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Studies of the effects induced in the electronic structure after Li deposition, and subsequent heating, on graphene samples prepared on C-face SiC are reported. The as prepared graphene samples are essentially undoped but after Li deposition the Dirac point shifts down to 1.2 eV below the Fermi level due to electron doping. The shape of the C 1s level also indicates a doping concentration of around $10^{14}$ cm$^{-2}$ after Li deposition, when compared with recent calculated results of core level spectra of graphene. The C 1s, Si 2p and Li 1s core level results show little intercalation directly after deposition but that most of the Li has intercalated after heating at 280°C. Heating at higher temperatures leads to desorption of Li from the sample and at 1030°C Li can no longer be detected on the sample. The single $\pi$-band observable from multilayer C-face graphene samples in conventional ARPES is reasonably sharp both on the initially prepared sample and after Li deposition. After heating at 280°C the $\pi$-band appears more diffuse and possibly split. The Dirac point becomes located
at 0.4 eV below the Fermi level, which indicates occurrence of a significant reduction in the electron doping concentration. Constant energy photoelectron distribution patterns extracted from the as prepared graphene C-face sample and also after Li deposition and heating at 280°C look very similar to earlier calculated distribution patterns for monolayer graphene.
I. INTRODUCTION

Studies of the effects induced by alkali metals deposited on graphene samples grown on Si-face SiC show in all cases\textsuperscript{1-9} a strong n-type doping of the graphene. For K\textsuperscript{1-2}, Rb and Cs\textsuperscript{3} the metal stays on the surface and does not penetrate graphene even after heating. For Li\textsuperscript{4-6} and Na\textsuperscript{7-9} on the other hand the metal at first also intercalates in between the carbon layers but with time also at the SiC interface, thus underneath the carbon buffer layer that forms upon growth of graphene on Si-face SiC. Heating at temperatures at around 300°C and 100°C, respectively, strongly promoted intercalation. For monolayer graphene samples the carbon buffer layer was shown to transform into a second graphene layer upon intercalation at the interface, resulting in a transformation from single layer to bilayer graphene electronic properties. Heating at higher temperatures resulted in de-intercalation and desorption of the metal from the sample.

For graphene grown on C-face SiC only very few studies of effects induced by deposited alkali metals have to date been reported\textsuperscript{10,11}. A main reason for this is that C-face and Si-face graphene for a long time have been thought to be fundamentally different\textsuperscript{12,13}. For Si-face graphene there is a general consensus about Bernal stacking and that multilayer graphene exhibits multiple $\pi$-bands\textsuperscript{14}. For C-face graphene on the other hand multilayer graphene samples in general show\textsuperscript{10,11,15,16,17} only a single $\pi$-band in conventional ARPES (Angle Resolved Photoelectron Spectroscopy). It has therefore been suggested that adjacent graphene layers on the C-face are rotated with respect to each other\textsuperscript{10,12,13,15,16}, and that this rotational disorder can explain an electronic band structure of isolated/decoupled layers. Other experimental results instead indicated\textsuperscript{17,18} the presence of $\mu$m-sized grains (crystallographic domains) of
graphene and that adjacent grains could have different azimuthal orientations. In a recent micro- and nano-ARPES investigation it was shown that such multilayer C-face graphene samples show\textsuperscript{19} a single linearly dispersing $\pi$-band in micro-ARPES, while nano-ARPES clearly reveal Bernal stacking and multiple $\pi$-bands in multilayer graphene grains. One thus has to keep in mind that conventional and also micro-ARPES from C-face graphene samples typically averages over so many crystallographic graphene grains, with different number of graphene layers, that the stacking can not be determined from such data. It is nevertheless of interest to investigate effects in the electronic structure of C-face graphene induced by a deposited alkali metal, and to compare with core level and $\pi$-band structure data for similarly treated Si-face graphene.

In this study the effects induced in the electronic structure of C-face graphene are investigated after depositing similar amounts of Li and after heating at similar temperatures as earlier done\textsuperscript{4-6} for Si-face graphene samples. The idea was to reveal if similar effects would be induced in the band structure and core levels. In particular if the Dirac point will shift downwards by about one eV after deposition and if more than one $\pi$-band can be observed after Li deposition and heating. Li ought to intercalate graphene on the C-face easier than on the Si-face since C-face graphene is known to form in smaller domains/grains and with a larger variation in the number of graphene layers and thus to have a higher density of grain boundaries and defects.

II. EXPERIMENTAL

Graphene samples grown on n-doped 6H-SiC(0001) substrates, from SiCrystal, were investigated using beam lines I311 and I4 at the MAXIV laboratory.
I311 is equipped with a modified SX-700 monochromator and the Photo Electron Spectroscopy (PES) end station used is built around a large hemispherical Scienta electron analyzer, providing a total energy resolution of 10 to 100 meV at photon energies from 45 to 450 eV. This end station was used for studies of the C 1s, Si 2p and L 1s core levels. Beam line I4, which is equipped with a SGM monochromator and a PHOIBOS 100 2D CCD Specs energy analyzer, was utilized for ARPES studies of the electronic band structure. The wide angular dispersion (WAM) lens mode was normally selected, providing an acceptant angle of ±14°. A Ta foil mounted on the sample manipulator was in both cases utilized as a reference sample for determining the Fermi level.

The graphene samples utilized in the core level studies were prepared by first heating the substrate in situ at 800 °C under a Si flux to create a Si rich 3x3 reconstructed surface, followed by heating at around 1050 °C for some minutes to obtain a C-rich surface with a graphene coverage of around 1 ML. Faint contributions from C-rich 3x3 and 2x2 reconstructed areas were then still discernable in collected LEED patterns. In the ARPES studies one sample prepared this way was investigated but also samples prepared in a furnace17,18 at 1900°C for 15 min in an Ar pressure of 850 mbar. The latter samples, characterized in an earlier investigation20 were shown to have fairly large domains where the number of graphene layers varied between 1 and 6. These samples produced considerably better band structure data and therefore the ARPES data shown below are from such samples. The graphene grain size is known to be considerably smaller for in situ prepared than for furnace grown samples. When specifying an average thickness of around 1 ML for an in situ prepared sample therefore most probably means that there are also areas with coverage of 2-4 ML and
areas with less than 1 ML coverage. The 3x3 and 2x2 reconstruction patterns observed in LEED indicate presence of areas with sub-monolayer coverage.

Deposition of Li was performed as earlier using a SAES getter source and with the sample at room temperature. Subsequent heating was carried out for two minutes at different selected temperatures. The sample temperature was determined using optical pyrometers in the temperature range 250-1100°C. Data collection was carried out with the sample at room temperature.

III. RESULTS AND DISCUSSION

C 1s spectra collected from one in situ prepared graphene sample before and after Li deposition and subsequent heating are shown in Fig. 1a). The spectrum from the as grown sample is modeled accurately using only two components, the G component from the graphene and the SiC component from the substrate. The energy separation of 2.1 eV and peak intensity ratio of around 2 (at 600 eV photon energy), determined between the G and the SiC components are consistent with previously determined values for an average graphene thickness of around 1 ML. After depositing Li on the surface both these components are seen to have broadened quite significantly and the G component has shifted ca. 0.5 eV to larger binding energy. After heating at 280°C the broadening of the G component is considerably reduced and it is shifted back about 0.2 eV while the substrate SiC’ component is shifted ca. 0.6 eV to lower binding energy. The energy separation between the G and SiC’ components has now increased to the largest value observed, 3.0 eV. This increase in energy separation has in earlier investigations on Si-face graphene been attributed to intercalation of the metal at the graphene/SiC interface, thus to a change in the interface dipole layer that increases the separation between the components. Heating
Fig. 1 C 1s spectra recorded before and after Li deposition and after subsequent heating at the temperatures specified. Contribution from graphene (G) and the SiC substrate appear clearly, at the 600 eV photon energy used.
at progressively higher temperatures is seen to result in a gradual decrease in the separation which indicates a gradual reduction of Li at the interface, since the initial C 1s spectrum is essentially restored after heating at 1030°C.

The corresponding set of Si 2p spectra in Fig. 2a) show a similar evolution after Li deposition and heating cycles. The Si 2p doublet from the SiC substrate is broadened after Li deposition and an additional component, labeled S1, shifted ca. 2.1 eV to lower binding energy appears. This shifted component is assigned to Si at the interface that has reacted with Li so a partial intercalation occurred at the interface directly upon deposition. After heating at 280°C the substrate SiC’ component is shifted ca. 0.9 eV to lower binding energy and appear additionally broadened. This is interpreted as earlier⁴-⁶ as due to that most of the Li is now intercalated at the interface so the SiC’ peak contains contributions from both the SiC substrate and from Si at the graphene/SiC interface that has reacted with Li. Upon increasing the heating temperature the peak shifts back gradually and the broadening is reduced so at 1030°C the initial Si 2p spectrum is essentially restored, which again indicates that the Li appears to have desorbed completely from the sample. That this is actually the case is verified by the Li 1s spectra shown in Fig. 2b). No Li can be detected after heating the sample at 1030°C. After deposition a Li 1s spectrum containing at least three components is obtained. In earlier studies on Si-face graphene⁴-⁶ four or even five Li 1s components could be identified and assigned to Li on top of the graphene, in between graphene layers and at the graphene/SiC interface. Therefore a peak fitting analysis of the core level spectra was carried out. Results for the Si 2p level for the as prepared surface are presented in Fig. 3a). They show that a weaker additional component, labeled E, apart from the SiC is required to adequately model this
spectrum. The relative intensity of this additional component, shifted ca. 0.5 eV to larger binding energy, is seen to be considerably higher in the 140 eV compared to in the 330 eV spectrum. This indicates that it originates from Si atoms in the uppermost layer(s) of the SiC substrate. The results for the Li 1s level directly after evaporation,

Fig. 2 Core level spectra recorded before and after Li deposition and after subsequent heating at the temperatures specified; a) Si 2p and b) Li 2p spectra collected at 140 eV.
Fig. 3  Si 2p and Li 1s spectra recorded at two different photon energies, and curve fitting results for the as prepared sample and after Li evaporation. The solid curves show the components and residual obtained in each fit.

in Fig. 3b), show that three components, labeled 1, 2 and 3, are sufficient to adequately model the Li 1s spectrum. The relative intensity of component “3” is clearly seen to increase with increasing photon energy, indicating that it corresponds to Li that has penetrated beneath the uppermost graphene layer. For the other two components the relative intensity decrease with increasing photon energy, which indicate that they both correspond to Li located on top of the graphene. Component “2” is, however, considerably broader than the other two and can contain unresolved components. This may be the reason why fewer components are observed in this case compared to earlier on the Si-face graphene. After heating at 280°C the Li 1s
spectrum become one broad feature, see Fig. 2b), having the same shape at photon energies from 100 to 240 eV. No component corresponding to Li on the surface of graphene can then be identified so all Li is suggested to be located at the interface or in between graphene layers. Upon further increasing the temperature the intensity of the Li 1s peak decreases gradually so at 600°C most, but not all, of the Li is desorbed from the sample. Thus the evolutions of the three different core level spectra tell the same story. That most of the deposited Li stays initially on top of the graphene and only a smaller amount intercalates. That most of Li is intercalated after heating at 280°C and that Li desorbs gradually after heating at higher temperatures so the initial sample is restored after heating 1030°C. It should be noted that the C 1s and Si 2p spectra, in Fig. 1 and 2a), are plotted to a constant peak height of the dominant feature while the Li 1s spectra, in Fig. 2b), are plotted to display the relative intensities, i.e. the number of counts per scan. No explanation of the additional E component in the Si 2p spectrum, or of the shoulder appearing ca. 2.5 eV after heating at temperatures from 380 to 600°C, was provided above. Oxide formation is an obvious candidate since Si 2p components shifted around 0.5 and 2.5 eV have earlier been reported upon oxidation of surfaces of SiC. However, no O 1s signal is detectable on the as grown sample or after heating at 1030°C, as illustrated in Fig. 4. A very weak O 1s signal is observable directly after Li evaporation and also after heating at temperatures from 380 to 600°C. The amount of oxygen on the surface that this signal corresponds to is too small to give rise to observable shifted oxide components in the Si 2p spectrum. Instead we tentatively suggest the additional component on the as grown sample to be connected to the procedure used for preparing graphene on C-face SiC, involving heating in a Si flux and subsequent annealing that may create some inhomogeneity in the composition of the outermost substrate layers. When analyzing
the Si 2p spectrum recorded after heating at 1030°C this additional component appeared with about the same relative intensity as on the as grown sample. For the component appearing after heating at 380 to 600°C, shifted ca. 2.5 eV to larger binding energy, in the Si 2p spectrum we have no explanation, when oxide formation was ruled out.

Fig. 4 O 1s spectra recorded before and after Li deposition and after subsequent heating at the temperatures specified.

Before turning to the band structure results we want to come back to the large broadening of the G component in the C 1s spectrum observed directly after Li deposition. This effect when an alkali metal is deposited on graphene has been observed in all earlier core level studies of Si-face samples\(^4\)\(^-\)\(^7\)\(^9\), but no convincing
explanation of this effect has been possible to give. However, a very recent calculation of core level spectra for pristine and doped free-standing graphene sheets\textsuperscript{23} provides an explanation of this broadening. The C 1s spectrum calculated for the pristine un-doped graphene, that is not metallic, showed a tailing on the high binding energy side that is characteristic of metallic systems. The peak shape was shown to vary with doping level in a characteristic way, and a doping concentration of 10\textsuperscript{14} cm\textsuperscript{-2} was shown (see Fig. 7 in Ref 22) to exhibit such a pronounced broad tailing on the high binding energy side as the G component shows after Li deposition in Fig. 1a). In 3D (three dimensional) metals the effects of collective excitations appear as discrete plasmon loss replicas. The 2D character of graphene means\textsuperscript{23}, however, that the collective excitations are 2D plasmons that have a completely different dispersion than in ordinary 3D metallic systems. The 2D plasmons give contribution from zero frequency and upward, which means that they contribute to the tail but also that no distinct plasmon loss replicas are distinguishable. If a constant 2D plasmon frequency is assumed discrete plasmon loss replicas are obtained\textsuperscript{24} on top of a doping induced asymmetry, but such discrete loss structures are not observed in the experimental spectra. This point is illustrated in Fig. 5 which show C 1s spectra recorded at 330 eV from the as grown sample, after Li deposition and after heating at 280°C. Also shown are results of peak fits using a Doniach and Sunjic lineshapes\textsuperscript{25}, that illustrate that the tailing for the as grown sample and after heating at 280°C can be reasonably modeled when assuming a larger asymmetry parameter, $\alpha$, in the latter case. After Li evaporation it is obvious that only a tail described by a larger asymmetry parameter can not provide a reasonable fit, since the spectrum contains additional structure in
Fig. 5  C 1s spectra recorded at 330 eV from the as grown sample, after Li evaporation and after heating at 280°C. Results of peak fits using a Doniach and Sunjic lineshape\textsuperscript{25} and different asymmetry parameters in the different cases are also included. These show that additional features appear as suggested in a recent theoretical work\textsuperscript{23}.

the tail that we have just simulated by adding a component that we ascribe to additional loss features. It is well known that alkali metals when deposited on graphene provide electron n-doping but to determine the doping concentration of graphene on different substrates from observed shifts in the C 1s level has not yet
been demonstrated. The energy separation between the Dirac point and the Fermi energy is on the other hand known to directly reflect the doping concentration. This energy separation is directly observed in ARPES spectra recorded around the \( \mathbf{K} \) point in the Brillouin zone of graphene and therefore such results are presented below.

The \( \pi \)-band recorded from a furnace grown C-face graphene sample around the \( \mathbf{K} \) point and along the A-\( \mathbf{K} \)-A’ direction (which is perpendicular to the \( \Gamma - \mathbf{K} - \mathbf{M} \) direction) using a photon energy of 33 eV is shown in the left panel of Fig. 2. The Dirac point is seen to be located very close to the Fermi level indicating essentially un-doped graphene. Since the graphene grain size on this sample was shown earlier to be only on the order of some micrometers, a few \( \pi \)-cones from domains of different azimuthal orientations could often be detected when moving the light spot over the sample but at some positions one \( \pi \)-cone dominated completely. The sample was always relocated to the same position, after Li deposition and subsequent heating, where only one \( \pi \)-cone appeared in the spectrum from the

Fig. 6 The \( \pi \)-band structure recorded close to the \( \mathbf{K} \) point and along the A-\( \mathbf{K} \)-A’ direction from the as prepared sample (left panel), after Li deposition (middle panel) and after heating at 280°C. A photon energy of 33 eV was used.
clean surface. Depositing Li on the sample shifts the \( \pi \)-cone downwards in energy, locating the Dirac point at ca. 1.2 eV below the Fermi level, as shown in the middle panel in Fig. 2. When assuming a linear dispersion of the \( \pi \)-band this energy separation of 1.2 eV gives an estimated\(^{26} \) electron doping concentration of about \( 1.0 \times 10^{14} \text{ cm}^{-2} \), which is precisely the doping concentration for which the shape of the C 1s core level spectra was calculated in Ref. 23. The electron doping concentration decreases quite drastically upon heating at 280°C. That is, after most of the Li has penetrated through the graphene and intercalated at the graphene/SiC interface, see the right panel in Fig. 6. Now the Dirac point is located at 0.4 eV, which indicates that the concentration has been reduced to a value of about \( 10^{13} \text{ cm}^{-2} \). The \( \pi \)-band also appears somewhat broader, in particular just below the Dirac point, which suggests that either the distribution of Li is no longer so homogeneous or that Li is intercalated in between graphene layers on areas, grains, that have a graphene coverage larger than 1 ML.

Since the Dirac point is shifted downwards from the Fermi level after Li deposition and heating at 280°C the \( \pi \)-band structure above and below the Dirac point can be investigated in somewhat greater detail and compared to that of that of the initial surface. Sets of ARPES spectra were therefore recorded close to the \( \overline{K} \) point and along the \( A - \overline{K} - A' \) direction (\( k_y \)) and in 0.25° steps over a fairly large angular range along the \( \overline{\Gamma} - \overline{K} - \overline{M} \) direction (\( k_x \)). From these sets cuts could be made to extract either the \( \pi \)-band structure along certain directions in the Brillouin zone or the
Fig. 7 The π-band structure recorded close to the $\bar{K}$ point for, a) and b), the as prepared sample and after Li deposition and heating at 280°C, f) and g). Photoelectron angular distribution patterns $E_i(k_x, k_y)$ around the $\bar{K}$-point extracted from recorded ARPES spectra collected from the graphene sample before, c), d), and e), and after Li deposition and heating at 280°C, h), i), and j). The wave vector $k_x$ is along $\Gamma - \bar{K} - M$ and $k_y$ along $A - \bar{K} - A'$. The photon energy was 33 eV.

angular distribution pattern, $E_i(k_x, k_y)$, at selected initial state energies. The π-band structure extracted along the $k_y$ and $k_x$ direction for the as prepared sample and after Li deposition and heating at 280°C are shown in Fig. 7a) and b) respectively f) and g).

The angular distribution pattern, $E_i(k_x, k_y)$, extracted at the Fermi energy, at 0.4 and 1.2 eV below the Fermi energy are shown in Figs. 7c), d) and e) for the as prepared graphene sample and in Figs. 7h), i), and j) after Li deposition and heating at 280°C. The intensity distribution and shape of these constant energy maps at and below the Dirac point agree well with patterns calculated\textsuperscript{27} for monolayer graphene. The
asymmetry in the intensity distribution and the appearance of the so called dark corridor\textsuperscript{28}. After Li deposition the patterns extracted at and below the Dirac appear fairly similar to those for the clean surface, see Figs. 7i), and j). The patterns now extracted above the Dirac point showed a flipped, “mirrored”, symmetry, see Fig. 7h), as predicted\textsuperscript{27} at energies located above the Dirac point for monolayer graphene. Apart from the shift in the Dirac point the only difference observed between the as prepared and Li exposed and heated sample is that the $\pi$-band and the $E_i(k_x,k_y)$ patterns are somewhat broader and more diffuse in the latter case. These observed effects in the band structure induced by Li deposition and heating are very similar to earlier findings\textsuperscript{11} after Na deposition and heating. Now we know, however, that the reason for these experimental results is that for C-face graphene the grain size is so small that when doing conventional or micro-ARPES an apparent monolayer $\pi$-band structure results\textsuperscript{19}. Nano-ARPES was actually required\textsuperscript{19} to observe the $\pi$-band structure of the individual grains, which revealed AB stacking within the grains also for C-face graphene.

IV. SUMMARY AND CONCLUSIONS

Studies of the effects induced in the electronic structure after Li deposition, and subsequent heating, on graphene samples prepared on C-face SiC are reported. The as prepared graphene samples were essentially un-doped but after Li deposition the Dirac point had shifted down to 1.2 eV below the Fermi level due to electron doping. After deposition the shape of the C 1s level also indicated a doping concentration of around $10^{14}$ cm$^{-2}$, when compared with recent calculated results of core level spectra of graphene. The C 1s, Si 2p and Li 1s core level results showed some intercalation after deposition but that most of the Li had intercalated after
heating at 280°C. Heating at higher temperatures led to desorption of Li from the sample and at 1030°C Li could no longer be detected on the sample. The single $\pi$-band observable from multilayer C-face graphene samples in conventional ARPES was reasonably sharp both from the initially prepared sample and after Li deposition. After heating at 280°C the $\pi$-band appeared more diffuse and possibly split. The Dirac point becomes located at 0.4 eV below the Fermi level, which indicated occurrence of a significant reduction in the electron doping concentration. Constant energy photoelectron distribution patterns extracted from the as prepared graphene C-face sample and also after Li deposition and heating at 280°C appeared very similar to earlier calculated distribution patterns for monolayer graphene.

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6 S. Watcharinyanon, L. I. Johansson, A.A. Zakharov, and C. Virojanadara, Surf. Sci. 606,


20 See Fig. 1 in Ref. 18, showing Low Energy Electron Microscopy (LEEM) images and
electron reflectivity curves extracted from different locations of one of the samples used in the present investigation, that reveal fairly large domains of graphene of one to five layers.


