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Surface electronic structure of K on Si(111)2 × 1 as a function of potassium coverage

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We have studied the room-temperature deposition of potassium on the cleaved Si(111)2×1 surface with direct and inverse photoemission. In contrast to the analogous cesium case as well as the prediction of a total-energy calculation, we find that the 2×1 reconstruction is stable against K adsorption. The measured energy dispersions of the unoccupied surface-state band for about half- and full-monolayer coverages indicate a crossing of the Fermi level along the $\bar{\Gamma}$-$\bar{J}$ azimuth, suggesting a metallic substrate surface, as calculated by Ciraci and Batra.

I. INTRODUCTION

In recent years there has been an increasing amount of research on alkali-metal deposition on silicon surfaces.[1-19] This strong interest has been triggered by the question as to how much charge is transferred from the adsorbed alkali atom to the semiconductor, in particular in the low-coverage regime. In the extreme case of a complete electron charge transfer the bonding becomes ionic, and the metallization as a function of coverage is caused by a partial filling of the semiconductor surface-state bands.[1-5] In the other case the charge transfer is fractional and rather small, and a weak covalent bonding explains the strong work-function reduction by a polarization-dependent interaction.[6,7] Some theories[8,9] also favor a mixed type of bonding, i.e., almost ionic at low coverage, while the covalent character increases with coverage.

Experimentally, the present interest started with electron-energy-loss measurements[10] of the plasmon dispersion and the interesting suggestion[11,12] that the K chains on a Si(100)2×1 surface may form a one-dimensional metal, which is in contrast to the substrate metallization of the ionic picture. On the other hand, a surface extended x-ray absorption fine-structure study[13] of this same surface produced a 20% larger value for the K-Si distance than that allowed for a fully ionic bonding.[1] Then, angle-resolved photoemission measurements[14-16] of Si(100)2×1–K and –Cs showed these surfaces to be semiconducting at full coverages. Two apparent surface-state bands were assigned to K 4*s* electrons in two Si dangling-bond states. Metastable deexcitation spectroscopy of cesium on Si(111)7×7 produced[17] clear evidence of a Cs 6*s*-derived level near the Fermi level with a redistribution of charge as a function of Cs coverage.

A common belief in the literature of alkali-metal-on-semiconductor research is the equivalency of the different alkali atoms (with the possible exception of Li), and in particular of potassium and cesium. Often, calculations performed for potassium are compared to experiments with cesium and vice versa. For example, the electronic-structure calculations of Ciraci and Batra[3] for Si(111)2×1–K were compared to photoemission results[18] of Cs on the same surface. Later, it was found from self-consistent total-energy calculations[4] that the 2×1 surface reconstruction is unstable against K adsorption, favoring a 1×1 structure which may become insulating at higher coverages.[4] In contrast, we have recently reported[19] that cesium destroys the 2×1 reconstruction of the cleaved Si(111) surface forming a new $\sqrt{3}\times\sqrt{3}R30°$ structure with a surface-state band which does not cross the Fermi level, i.e., this surface remains semiconducting at saturation coverage.

In the present paper we present the corresponding results of potassium deposited on Si(111)2×1. Contrary to the total-energy calculations, the 2×1 reconstruction persists throughout the entire coverage range, but the surface-state band does cross the Fermi level about midway along the $\bar{\Gamma}$-$\bar{J}$ axis, indicating a metallization. The overall shape and bandwidth of the surface-state band is consistent with Ciraci and Batra's calculations[3] for one K atom per 2×1 unit cell, which is essentially the clean-surface band structure with the Fermi level shifted so that it cuts through the unoccupied part rendering the surface metallic. On the other hand, the electronic-structure calculations of Ishida *et al.*[6] also provide a surface-state band of mostly K 4*s* character, which cuts E_F along the $\bar{\Gamma}$-$\bar{J}$ as well as the $\bar{\Gamma}$-$\bar{J}'$ direction, which is not confirmed by our measurements.

II. EXPERIMENT

The experiments reported below were performed in a two-chamber UHV apparatus.[20] The base pressures in the spectrometer and in the preparation chambers were in the 10^{-11}-mbar range. The system is equipped with inverse and ultraviolet (direct) photoemission spectroscopy, IPES and UPS, respectively. Only IPES was working in the angle-resolved mode. Low-energy electron diffraction (LEED) allows the surface crystallographic order to be checked. The IPES experiments were carried out in the isochromat mode, which detects 9.5 eV photons with a Geiger-Müller-type counting tube equipped with a SrF_2 window. An electrostatically focused electron gun with BaO cathode and the photon detector were fixed relative to one another at an angle of 30°. The angle of incidence θ of the electrons was varied by rotating the sample. The electron-beam divergence was better than 4°, resulting in a resolution of the wave vector $k_{\parallel}$ of $\Delta k_{\parallel}=0.08$ Å^{-1} with an overall energy resolution of 0.35 eV in IPES. The overall energy resolution of the 180°-hemispherical electron energy analyzer for UPS was estimated to be 0.15 eV. The latter were derived from the width of the Fermi-level onset for a tantalum foil which could be interchanged with the silicon crystal. The position of the tantalum Fermi level E_F was used as the energy reference.

Single-crystalline bars of p-doped silicon (resistivity $\rho \simeq 0.05$ Ω cm) with a cross section of 5×5 mm^2 were cleaved using a knife-and-anvil technique. By cleaving along the $[\bar{2}11]$ direction, single domain 2×1 reconstructed surfaces were produced and checked with LEED. UPS showed (cf. Fig. 1) a strong contribution from the occupied dangling-bond surface state. Evaporation of K was done by passing current through a well outgassed dispenser oven (SAES Getters), with the substrate held at room temperature. During evaporation the pressure never exceeded 1×10^{-10} mbar, while the base pressure was always better than 5×10^{-11} mbar. The evaporation rate was checked with a crystal monitor, but the actual coverage was determined from the change of the secondary electron cutoff energy in UPS. Figure 2 shows the change in cutoff energy for a cleaved Si(111) surface exposed to successive evaporations of K. After the first evaporation, a downward band bending of 0.17 eV was observed from the shift of the uppermost Si valence state, similar to the case for cesium.[18,19] The cutoff decreases almost linearly until it reaches a saturation value of -3.45 eV in agreement with the findings of Oellig and Miranda.[21] Up to the saturation region of the cutoff energy and thus of the work function, a well-ordered 2×1 LEED pattern was observed. We assign the saturation of the cutoff to the completion of the first monolayer. In Fig. 2 the cutoff energy reaches a minimum after three minutes of evaporation and starts to increase again. From the change in the valence-band emission (see uppermost curve in Fig. 1, at 5.5 eV) we believe this to be an effect of contamination. The apparent lifetime of the monolayer K-covered surface was approximately two hours during measurements.

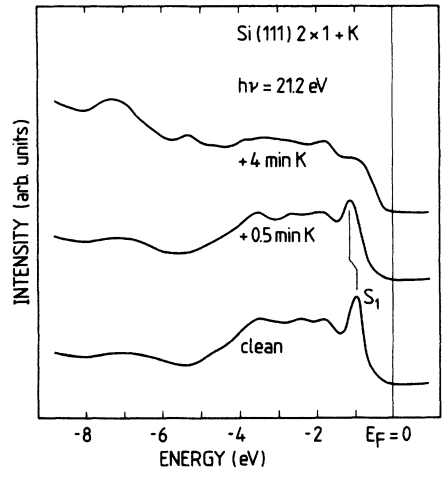

FIG. 1. Angle-integrated ultraviolet photoemission spectra of Si(111)2×1 at $h\nu=21.2$ eV for increasing K evaporation times. Note the shift of the surface-state feature S_1 to 0.17 eV lower energies indicating a downward band bending.

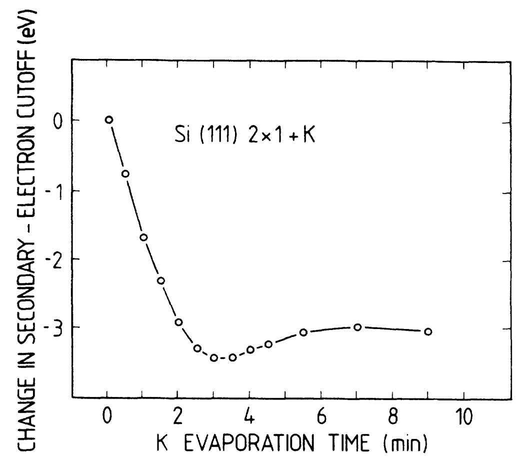

FIG. 2. The change in the cutoff energy for secondary electrons in UPS from the Si(111)–K surface as a function of K evaporation time. The minimum at 3 min is defined as the saturated-monolayer coverage which still exhibits a 2×1 LEED pattern.

III. RESULTS AND DISCUSSION

First we discuss the development of the unoccupied electronic states as a function of K coverage. In Fig. 3

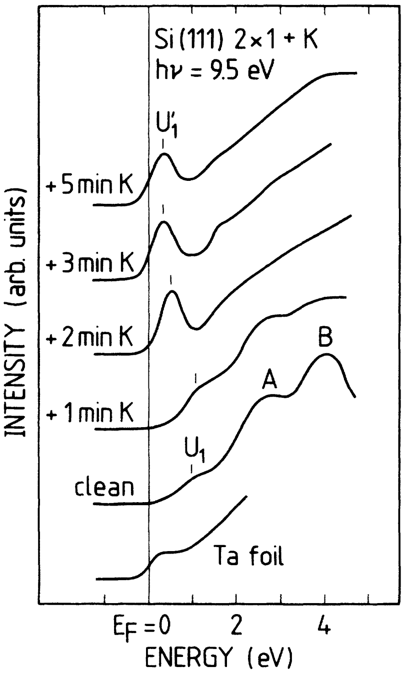

FIG. 3. Normal-incidence inverse photoemission spectra of Si(111)2×1 at $h\nu=9.5$ eV as a function of K evaporation time. Note the development of a K-induced surface state U_1' after U_1 of the clean silicon surface has disappeared.

we show the normal-incidence inverse photoemission spectrum of clean Si(111)2×1 with the well-known U_1 surface-state feature and the two bulk conduction-band peaks A and B.[22] As reference spectrum for the energy zero we have included a clean tantalum spectrum (lower curve). Similar to the K/GaAs(110) system[23] we observe the occurrence of a new K deduced surface state near the position of U_1, which grows in intensity and shifts toward E_F with increasing coverage. At the saturation monolayer coverage (3-min K spectrum) it has reached the Fermi level and does not change anymore. The bulk features A and B disappear with increasing potassium deposition. Although this new K-induced peak U_1' indicates this composite surface becoming metallic, we realize that the corresponding UPS curve for the 4-min K coverage in Fig. 1 does not exhibit any spectral intensity near E_F. We also remember that the K/GaAs(110) surface stayed semiconducting.[23] So did the monolayer-covered Cs/Si(111) surface[19] which, however, produced a structural change of the surface as compared to the present K/Si(111) system ($\sqrt{3}\times\sqrt{3}R\,30°$ versus 2×1).

In order to check on the predicted metallization of the surface and in particular of the filling of the 2×1 surface state and resulting Fermi-level shift with coverage, we have picked two coverages, 2 and 3 min of K evaporation, and performed angle-resolved IPES measurements along the main symmetry directions of the surface Brillouin zone. For the saturated-monolayer (3-min) coverage this is shown in Figs. 4 and 5 for both azimuths, respectively. The $\bar{\Gamma}$-$\bar{J}'$ azimuth (Fig. 4) shows a dispersion behavior with the U_1' peak shifting away from the Fermi level excluding an interpretation in terms of a metallization effect. However, the data taken along the $\bar{\Gamma}$-$\bar{J}$ azimuth (cf. Fig. 5) exhibit spectral changes as a function of polar angle which we believe indicate the crossing of E_F and therewith indeed a metallic character. In both cases the pronounced peak at the $\bar{\Gamma}$ point, which is already close to E_F, disperses a little further down with increasing θ, but the main effect is more or less a drop in intensity for $\theta \geq 25°$ (see Fig. 5).

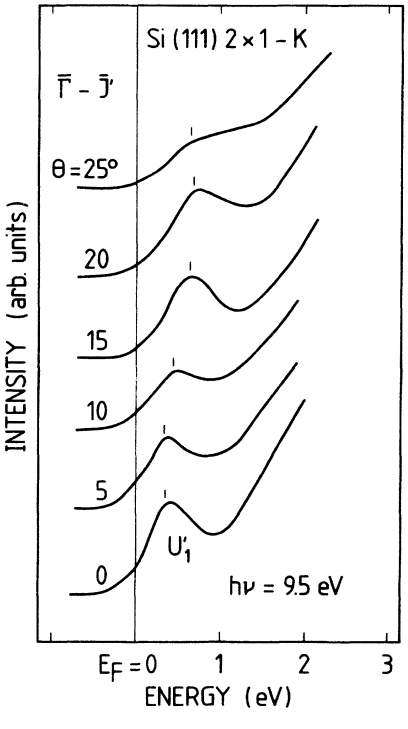

FIG. 4. Angle-resolved inverse photoemission spectra at $h\nu$=9.5 eV for different incidence angles θ, probing states along the $\bar{\Gamma}$-$\bar{J}'$ line of the Si(111)2×1–K surface Brillouin zone.

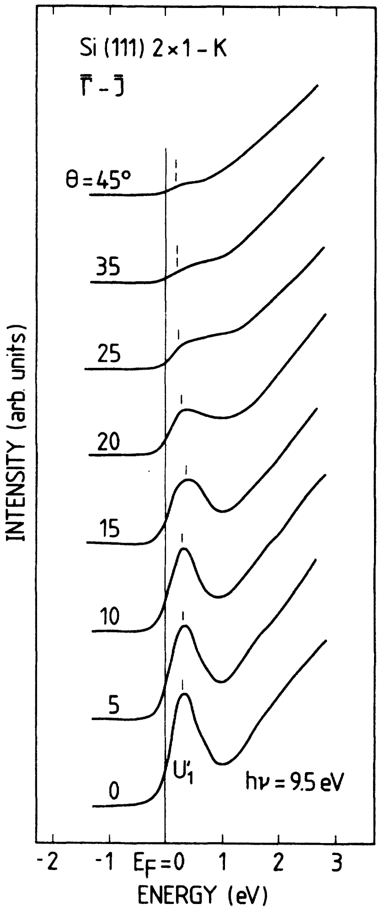

FIG. 5. As in Fig. 4, but probing states along the $\bar{\Gamma}$-$\bar{J}'$ line of the Si(111)2×1–K surface Brillouin zone.

A drop in intensity with a maximum intensity still observable is consistent with a band dispersing through the Fermi level and a spectrometer of finite energy resolution monitoring this crossing. We have simulated such behavior by assuming a Lorentzian peak shape (full width at half maximum FWHM = 100 meV), convoluted it with a Gaussian spectrometer function of different FWHM's (ΔE=20, 100, 300, and 500 meV) and a 293-K Fermi function. For details see Ref. 24. The closer the Lorentzian peak with its initial-peak position moves towards the Fermi level, the more the final-peak position, i.e., the one after the convolutions, deviates from the initial position. As can be seen in Fig. 6(a) this effect scales with the energy resolution ΔE which in this simple simulation could be caused by an energy and/or $\mathbf{k}$ broadening.

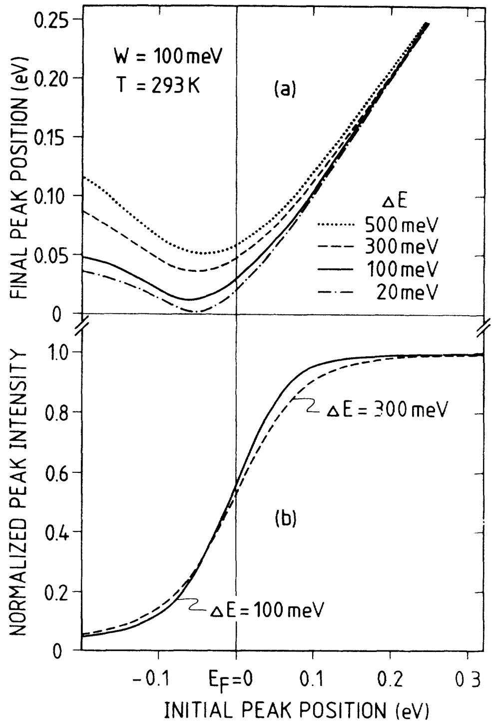

FIG. 6. Simulation of a spectral feature moving through the Fermi level. A Lorentzian curve (FWHM = 100 meV) with initial peak position is convoluted with Gaussian spectrometer functions (FWHM's $\Delta E = 20$, 100, 300, and 500 meV) and a 293-K Fermi function. The resulting new peaks are plotted as final- vs initial-peak positions in the upper panel (a) and their normalized intensities in the lower panel (b). For more details see Ref. 24.

In other words an energetic broadening keeps the final peak position of a band crossing E_F almost constant but its intensity decreases. The latter becomes clear from Fig. 6(b). We believe that the behavior just described applies at least qualitatively to the spectral changes of U_1' in Fig. 5. Quantitatively there is still a discrepancy between our simple simulation and the data of Fig. 5. The minimum peak position of U_1' is about 0.25 eV above E_F in Fig. 5, while the simulation in Fig. 6(a) allows less than 0.1 eV even for the worst resolution ($\Delta E = 500$ meV). Neglect of the background could be one reason for the discrepancy. A similar crossing of E_F was observed[25] in IPES measurements of Na, K, and Cs on Al(111).

With all these imperfections in mind we see from Fig. 6(b) that the actual crossing of the Fermi level occurs when the intensity of the peak drops to half its maximum value. Applied to Fig. 6 this would mean that the U_1' surface-state feature crosses E_F between $\theta = 20°$ and 25° corresponding to $k_{\parallel} \sim 0.5$ Å^{-1}. In Fig. 7 we have plotted the peak positions of U_1' from Figs. 4 and 5 together with the calculated surface-state bands of Ciraci and Batra (Ref. 3, solid line) and Ishida *et al.* (Ref. 6, dashed lines). Both calculations were performed for one potassium atom per 2×1 surface Brillouin zone. First we note that both calculated surface-state bands cross the Fermi level around $k_{\parallel} = 0.6$ Å^{-1} in agreement with our above argument for the crossing of the measured surface-band dispersion. This branch of the band makes the surface metallic and has π^* character as it originates from the clean 2×1 surface-state band. In Ishida *et al.*'s calculation the K 4*s* band disperses downwards in going from $\bar{J}$ to $\bar{\Gamma}$. To avoid a crossing with the Si π^* band a hybridization gap of about 0.8 eV at $\bar{\Gamma}$ opens up, which produces another Fermi-level crossing along the $\bar{\Gamma}$-$\bar{J}'$ direction. Checking with Fig. 4 in which the IPES curves along this azimuth are presented, we do not find any evidence for this second crossing. Instead, the U_1' surface-state feature exhibits an upward dispersion. It is plotted in Fig. 7 and resembles in its overall shape and bandwidth the upper branch of the π^* surface-state band of Ishida *et al.*[6]

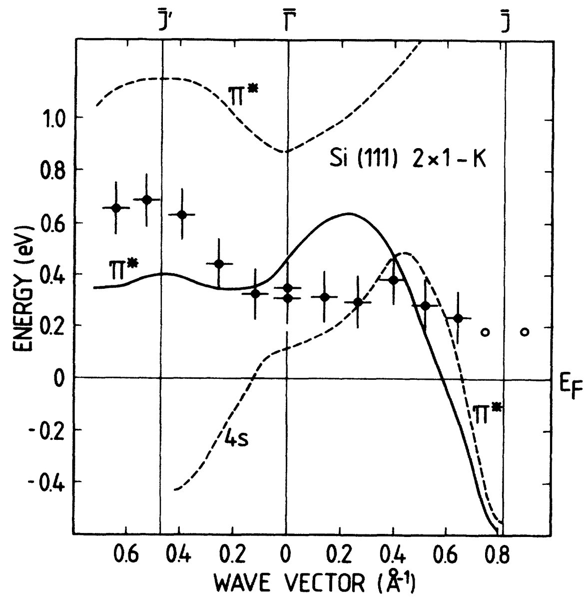

FIG. 7. The energy dispersion $E(k_{\parallel})$ of the U_1' surface-state feature as derived from Figs. 4 and 5. The crosses indicate the estimated uncertainty. The solid line represents the calculated surface-state band of Ciraci and Batra (Ref. 3), the dashed lines the ones by Ishida *et al.* (Ref. 6), both for one K atom per 2×1 surface Brillouin zone.

In the calculations of Ciraci and Batra[3] the bonding is ionic and the K 4*s* valence-electron charge is donated to the unoccupied Si π^* surface-state band resulting in a filling and concomitant shift of the Fermi level to higher energies. At the monolayer coverage, i.e., one K atom per 2×1 surface unit cell, this rise is 0.7 eV with respect to the valence-band edge.[3] For lower coverages, the Fermi-level shift should be less pronounced. In order to check this we have also performed angle-resolved IPES measurements for a 2-min K coverage corresponding to a work-function change of $\Delta\phi = -2.9$ eV (cf. Fig. 2). The results are shown in Fig. 8. We note the K-induced surface-state feature U_1''. Similar to the monolayer-covered surface in Fig. 5 we again observe a decrease in peak intensity with increasing polar angle. As discussed at length above we interpret this behavior to be the

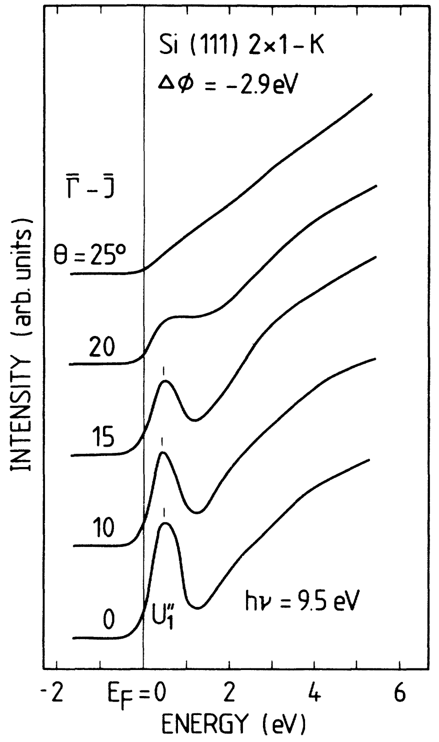

FIG. 8. As in Fig. 5 probing states along the $\bar{\Gamma}$-$\bar{J}$ line of the 2×1 surface Brillouin zone, but for a coverage below the saturated-monolayer, i.e., for $\Delta\phi=-2.9$ eV (cf. Fig. 2).

Fermi-level crossing of U_1'' as well. However, in contrast to the picture developed by Ciraci and Batra,[3] the crossing occurs at a smaller θ, i.e., between 15° and 20° (cf. Fig. 8). In particular, compare the 25° spectra of Figs. 5 and 8. A lower position of E_F in Fig. 7 should leave more spectral U_1'' intensity in Fig. 8 for $\theta \geq 25°$ than in Fig. 5 with the higher coverage and thus higher Fermi-level position. On the other hand, we have to doubt that a coverage below the saturated monolayer consists of an ordered overlayer, although LEED exhibited a 2×1 pattern for this coverage too. Hence $k_{\parallel}$ may not be a good quantum number, and angle-resolved measurements should be taken with caution.

Finally we mention that a metallic surface as derived from angle-resolved IPES measurements does not contradict our angle-integrated UPS measurements in Fig. 1 where we do not find any spectral intensity at E_F. The crossing of E_F happens only at certain points of the surface Brillouin zone and would be averaged out in an angle-integrated measurement. In addition, our isochromat energy of $h\nu=9.5$ eV provides a better cross section for s,p electrons than the He I photon energy of 21.2 eV. Only angle-resolved UPS measurements will allow the surface-state band to be mapped within the occupied part of the surface electronic structure as well and the complementary Fermi-level crossing to be found from lower energies upwards. Such experiments will be performed in the near future.

In summary, we have measured angle-resolved inverse photoemission spectra of the Si(111)2×1–K surface. This saturated-monolayer coverage is defined by the minimum of the work function. The plot of the energy dispersion of a K-induced surface-state feature reveals a Fermi-level crossing which renders this surface metallic in agreement with calculations by Ishida *et al.*[6] and Ciraci and Batra,[3] both performed for one K atom per surface unit cell. Calculations for higher coverages[3] do not agree with our measured energy dispersion. Its general shape and width certainly agree better with Ciraci and Batra's calculated bands. All this is different from the monolayer-covered cesium surface which remained semiconducting and exhibited a $\sqrt{3}\times\sqrt{3}R\,30°$ surface reconstruction. This points to quite a different behavior of potassium and cesium interacting with silicon surfaces in general.

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