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# Local electronic properties of adsorbed Li on hydrogen-terminated Si(111)-(1×1):H surfaces

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The adsorption of Li on hydrogen-terminated Si(111)-(1×1):H surfaces was studied by NMR (determination of $T_1$ times in nuclear spin relaxation experiments). Most of the experiments were performed at an extremely low Li coverage around $10^{-3}$ monolayers. For a heavily *n*-doped sample with a carrier concentration beyond the Mott limit, the temperature dependence of the relaxation rates $\alpha=1/T_1$ points to a metallic behavior. For the moderately *n*- and *p*-doped samples the relaxation rates are independent of the kind of doping. Their temperature dependences display a thermally activated behavior. They can be understood within the well-established theory of $T_1$ times in semiconductors, reformulated for two-dimensional systems.

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Among the semiconducting Si surfaces the hydrogen-terminated Si(111):H(1×1) one preserves the elementary (1×1) unit cell of the Si(111) surface. It has no electronic surface states in the fundamental band gap. Thus, the metal-to-semiconductor contact can be studied without the complications introduced through such states. Several groups already addressed alkali-metal adsorption on hydrogen-terminated Si(111)-(1×1):H surfaces experimentally[1–7] as well as theoretically.[6–9] For *n*-doped samples one finds alkali-metal-induced surface states in the vicinity of the conduction band minimum (CBM) that pin the Fermi energy at low coverage. For *p*-doped material with $E_F$ near the valence band maximum (VBM) already low alkali-metal adsorption leads to a jump of $E_F$ up to the conduction band minimum. Experimentally, this picture was corroborated through core level photoelectron spectroscopy of the Fermi energy position.[1–4] Theoretically, the density of states (DOS) around the CBM is found to be alkali-metal derived.[8,9] With photoemission, the density of states around the band gap is tested for submonolayer Li adsorption. Surprisingly the expected feature at $E_F$ was found only for *n*-doped material. It is absent for the *p*-doped one.[7] In contrast, only a very weak photoemission intensity appeared spreading over the whole gap.

This situation asks for independent cross checks by means that are locally sensitive to electron densities at the adsorbed alkali-metal atom. Nuclear magnetic resonance (NMR) utilizes the local nature of the nuclear moments to probe almost in a pointlike manner.[10,11] Therefore we resumed our previous $\beta$-detected nuclear magnetic resonance ($\beta$-NMR) experiments (measurements of $T_1$ times[10,11]) to study the electron density of states at the adsorbates locally. The experiment described here is an extension of previous ones,[5,6] but now with the main advantage of an increased magnetic field strength over the NMR region (up to 0.8 T instead of only up to 0.13 T previously). This is advantageous since at higher magnetic fields relaxation processes with long correlation times, as those caused, for example, by diffusion, are suppressed effectively.[10–12] Thus electronic properties are more pronounced.

The experiments were performed in a dedicated UHV apparatus (base pressure $3\times10^{-11}$ mbar). Conventional analytical techniques are used along with the $\beta$-NMR.[13] The latter utilizes $\beta$-decaying nuclear spin polarized radioactive $^8$Li atoms as a probe. Getter sources provide stable Li when higher surface coverage is needed. A homemade fast load lock is connected to the UHV chamber. It provides rapid transfer of the wet chemically prepared hydrogen-terminated Si(111)-(1×1):H samples. Details of the load lock concept, of the wet chemical treatment, and of the transfer to the UHV can be found elsewhere.[6,14] The highly ordered wet chemically hydrogenated surface is termed "hydrogen terminated" in accordance with the literature.[14,15] The cleanliness of the surface was monitored by Auger electron spectroscopy. For a "clean surface" the ratios of O(*KLL*)/Si(*KLL*) and C(*KLL*)/Si(*KLL*) Auger intensities had to be below 0.02.

An important, but unusual instrument, is the source providing a polarized $^8$Li atomic beam of thermal velocity.[13] At the site of the sample it provides a thermal atomic beam of about $10^8$ lithium atoms/s, mainly the primary $^7$Li used for the production of $^8$Li in the $^2$H($^7$Li,$^8$Li)$^1$H nuclear reaction. The beam contains a small amount of about $10^4$ atoms/s of the nuclear spin polarized radioactive isotope $^8$Li (polarization 0.8 to 0.9). $^8$Li is a $\beta$-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 $\beta$ decay. The asymmetry $\epsilon$ of the $\beta$-electron intensity with respect to the magnetic field is measured by scintillator telescopes at $N(0^\circ)$ and $N(180^\circ)$; $\epsilon$ is proportional to the nuclear polarization of the adsorbed $^8$Li ensemble. Systematic errors in the determination of $\epsilon$ are eliminated by performing the experiment with the reversed $^8$Li beam polarization as well. During the $\beta$-electron detection period the $^7$Li ion beam, as the main source of background signals, is switched off.

$^8$Li possesses a nuclear spin $I=2$. Therefore the decay of nuclear polarization with time (relaxation) can be expressed in general as the sum of four exponentials.[12] It is not always possible to disentangle them with high enough precision. However, the slowest relaxation rate could always be determined accurately. We therefore concentrate in this paper only on $\alpha_{\text{slow}}\hat{=}\alpha=1/T_1$ in describing $\epsilon(t)$

$$\epsilon(t)=\epsilon_0 e^{-\alpha t}=\epsilon_0 e^{-t/T_1}. \tag{1}$$

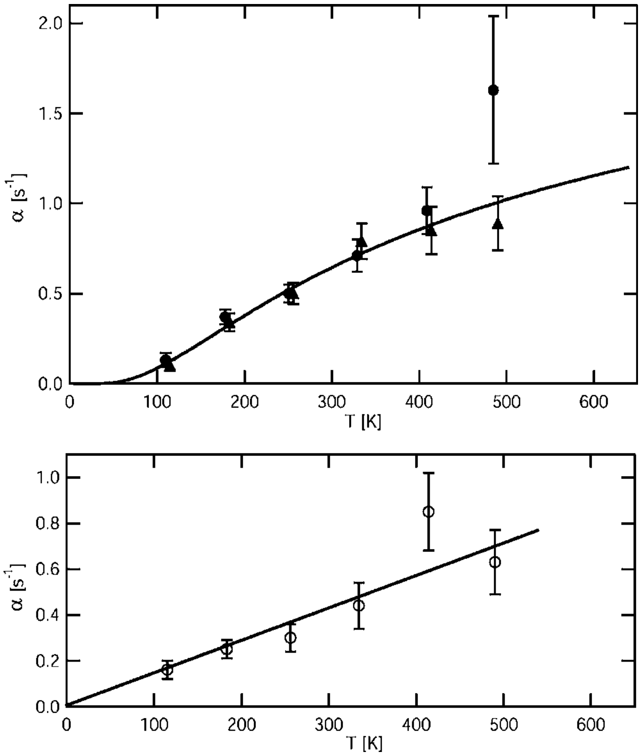

FIG. 1. Nuclear spin relaxation rates $\alpha = 1/T_1$ as a function of the substrate temperature for $^8$Li adsorbed on a hydrogen terminated Si(111)-($1\times1$) surface. The data points were taken at a magnetic field of 0.8 T. In the upper part the data for the moderately $n$-doped samples (round dots) were shifted by −5 K in order to distinguish them from the ones for the moderately $p$-doped samples (triangular symbols). The solid line is a fit to the data according to Eq. (2), assuming a Li coverage of $10^{-3}$ ML. (For details, see text.) The lower part displays data obtained for a heavily $n$-doped sample, already beyond the Mott limit and thus metallic. A linear fit to the data is shown.

Nuclear spin relaxation rates $\alpha$ are shown in Fig. 1 for moderately and heavily doped samples in an external magnetic field of 0.8 T. The data is presented as a function of surface temperature. The heavily $n$-doped (Sb) material (33 mΩ cm) has a carrier concentration of about $6\times10^{18}/\mathrm{cm}^3$ and is already beyond the Mott limit.[16] The relaxation rate in this case (lower panel) is consistent with Korringa relaxation, i.e., $\alpha \sim T$, which is typical for a metallic system.[10,11] The lower doping leads to higher relaxation rates (upper panel) with a qualitatively different temperature dependence.

Although the highly doped sample is beyond the Mott limit, one cannot expect that the description of the relaxation rates can be based on the interaction of the nuclear spins with the moments of "free" electrons, occupying plane-wave Bloch states (noninteracting electron gas).[6] We therefore adopt here the correlation time formalism[17] for partly localized electrons. (For details, see Appendix B in Ref. 6.) Choosing as correlation time $\tau_e$, the "lifetime of residence" of an electron at the $^8$Li site, the relaxation rate becomes proportional to $\tau_e \mathrm{DOS}(\epsilon_F) T$, where $\mathrm{DOS}(\epsilon_F)$ is the electronic density of states at the Fermi energy. Thus, an increasing correlation time $\tau_e$, is equivalent to an increasing localization, which leads to an increasing nuclear spin relaxation rate as compared to a free electron system. This interpretation is corroborated by the fact that the relaxation rates indeed become larger for the metallic heavily doped $n^+$ sample as compared to the ones observed, e.g., for the real metallic Ru(001) surface.[12]

Figure 1 (upper panel) shows the temperature dependence of the relaxation rates for $^8$Li on hydrogen-terminated Si(111) surfaces of moderately $n$- or $p$-doped wafers (conductivity around 10 Ω cm). After chemical treatment and transfer the samples were annealed by heating to 600 K for several minutes prior to data taking. Within the error bars the observed relaxation rates do not depend on the kind of doping. The relaxation rate is not "Korringa-like," i.e., $\alpha/T \neq \mathrm{const}$; in contrast, they seem to approach zero at 70 K already. The rates were found to be magnetic field independent beyond a field of 0.3 T (not shown). Altogether the surface shows no sign of clear metallic behavior. The findings have to be contrasted to previous experiments where hydrogen-covered, i.e., in vacuum prepared, Si(111) surfaces of weakly doped samples were studied at a much lower magnetic field (below 0.1 T).[5,6] These structurally less perfect surfaces showed also dopant independent relaxation rates as here. But the rates were compatible with Korringa relaxation and about 40% lower than observed here. The latter point is surprising since a lower field usually leads to increased relaxation, thus highlighting the (probably structural) differences in these surfaces, i.e., hydrogen terminated (here) versus hydrogen covered (previous).

On the "perfectly" hydrogen-terminated surface it is difficult to understand how relaxation occurs. The independence of the magnetic field, the increase with temperature and reasonable size points to electronic interaction, i.e., fluctuations of the electronic spin density at the Li adsorbates.[10] On the perfect surface, this spin density does not exist. In what follows we want to argue that stable lithium accompanying the radioactive one serves as a surface dopant.

The length of time an individual crystal was used in the experiment was determined by the surface cleanliness. The data points of Fig. 1 were obtained by collecting data over about a day, until the ratio of either the C/Si- or the O/Si-Auger lines reached 0.02. Thus unpolarized $^7$Li was accumulated up to about $10^{-3}$ to $10^{-2}$ monolayers (ML).

On metals or non-hydrogen-covered semiconductor surfaces this buildup is prevented by flashing the surface to 1000 K every hour or so. This has been done in previous experiments.[5,6,18] Such a procedure is not feasible for hydrogen-terminated surfaces;[6] otherwise hydrogen would always desorb together with the Li and a new surface would have to be prepared every hour.

Therefore we conclude that Li atoms themselves adsorbed during the nuclear spin relaxation measurements act as dopants of the surface. Electrons from their donor levels are excited easily into the conduction band and thus the nuclear spin relaxation due to Fermi contact interaction is observable also at low temperatures. This assumption is supported by theoretical results that find that Li adsorbs at the $h_3$ threefold hollow site and indeed causes density of states near the bottom of the valence band.[6,7] As mentioned already above, the

Li coverage may increase up to about $10^{-2}$ ML during data taking. If all adsorbed Li atoms contribute to an $n$-type doping of the surface, the dopant density of the surface exceeds the doping concentration for the bulk dopants by far. Thus we expect relaxation rates independent of the type of bulk doping and independent of the magnetic field due to the electronic nature of the interaction. A thermally activated relaxation rate has been derived:[18]

$$\frac{1}{T_1} = \frac{2\pi}{\hbar}\frac{32\pi^2}{9}\mu_e^2\left(\frac{\mu_{Li}}{I}\right)^2 |\Phi(0)|^4 \rho^{(2)} n^{(2)}(T). \qquad (2)$$

$\mu_e$ and $\mu_{Li}$ denote the magnetic moments of the electron and the $^8$Li nucleus, respectively, $|\Phi(0)|^2$ the (energy independent) probability to find an electron at the nucleus (and thus a dimensionless number) and $\rho^{(2)}$ the energy independent density of states per volume of a two-dimensional free electron gas that is localized in the third dimension perpendicular to the surface within a rectangular barrier of width $L$.[19] (Contrary to the original work of Abragam,[10] $\rho^{(2)}$ denotes the total density of states and not the one for one specific spin state.) The only temperature-dependent factor in Eq. (2) is the two-dimensional electron density $n^{(2)}(T)$ in the conduction band for a nondegenerate electron gas. (For an analogous formula for three dimensions see, e.g., Ref. 19.) It depends on $n_D^{(2)}$, the area density of the donors, and on $E_D$, their binding energy relative to the conduction band minimum. For low enough temperatures $n^{(2)}(T)$ becomes proportional to $T\exp(-E_D/kT)$, which agrees favorably with the thermally activated behavior observed experimentally (Fig. 1). For a more detailed discussion, see Ref. 18.

In the experiments the Li dose stems solely from adsorbed Li out of the atomic beam during data taking. Thus, the Li coverage is known to be small, but not exactly how small. This situation was analyzed previously, assuming a coverage between $10^{-2}$ and $10^{-4}$ (Fig. 6 in Ref. 18). There it turned out that for temperatures up to the inflection point, the quality of the fit did not depend on the coverage assumed. Therefore the solid line in Fig. 1 displays a fit assuming as Li coverage $\Theta = 10^{-3}$ only. It yields a donor energy of $E_D \approx 40 \pm 8$ meV, quite in agreement with the value found for Li doping of bulk silicon.[20]

In addition, at a Li coverage of $0.25 \pm 0.04$ ML, a temperature dependence of the relaxation rates was determined experimentally (Fig. 2). It looks similar to the one in Fig. 1 but the size of the relaxation rates decreased. Again, the relaxation rates are of electronic origin as their magnetic field independence indicated (not shown here). The solid line in Fig. 2 was obtained using a coverage of $\Theta = 0.25$ ML in Eq. (2). Since the relaxation rates are smaller as compared to the low coverage ones in the upper part of Fig. 1, the donor energy turned out to be only $E_D \approx 22 \pm 8$ meV. This result was not very sensitive to the exact value of Li coverage used. It remained the same if the coverage was varied by 0.05 in both directions. The result indicates a reduction of the donor energy. As discussed recently[6] one might argue that at a coverage of 0.25 ML, the 2$s$ orbitals of Li will start to overlap and begin to form a delocalized two-dimensional electron gas (metallic layer). This certainly diminishes the donor energy.

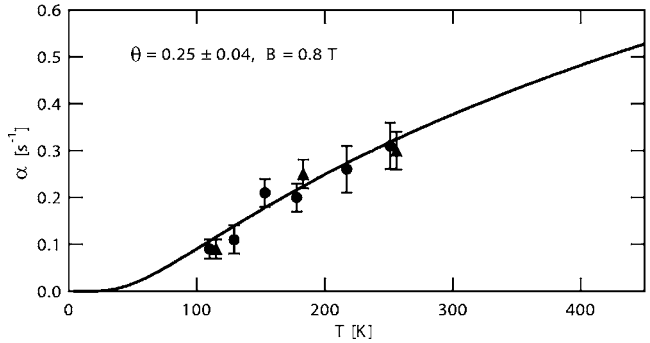

FIG. 2. Temperature dependence of the nuclear spin relaxation rates $\alpha = 1/T_1$ observed for a Li coverage of $\Theta = 0.25 \pm 0.04$ ML and a magnetic field of $B = 0.8$ T. The fitted curve was obtained similarly to the one in the upper part of Fig. 1. The data points obtained with the $n$-doped sample (round dots) were shifted by −5 K in order to distinguish them from the ones obtained with the $p$-doped sample.

In summary, one of the main goals of this experiment was to investigate whether nuclear spin relaxation rates (inverse $T_1$ times) determined at Li nuclei adsorbed on the hydrogen-terminated Si(111)-$(1\times1)$:H surface depend on the doping type of the sample. For the moderately doped samples (around $10^{15}/\text{cm}^3$), as also used in photoelectron experiments[7] no such dependence could be detected whatever coverage, surface temperature, and external magnetic field was chosen. Moreover, from the studies a consistent picture of the relaxation rates emerged. It relies strongly on the results of all electron FLAPW calculations,[6,7] which showed that in agreement with other theoretical work[8,9] alkali metals such as Li adsorb as a surface donor on the $h_3$ hollow site and generate density of states near to the CBM. As usual, all the calculations have been performed for undoped material. Even though charge compensation may play a role for the $p$-doped sample, one cannot see how moderate bulk doping of about $10^{15}/\text{cm}^3$, that is about $10^{10}/\text{cm}^2$ [or about one charge carrier per $7\times10^4$ $(1\times1)$ unit cells], can affect the surface band structure considerably. This number is much smaller than the $7\times10^{11}/\text{cm}^2$ electrons injected by $10^{-3}$ ML of adsorbed Li. Consequently, the description of the data obtained for Li adsorption on moderately $n$- and $p$-doped samples was based on the well-known theoretical description of nuclear spin relaxation in semiconductors, which was reformulated recently for two-dimensional systems such as surfaces.[18] Fitting the data yields reasonable donor energies.

The doping-independent relaxation rates are in severe contradiction to the results of a recent photoelectron spectroscopy experiment.[7] It finds only for the $n$-doped samples a finite density of states around the Fermi energy. To explain this result the authors propose a doping-dependent Li adsorption site: For the $n$-doped materials the threefold hollow site $h_3$, where Li acts as a donor, and for the $p$-doped material a substitutional site where according to FLAPW calculations[6,7] Li generates additional density of states right within the valence band. Such a picture certainly does not fit to the present experimental observations, since the finite (electronic) relaxation rates for the *p*-doped samples require fluctuating electronic spins and thus empty states in the vicinity of the CBM.

At a first glance one might think that the orders of magnitude higher solubility of Li in *p*-doped Si as compared to the *n*-doped one[21] might offer an explanation for the results of the photoelectron experiments[7] in form of subsurface Li for the *p*-doped samples only. This explanation is excluded, however, by the present results obtained for a coverage of 0.25 ML and $T < 250$ K, which do not show any dependence on the kind of sample doping used (Fig. 2). Thus the activation energy for the transfer of Li from the surface into the bulk has to be high enough (at least 1 eV) to prevent significant diffusion of Li into the bulk at temperatures below 250 K. A surface near bulk doping would occur due to the much lower bulk diffusion energy of Li in Si of 0.66 eV.[21]

In the photoelectron experiments, Li was adsorbed at temperatures around 100 K only and kept at this temperature during the experiments. Thus, subsurface Li for Li adsorption on the *p*-doped sample is only a very unlikely explanation of the seemingly contradictory results of the present NMR experiment and the former photoelectron experiments. Therefore, though strange, this problem can be solved easily only by assuming that the features found in the photoelectron spectroscopy experiment are not connected to the local properties of adsorbed Li. It is presently unclear, what could cause such properties. Certainly, detailed calculations for both photoelectron spectra and relaxation rates would be highly welcomed.

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