Novel Bi-Polaronic Ground State in K/Si(111):B*  

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We report here on low energy electron diffraction (LEED), Auger spectroscopy, scanning tunneling microscopy (STM) and angle-resolved photoemission (ARPES) studies of ultrathin films of K/Si(111)-√3×√3R30:B. A potassium-induced surface state is evidenced being maximum at the saturation coverage. ARPES data clearly evidence the folding of the K-induced surface band near the expected k_F attesting of a large Mott gap Δ = 500 meV and a very narrow measured bandwidth W = 140 meV. This clearly signs the strongly correlated nature of this material. Nevertheless, by decreasing the temperature, a novel insulator to insulator surface phase transition is observed characterized by a doubling of the unit cell together with a stabilization of the surface band. In addition, the linear temperature dependence of the ARPES linewidth suggests these materials are characterized by a strong electron-phonon coupling. Therefore, such a phase transition can be explained if the electron-phonon coupling is large enough to compensate the strong on-site repulsion defining a bi-polaronic insulating ground state instead of a Mott-Hubbard one. [DOI: 10.1380/ejssnt.2009.259]

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I. INTRODUCTION

Semiconductors are usually considered as prototypes for the band insulator, both charge and spin excitations being cancelled by the semi-conducting gap. Nevertheless, the Si(111) surface is characterized by the presence of dangling-bonds (DB) which can reorganize in the well-known 7 × 7 surface reconstruction. Therefore, a half-filled DB-based surface state appears inside the gap giving a metallic character to this originally semi-conducting surface [1, 2]. In boron-enriched (p-doped) silicon materials, the segregation of B dopants at surface leads to a √3×√3R30 surface reconstruction associated with a surface metal-insulator transition in agreement with band structure calculations [3, 4]. Doping this interface with alkali atoms (electron donors) leads to completely different physical properties [5, 6]. Indeed, the reduction of the bandwidth together with the reduction of screening of the interactions at surface have been shown to lead to a Mott transition implying sp states, the Harrison criterion U/W >> 1 being reached here only at surface. 1/3 K ML/Si(111)-√3×√3R30 : B (K/Si:B) has been first proposed to have a Mott-insulator ground state in 1997 [7, 8]. Then, such a Mott state at surface has been identified as a generic property of semiconducting surfaces having a √3×√3 surface reconstruction [9] i.e. presenting a triangular pattern such as SiC(0001) [10, 11], C/Si(111) [12] and more recently Sn/Ge(111) at low temperature [13]. Moreover, it has been proposed that non-negligible exchange coupling between neighboring dangling bonds electron could lead to the formation of a half-filled frustrated antiferromagnetic triangular network at surface [7, 10, 15, 16]. More recently, the possible occurrence of superconducting properties upon doping has been emphasized justifying thus the great interest for these semiconducting surfaces [17]. Angle-resolved photoemission spectroscopy (ARPES) is known to be a powerful tool since it provides great insights in the nature of the single particle excitation spectra, especially in correlated systems. Nevertheless, the results are sometimes questionable in correlated bulk-like materials due to the surface sensitivity of this technique. In the case of correlated semiconducting surfaces considered here, the situation is clearer since only the surface and interface physical properties are relevant. We report here on structural and spectroscopic investigation of K/Si:B as function of the temperature to search for the real ground state of these materials. In particular, a novel surface phase transition is evidenced by LEED at low temperature together with a stabilization and a narrowing of the surface state band as seen by photoemission. All the experimental features discussed in the following give arguments for a redefinition of the ground state of K/Si:B as a (surface) bi-polaronic insulator rather than a Mott-Hubbard one. This is expected in the Holstein-Hubbard model if the electron-lattice coupling g is enough to overcompensate the on-site electron repulsion U leading to negative U-centers [18] as already proposed for Na/GaAs(110) [19, 20].

II. EXPERIMENTAL DETAILS

The measurements were carried out in a UHV setup composed of a Molecular Beam Epitaxy (MBE) chamber for the elaboration and characterization of the surfaces connected to a low temperature STM/STS and an ARPES set-up. The Si(111) substrates (a_111 = 3.85 Å) originate from a 2.5 inch silicon wafer highly enriched with boron atoms in order to reach sufficiently low resistivity (ρ = 10^−3 Ω·cm) to avoid charging effects. Then, the √3×√3R30 surface reconstruction (a_3√3×√3 = 6.66 Å) has been obtained by several short annealing at 1450 K with a direct-current heating set-up to remove the native oxide followed by a few hours heating at 1100 K to favor the segregation of boron atoms at surface. The average density of boron vacancies has been con-
trolled by STM topography with a low temperature Omicron STM in order to be minimized. Then, the K/Si:B interface has been prepared by evaporation of alkali atoms from a SAES getter with a deposition rate of 0.13 monolayer/nm in a vacuum better than $5 \times 10^{-10}$ mbar. The $K_{LM1}$ Auger line allowed us to monitor precisely the alkali coverage. ARPES data have been recorded with a high resolution Scienta SES-200 analyzer coupled to a high intensity UVS-300 Specs discharge lamp operating at $h\nu = 21.2$ eV (He-I mode) at a pressure of $10^{-5}$ mbar in the ionisation chamber ($10^{-9}$ mbar in the photoemission chamber). The energy resolution was better than 10 meV (for pass-energy 10 eV) and angular resolution better than 0.4 degree corresponding to a k resolution better than 0.015 Å$^{-1}$. The 2D detector allows to record accurately the emission spectra between -8 and +8 degrees i.e. over half the $\sqrt{3} \times \sqrt{3}$ reconstructed Brillouin zone in less than ten minutes permitting to avoid surface contaminations.

### III. RESULTS AND DISCUSSION

The cristallographic structure of the Si:B interface is presented on the Fig. 1(a). A boron enriched surface has been obtained following the procedure described in the section devoted to the experimental details. Previous photodiffraction measurements [3] and ab initio calculations [4] have clearly established the occupation of the pentavalent $S_5$ sub-surface site by boron atoms leading to the well known $\sqrt{3} \times \sqrt{3}$ surface reconstruction, the surface hexagonal unit cell being 30 degrees turned compare to the initial (1 x 1) unit cell. The presence of the surface reconstruction has been monitored by STM at 80 K and LEED in the 80-300 K range as presented in Fig. 1(b). Under appropriate conditions (see experimental details), a nearly free of defects surface reconstruction is obtained as monitored by STM. Indeed, as previously reported [21], B vacancies appear as bright spots in positive BIAS voltages due to a well defined unoccupied localized state close to 500 meV above the Fermi level. Therefore, the number of vacancies can be controlled and minimized to 0.015 per nm$^2$ by adjusting the annealing temperature. On the Si(111) surface, the dangling bonds (DB) are known to be reorganized in a $7 \times 7$ surface reconstruction, the weakly dispersive adatom half-filled surface state ensuring the (moderate) metallic character of this surface [1]. At the opposite, the Si(111)-$\sqrt{3} \times \sqrt{3}$R30:B substrate exhibits a semiconducting behavior as demonstrated by the photoemission spectra recorded on the substrate (dashed line in Fig. 2(b)). Indeed, DB electrons are trapped by boron impurities leaving an empty DB (surface) state as shown by previous experiments [22] and well accounted by one-electron band structure calculations [4].

Then, evaporation of K adatoms at room temperature has been monitored by Auger spectroscopy as presented in Fig. 2(a). The $Si_{KLL}$, $B_{KLL}$ and $K_{LM1}$ Auger lines are clearly identified on the spectra corresponding to a deposition time t=100 s. Plotting the $K_{LM1}/Si_{KLL}$ intensity ratio as function of t allows us to evidence its saturation around t=130 s. Indeed, according to previous studies, the room-temperature sticking coefficient fall down after the completion of the first layer. This corresponds also to the saturation of the workfunction observed usually in these systems [6]. Therefore, the room-temperature saturation coverage is defined as one K atom per reconstructed unit cell i.e. 0.33 ML K/Si:B. As evidenced by previous photoemission studies on core-levels, a charge transfer through the Si(111) surface occurs due to hybridization between singly occupied 4s alkali orbitals and empty 3$p^3$ silicon orbitals [5, 6, 22]. According to recent DFT calculations [23], the chemisorption of K adatoms should take place preferably at the highly coordinated $H_3$ site (red dashed circles in Fig. 1(a)). Nevertheless, to our knowledge, there are no such experimental evidences up to now. The LEED pattern obtained at room temperature for the
saturation coverage is presented in Fig. 4(a). It indicates the $\sqrt{3} \times \sqrt{3}R30$ surface reconstruction is conserved upon K adsorption up to one adatom per surface reconstructed cell as in previous measurements. Then, a new K-induced surface state is known to be formed [5, 6]. This state has been established to be metallic at half-filling i.e. at saturation coverage by ab-initio calculations [23]. According to previous experimental results, the K-induced surface state we have measured, presented in Fig. 2(b), remains insulating up to 0.33 monolayer. This has been first interpreted as originating in a Mott metal-insulator transition induced by the reduction of the bandwidth at surface due to the reduction of the effective coordination number [7, 8].

The lower and upper Hubbard surface bands have been clearly identified by photoemission and inverse-photoemission and the full Mott gap previously established to be roughly 1.5 eV [7]. The new angle resolved photoemission data presented here has been obtained with an energy and momentum resolution one order of magnitude better than in previous works providing additional features. First, the coverage dependence of this surface state, so-called $S_1$ state, behaves as for an impurity (localized) level. Indeed, Contrary to what is expected in band theory, its energy position evolves only slightly with the filling (doping) as shown in Fig. 2(b). In addition, its spectral intensity is maximum close to the saturation coverage as already observed for similar interfaces [19, 20]. At the opposite, the $S_2$ feature have been previously identified as originating from the substrate band-structure and are only slightly modified by K adsorption [6]. The surface state dispersion obtained along the $\Gamma - M'$ high symmetry line of the hexagonal reconstructed Brillouin zone (BZ) is presented in Fig. 3 for the optimal coverage. A new fact is that a clear band-folding of the surface state occurs for a k-value close to half of the BZ ($0.3 \, \text{Å}^{-1}$), this value corresponding to the expected $k_F$ obtained from tight-binding calculations. This is probably due to the opening of the correlation-induced Mott gap expected at half-filling if $U$ becomes larger than $W$. In addition, a weak but significant dispersive behavior is clearly established with a measured bandwidth $W_{\text{exp}} \approx 140$ meV (dotted line in Fig. 3). This indicates a strong renormalization of the experimental bandwidth compare to the one obtained from band structure calculations $W_{LDA} \approx 300$ meV [23]. This is probably due to the real part of the self-energy usually observed for strongly correlated systems. The maximum of the dispersion is obtained for $k_{\text{Max}} = 0.3 \, \text{Å}^{-1}$ and $E_{\text{Max}} = 760$ meV. In the Hubbard scheme, the average binding energy gives the effective coulombic repulsion $U/2 \approx 0.75$ eV leading to a measured $U/W$ ratio considerably larger than 1. Analysis of the 2nd derivative of the peak close to $E_F$ leads to a substantial Mott gap $\Delta_{\text{Mott}} \approx 500$ meV. At this stage, the K/Si:B interface behaves as a Mott-Hubbard material as proposed for a great number of such semiconducting surfaces presenting a $\sqrt{3} \times \sqrt{3}R30$ surface reconstruction as SiC(0001) [11], Sn/Ge(111) or Si(111) at low temperature [13, 14] and as predicted for C/Si(111) [12].

Nevertheless, one should first remark a strong intrinsic broadening of this surface state at room-temperature ($\approx 600$ meV) even considerably larger than the bandwidth. More, the shape of the surface state is strongly k-dependent and the integration along the $\Gamma - M'$ direction leads to a broad gaussian line. Wuetering and co-workers [7] have proposed to interpret this anomalous broadening as a possible Franck-Condon envelop originating from the strong coupling to the lattice. Indeed, in the non-adiabatic regime, the electron-phonon coupling (EPC) influences both the energy and the lifetime of the quasi-particle bands measured by photoemission through modifications of real and imaginary part of the self-energy. Hence, the coupling of the quasi-particle bands with a phonon continuum or with a specific localized phonon mode usually leads to a temperature-dependent broadening of the linewidth when the temperature is comparable to the Debye temperature or the typical phonon energy [25]. Under these assumptions, the linewidth is usually described by $\Gamma = \Gamma_0 + 2\pi \lambda k_BT$. $\lambda$ being the mass enhancement parameter given by $\lambda = (m* - m_0)/m_0$. Therefore, in presence of a strong e-ph coupling, the linewidth should vary linearly with the temperature indicating a strongly renormalized effective mass. It is interesting to notice that
the condition $\lambda$ larger than 1 supports the idea that the system should become unstable toward a reconstruction or some form of phonon-mediated pairing [25]. The non negligible role of EPC on the Si(111) surfaces has been emphasized a long time ago [26, 27]. Recently, a strong mass enhancement factor $\lambda = 1.01$ has been extracted from ARPES data obtained on the Si$(7\times7)$ metallic surface state in the 30-300 K temperature range [28].

Therefore, the temperature dependence of the photoemission spectra of K/Si:B near the optimal coverage has been investigated as well as possible structural changes.

A comparison between LEED patterns obtained at 300 K and 220 K for the saturation coverage is presented in Fig. 4. New diffraction peaks appear clearly in the low temperature diffraction pattern indicating a novel $2\sqrt{3}\times\sqrt{3}$ phase at low temperature. This implies a doubling of the surface lattice periodicity along the two initial $\sqrt{3}\times\sqrt{3}$ crystallographic axes or the possible existence of three domains with the doubling of the unit cell occurring only in one direction. The spot widths are slightly larger with a small additional background. Nevertheless, a rather well established structural ordering is obtained at 220 K. At the same time, the overall surface band is shifted to higher binding energies ($\delta E = 60$ meV) between 300 and 200 K indicating a stabilization of the electronic structure. This is evidenced by the temperature dependence of the energy dispersion curve obtained at $k_{\text{max}}$ presented in Fig. 5(a). In addition, the shift occurs only on the surface band $S_1$, whereas the $S_2$ and $S_3$ features remains unchanged indicating no photovoltage or charging effects occur (not presented here). A more detailed study of the transition indicates that hysteresis effects are strong. The transition temperature has been evaluated to be roughly $T_c \approx 270$ K. In addition, a continuous narrowing of the surface bands clearly appears with decreasing temperature from 300 to 100 K. Indeed, by plotting the width (FWHM) of the energy dispersion curves obtained at $k_{\text{max}}$ as function of the temperature, a linear behavior is clearly established in Fig. 5(b). In addition, we have not observed significant changes of the photoemission line width close to the transition. From this dependence, we have extracted a mass enhancement factor $\lambda = 1.06$ close to the value obtained on the Si$(7\times7)$ surface [28] indicating that this material is also characterized by a strong e-ph coupling. Such a quasi-linear variation is valid for temperature higher than the Debye frequency but is usually experimentally observed over a wider temperature range as revealed by previous works on these surfaces [28]. Hence, these results clearly demonstrate the occurrence of a new insulating to insulating phase transition involving a doubling of the unit cell due to strong electron-phonon interactions.

On the theoretical point of view, the Holstein-Hubbard model, including both on-site repulsion $U$ and electron-phonon coupling $g$ has been intensively studied in 1D [30], 2D [29] or in infinite dimension [18, 31]. For small $g$ and/or $U$ values, the ground state is shown to be metallic at half-filling (but unstable in quasi-one dimensional material through charge density waves instabilities). At large $U$, a correlation induced Mott-insulating phase occurs as previously proposed for the alkali/Si:B interface concerned here. Nevertheless, in case of strong e-ph coupling (known as the anti-adiabatic case), a bi-polaronic insulating ground state (BPI) is promoted characterized by the formation of electron pairs trapped by their self-induced ionic displacements in an area of the of the order of the lattice constant (local dimerization and charge ordering). Therefore, a new effective electron-electron interaction $U_{\text{eff}}$ can be defined resulting from the competition between the coulombic repulsion and the attractive energy due to the formation of the bi-polaron leading to $U_{\text{eff}} = U - 2g^2/\omega_0$, with $E_{\text{BP}} = 2g^2/\omega_0$ being the binding energy of the bi-polaron [18]. In the present case, we can exclude the weak-coupling charge density wave (or Peierls) scenario since the high temperature phase is strongly insulating. Therefore, we propose to interpret this novel transition as a stabilization of the bi-polaronic phase at low temperature. Indeed, a periodic lattice deformation takes place due to the alternation of doubly occupied sites and unoccupied sites, the coupling to the lattice being high enough to compensate the electron repulsion leading to negative U-centers as already proposed for al-

![FIG. 3: (a) Energy dispersion curves obtained for $k_F$, $k_{M\text{ax}}$ and $k_{M'}$ at room-temperature for 0.33 ML K/Si:B; (b) corresponding ARPES intensity map measured along $\Gamma - M'$; expected tight-binding dispersion (red dashed-dotted line), experimental dispersion (black-dashed-line).]

![FIG. 4: LEED pattern obtained for 0.33 monolayer K/Si:B above (T=300 K) and below (T=220 K) the transition temperature]
kali ultra-thin layers deposited on GaAs(110) [19, 20].

IV. CONCLUSION

The structural and electronic properties of the K/Si:B interface have been studied as function of the temperature and corresponding linewidth in the inset as function of temperature. A novel $\sqrt{3} \times \sqrt{3} \rightarrow 2\sqrt{3} \times \sqrt{3}$ phase transition has been evidenced connecting two insulating phases. In addition, we have shown these materials are characterized by a strong e-ph coupling. As a consequence, we have proposed to describe the ground state of K/Sl:B as a bi-polaronic phase rather than a Mott-Hubbard one as previously proposed. As a consequence, due to their bounded nature, bi-polarons should carry a singlet spin state making these surfaces non-magnetic at low temperature contrary to previous speculations. In addition, the substitution with other alkali atoms should provide the way to modify microscopic parameters such as bandwidth, e-e repulsion, or e-ph coupling by modifying charge transfers, local arrangement of adatoms or adatom masses. Thus, these semiconducting surfaces give the opportunity to study the physical properties of correlated materials in presence of a strong e-ph coupling, especially the limit of the bi-polaronic phase, with adequate surface science techniques.

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