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Li-induced metal-semiconductor-metal transitions on the Si(111)-(7×7) surface: A work function, photoemission, and NMR study

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The metallic (7×7) reconstructed Si(111)-surface undergoes with increasing Li coverage a metal-semiconductor-metal transition as seen in work function changes, photoelectron spectra and T_1 times determined in NMR experiments. From zero coverage to about 0.12 ML the partly delocalized electron gas of the originally metallic Si(111)-(7×7) surface becomes increasingly localized. Around 1 ML Li coverage the surface becomes semiconducting and its properties may be understood in a simple local bonding picture in which the $(sp)^3$-Si orbitals hybridize with the 2*s*-Li orbital. A further increase of coverage leads to a metallic overlayer.

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I. INTRODUCTION

Due to its dangling bonds the (7×7) reconstruction of the Si(111) surface has many hallmarks of a metallic surface. Recently, not only a parabolic dispersive band located at the center of the (7×7) Brillouin zone has been identified[1] but also "Korringa-like nuclear spin relaxation," was observed in nuclear magnetic resonance (NMR) experiments on Li, adsorbed at extremely low coverages as a 10^{-3} monolayer (ML) and below.[2] That is on average only one Li atom per 20 unit cells of the (7×7) reconstruction. Nuclear spin-lattice relaxation rates, denoted as $\alpha=1/T_1$, describe the rate of change of the nuclear polarization (magnetization) towards thermal equilibrium [Eq. (2)]. In classical NMR experiments[3–6] T_1 denotes the built up time; here it denotes the decay time of the polarization, since its initial value is far above the one of thermal equilibrium (see Sec. II).

Relying on common wisdom, the observation of "Korringa-like" nuclear spin relaxation—magnetic-field-independent relaxation rates linear in temperature—is considered as a univocal sign for the "metallicity" of a system.[3–5,7] In what follows, we will be more careful and consider it as a sign for an at least partly delocalized electron gas with correlation times much shorter than the electron Larmor period for the magnetic field used. A recent discussion of electron localization and electric conductance in the (7×7) reconstruction can be found in Ref. 8.

In contrast to the plain Si(111)-(7×7) surface, the hydrogen terminated Si(111)-(1×1):H one has saturated dangling bonds and is semiconducting, the latter being proven as well experimentally[9–13] as theoretically.[2,14–17] Adsorbing, however, on the Si(111) surface at room temperature chemically equivalent alkali-metal atoms, instead of hydrogen reflection high energy electron diffraction (RHEED) and low electron energy diffraction (LEED) patterns, show a new appearing superstructure, called δ-7×7 or 7×1, while the original (7×7) superstructure is disappearing.[18–21] Its geometrical structure is not clarified finally. Comparing ultraviolet photoelectron spectra (UPS) for the adsorption of K and Cs (Refs. 22–25) with those obtained for Li (Refs. 18 and 26) similarities but also differences appear. UPS experiments on adsorbed K and Cs display with increasing coverage a vanishing density of states around the Fermi energy.[22–24,26,27] While for K adsorption and also for Li adsorption, as shown in Sec. III, the density of states at the Fermi energy vanishes for saturation coverages; it is already recovered for Na and Cs adsorption.[28] Thus at saturation coverage the (7×7) surface becomes semiconducting for Li and K adsorption, but is metallic if Na and Cs is adsorbed. Beyond saturation coverage UPS experiments indicate for K and Cs adsorption a metallization of the surface, while for Li adsorption at room temperature the formation of silicides is reported.[18] In contrast to the other alkali-metals Li may diffuse at room temperature into the Si(111) bulk.[29,30] Since the amount of Li diffusing into the bulk depends crucially on its solubility in Si and on temperature, low enough temperatures (around 100 K) and the choice of *n*-doped material is essential to suppress it.

Metastable-atom deexcitation spectroscopy (MDS) experiments detected even at low coverage (no calibration) remaining valence electrons on the adsorbed Li atoms which provides clear evidence of a partially occupied Li resonance.[29] Theoretically, this is explained by adsorption at the adatom dangling bonds.[31] This adsorption site is also adopted for low coverage K and Cs adsorption, as UPS experiments show.[22–24] The results are supported by recent high-resolution electron energy loss spectroscopy (HREELS) experiments which find a clear signature for a metal-semiconductor transition at the early stage of Na and Cs adsorption by completely filling half-filled Si-adatom dangling bonds.[28]

An understanding of the coverage-dependent metal-semiconductor-metal transition driven by alkali-metal adsorption on the Si(111)-(7×7) surface obviously requires not only a thorough discussion of the nature of the chemical bond between the alkali-metal atom and the substrate (the past battles on this question became focused within the phrase "ionic versus covalent binding"), but one must address also the issue of electron localization, for which the structure and density of overlayer atoms are apparently crucial parameters.[23,24,32–34] UPS, HREELS, and Auger electron spectroscopy (AES) experiments are suitable techniques to study chemical bonds. The observation of nuclear spin depolarization (relaxation) in β-NMR (measurement of relaxation rates[3–6]), which are now feasible for Li adsorbates on semiconductors[2,13,35] is the ideal tool to study localization phenomena, since its result is proportional to the electron correlation time (see Appendix B in Ref. 2 for details).

The description of β-NMR experiments for the Li induced metal-semiconductor-metal transitions on Si(111)-(7×7) will therefore be the central part of this paper. For an interpretational support we embed these results, however, into work function change ($\Delta\Phi$) and UPS results, which were obtained parallel over the years.

II. EXPERIMENTAL

The experiments have been performed in two UHV apparati in Marburg and at the Max-Planck-Institute for Nuclear Physics in Heidelberg (base pressure below 3×10^{-11} mbar), both equipped with NMR facilities aside from conventional surface science techniques as temperature programmed desorption (TPD), LEED, AES, and $\Delta\Phi$ measurement devices. The experiment in Marburg has been described briefly recently.[36–38] It was used for $\Delta\Phi$ and UPS measurements. It has an atomic beam facility together with a "retarding field" assembly to determine as a function of Li coverage also *in situ* work function changes. In addition, UPS measurements using a He light source in connection with a hemispherical mirror analyzer (HMA) were possible.

The experiments were performed on commercially grown *n*-type phosphorous-doped Si(111) samples with a resistivity of 4 to 10 Ω and a miscut of less than 0.3°. The crystals were mounted in an ultrahigh vacuum (UHV) chamber without any prior preparation and cleaned *in situ* by heating to 1450 K to remove carbon contamination. Annealing for 30 min at 1200 K followed by slow cooling during the ’1×1’$\leftrightarrow 7\times7$ phase transition led to samples that showed no contamination in Auger spectra (the Si signal-to-noise ratio was greater than 1000) and sharp 7×7 LEED patterns. The samples were heated resistively by an ac current.

The β-detected NMR experiments were performed in Heidelberg utilizing nuclear spin polarized radioactive ^{8}Li as a NMR probe. Together with the radioactive Li also stable Li adsorbs always. Since it has also been described in detail recently[2,35,39–41] we sketch this tool only briefly. The UHV chamber used in this part of the experiments was equipped with a homemade load lock for a fast transfer of the silicon crystals. The samples used were also moderately $n(P)$-doped Si(111) crystals with a misorientation of $<0.5°$. They were prepared with a wet chemical procedure outside the UHV chamber as hydrogen-terminated Si(111)-(1×1):H surfaces.[2,42] This detour was chosen in order to deal outside the UHV chamber with rather inert surfaces, which, moreover, are improved in their properties during the wet chemical treatment. These wet chemically prepared samples were transferred into the UHV chamber via the fast load lock and clamped onto a small Mo plate. Heating was achieved by electron bombardment from the backside of the Mo plate, cooling by contact of the sample holder to a liquid nitrogen reservoir. After the sample was transferred into the UHV it was flashed to about 1200 K in order to remove the adsorbed hydrogen and to prepare the (7×7) reconstruction. Afterwards a clear (7×7) LEED pattern was observed. The cleanliness of the surface was monitored by AES. (The ratio of carbon and oxygen Auger lines to the Si one was kept below 0.01 always.)

The UHV chamber was connected via a differential pumping section to the chamber in which the source for a thermal nuclear spin polarized ^{8}Li atomic beam was installed. Radioactive ^{8}Li with a half-life of only 0.84 s was produced *in situ* by bombarding a deuterium gas target with a 24 MeV ^{7}Li^{3+} ion beam from the MP-tandem accelerator at the MPI for Nuclear Physics in Heidelberg including the ^{2}H(^{7}Li,^{8}Li)^{1}H nuclear reaction. Its nuclear spin $(I=2)$ was polarized by optical pumping in a magnetic field either in the $m=+2$ or in the $m=-2$ state (positive and negative polarization). The source provided at the site of the sample a thermal atomic beam of about 10^8 lithium atoms/s containing a small amount of about 5×10^4 atoms/s of the nuclear spin polarized radioactive isotope ^{8}Li.[34] Only these ^{8}Li atoms served as probes for the measurements of T_1 times (nuclear spin relaxation rates $\alpha=1/T_1$.

^{8}Li is a β-decaying nucleus with a half-life of $T_{1/2}=0.84$ s. Spin polarization of the adsorbate ^{8}Li itself can therefore be detected via the directional asymmetry of the β decay. The asymmetry ϵ of the β-electron intensity with respect to the magnetic field is measured by scintillator telescopes.[35] The nuclear polarization P of the ^{8}Li ensemble is determined from the observed asymmetry ϵ as

$$\epsilon=\frac{N(0\,°)-N(180\,°)}{N(0\,°)+N(180\,°)}=-\frac{1}{3}P. \tag{1}$$

Here $N(0°)$ denotes the count rates for electrons emitted along the direction of the magnetic field, while $N(180°)$ denotes the ones opposite to it. The factor $\left(-\frac{1}{3}\right)$ reflects to properties of the ^{8}Li β decay (the allowed Gamow-Teller decay[43]). Systematic errors in the determination of ϵ are eliminated by performing the experiment with the reversed polarization P as well. Details of the signal detection can be found in Refs. 41 and 44.

The nuclear spin relaxation experiments consist basically of three subsequent steps which are repeated many times. It starts with a filling period (typically 1.5 s) during which ^{8}Li is produced and accumulated in the thermalizer.[39] Afterwards it is released while production is still going on. An atomic beam is formed and nuclear spin polarized by optical pumping. The thermal ^{8}Li atoms are adsorbed on the surface for 0.5 s. Finally during the detection period of 4 s the β-electron asymmetry ϵ [Eq. (1)] is measured as a function of time. During the detection period the ion beam, as the main source of background signals, is switched off. Figure 1 displays as a typical example $\epsilon(t)$ data for ^{8}Li adsorption on a Si(111) surface kept at $T=110$ K and at a magnetic field of 0.8 T.

Since ^{8}Li has a nuclear spin $I=2$ the decay of nuclear polarization with time can be expressed in general as the sum of four exponentials. (For details see Ref. 45 and Appendix

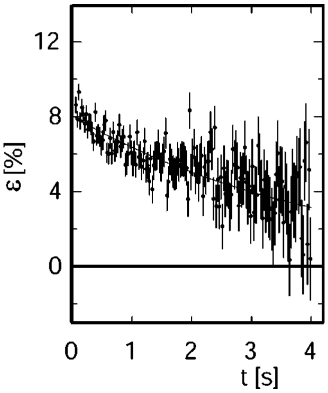

FIG. 1. Observed asymmetry ϵ as a function of time for Li adsorbed at 110 K and at a magnetic field of 0.8 T on a Si(111) -(7×7). The data are fitted according to Eq. (2) to one exponential yielding $\alpha=(0.24\pm0.01)$ or $T_1=(4.17\pm0.17)$ s.

A of Ref. 46.) However, as in Fig. 1 often only one exponential was sufficient to describe the data. It determines the relaxation rate $\alpha=1/T_1$ defined through

$$\epsilon=\epsilon_0 e^{-\alpha t}=\epsilon_0 e^{-t/T_1}. \tag{2}$$

The fit to the data in Fig. 1 yielded $\alpha=0.24\pm0.01$ or $T_1=(4.17\pm0.17)$ s.

We close this section with the remark that contrary to conventional NMR experiments[3–6] the determination of α or T_1 does not require the application of resonant rf fields, since the initial spin polarization P of the ^{8}Li ensemble of about 0.8 exceeds the thermal polarization in an external field by a factor of about 10^5.

III. EXPERIMENTAL RESULTS

In previous investigations of alkali-metal adsorption on semiconductor surfaces unfortunately the absolute coverage in monolayers and more important in number of adsorbate atoms per surface substrate atom was mostly not known, and if at all, only poorly.[18,19,22–24,26,29,47–50] For Li adsorption on Si we have put much effort into this question of employing TPD data and their correlation with well studied superstructures, mainly the Li induced (3×1) reconstruction,[36,37,51] which at saturation has a coverage of 1/3 in terms of the number of Si-surface atoms. In what follows, the amount of coverage always refers to this work.

Figure 2 displays the work function change at 90 K of a Si(111)-(7×7) surface as a function of coverage. It was determined with the diode method described in detail elsewhere.[38] A much lower temperature had to be chosen for the determination of $\Delta\Phi$ with adsorbed Li, as compared to $\Delta\Phi$ investigations for the other alkali-metals (Na, K, Cs) performed commonly at room temperature (300 K).[24,48,49] Experiments preceding the ones presented here showed that the LEED pattern taken parallel to the $\Delta\Phi$ data for Li are only at temperatures below 150 K similar to the ones observed for the other alkali metals. Moreover, even at 400 K, it was not possible to detect via LIF (laser-induced fluorescence) for Li adsorption any desorbing Li during exposure.

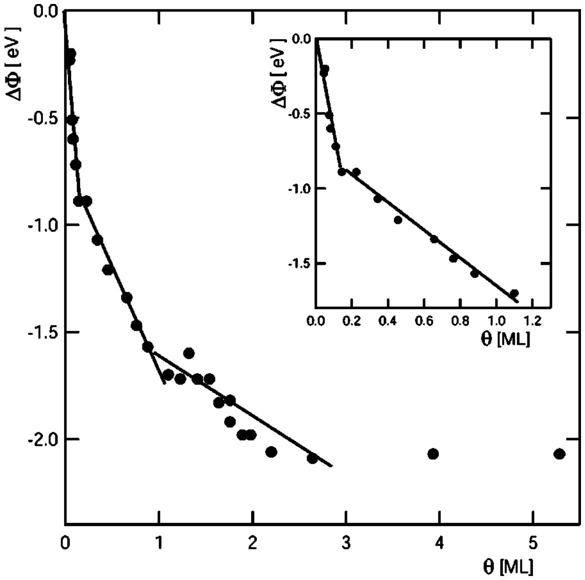

FIG. 2. Work function change $\Delta\Phi$ as function of Li coverage Θ. The surface was covered with Li at 90 K.

On one hand, this points to a coverage-independent sticking coefficient of one and, on the other hand, to the possibility that at these elevated temperatures Li might diffuse already into the bulk[29,30] or forms silicides.[18] First, in Fig. 2 the change in work function increases steeply up to about $\Theta\approx0.12$ ML (see the inset). Then it starts to level off, changing its slope twice around 0.12 and around 1 ML in order to approach a constant value in between 2 and 3 ML Li coverage. In contrast to the adsorption of the other alkali metals it does not exhibit a minimum.[28,48,49] Further details of the work function change shall be discussed together with the coverage-dependent UPS and NMR results in Sec. IV.

Figure 3 displays the UPS results as a function of Li coverage. They were obtained with 21.2 eV photons from a He light source incident under 45° to the surface normal and a hemispherical mirror analyzer (HMA) to observe the electron spectra. Photoelectrons emitted along the surface normal were detected without further apertures. The sample was put on a 10 V potential and the resolution amounted to about 50 mV. The absolute Li coverage was determined by TPD, as described in a separate paper.[51] Because of the low temperature chosen, surface photovoltage effects[52] (SPV) shift the spectra for the uncovered surface by about 400 meV to higher kinetic energies as compared to a spectrum obtained at room temperature. Since SPV effects probably also depend slightly on coverage, on the temperature-dependent morphology, and on the electronic structure of the surface which could not be controlled sufficiently, the spectra indicate only the photoelectron energies and not the Fermi energy.

The spectra of the plain surface displays all the well known features of the Si(111)-(7×7) reconstruction,[53–57] in particular the well known (unresolved) adatom derived states S_1 and S_1'. Its high energy tail leaks over the Fermi energy causing the metallicity of this reconstruction. This state indicates also roughly the position of the Fermi energy. The state S_2 can be associated with the fully occupied rest atom dangling bonds. A comparison with UPS spectra for adsorbed K

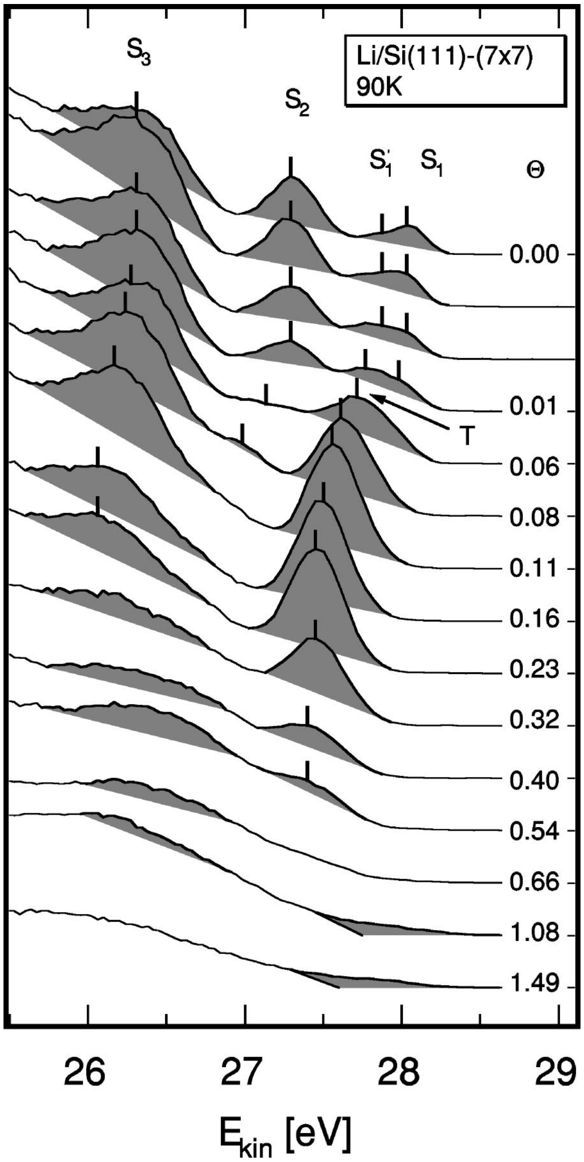

FIG. 3. As a function of Li coverage on the Si(111)-(7×7) surface UP spectra determined at 90 K under normal emission with photons of 21.1 eV energy impinging on the surface under an angle of 45°. The Li coverage Θ is given in the column on the right side in ML.

and Cs (Refs. 48 and 49) confirms that only at sufficiently low surface temperatures Li adsorption yields spectra with features similar to the ones obtained for adsorption of the heavier alkali metals. The gross features of all these data indicate that the states S_1, S_1, and S_2 fade away quickly with increasing alkali-metal coverages, and thus the metallicity of the surface, too. A more deeply bound state (T) appears already near 0.06 ML coverage. We will discuss these features in connection with the NMR data. (Sec. IV) For coverages beyond 1 ML the surface conductivity is restored for the lighter alkali-metal adsorbates (Li, Na, K).

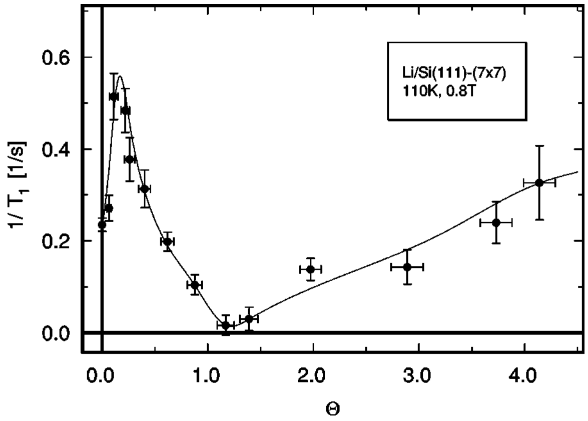

FIG. 4. Relaxation rates observed as a function of coverage of Li adsorbed on a Si(111)-(7×7) surface. The sample is held at a temperature of 110 K and in a static external magnetic field of $B=0.8$ T parallel to the surface normal. The solid line is a guide to the eye. The Li coverage Θ is given in ML.

Figure 4 displays the observed relaxation rates as function of Li coverage for a magnetic field of 0.8 T and a surface temperature 110 K. The observed value for the lowest coverage, around 10^{-3} ML, agrees favorably with recently published ones.[2,58] As discussed previously in these papers, the finite relaxation rate is closely related to the metallicity of the (7×7) reconstruction of the Si(111) surface. Furthermore, the rather large relaxation rates observed for this system as compared to ^{8}Li adsorption on metals are in accordance with electron localization in the adatom dangling bonds [longer correlation times τ_e; Eq. (3) in Sec. IV]. Increasing the coverage, the relaxation rates first increase steeply by more than a factor of two and reach a maximum around a coverage of $\Theta=0.12$ ML. Beyond this coverage the relaxation rate decreases steeply approaching a value consistent with zero within the error bars at a coverage of about 1.2 ML [$\alpha=(0.0.18\pm0.020)\ \mathrm{s}^{-1}$]. It is tempting, even at that point of the discussion, to interpret this result as an indication that around a coverage of 1 ML the surface becomes semiconducting. (Due to the limited number of data points around 1 ML the exact coverage range in which α vanishes could not be determined.) Increasing the coverage further, the relaxation rates increase again reaching finally beyond a coverage of 4 ML a value found also for higher Li coverages on a metal surface as Ru(001).[59]

An interpretation of the data of Fig. 4 in terms of electronically driven relaxation ("Korringa relaxation") requires magnetic-field-independent relaxation rates.[3–5] In this context their magnetic field independence has been tested in some detail at several coverages (Fig. 5). The observed data at four different coverages display no magnetic field dependence, whatsoever. (A $1/B^2$ dependence would be expected if the relaxation would be caused by surface diffusion.[35,46,59])

A detailed discussion and comparison of the coverage dependence of all three measured quantities—ΔΦ data, UP spectra, and the relaxation rates $1/T_1=\alpha$—will follow in the next section.

IV. DISCUSSION AND CONCLUSIONS

In order to understand in more detail the coverage dependencies of the relaxation rate $\alpha=1/T_1$ of the work function

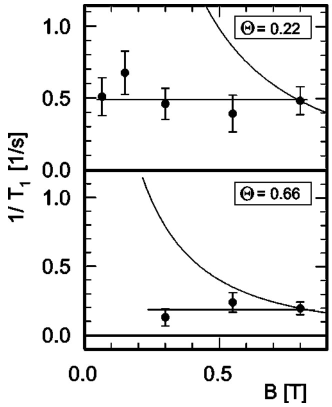

FIG. 5. Magnetic field dependence of the relaxation rates at 110 K for Li adsorbed on the Si(111)-(7×7) surface at coverages Θ of 0.22 and 0.66 ML. The curves decreasing with magnetic field proportional to $1/B^2$ indicate the expected magnetic field dependence if diffusion plays the dominant part as a source for fluctuating fields.

change ΔΦ and of the UP spectra we recall that at low coverages alkali-metal atoms as Li adsorb with large probability at an empty adatom dangling bond. This is based on theoretical and experimental investigations[28,31] and also intuitively expected. The (7×7) reconstruction of the Si(111) surface reduces the number of the 49 dangling bonds of the unreconstructed surface to 19 on the expense of considerable stress within the surface. The electrons in the six rest atom dangling bonds and in the corner hole are bound well below the Fermi energy and are therefore filled with two electrons. In particular due to intraside Coulomb repulsion the remaining five electrons occupy 5 of the 12 adatom dangling bonds leading to a degenerate surface electron gas (metallic surface) which pins the Fermi energy.[60–65] Thus we expect that at low coverages Li will adsorb at an empty adatom dangling bond. Because of intraside Coulomb repulsion its electron will become part of the degenerate surface electron gas formed by the electrons already in the adatom dangling bonds. This is in accordance with the observed magnetic field independence of the relaxation rates (Fig. 5) which points to fluctuating electron spins (magnetic moments) as the source of the fluctuating fields causing the nuclear spin relaxation.

There can be up to six adsorbed Li atoms per (7×7) unit cell, until this picture breaks down (coverage up to $\Theta = 6/49 = 0.12$). For the seventh adsorbed Li atoms per unit cell in the average all adatom dangling bonds are occupied by one electron. Because of the intraside Coulomb repulsion the energetic degeneracy of its electron would be lifted. It would start to localize if no structural changes would occur. And indeed, at a coverage of about $\Theta = 0.12$ remarkable changes in the measured quantities are observed: The change in work function changes its slope and it becomes less steep (Fig. 2); in the UP spectra the S_1 and the S_1' peaks have already faded and merged into the broad T peak which begins to reduce its intensity around a coverage of 0.12 (Fig. 3). Most dramatically, however, this coverage appears within the $1/T_1$ data (Fig. 4). With increasing Li adsorption they first rise from lowest coverages by about a factor of two and reach a maximum around $\Theta = 0.12$, beyond which they decline steeply in order to finally reach a value consistent with zero around 1 ML.

One may wonder why the relaxation rates increase if the states which cause the metallicity of the (7×7) reconstruction are disappearing and localization plays an increasing role. Nuclear spin relaxation of electronic origin relies on fluctuating electronic spins (magnetic moments). Choosing as electron correlation time τ_e, the "lifetime of residence" of an electron at the ^{8}Li site for metalliclike systems, the T_1 time turns out to be proportional to[2]

$$\alpha = \frac{1}{T_1} \propto |\langle|\Psi(0)|^2\rangle|^2 \mathrm{DOS}(\epsilon_F)\tau_e T, \tag{3}$$

whereby $|\langle|\Psi(0)|^2\rangle|$ is the probability per atomic volume to find an electron at the Li nucleus and DOS (ϵ_F) is the electronic density of states at the Fermi energy. Clearly, an increasing correlation time τ_e which is equivalent to increasing localization will lead to an increasing relaxation rate $\alpha = 1/T_1$ as long the electrons at the Li nucleus are able to fluctuate in time.

The relaxation rate decreases steeply beyond 0.12 ML coverage. In parallel the change in work function become less steep and the T peak in the UP spectra begins to fade fast. According to results obtained with Na (Ref. 49) the adatom states probably do not pin the Fermi level anymore and consequently band bending moves the Fermi level towards the valence band maximum causing eventually a leveling off of the work function change with coverage. The UP spectra indicate that all states within the band gap start to disappear and the surface becomes gradually semiconducting. One may speculate that as for K and Cs adsorption,[22,23] and also for the Li one, the adatom states hybridize with the Li 2s orbitals moving the former adatom states down below ϵ_F. In parallel, bonding to the Li atoms reduces the energy splitting between the adatom and rest atom states and increases their mutual interaction. At saturation coverage, the surface is completely reconstructed to a δ-7×7 surface at higher temperature and probably a more or less ordered (1×1) one at lower temperatures. Localization effects have disappeared and the semiconducting nature of the Li/Si(111)-(7×7) interface can be simply understood in a local bonding picture as depicted for K in Fig. 10(a) of Ref. 23. At that point, around 1 ML the relaxation rate vanishes. [For $\Theta = 1.2$ ML, $\alpha = 1/T_1 = (0.018 \pm 0.020)$ s^{-1}]. This demonstrates convincingly that the surface really became semiconducting (see a discussion of relaxation rates for semiconducting surfaces in Refs. 13 and 35).

Beyond 1.2 ML coverage the work function still becomes a little bit lower until it reaches saturation in between 2 and 3 ML. That may be caused by a change of the electron affinity while the Fermi level probably stays constant. In this coverage regime the relaxation rates increase already. Excess Li (with respect to the coverage $\Theta = 1.2$ ML around which the surface becomes semiconducting) may act as a dopant. In a simple picture for relaxation in two-dimensional semiconductors[13,35] the rate should first increase with the square root of the excess amount of Li, that is approximately with $\sqrt{(\Theta/ML)-1.2}$ until a metallic layer starts to grow. (For lack of enough data points beyond 1.2 ML an explicit fit to a square root behavior was not feasible.) At the maximum coverage, the relaxation rate reaches $(0.33\pm0.08)\ \mathrm{s}^{-1}$, a value comparable to the one for relaxation of Li in lithium at the present sample temperature[66] ($\alpha=0.39\ \mathrm{s}^{-1}$).

In conclusion we may state that for Li adsorption on the Si(111)-(7×7) surface the coverage dependencies of all three quantities measured—work function changes, UP spectra, and nuclear spin relaxation rates—can be understood, at least qualitatively, in a consistent picture. The main feature appearing is a metal-semiconductor-metal transition in which firstly the metallic (7×7) reconstruction becomes semiconducting around 1 ML adsorbed Li, which converts again into a metallic Li surface layer for multilayer adsorption. The discussion shows, furthermore, that localization effects are very important in the region where the surface changes from metallic to semiconducting properties. In this respect, it would be certainly very desirable if at least for the benchmark coverages where the interface changes its properties considerably (low coverage, $\Theta=0.12$ ML, $\Theta\approx1$ ML) all electron density functional calculations which are now feasible for semiconductors[2,67–69] would be available. Their quantitative results would be able to judge the qualitative arguments presented here. Moreover, such calculations would be a perfect testing ground whether localization effects can nowadays be incorporated into such codes, and if so, to what degree.

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