Lithium adsorption on the SrTiO$_3$(100) surface

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Abstract
In this paper we study the kinetics of Li adsorption on the SrTiO$_3$(100)
(STO(100)) surface at room temperature (RT). The study took place in an ultra-
high vacuum (UHV) by low-energy electron diffraction (LEED), Auger electron
spectroscopy (AES), electron energy-loss spectroscopy (EELS), temperature-
programmed desorption (TPD) and work function (WF) measurements. At low
Li coverage ($\theta < 0.5$ ML), Li adsorbs as isolated atoms, whereas at higher
coverage it intermixes with the oxygen of the substrate and/or it intercalates
into the substrate. The sticking coefficient of Li on STO(100) is constant. The
lithium remains in a non-metallic state on the surface. After heating at 1100 K,
part of the Li remains on the surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Strontium titanate, SrTiO$_3$ (STO), is one of the perovskite-type oxide compounds which is of
great technological and scientific interest. It is used as a substrate for the growth of high-T_c
(critical temperature) superconductors [1–3], as high-temperature oxygen sensors [4, 5] and as
a buffer material for the growth of GaAs on Si [6].

Metallic films on oxide substrates are relevant to crystal growth, catalysis, gas sensor
operation, etc [1–7]. When metals are deposited on metal oxide surfaces, interesting surface
chemistry can take place.

Thin alkali films on surfaces are very interesting because of their technological
applications (promotion in heterogeneous catalysis, enhancement of the oxidation, etc) and
their fundamental importance as simple adsorption systems [8–10]. The electrochemical Li
insertion into metal oxides is a research area of high current interest because of its importance
in the development of new high energy-density batteries.

In this contribution, we report on the adsorption of Li on the STO(100) surface at room
temperature (RT). The study took place in an ultra-high vacuum (UHV) environment by

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Auger electron spectroscopy (AES), electron energy-loss spectroscopy (EELS), low-energy electron diffraction (LEED), temperature-programmed desorption (TPD) and work function (WF) measurements.

2. Experimental details

The experiments were performed in an UHV chamber with base pressure 10^{-10} mbar. The chamber was equipped with a four-grid LEED optics, a cylindrical mirror analyser (CMA) with energy resolution 0.3% for AES and EELS measurements, a quadrupole mass spectrometer (QMS) for TPD measurements and an electron gun for relative WF measurements. The system was also equipped with an Ar^+-ion sputtering system and heating facilities for sample cleaning. The AES and EELS measurements were recorded in the first derivative mode. Lithium was evaporated from a well-degassed SAES dispenser. The procedure used for the Li dose calibration is the following. A Si(111) single-crystal surface was exposed to the Li flux using the same heating current (8.0 A) as that used during Li deposition on STO, and the Auger Li (50 eV) peak height was recorded as a function of the Li dose. The first Li layer on Si(111) was monitored at the first break of the curve. The density of the Li layer on the Si(111) surface is 7.8×10^{14} atoms cm^{-2} [11]. From this we estimated each Li dose to be 1.3×10^{14} atoms cm^{-2}. (Each dose corresponds to an exposure time of 30 s.) One monolayer of Li on STO(100) corresponds to 1.3×10^{15} atoms cm^{-2} and is reached after ten doses of Li deposition. For the above calibration we assumed that the sticking coefficient of Li is the same on both surfaces.

The STO(100) sample, with dimensions $(10 \times 5 \times 1)$ mm^3, was provided by Crystal GmbH. The sample was polished on one side and was doped by Fe acceptors (0.14 wt%). The sample was mounted into a Ta case with a Ta foil strip uniformly pressed between the case and the sample, and it was heated by passing current through the Ta foil strip. The temperature was measured by a Cr–Al thermocouple, spot welded onto the back side of the case and calibrated with an infrared pyrometer. The surface was cleaned by heating at 1050 K for several hours. This procedure produces a good 1×1 LEED pattern. However, a small amount of carbon contamination was detected by Auger spectroscopy. The carbon contamination was removed by Ar^+ bombardment (2 keV, 1 μA) and subsequent heating at 900 K. The substrate was considered clean when the carbon (C (273 eV)) to oxygen (O (520 eV)) Auger peak height ratio was less than 5%.

3. Results and discussion

Lithium adsorption on the STO(100) surface causes a gradual decrease of the intensity of the substrate LEED spots, whereas the background of the picture increases. Above about one monolayer of Li deposition the LEED pattern of the substrate almost disappears. The disappearance of the LEED pattern at relatively low Li coverage indicates the possibly that the Li causes a reconstruction of the STO surface.

Figure 1 shows the Auger peak intensity of Li (43 eV), Li (48 eV), O (520 eV), Ti (380 eV) and Sr (76 eV) as a function of Li deposition on the STO(100) surface at RT. As seen in figure 1, the intensity of the Sr (76 eV) Auger peak decreases rapidly with Li deposition because of the low escape depth of the low-energy electrons. The intensity of the O (520 eV) and Ti (380 eV) Auger peaks decreases with the same rate at low Li coverage (<10 D). This is expected because the escape depth for the electrons of both peaks is almost the same. However, at higher Li coverage the O (520 eV) Auger peak remains almost constant, whereas the Ti (380 eV) decreases continuously. This difference can be explained by a reconstruction of the surface, which moves oxygen atoms to the surface. The reconstruction of the surface
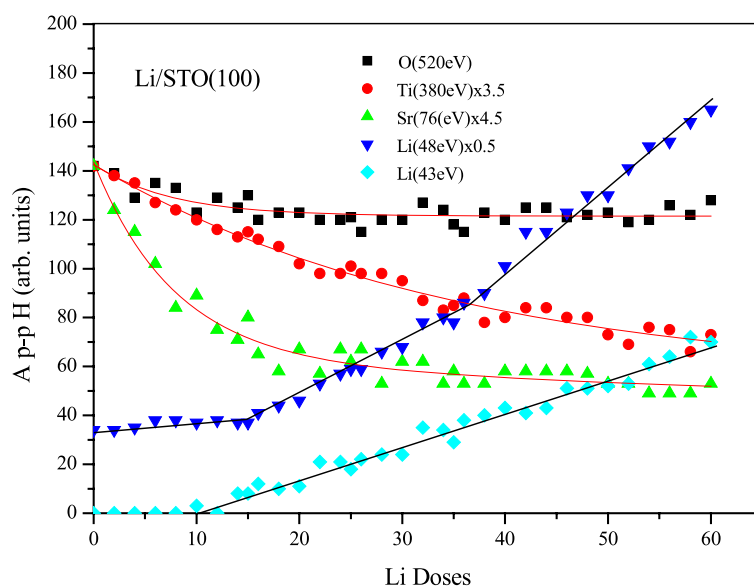
Figure 1. The Auger peak to peak height (Ap-pH) of Li (48, 43 eV), Ti (380 eV), Sr (76 eV), and O (520 eV) versus Li dose on the STO(100) surface at RT. The Ti (380 eV) Ap-pH has been multiplied by 3.5 and the Sr (76 eV) by 4.5 for comparison reasons.

during Li deposition above 1.0 ML is consistent with LEED observations. We cannot preclude also a partial insertion and/or intercalation of Li into the substrate. Lithium intercalation has been also observed during Li deposition onto the $TiO_2(110)$ surface [12, 13].

The intensity of the Li Auger peaks is almost constant up to about ten doses (1.0 ML). The intensity of the Li (48 eV) peak is not zero at zero Li coverage because it is overlapped with the low-energy Auger peaks of $SrTiO_3$. Above ten doses of Li deposition, the intensity of the Li (48 eV) and Li (43 eV) increases linearly with Li deposition. All Li-correlated Auger peaks have been previously detected during oxygen adsorption on Li films [14]. All peaks have been assigned to interatomic transitions initiated by a 1s hole on Li atoms. The 48 eV Li Auger peak is associated with the Li(1s)Li(2s)Li(2s)′ interatomic transition, where the prime denotes a neighboring Li atom. This is because there cannot be more than one valence hole on the same Li atom. The 43 eV peak appears above 10 doses of Li deposition. This peak is associated with a Li–O interatomic Auger transition. The stability of the Li-related Auger peaks up to ten doses of Li deposition indicates that Li at low coverage (<1.0 ML) adsorbs on the surface as isolated atoms. As the coverage increases the Li–Li interaction increases, in agreement with the evolution of the Li KVV′ Auger transition. The appearance of the 43 eV peak (which has been assigned as the Li (1s), O (2p), O (2p) Auger transition), above ten doses of Li deposition is consistent with the reconstruction of the surface and the intermixing of the Li with oxygen, which increases the Li–O interaction. Analogous peaks have been also measured during Li deposition on semiconducting [11] and metallic substrates [15, 16].

Figure 2 shows the work function change, $(\Delta\Phi)$ versus Li deposition on the STO(100) surface at RT. The work function of the STO surface decreases rapidly from its clean surface value, up to about ten doses of Li deposition, and remains almost constant at higher coverage. Within experimental error, no minimum is observed, similarly to a characteristic of the alkali adsorption on metallic and semiconducting surfaces [17, 18]. The initial dipole moment of Li adatoms, at very low coverage, was calculated by the Helmholtz equation [19] to be 2.0 D
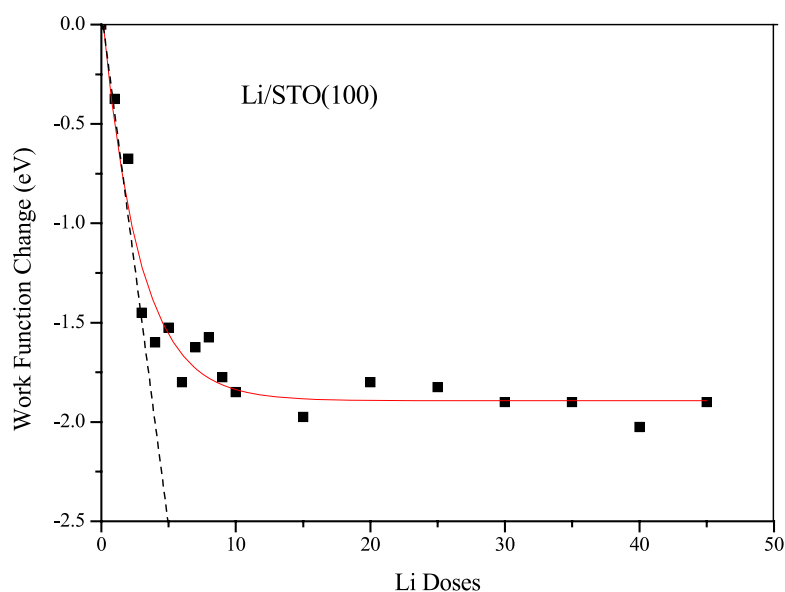
Figure 2. The WF change, $\Delta\Phi$, of the STO(100) surface as a function of Li dose at RT.

(debye unit). This value is the same with the theoretical value, 2.0 D, as it was calculated by Hartman [19], whereas it is much higher than the value of 0.6 D which was measured after Li deposition on Ni(110) surface [16]. This difference is attributed to the different adsorption geometry of Li atoms on the two substrates. At higher coverage the slope of the work function curve decreases gradually and ultimately becomes zero at about 1 ML coverage. This shows that the dipole moment of the Li gradually decreases. The behavior of the work function is consistent with the Auger measurements. The maximum work function change is 1.9 eV. Analogous results have been measured during Li deposition on the TiO_2(110) surface [12]. If we assume the work function of the clean surface equal to 3.4 eV [20], the work function of the Li/STO system at high coverage is 1.5 eV, a value which is lower than the work function of metallic Li (2.4 eV) [20]. This is an indication that Li is in a non-metallic state on the STO surface up to the coverage we examined ($\sim$5 ML). This is consistent with the Auger measurements and the Li–O intermixing on the surface.

Figure 3 shows a series of temperature-programmed desorption spectra of Li after Li deposition on the STO(100) surface at RT. The heating rate was constant 15 K s^{-1}. The TPD spectra show a strong double peak at $\sim$1100 K and a smaller one at about 1000 K, which never saturated with Li deposition. At very high Li coverage ($>$20 D) a very small peak is developed at 640 K. The lack of saturation of the main high temperature desorption peaks suggests that Li remains in a non-metallic state and reflects the desorption of Li from some Li–O intermixed multilayer rather than desorption of Li from sites on the STO surface, in agreement with the suggested surface reconstruction and Li–O intermixing.

The area under the TPD spectra is proportional to the desorbed amount. The area under the TPD spectra of Li versus the number of Li doses is shown in figure 4. The slope of this curve is proportional to the sticking coefficient of the adsorbate. As is shown in figure 4, the area increases linearly with Li deposition, which means that the sticking coefficient of Li on STO is constant. The deviation from linearity at high Li coverage ($>$15 D) is attributed to a partial insertion (intercalation) of Li into the substrate. We preclude a change of the sticking coefficient
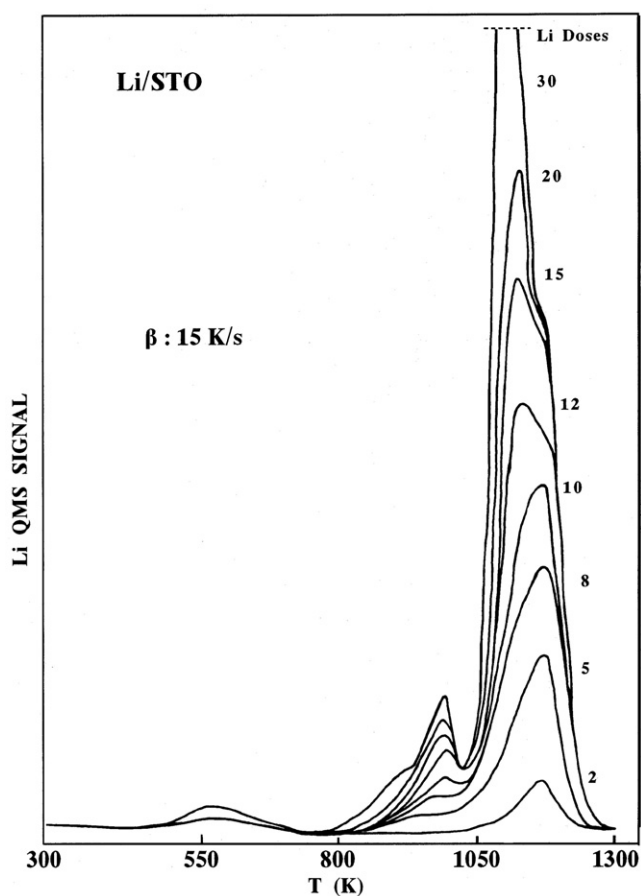
Figure 3. TPD measurements of Li after different amounts have been deposited on the STO(100) surface. The heating rate is 15 K s^{-1}.

above 14 doses because the Auger measurements (figure 1) do not show such a behavior. The desorption energy of the low-temperature Li desorption peak (640 K) can be roughly estimated by the Seebauer equation [21]. Using a pre-exponential factor of $\nu = 10^{13}$ s^{-1}, we found 1.7 eV/atom for the 640 K TPD peak. This value is close to the cohesive energy of metallic Li (1.63 eV/atom) [22]. The area under the 640 K is very small, indicating that no metallic Li overlayer is formed, in agreement with the work function measurements and the results of Li on TiO$_2$(110) [12]. We did not observe any Li–O compound in the TPD spectra.

The electron energy-loss spectra (not shown here) of STO do not show any substantial change during Li deposition. The intensity of all peaks in the measured energy range, 0–40 eV, decreases gradually, but are all visible even after 4 ML deposition. This behavior is different from that of K on the STO(100) surface [23]. In that case the 12.5 eV loss peak, which has been attributed to an excitation from O to Ti(3d), decreases rapidly and disappears after 1 ML of K deposition. This behavior has been attributed to a charge transfer from K (4s) to Ti (3d), which is empty in the clean STO. The charge transfer fills in the Ti -3d level and leads to a decrease of the excitation probability. The charge transfer indicates an ionic binding of K on STO. In our case the 12.5 eV loss peak remains even after 4 ML of Li deposition and indicates a covalent rather than ionic binding of Li on STO.

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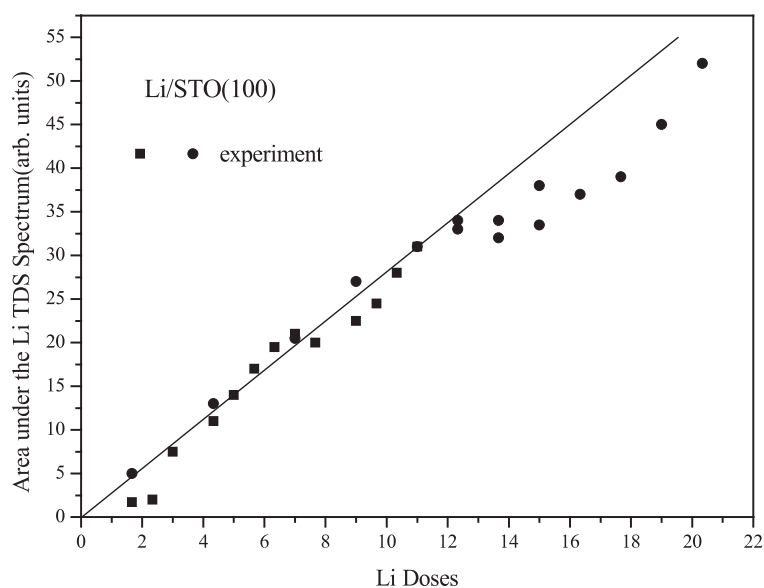
Figure 4. Integrated desorption flux of Li versus deposition on the STO(100) surface. The two different symbols correspond to different experiments.
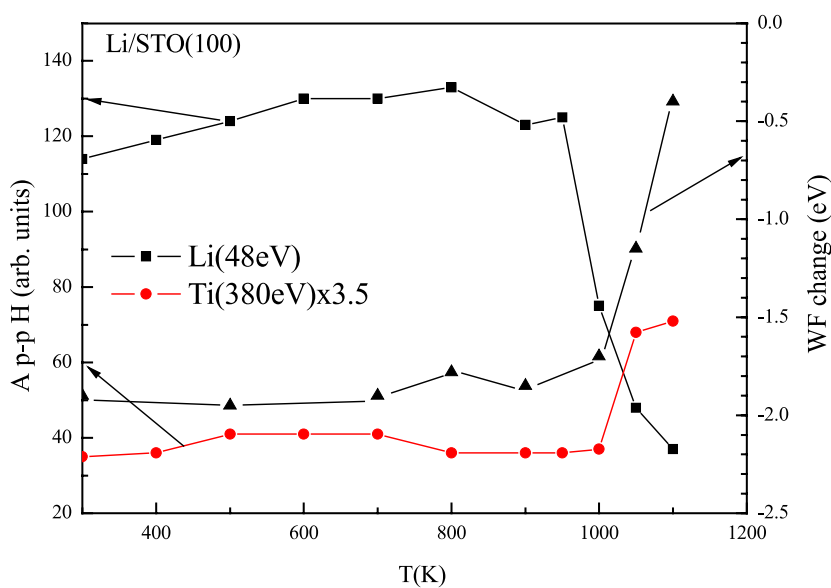
Figure 5. The Ap-pH of Li (48 eV), O (520 eV), Ti (380 eV) and the WF change as a function of annealing temperature for 20 s anneals.

Figure 5 shows the change of the Li (48 eV), O (520 eV), and Ti (380 eV) Auger peak intensities as well as the change of the work function of the system Li/STO(100) as a function of temperature. The initial Li coverage is 4 ML. The annealing time was 20 s, and the measurements were made near 300 K after the sample cooling. The work function is constant up to 600 K and increases at higher temperature. The final value of the work function after

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heating at 1100 K for a long time is 0.18 eV below the value of the work function of the clean STO(100) surface. This is attributed to a small amount of Li which remains on the surface after heating at 1100 K. The Ti (380 eV) Auger peak remains constant up to about 1000 K and increases rapidly at higher temperature because of Li desorption. The Li (48 eV) Auger peak increases gradually up to 800 K and then decreases rapidly. The initial increase of the Li (48 eV) Auger peak is attributed to a partial deintercalation of Li to the surface. After heating of the sample at 1100 K for a long time the intensity of the Li (48 eV) Auger peak does not go back to its value before Li deposition. This indicates that part of Li remains on the surface after heating at 1100 K, in agreement with the work function measurements. This amount of Li is removed from the surface by Ar-ion bombardment.

4. Summary

The kinetics of Li adsorption on the SrTiO$_3$(100) surface has been studied at RT by LEED, AES, EELS, TPD and WF measurements in UHV. At low Li coverage (<1.0 ML) Li adsorbs as isolated ions with relatively high dipole moment. Above 1.0 ML coverage, part of the oxygen moves to the surface and intermixes with Li atoms. The sticking coefficient of Li on STO(100) is constant, and the Li overlayer is in a non-metallic state. There is not any indication of Li oxidation on the STO(100) surface. Part of the lithium intercalates into the substrate. At high temperatures most of the lithium desorbs from the surface.

Acknowledgment

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