Electric field gradients from NMR measurements on the Si(111)3 × 1–Li reconstruction

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New Journal of Physics 3 (2001) 1.1–1.11 (http://www.njp.org/)
Received 5 October 2000; online 5 March 2001

Abstract. The Li-induced formation of the 3 × 1 reconstruction of the Si(111) surface has been investigated by nuclear magnetic resonance (NMR) on the Li nuclei. Two different electric field gradients (EFGs) were observed simultaneously and could be assigned to the EFG of Li adsorbed on Si(111)7 × 7 and Li involved in the 3 × 1 reconstruction. The observed EFGs are positive, indicating a Li adsorption site not above but rather within the reconstruction. The implications of these findings on some of the proposed structural models of the 3 × 1 reconstruction are discussed.

1. Introduction

The structure of the metal-induced Si(111)3 × 1 reconstruction has been the subject of many experimental and theoretical investigations since it was first discovered by Le Lay on adsorption of Ag [1]. The nature of the family of the 3 × 1 reconstructions is still far from being fully understood, but there is at least a consensus on some of its properties. Based on the similarity between low-energy electron diffraction (LEED) intensity–voltage (I–V) curves for the Li-, Na-, Ag-, and Mg-induced 3 × 1 structure [2–4], it is considered to be a substrate reconstruction rather than an adsorbate overlayer structure. The surface is semiconducting with a bandgap of about 1 eV [5]. The absolute metal coverage is one-third of a monolayer (ML), as determined by various experimental techniques for different adsorbates [6–10]. One ML is defined as $7.8 \times 10^{14}$ cm$^{-2}$, the density of Si atoms in the top layer of the bulk-terminated 1 × 1 structure.

Amongst the proposed structural models, five are consistent with most properties of the 3 × 1 reconstruction established to date. Namely, these are the Seiwatz model [8,9], the extended...
Pandey model [11, 12] and the more recent `560560’ model [13–15], the similar honey-comb chain-channel (HCC) model [16] and the double-π-bonded chain (DπC) model [17].

From energy considerations it seems to be obvious that the metal atoms act as electron donors, saturating the remaining Si dangling bonds in the $3 \times 1$ reconstruction. This aside, very little is known on the role of the metal atoms in the reconstruction itself, due to a lack of experimental as well as theoretical information on the metal atoms. For example, LEED and x-ray scattering experiments are insensitive to Li since the scattering cross sections are too small [14]. Density-functional calculations (DFTs) are also unable to determine the Li position, since the energy differences between various binding positions were found to be negligible [14].

In this paper we present nuclear magnetic resonance (NMR) measurements from which the electric field gradient (EFG) at the nucleus of $^6$Li adsorbed on Si(111) is determined. Two different EFGs are seen in this experiment. They can clearly be assigned to Li atoms that are adsorbed on the $7 \times 7$ reconstruction and to Li atoms that are involved in the $3 \times 1$ reconstruction. The EFG is a very local quantity and is directly related to the charge density around the nucleus of the adsorbate probed by NMR. It is therefore a quantity that is sensitive to the geometry and electronic structure around the nucleus. In principle, the value of the EFG can be calculated from electron density distributions obtained from DFT calculations, unless pseudo-potential methods are used to approximate the wavefunctions in the vicinity of the nucleus. However, no ab initio all-electron DFT calculations on this problem are known to date. Nevertheless, qualitative conclusions on the binding geometry of the Li atoms can be drawn from the sign of the observed EFGs.

2. Experimental set-up

The experiments were performed on commercially grown n-type phosphorus-doped Si(111) samples with a resistivity of 4 to 10 Ω cm and a miscut of less than 0.3°. The crystals were mounted in a ultra-high 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 $7 \times 7 \leftrightarrow 1 \times 1$ phase transition led to samples that showed no contamination in Auger spectra (the Si-signal to noise ratio was greater than 1000) and sharp $7 \times 7$ LEED patterns. The samples were heated resistively by an ac current at 1.2 MHz. This frequency is well above the Larmor frequency of the NMR experiments, so that due to a motional narrowing process, the magnetic field produced by the heating current does not affect the NMR spectra. The temperature was measured and controlled by an infrared pyrometer.

In order to overcome the sensitivity problems that make conventional NMR techniques unsuitable for surface studies, highly nuclear spin polarized $^6$Li atoms (nuclear spin $I = 1$) from an external source are used (figure 1). Basically the source works as follows. Metallic lithium is heated in an oven. Its vapour expands into a vacuum through a nozzle and is formed into an atomic beam by a skimmer. The Li atoms are then polarized by a combination of a Stern–Gerlach-type quadrupole magnets and radio frequency (RF) transitions. Their polarization is determined by laser induced fluorescence (LIF) [18] before they adsorb on the sample surface. The sample is held in a static magnetic field $B_0$ (up to 40 mT, oriented parallel to the surface normal) which is superimposed by an RF field of variable frequency $\nu$ (several hundred kilohertz, perpendicular to $B_0$). To obtain an NMR spectrum, the nuclear spin polarization of the desorbing Li atoms (population of the $m$-sublevels with $m = -1, 0, +1$) is again measured via LIF, while the frequency of the RF field is swept over the Larmor-frequency $\nu_L$ of the nucleus ($\nu_L = \mu B_0/\hbar$,
Figure 1. Schematic diagram of the experimental set-up. MFT and SFT are high-frequency transitions to switch the $m$-state population of the atomic $^6$Li beam.

$\mu = 0.82\mu_N$ is the nuclear dipole moment of $^6$Li). When the RF frequency corresponds to the energy difference between hyperfine levels of $^6$Li (see insert to figure 2(a)), a dip in the nuclear spin polarization of the desorbing atoms is observed (figure 2). More detailed descriptions of the experimental set-up and the general principle of the NMR experiments can be found in [19–21] respectively.

3. Experimental results

Figure 2(b) shows an NMR spectrum of $^6$Li on Si(111) taken at a surface temperature of $T = 1100$ K and a magnetic field of $B_0 = 27$ mT. The figure displays the relative polarization effect $\varepsilon/\varepsilon_0$ as a function of the RF frequency, where $\varepsilon_0$ is determined outside the NMR resonance. Consider the transition between the $m = -1$ and $m = 0$ sublevels as an example: the polarization effect is assessed by alternately preparing the atomic beam such that the atoms are predominantly populating the sublevels $m_{\text{beam}} = -1$ and $m_{\text{beam}} = 0$. For both beam preparations the population $N_{-1}$ of the sublevel with $m = -1$ of the desorbing atoms were determined by LIF. From the obtained $N_{-1}(m_{\text{beam}})$ the polarization effect

$$\varepsilon = \frac{N_{-1}(-1) - N_{-1}(0)}{N_{-1}(-1) + N_{-1}(0)}$$

is calculated, which is a normalized measure of the polarization of the desorbing Li atoms [20]. The quantity $\varepsilon$ has the advantage of being independent of systematic errors in the measurements, such as fluctuations of the Li beam intensity, etc. If an RF field with a frequency identical to the energy difference between the two sublevels $m = -1$ and $m = 0$ is irradiated onto the sample, transitions between these two sublevels occur. If the intensity of the RF field is sufficient, the population of these two sublevels becomes equal ($\varepsilon = 0$).
Two dips in the relative polarization effect $\varepsilon / \varepsilon_0$ can be seen. They are centred around the Larmor frequency, $\nu_L$. The two lines are about $\Delta \nu_1 = 1$ kHz apart from each other. In the absence of an EFG at the $^6$Li adsorbate nucleus, both lines would be found at the Larmor frequency itself. The interaction of the nuclear quadrupolar moment $Q$ of the $^6$Li atoms with an EFG leads to the observed line splitting. From the line separation $V_{nn}$ can be determined, which is the projection of the EFG on the axis of the static magnetic field (parallel to the surface normal in this case) [22]:

$$\Delta \nu = 6\nu_Q = \frac{3eQ}{2\hbar}V_{nn} \quad \text{for } I = 1. \quad (2)$$

The use of different beam preparations allows identification of the lines: the line at the lower frequency (open symbols) corresponds to a transition between the nuclear spin sublevels $m = -1$ and $m = 0$ and the line at the higher frequency (full symbols) corresponds to a transition between

Figure 2. (a) Splitting of the nuclear sublevels of $^6$Li due to the interaction of the magnetic nuclear dipole moment with the (external) magnetic field and an additional interaction of the nuclear electric quadrupole moment with an electric field gradient. (b) NMR spectra for $^6$Li adsorbed at 27 mT on a Si(111) surface at a temperature of $T = 1100$ K. The empty symbols denote the $m = -1 \leftrightarrow m = 0$ transition, the full symbols the $m = 0 \leftrightarrow m = 1$ transition. (c) The same as (b) but at a temperature of 970 K.
the sublevels \( m = 0 \) and \( m = 1 \). From the order of their appearance the sign of the EFG can be determined; it is positive in this case and its value derived from (2) is \( V_{nm}^{(1)} = +3.3 \times 10^{15} \text{ V cm}^{-2} \).

The mean residence time of Li on Si(111) at this temperature is about 50 ms [20] and the atomic beam intensity was approximately 1 ML/16 s, which leads to an equilibrium Li coverage of \( \Theta = 3 \times 10^{-3} \text{ ML} \). For such a low Li coverage, it can be assumed that the structure of the Si(111) surface is undisturbed and still exhibits the \( 7 \times 7 \) reconstruction. The maximum polarization effect of the desorbing Li atoms is \( \varepsilon_0 = 0.4 \), which is slightly lower than expected from the polarization of the Li atoms in the atomic beam prior to adsorption. This loss of polarization stems from nuclear spin relaxation effects during the residence of the \( ^6\text{Li} \) atoms on the surface.

Figure 2(c) then shows an NMR spectrum recorded at a lower surface temperature of \( T = 970 \text{ K} \). Due to a longer mean residence time, nuclear spin relaxation on the surface is greater and the maximum polarization effect observed drops to \( \varepsilon_0 = 0.04 \), resulting in noisier data. In addition to the two lines that are also seen at \( T = 1100 \text{ K} \) (figure 2(b)), a second pair of lines with a frequency separation of \( \Delta \nu_2 = 2.8 \text{ kHz} \) appears. This corresponds to an EFG of \( V_{nn}^{(2)} = +9.4 \times 10^{15} \text{ V cm}^{-2} \). As recently seen in a combined LEED and isothermal desorption study [23], the longer residence time of the Li atoms and thus higher Li coverage (approximately 0.04 ML at this temperature and atomic beam intensity) leads to the formation of \( 3 \times 1 \) reconstructed patches on the surface. The second, larger EFG is therefore assigned to that experienced by Li atoms involved in the formation of the \( 3 \times 1 \) structure.

A more detailed examination of the temperature-dependent appearance of the two EFGs is shown in figure 3 for two different atomic beam intensities. The noise levels are lower for the \( m = 0 \leftrightarrow m = 1 \) transition due to more efficient atomic beam preparation. Only this preparation is therefore used in this experiments. Care was taken to check that the magnitude of the external magnetic field and thus the Larmor frequency did not shift during the measurement. The EFG can then be extracted from the position of just one line and the Larmor frequency. For temperatures higher than 980 K, only the EFG of Li on the \( 7 \times 7 \) reconstruction is observed. For lower temperatures, the EFG assigned to Li in the \( 3 \times 1 \) structure develops: first in the case of the higher atomic beam intensity of 1 ML/16 s, and then also in the case of the lower beam intensity of 1 ML/24 s. Down to 960 K a coexistence of both EFGs is seen, but below this temperature only the EFG due to the \( 3 \times 1 \) reconstruction can be observed.

Figures 4(a) and 4(b) summarize the temperature dependence of the NMR lines. They show the relative depths of the lines \( \Delta \varepsilon/\varepsilon_0 \), taken from Lorentzian fits to the spectra, for the higher (figure 4(a)) and the lower (figure 4(b)) atomic beam intensity. The temperature at which the transition between the two EFGs occurs (broken line in figure 4) clearly depends on the atomic beam intensity. In figure 4(c) the linedepth is plotted against the Li equilibrium coverage, which is determined by a combination of temperature programmed and isothermal desorption measurements (see [23] for details). The depths of the NMR lines for different atomic beam intensities are seen to obey the same coverage dependence. The transition from one EFG to the other is therefore an effect of the Li coverage rather than of the surface temperature. The development of the NMR line assigned to Li in the \( 3 \times 1 \) structure starts at a coverage of 0.02 ML and becomes the dominant line at a coverage of 0.03 ML. This is consistent with the results from the isothermal desorption study [23] where a critical Li coverage of approximately 0.03 ML was found for the \( 3 \times 1 \) structure to nucleate and grow.

Figure 5 shows the extracted EFG as a function of surface temperature. The value of the EFG associated with the \( 3 \times 1 \) structure is constant within the measured temperature range whereas the EFG assigned to the \( 7 \times 7 \) reconstruction decreases linearly with temperature. Similar
linear temperature dependences of EFGs have been reported for several adsorbate/substrate systems [24]. A satisfying explanation for this effect is still lacking.

The two different values of the EFG of Li on Si(111) have already been observed, but were not assigned to different surface reconstructions [25]. In the former study, a temperature and coverage dependent shift of one EFG between the two values rather than the simultaneous appearance of two EFGs was seen. The sample used in that experiment was less well characterized, in particular the miscut was greater and the preparation of the $7 \times 7$ structure was performed less carefully (e.g. faster cooling down through the $7 \times 7 \leftrightarrow 1 \times 1$ phase transition). Furthermore, the static magnetic field was less homogeneous than in the present study. Either fact could explain the contrasting observations. First, a greater miscut and a faster cooling procedure result in smaller terraces, which only allow the formation of small $3 \times 1$ domains. This could have led to the observation of just one line due to an averaging motional narrowing process (see below). Second, an inhomogeneous magnetic field could have resulted in insufficient instrumental resolution to resolve the two distinct lines.

4. Discussion

Two features of the data need further discussion: the narrow line width in the NMR spectra and the existence of two well separated EFGs under the condition of fast diffusion, where one would
Figure 4. (a) and (b) Depths of the NMR lines as a function of surface temperature for the two different atomic beam intensities. (c) The same data plotted against the Li coverage. The coverage was determined from temperature programmed and isothermal desorption measurements.

expect only one motional narrowed EFG [26, 27], and the large difference of the EFGs for the two reconstructions.

In general, the existence of two binding environments for the Li atoms that differ in their EFGs and mean residence times does not necessarily lead to the observation of two pairs of lines in the NMR spectra. If the mean residence time that the Li atoms dwell in one binding environment before they diffuse to the other one is shorter than \(1/\Delta \nu\) (\(\Delta \nu = \frac{1}{2}(\Delta \nu_2 - \Delta \nu_1)\)), only one pair of lines at an intermediate position is seen. A Monte Carlo simulation was performed to examine
this effect, which is known as motional narrowing, more quantitatively. The simulation shows that the Li nuclei have to experience one EFG continuously for more than $5 \times 1/\Delta \nu$ before this EFG shows up in the spectra in terms of separate lines [28]. From the data of figure 2(c), $\Delta \nu$ is found to be about 750 Hz. Thus, the adsorbed $^6$Li atoms must stay on average for more than $t = 6.7$ ms in one binding environment, in order for separate lines to be observed (a similar number is obtained by discussing the width of the NMR lines). This rules out the possibility that the two different EFGs are just due to two different binding sites within the same unit cell and strongly supports the assignment of the two EFGs to differently reconstructed patches.

From the minimal time the Li atoms must stay in one $3 \times 1$ reconstructed patch and the size of the patch, a lower limit for the Li diffusion constant can be derived. From the miscut of the crystal and from atomic force micrographs the mean terrace width of the surface was determined to be approximately 1 $\mu$m. This figure may be used as an appropriate order of magnitude of the maximum size of the $3 \times 1$ patches. For isotropic two-dimensional diffusion, the mean distance squared $\bar{x}^2$ that an adsorbate can cover within the time $t$ is given by [29]

$$\bar{x}^2 = \frac{a^2}{\tau_{\text{diff}}} t$$

(3)

where $\tau_{\text{diff}}$ denotes the mean time for one diffusion jump of length $a$. To a first approximation $a$ is given by the Si(111) lattice constant ($a = 3.84$ Å); $t = 6.7$ ms then results in $\tau_{\text{diff}} \simeq 1$ ns. At a temperature of 960 K, where the $3 \times 1$ peak is fully developed, this leads to a diffusion energy of approximately 0.8 eV, where a prefactor of $10^{-13}$ s is presumed. Since the patch size is likely to be smaller than the above assumed upper limit of the terrace width, the diffusion energy could be even larger. The high value of the diffusion energy could be due to the fact that all dangling bonds in the $3 \times 1$ structure are saturated by Li atoms, which is also evident from the high Li desorption energy of 3.2 eV [23]. Diffusion would then involve site switching via unfavourable sites and therefore high barriers.

The value of the EFG $V_{nn}$ is directly correlated with the charge density distribution $\rho(\vec{r})$
Figure 6. The influence of the electron density around the Li atom on the sign of the EFG: electrons outside the $54.7^\circ$ cone within the hatched area equatorial around the Li atom contribute with a positive sign to the EFG, electrons above or below the Li atom within the $54.7^\circ$ cone contribute with a negative sign.

around the Li nucleus:

$$V_{nn} = \int \rho(\vec{r}) \frac{3 \cos^2 \theta_n - 1}{r^3} d\vec{r}$$

where $\theta_n$ denotes the angle between $\vec{r}$ and the surface normal (figure 6). This quantity could in principle be determined from the results of structure calculations using DFT. Because of the $1/r$ dependence in (4) the charge density $\rho$ close to the nucleus is most important for the EFG. A successful attempt to calculate an EFG on surfaces has recently been achieved for Li adsorbed on Ru(111) using a full-potential linearized augmented plane wave all-electron calculation [30]. Agreement between measurements and theory within a factor of two was found. A calculation for the structurally more complicated Si surface is still missing. However, some qualitative conclusions can be drawn from (4). The $(3 \cos^2 \theta_n - 1)$ term changes its sign at $\theta_n = 54.7^\circ$. Thus, a cone with this opening angle is defined around the Li nucleus, as shown in figure 6. Electrons within this cone below or above the Li nucleus contribute with a negative sign to $V_{nn}$, whereas on the other hand electrons equatorial around the Li atoms outside that cone contribute with a positive sign. A negative sign of the EFG is therefore an indication for an adsorption situation where the adsorbate sits well above the surface with the binding electrons in between the adsorbate and the surface. One would expect negative EFGs for top or bridge sites on closely-packed flat surfaces, as in fact was observed for Li adsorption on a W(110) surface [31]. A positive sign of the EFG, on the other hand, is a sign that the adsorbate is sunk into an open surface structure so that the binding electrons surround the adsorbate. This was indeed observed for adsorption of Li on the more open W(100) and W(211) surfaces [31].

The EFG of Li on the $3 \times 1$ reconstruction shows the largest positive value ever seen on surfaces. This is in clear contradiction with a situation where the electron density due to the binding electrons is directly beneath the Li atoms and points towards an adsorption geometry where the Li atoms are embedded in the top Si layer(s). It is reasonable to assume that the remaining dangling bonds of the $3 \times 1$ reconstruction are the most probable binding sites for the Li atoms. Thus, since both the Seiwatz [8, 9] and the extended Pandey chain models [11, 12]
provide only dangling bonds almost along the surface normal, they are not compatible with a positive EFG (see [32] for an overview, including schematic drawings of the different structural models). This is also in accordance with the conclusions drawn from the result of a recent STM study by Saranin et al [32]. The authors determined the top Si atom density to be $\frac{2}{3}$ ML and also discard the Seiwatz and extended Pandey models, which have a Si density of $\frac{2}{3}$ and 2 ML, respectively. The three more recently published models, the ‘560560’ [13–15], HCC [16] and DπC models [17], all have dangling bonds tilted away from the surface normal. The ‘560560’ and the HCC model both contain a narrow empty channel into which a dangling bond protrudes from the side. A Li position in or slightly above these channels would lead to electron density beside the adsorbed Li atoms, as seen, for example, in the charge density plots in [16]. They are therefore in agreement with the observed positive EFG. The DπC model consists of two $\pi$-bonded chains. The alkali metal atoms are thought to be in a threefold position between the two chains. Providing that the three bonds (one to the Si atom underneath, two to the side) have a similar charge density, this binding position would also lead to a positive EFG.

To summarize, the Li-induced formation of the $3 \times 1$ reconstruction of Si(111) has been investigated by NMR on Li nuclei. The electric field gradients of Li adsorbed on the $7 \times 7$ structure and of Li involved in the formation of the $3 \times 1$ reconstruction could be observed simultaneously and were found to be $3.3 \times 10^{15}$ V cm$^{-2}$ and $9.4 \times 10^{15}$ V cm$^{-2}$, respectively. The absence of motional narrowing for the two EFGs allowed the diffusion energy of Li in the $3 \times 1$ structure to be estimated to be at least 0.8 eV. The observed EFGs are positive, indicating a Li adsorption site not above but rather within the reconstruction. A few of the proposed structural models for the $3 \times 1$ reconstruction can be ruled out by these findings.

Acknowledgments

Dr H J Jänsch (Marburg) contributed with many stimulating discussions. This work was supported, in part, by the Deutsche Forschungsgemeinschaft (DFG), Bonn, under contract Fi 311/4-2.

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New Journal of Physics 3 (2001) 1.1–1.11 (http://www.njp.org/)
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