A low-energy electron microscopy and x-ray photo-emission electron microscopy study of Li intercalated into graphene on SiC(0001)

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\textbf{Abstract.} The effects induced by the deposition of Li on 1 and 0 ML graphene grown on SiC(0001) and after subsequent heating were investigated using low-energy electron microscopy (LEEM) and x-ray photo-emission electron microscopy (XPEEM). For 1 ML samples, the collected photoelectron angular distribution patterns showed the presence of single $\pi$-cones at the six equivalent K-points in the Brillouin zone before Li deposition but the presence of two $\pi$-cones ($\pi$-bands) after Li deposition and after heating to a few hundred °C. For 0 ML samples, no $\pi$-band could be detected close to the Fermi level before deposition, but distinct $\pi$-cones at the K-points were clearly resolved after Li deposition and after heating. Thus Li intercalation was revealed in both cases, transforming the carbon buffer layer (0 ML) to graphene. On 1 ML samples, but not on 0 ML, a ($\sqrt{3} \times \sqrt{3}$) R30° diffraction pattern was observed immediately after Li deposition. This pattern vanished upon heating and then wrinkles/cracks appeared on the surface. Intercalation of Li was thus found to deteriorate the quality of the graphene layer, especially for 1 ML samples. These wrinkles/cracks did not disappear even after heating at temperatures $\geq$500 °C, when no Li atoms remained on the substrate.

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The recent realization of two-dimensional (2D) graphene sheets has raised much interest among researchers in trying to make use of their peculiar electronic structure. Electrons in an isolated graphene sheet form a 2D gas of massless Dirac fermions [1, 2] that provide unique electron transport properties. In real electronic device, however, the graphene electronic properties are affected by elastic deformations, interlayer coupling and interactions with the substrate. In particular, for a graphene sheet prepared epitaxially on a SiC(0001) substrate, it is known that the first carbon layer, the so-called ‘buffer layer’ or 0 ML graphene layer, has no graphitic electronic properties and acts as a layer that allows the next carbon layer to behave electronically like an isolated graphene sheet. This buffer layer is known to bond covalently [3, 4] to Si atoms in the first Si-C bilayer of the SiC(0001) substrate. The remaining unsaturated dangling bonds in this first bilayer of the substrate result in a pinning of the Fermi level [5]. The buffer layer is therefore regarded as a major obstacle to the development of future electronic devices from graphene grown on SiC(0001). To find different ways of decoupling the buffer layer from the substrate is therefore of great interest. This was recently accomplished by hydrogen [6, 7] and gold [8] intercalation and we therefore investigated the effects of lithium layers deposited on graphene sheets grown on the SiC(0001) substrate. One reason is that it is known that a graphite intercalation compound (GIC) can be obtained by depositing Li metal on graphite. Moreover, Li-GICs are of interest for the development of rechargeable Li-ion batteries, for which the lifetime is particularly crucial. It has been claimed that graphitic anodes suffer severe surface structural disordering upon prolonged cycling in such batteries, which shortens their lifetime [9–11]. Graphene may be a better material than graphite for such applications since it is said to have a high elasticity and to be extremely strong and chemically inert. No fundamental experimental study of Li adsorption on high-quality graphene sheets prepared on SiC substrates has, to our knowledge, been reported so far. Therefore, we pursued the detailed experimental investigation reported below using a spectroscopic photoemission, low-energy electron microscope (SPELEEM) instrument.

We show that dramatic changes in the electron band structure and in the morphology of monolayer graphene grown on the silicon-terminated 6H-SiC(0001) surface are induced after Li deposition. Changes in the morphology of the graphene sheet are detected immediately after deposition and are even more emphasized after subsequent heating cycles at temperatures of a few hundred °C. A transformation from monolayer graphene to bilayer graphene is unambiguously demonstrated by recorded momentum-resolved photoelectron diffraction patterns, which reveal the \((E, k_x, k_y)\) electron band structure over the whole hexagonal Brillouin zone (BZ). The two bands detected after Li deposition do not appear as sharp and distinct as the single band present on monolayer graphene before deposition. This may be partly caused by the defects and disorder observed to be induced by the deposited Li. A comparison is also made with 0 ML graphene grown on 6H-SiC(0001), i.e. a sample that has only the carbon buffer layer at the surface. Also, for this sample, significant differences are observed in both the electronic structure and morphology after Li deposition. The electronic structure shows a clear transformation from the very faint electronic structure observed close to the Fermi level for the carbon buffer layer to sharp \(\pi\)-cones around the K-points in the BZ that are typically observed for monolayer graphene. Fewer defects and disorder appear to be induced by the deposition of Li on the 0 ML sample compared to the 1 ML sample.

Growth of large homogeneous area 1 ML graphene on a 6H-SiC(0001) substrate was performed [12, 13] in an inductively heated furnace at a temperature of 2000 °C and at an ambient argon pressure of 1 atm. Similar conditions but with a somewhat shorter time were
Figure 1. (a, b) LEEM images taken from monolayer graphene (1 ML) grown on a 6H-SiC(0001) substrate: (a) at an FOV of 50 µm and an energy of −0.38 eV and (b) at an FOV of 25 µm and an energy of 0.0 eV. (c) LEEM image taken after Li deposition: FOV, 50 µm, and energy, −1.2 eV. (d) μ-LEED image collected at $E_{\text{Kin}} = 40$ eV after Li deposition. (e, f) LEEM images taken after annealing at 180 and 260°C, respectively: FOV, 20 µm, and energy, −0.02 and 1.0 eV, respectively.

used for preparing large homogeneous area 0 ML graphene on 6H-SiC(0001). The morphology, thickness and electronic structure of these samples were investigated using the SPELEEM instrument on beamline I311 at the MAX synchrotron radiation laboratory. This microscope has a spatial resolution better than 10 nm in the low-energy electron microscopy (LEEM) mode. High energy and momentum resolution in the x-ray photo-emission electron microscopy (XPEEM) mode is obtained by using an energy filtering function. This is realized utilizing a hemispherical analyzer in the electron optical path, and the lenses of the image column transfer independently the image plane and the back focal plane of the objective through the system [14].

Linearly s-polarized radiation of the first harmonics of the undulator was used for the excitation, at normal incidence on the sample surface. A few monolayers of Li were then deposited in situ from a metal dispenser (SAES getters) and subsequent heating cycles were carried out live in front of the objective lens.

A large and homogeneous monolayer graphene sample grown on SiC(0001) is shown by the LEEM image in figure 1(a), using a field of view (FOV) of 50 µm. The electron reflectivity curve recorded from, respectively, the bright grey area and the small darker islands shows single and double dip(s)/minimum(a). Thus, the bright area in figure 1(a) represents monolayer graphene, while the darker areas/islands represent bilayer graphene but also contain small dark spots where three layers of graphene have formed. The weak lines seen across the sample surface represent steps and illustrate the step bunching that occurs on the SiC substrate during graphene
Figure 2. (a–c) Photoelectron angular distribution pattern collected from 1 ML graphene at an initial state energy of (a) 1.7 eV, (b) 1.2 eV and (c) 0.2 eV below the Fermi level, using a photon energy of 35 eV. (d–f) Patterns collected from the 1 ML graphene sample after Li deposition and annealing at 330 °C and at the same initial state energies as in (a–c), respectively.

growth. These lines are more clearly seen in the close-up LEEM image displayed in figure 1(b), where an FOV of 25 μm was utilized. Images recorded immediately after Li deposition show significant differences, as illustrated in figure 1(c). The surface appears rougher and grainy after Li deposition but is nevertheless well ordered, as illustrated by the μ-LEED pattern shown in figure 1(d). In addition to the (1 × 1) graphene spots, weaker spots corresponding to a (√3 × √3) R30° reconstruction are also clearly visible in this diffraction pattern. What possibly can give rise to this structure is the formation of a C6Li compound as suggested by Farjam and Rafii-Tabar [15], or Li adsorption in the hollow sites on graphene. The Li deposited was, as expected, found to change the work function of the sample, and different electron energies had then to be used to reveal similar details and contrasts in the LEEM images as in figure 1(a).

The surface morphology was surprisingly found to deteriorate and not improve after heating at different temperatures. At 180 °C a mosaic-like pattern was observed in the LEEM image, as illustrated in figure 1(e). This mosaic pattern is suggested to be due to distortions in the graphene layer induced by the tension caused by deposited Li atoms. After heating the sample at 260 °C the pronounced mosaic pattern could no longer be observed. However, wrinkles along the steps could be observed, and defects appear to have developed on the monolayer terraces, as shown in figure 1(f). The morphology remained the same also after heating at temperatures up to about 350 °C.

The (E, kx, ky) electronic band structure was investigated before and after Li deposition using energy filtered XPEEM [14]. 2D momentum-resolved photoelectron angular distribution patterns recorded, using a photon energy of 35 eV, at three different initial state energies are shown in figure 2. The typical electronic band structure of monolayer graphene [16, 17], i.e. the
Figure 3. (a, b) LEEM images taken from 0 ML graphene (a) before and (b) after Li deposition, at an FOV of 25 µm and an energy of −0.4 and −1.3 eV, respectively. (c) µ-LEED image collected at $E_{\text{Kin}} = 40$ eV after Li deposition. (d) LEEM image taken after heating the sample at 340°C: FOV, 25 µm, and energy, −1.4 eV.

single π-cones at the six equivalent K-points in the first BZ, can be observed in figures 2(a)–(c). The initial state energies in the figure are 1.7, 1.2 and 0.2 eV below the Fermi level, respectively, since the Fermi level was determined to be located at $E_{\text{SV}} = 30.2(\pm 0.1)$ eV. After Li deposition and also after heating at 330°C the π-cones appear somewhat broader and less distinct, as illustrated in figures 2(d)–(f). This is due to the appearance of two π-bands (i.e. two π-cones) that are most clearly visible in the pattern collected at the smallest initial state energy. The theoretical investigation of photoemission constant-energy maps for bilayer graphene showed such π-bands [18], and this thus indicates that Li atoms have succeeded in getting through the graphene and buffer layer and transform the carbon buffer layer into a second graphene layer. This also agrees well with our recent core level observation of Li intercalation into epitaxial monolayer graphene on SiC(0001) [19].

A similar experiment was performed on 0 ML graphene grown on SiC(0001), i.e. a sample with only the carbon buffer layer on the surface. A typical LEEM image of this 0 ML graphene sample is shown in figure 3(a), at an FOV of 25 µm. The bright area in the figure represents 0 ML graphene since electron reflectivity curves recorded from this area showed no pronounced dip/minimum. However, smaller dark stripes and spots are also clearly visible on the surface, and electron reflectivity curves collected showed them to represent 1 ML graphene since the curves contained one pronounced dip/minimum. The surface morphology was found to change immediately after Li deposition, as illustrated by the LEEM image in figure 3(b). The surface appears rougher and several dark spots of different sizes are now presented on the surface. The µ-LEED patterns recorded after Li deposition showed no new reconstruction, as for the 1 ML
Figure 4. (a, b) Photoelectron angular distribution patterns collected from 0 ML graphene at an initial state energy of (a) 1.2 eV and (b) 0.2 eV below the Fermi level, using a photon energy of 35 eV. (c, d) Patterns collected from the 0 ML graphene sample after Li deposition and heating at 350°C at the same initial state energies as in (a, b), respectively.

graphene sample. For this 0 ML sample, a distinct and intense \((6\sqrt{3} \times 6\sqrt{3}) R30^\circ\) diffraction pattern was observed before Li deposition, whereas only \((1 \times 1)\) graphene spots and weaker spots from the SiC(0001) substrate can be observed after the deposition, as shown in figure 3(c). This clearly shows that the \((6\sqrt{3} \times 6\sqrt{3}) R30^\circ\) pattern is eliminated/quenched by the deposited Li. It also suggests that the \((\sqrt{3} \times \sqrt{3}) R30^\circ\) pattern observed on the 1 ML graphene sample after Li deposition is probably not due to Li atoms adsorbed on top of graphene, since similar diffraction spots would then be expected to be seen also on the 0 ML sample. After annealing the sample at 340°C, the surface morphology appears to have improved, see figure 3(d), because the bright area looks less rough, but dark spots are still present. It should be noted that no mosaic-like pattern or wrinkles could be observed on this 0 ML sample after Li deposition and heating. One could speculate about the fact that since the π-electrons in the buffer layer are covalently bound to the SiC substrate unlike the π-electrons in free standing graphene, or in graphene layers grown on top of the buffer layer, they have no opportunity to bond with Li atoms on the surface and create the \((\sqrt{3} \times \sqrt{3}) R30^\circ\) reconstructed pattern as found in the case of 1 ML graphene. However, the μ-LEED pattern in figure 3(c) suggests the carbon layer to be decoupled from the substrate after Li deposition and photoelectron angular distribution patterns collected after deposition show that the π-electrons then form cones like for monolayer graphene, although with the Dirac point shifted down by about 1 eV from the Fermi level.

A mapping of the \((E, k_x, k_y)\) electronic band structure for the 0 ML sample before and after Li deposition was carried out as shown in figure 4. The 0 ML sample showed as expected [3, 4] very faint electronic structures below 1 eV but no π-band close to the Fermi level, as illustrated by the photoelectron angular distribution patterns in figures 4(a) and (b), which were collected at initial state energies of 1.2 and 0.2 eV below the Fermi level. A single π-cone at the six
Figure 5. LEEM images taken at an FOV of 15 µm from a sample with a mixture of 0 and 1 ML graphene areas grown on SiC(0001): (a) before deposition and at an electron energy of 0.4 eV, (b) after Li deposition and at an electron energy of 4.5 eV, (c) after heating at 180 °C and at an electron energy of 6.7 eV and (d) after heating at 260 °C and at an electron energy of 6.8 eV.

equivalent K-points in the BZ, characteristic of monolayer graphene, appeared immediately after Li deposition, however. These cones, which became somewhat sharper and distinct after heating at 350 °C, are shown in figures 4(c) and (d). When comparing these distribution patterns with those of the 1 ML graphene sample before Li deposition (figures 2(a)–(c)), one can immediately see that the Dirac point is located about 1 eV lower in figures 4(c) and (d). This indicates electron doping of the graphene layer created by Li intercalation on the 0 ML sample. It now becomes obvious, when looking carefully at figures 2(e) and (f), that there are two π-cones (π-bands), shifted in energy relative to each other, that give rise to the more diffuse distribution patterns obtained after Li intercalation of the 1 ML sample compared to the sharp distribution patterns in figures 4(c) and (d) from the single π-cones observed after Li intercalation of the 0 ML sample.

To further confirm our observations about the effects on Li intercalation of 0 and 1 ML graphene, a sample with a mixture of larger areas of 0 and 1 ML graphene was prepared. This then ensured that the amount of Li deposited and the heat treatment are as similar as possible for the 0 and 1 ML graphene areas investigated. A representative LEEM image of this sample is shown in figure 5(a). The bright and darker areas in figure 5(a) represent 1 and 0 ML graphene as observed by the electron reflectivity curve recorded from these areas. Immediately after Li deposition the surface morphology appears, as expected, more uneven and rough on both the 0 and 1 ML areas, as seen in figure 5(b). After heating the sample to 180 °C, see figure 5(c), the 1 ML areas still look fairly rough, but interestingly this does not appear to be the case for the 0 ML areas. A more pronounced effect is observed after the sample was heated to about
260 °C; then cracks are visible everywhere on the 1 ML areas but not on the 0 ML areas, as seen in figure 5(d). These observations agree well with those made on the earlier investigated 0 and 1 ML graphene samples, which rules out any dependence on the amount of Li deposited on the surface or difference in heating temperature. The morphology of the topmost graphene layer obtained after Li deposition and heating is different for 1 and 0 ML samples. Cracks and wrinkles appear to be present on the 1 ML areas but not on the 0 ML areas.

Electron reflectivity curves were also recorded from the 1 and 0 ML areas after Li deposition. Two dips were then clearly observed in the reflectivity curve from the Li-intercalated 1 ML area. The separation between the dips was, however, found to be larger than the separation observed for an ex situ grown 2 ML graphene [12] sample. The reflectivity curve from the 0 ML area showed no pronounced dip/minimum before Li deposition but a weak dip/minimum at an energy of about −0.7 eV after deposition. Upon heating the sample, the dips in the reflectivity curves first became somewhat sharper, but then with increasing temperature they gradually changed back and looked similar to before deposition. One actually had to heat the sample to about ≥500 °C before the measured electron reflectivity curves looked essentially the same as before the Li deposition. Such heating did not restore the surface morphology; however, it remained poor since cracks and defects like those in figure 5(d) were still discernible.

In summary, we have by using LEEM and XPEEM studies successfully demonstrated Li intercalation into both 1 and 0 ML graphene samples grown on SiC(0001). For the 1 ML sample, the recorded photoelectron angular distribution patterns showed the existence of single π-cones at the six equivalent K-points in the BZ before Li deposition. After Li deposition and also after heating up to temperatures of about 350 °C, the patterns showed the existence of two π-cones (π-bands). For the 0 ML sample, distinct π-cones at the K-points in the BZ were clearly resolved after Li deposition and heating, while no π-band could be detected close to the Fermi level on the initial surface. After Li deposition on the 1 ML sample the Li atoms are suggested to initially bond with graphene π-electrons and produce a new reconstructed surface and the (√3 × √3) R30° diffraction pattern observed. This pattern was found to vanish immediately upon heating the sample and then cracks/wrinkles appeared on the surface. For the 0 ML sample, no (√3 × √3) R30° diffraction spots were detected after Li deposition. Li intercalation was found to deteriorate the quality of the graphene layer, especially for the 1 ML graphene sheet where wrinkles/cracks and defects were clearly seen to form. These wrinkles/cracks did not disappear even after heating at temperatures of 500–1000 °C and no Li atoms remained on the substrate. For the 0 ML graphene sample, fewer wrinkles/cracks were observed to form on the surface after Li deposition and heating. A sample with a more even mixture of 0 and 1 ML graphene was also prepared and studied. The results obtained confirmed the observations made on the two other samples and that differences in the substrate quality, amount of Li deposited and the heating cycle applied were not the reasons for the difference in quality observed for the Li-intercalated graphene on 0 and 1 ML samples. The observed deterioration in quality of graphene upon Li intercalation may be one reason to explain why the efficiency of a fuel cell reduces with usage.

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