 eV) and *LMM* (244 eV) Auger decays. We chose the more surface-sensitive *LMM* detection mode for the final analysis. This choice was made due to some artifacts in the *KLL* spectra presumably due to trace amounts of Ni from the alkali-metal getter which were detectable on top of the EXAFS oscillations above the wave vector $k = 7$, although no traces of nickel were detected in our AES spectra. The *LMM* spectra could be monitored up to the k value of 7.9. Above this the strong K 1s photoemission line swept through the detection window. We found that despite sample cooling to -120 °C the EXAFS signal from the K/Si interface was very weak and also strongly attenuated for higher k values. Figure 1 presents the glancing incidence K *LMM* Auger yield spectra from two samples of equal absorption jump (total of 60 sweeps). In the insert we feature in more detail the EXAFS part of the spectrum (χ) in the wave vector k space weighted by k^2 . The glancing incidence was chosen so as to maximize the EXAFS sensitivity to the K—Si bond length which is the quantity of prime interest in this work. To experimentally determine the distance one needs phase shifts

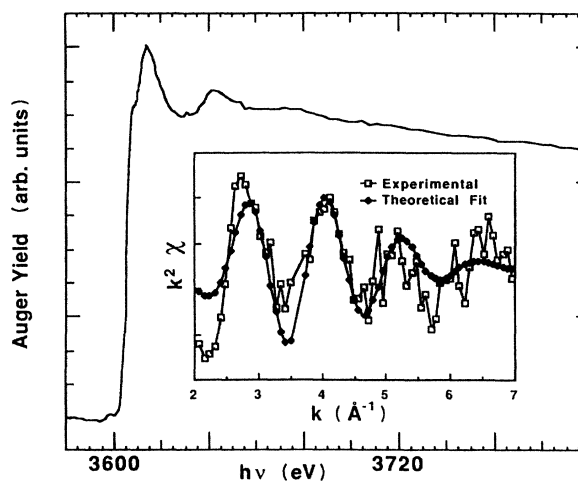


FIG. 1. The K 1s absorption spectra for $\frac{1}{2}$ ML K on Si(100) 2×1 taken by monitoring the surface sensitive *LMM* transition and normalized to the incident flux as described in the text. The insert shows the extracted fine structure and the theoretical fit which yields the bond length determination of 3.14 Å.

from a suitable standard crystal. KCl is a good candidate. Unfortunately, KCl was found to be very unstable when exposed to the x-rays. Even after a single sweep (20 min) the beam caused a visible discoloration of the crystal (probably due to the formation of the F centers) and dramatic changes in the spectra structure. For the bond-length determination we thus used as reference the crystalline Si phase shifts corrected using theoretical values from Teo-Lee¹³ to account for the fact that K is the central atom. This procedure provided a K—Si bond length of 3.14 Å. The uncertainty of this determination which takes into account reliability of the phase-shift determination and possibility of the anharmonic vibrational effects¹⁴ is ± 0.10 Å. The corresponding fit is presented together with the raw data in the insert in Fig. 1. It is important to note that the visual inspection of the fine structure shows 4 full oscillations. Thus just from visual inspection of the spectra, we know that the bond length must be significantly larger than 2.4 Å which is the Si—Si distance and whose spectra exhibit only 3 oscillations in the same k range. We also studied the SEXAFS for the normal light incidence. In this configuration the signal was even weaker and we did not attempt to make any firm conclusions from these data. The data for this configuration are less suitable for the K—Si distance determination, however, they could provide information on the adsorption geometry which for the system at hand has not yet been experimentally established. However, the near-edge structure (not shown) for normal incidence was significantly different than that for glancing incidence. This result shows that K does not form islands on the surface and that Si is indeed involved in the bonding. This correlates well with our LEED results which show the 2×1 reconstruction for the studied overlayers.

It is interesting to note that the bond length of 3.14 Å obtained in this investigation for the K/Si(100) 2×1 interface for $\frac{1}{2}$ ML of K happens to be identical to the sum of covalent radii (Si, 1.11 Å, K, 2.03 Å). This result is in disagreement with total-energy pseudopotential calculations of Ciraci and Batra¹ and thus questions the con-

clusions coming from the assumption of an extremely short ionic bond. The agreement with recent calculations of Kasowski and Tsai² is reasonable. This is also in agreement with a rather low temperature of desorption of alkali metals on a silicon surface which suggests a weak overlayer-substrate interaction consistent with a longer bond (600 °C for K).¹⁵ This bonding corresponds to a limited interaction between the substrate and the overlayer and is consistent with the formation of the one-dimensional metallic chains along the [110] direction as suggested by the interpretation of elementary excitations and other experimental data as well as theoretical calculations of Kasowski and Tsai.²

In conclusion, we report a SEXAFS study of the K/Si(110) 2×1 interface. The K—Si bond length was found to be 3.14 Å which indicates weak overlayer-substrate interaction. The result justifies the physical model proposed on the basis of earlier experimental findings (described in the introduction) and questions the results of recent pseudopotential calculations. The different conclusions of the theoretical work are a direct consequence of very short bond length which is shown to disagree with our experimental determination. On this basis we argue against the model of Ciraci and Batra which in principle could provide an alternative interpretation of some phenomena. This disagreement is somewhat puzzling as the total-energy pseudopotential calculations are believed to be "state of the art" in application to the metal-semiconductor chemisorption.

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*On leave from Service de Physique des Atomes et des Surfaces, Commissariat à l'Énergie Atomique, CEN Saclay, 91191 Gif-sur-Yvette, France.

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