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Original Publication:

Chao Xia, Leif I Johansson, A A Zakharov, Lars Hultman and C Virojanadara, Effects of Al on epitaxial graphene grown on 6H-SiC(0001), 2014, Materials Research Express, (1), 1.

<http://dx.doi.org/10.1088/2053-1591/1/1/015606>

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Effects of Al on epitaxial graphene grown on 6H-SiC (0001)

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Received 6 November 2013, revised 9 January 2014

Accepted for publication 28 January 2014

Published 03 March 2014

Materials Research Express 1 (2014) 015606

doi:[10.1088/2053-1591/1/1/015606](https://doi.org/10.1088/2053-1591/1/1/015606)

Abstract

Aluminum was deposited on epitaxial monolayer-grown graphene on SiC (0001). The effects of annealing up to 1200 °C on the surface and interface morphology, chemical composition, and electron band structure were analyzed *in situ* by synchrotron-based techniques at the MAX Laboratory. After heating at around 400 °C, Al islands or droplets are observed on the surface and the collected Si 2p, Al 2p, and C 1s core levels spectra indicate Al intercalation at the graphene SiC interface. Also, the original single π -band splits into two, indicating decoupling of the carbon buffer layer and the formation of a quasi-free-standing bilayer-like electronic structure. Further heating at higher temperatures from 700 to 900 °C yields additional chemical reactions. Broader core level spectra are then observed and clear changes in the π -bands near the Dirac point are detected. More electron doping was detected at this stage since one of the π -bands has shifted to about 1.1 eV below the Fermi level. Different ordered phases of (7×7) , (4×4) , $(1 \times 1)_{\text{Al}}$, and $(1 \times 1)_{\text{G}}$ were also observed on the surface in this temperature range. The original single π -band was restored after heating at ~1200 °C, although an Al signal was still able to be detected.

Keywords: epitaxial graphene, SiC, aluminum, ARPES XPS, LEEM XPEEM

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1. Introduction

Graphene, one single layer of graphite, is one of the most promising candidate materials for future electronic devices [1, 2]. It has fascinating electronic, mechanical and thermal properties that are suitable for fast and durable electronic devices. In particular, epitaxial graphene grown on Si-terminated silicon carbide (SiC) substrates by thermal graphitization is considered to be one of the most convenient methods to obtain a single layer graphene that is suitable for device operation at high temperature, high voltage environments.

The choice of metal to be used as a contact material for graphene-based electronic devices is still an open question. Aluminum (Al) is one of the most commonly used metals in SiC-based electronics. It has been reported that Al-6H-SiC provides good rectification characteristics with low reverse leakage current [3]. Al is also easy to use, abundant in nature and inexpensive. It has, however, not yet been revealed if Al provides a good choice of contact material for graphene-based electronic devices. Al can form ternary compounds, such as Al_4SiC_4 and $\text{Al}_4\text{Si}_2\text{C}_5$, having desirable ceramic properties [4]. Theoretical studies predict that Al-doping makes graphene significantly more reactive, which can be utilized in sensor applications [5–8]. If these predictions are true, then they may have a significant impact on future graphene electronic technology. If, for example, Al changes the electric field at the graphene/SiC interface, it will affect the surface band bending, which is crucial for rectifying devices. Single layer, (i.e., single π -band) electronics or bi-layer graphene (i.e., two π -bands) electronics are typically carefully selected for specific devices. However, if this property can be changed just by varying the temperature by a few hundred degrees, then the device may be unreliable. Moreover, the formation of different compounds at the graphene/SiC interface, or on the graphene surface, may change the intrinsic doping level and affect device properties. There have been no previous reports of detailed studies of the chemical composition, surface morphology, electronic structure and atomic structure before or after Al deposition on epitaxial graphene, or after subsequent heating. We have, therefore, performed such studies, which are timely and relevant, to determine if Al may provide a good choice of contact material for graphene-based devices.

Our results show that no change in the electronic π -band structure and no chemical reaction occurred after Al deposition on graphene at room temperature. After heating the samples to temperatures $>350^\circ\text{C}$, clear and distinct changes were observed. The Al was found to fully intercalate at the interface after heating the sample at 400°C and the graphene electronic properties consequently changed from a single π -band to two π -bands. Further heating at temperatures from 700°C to 1200°C induced more changes in the chemical composition, and in the electronic band structure and graphene doping level concentration. These findings are presented and discussed below.

2. Experiment

The morphology, chemical composition, electronic structure and atomic structure were investigated using low energy electron microscopy (LEEM), x-ray photoelectron microscopy (XPEEM), photoelectron spectroscopy (PES), angle resolved photoelectron spectroscopy (ARPES), and selected area low energy electron diffraction (micro-LEED) at beamlines I311 and I4 at the MAX Laboratory in Lund, Sweden. Beamline I311 is equipped with a modified

SX-700 monochromator, which provides light for two end stations. The first station is built around a large hemispherical Scienta electron analyzer. The total energy resolution determined by the operating parameter used of <10 to 100 meV at photon energy from 45 to 450 eV and of <300 meV at photon energies from 600 to 750 eV, which were selected in the high resolution core level studies reported below. The second station is equipped with a spectroscopic photoemission LEEM (SPELEEM) instrument. This microscope has a spatial resolution better than 10 nm in the LEEM mode. Changes in the surface morphology with heating temperature could, in the SPELEEM station, be investigated live in front of the objective lens. Angle resolved photoelectron spectroscopy studies were performed at beamline I4, which is equipped with a spherical grating monochromator (SGM) and PHOIBOS 100 two-dimensional (2D) Specs energy analyzer. A low angular dispersion lens mode was selected, which provided an acceptance angle of $\pm 7^\circ$.

Graphene was grown on nominally on-axis 6H-SiC(0001) substrates, which were cut from a production grade n-type wafer from SiCrystal, having a misorientation error within 0.06° , and the Si face was chemically and mechanically polished. The substrates were cleaned using the RCA method and HF etching to remove surface oxides and contaminations. Monolayer graphene was grown by heating the substrate at a temperature of 1300°C for three minutes at a base pressure of approximately 10^{-7} mbar [9]. Al was then thermally deposited on the graphene sample while the sample was kept at room temperature. The amount of deposited Al was estimated to be $\sim 3 \text{ \AA}$ for the samples used in the PES and ARPES experiments from measured core level intensity ratios, while in the LEEM and XPEEM experiments it was around $\sim 9 \text{ \AA}$. The effects induced on the graphene sample were studied after deposition and subsequent heating at different temperatures.

Sample holders for direct current heating were used in the PES/ARPES end stations, while an electron beam heating sample holder was used for the SPELEEM experiment. The heat distribution to the sample appeared slower for the electron beam heating system. Therefore, we selected to heat for one minute at each temperature in the PES/ARPES stations and for two minutes in the SPELEEM station.

3. Results and discussion

The micro-LEED and LEEM data collected from one epitaxial monolayer graphene sample are provided in figure 1. The diffraction pattern in figure 1(a) shows intense (1×1) spots from graphene and also the $6\sqrt{3} \times 6\sqrt{3} \text{ R } 30^\circ$ reconstruction from the carbon buffer layer formed underneath on the SiC substrate. The LEEM image in figure 1(b), collected at a field of view (FOV) of $50 \mu\text{m}$, indicates the graphene to be homogeneous. The extracted reflectivity curves correspondingly showed that it was monolayer graphene. Deposition of about 9 \AA of Al on the sample changes the diffraction pattern quite dramatically, as can be seen in figure 1(c). Six dominating spots in a ring-like pattern then appear which correspond to a slightly different unit cell size compared to both graphene and the SiC substrate. This ring-like diffraction pattern is interpreted to correspond to Al(111) facets formed on the surface, which exhibits an azimuthal rotational disorder on the surface. LEEM also shows changes of the surface morphology directly after Al deposition, as illustrated by the image in figure 1(d), which was collected at a FOV of $25 \mu\text{m}$. The Al appears to be distributed quite uniformly on the surface and no signs of droplets are found. The sample was then gradually annealed at different temperatures from

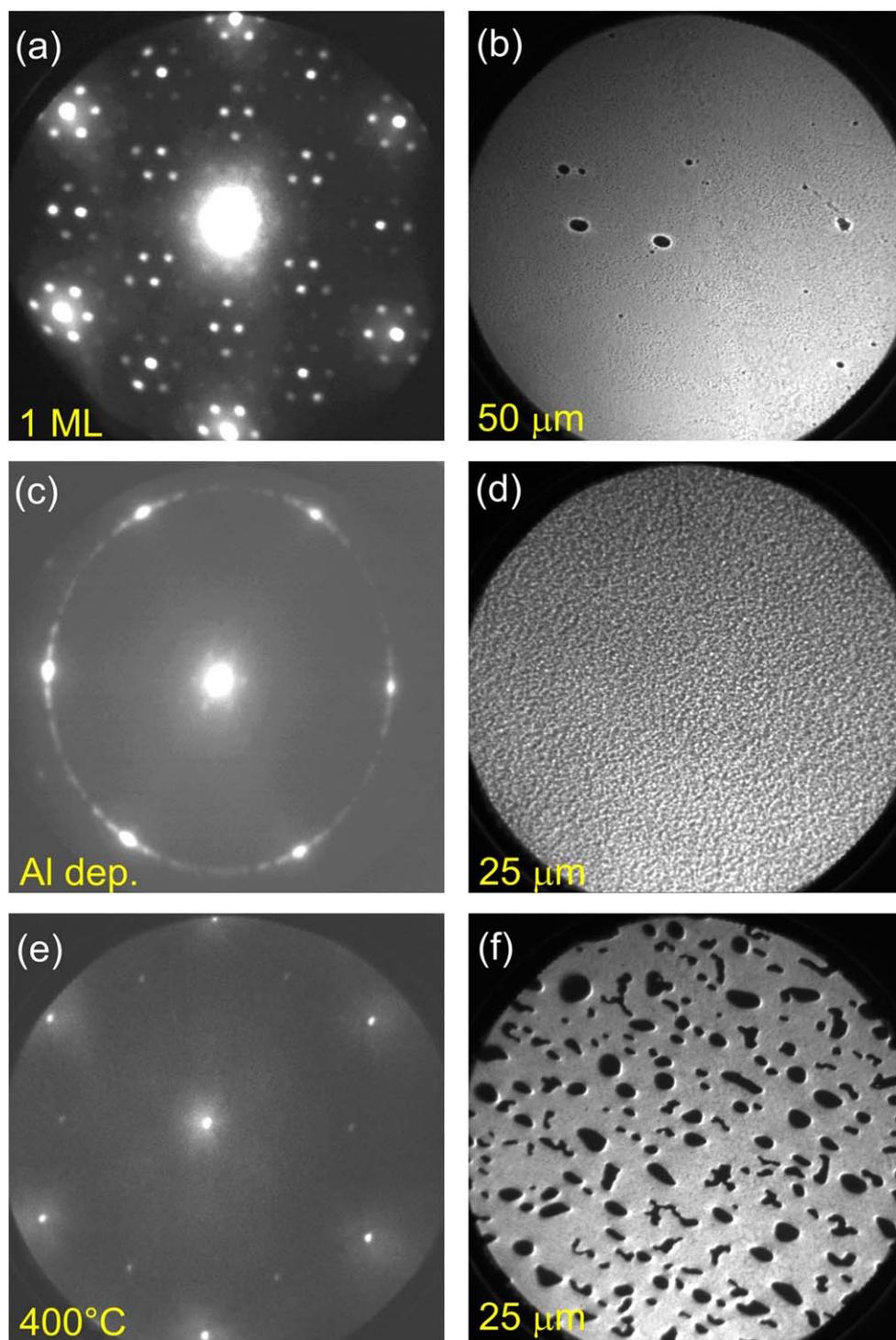


Figure 1. Selected area LEED patterns and corresponding LEEM images collected from (a)–(b) a 1 ML graphene sample grown on SiC(0001), (c)–(d) after Al deposition, and (e)–(f) after heating at 400 °C. The E_{kin} used in the μ -LEED patterns was 45, 54, and 95 eV, respectively in (a)–(e), and the probing area was 5, 1.5, and 1.5 μm , respectively. The energy selected in the LEEM images was -0.4 , -0.4 , and 4.8 eV in, respectively, (b)–(f).

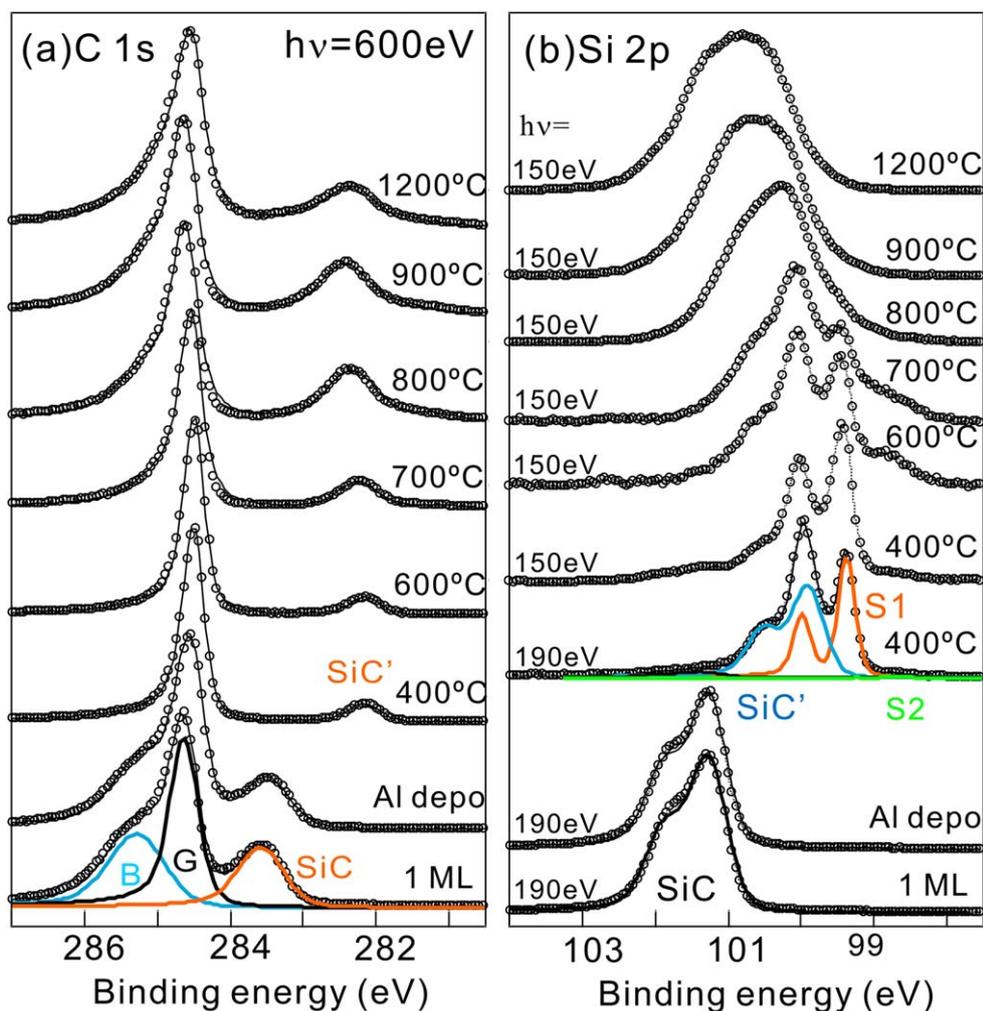


Figure 2. (a) C 1s spectra recorded using a photon energy of 600 eV from a 1 ML graphene sample, after Al deposition and after subsequent heating at different temperatures. (b) A similar set of Si 2p spectra recorded using photon energies of 190 eV and 150 eV. The lower photon energy is selected to demonstrate the appearance of a weak surface component (S2) after heating at ≥ 400 °C.

400 °C to 1200 °C. After heating at 400 °C, only the (1×1) spots from graphene (dominant) and SiC (weaker) are observed in the LEED pattern, as seen in figure 1(e). This illustrates that Al has induced changes in the interface region since the interface buffer layer $6\sqrt{3} \times 6\sqrt{3}$ spots are no longer observed. The LEEM image in figure 1(f) also shows drastic changes in the surface morphology after this heating. Islands of Al (the dark spots) seem to have formed on the surface at this temperature.

High-resolution core level photoemission investigations were performed, both before and after Al deposition and subsequent heating. A set of the C 1s core level spectra that were collected are displayed in figure 2(a). The spectrum from the as-prepared monolayer graphene sample (bottom spectrum) is composed of three components, originating from SiC substrate (SiC), graphene (G), and interface carbon buffer layer (B). After Al deposition no significant changes in relative peak intensities and binding energies are observed. However, directly after

heating at 400 °C, the substrate signal (SiC) is observed to have shifted by 1.3 eV to the lower binding energy (and is now labeled SiC' in the figure) and no signal from the interface buffer layer (B) is detected. The latter agrees and confirms the absence of the buffer layer ($6\sqrt{3} \times 6\sqrt{3}$) spots in the LEED pattern recorded after heating at this temperature, see figure 1(e). In addition, the G/SiC' peak intensity ratio after heating is seen to have increased by more than three times compared to the as-prepared graphene sample, and can also be seen after Al deposition. This suggests the transformation of the carbon buffer layer into a quasi-free-standing graphene layer. The shift of the substrate SiC component to the lower binding energy is attributed to the formation of a dipole layer at the interface that changes the coulomb charge environment in the interface region. A similar effect has been reported earlier in the case of Li, hydrogen, and Si intercalation [10–13]. When increasing the heating temperature, no significant changes are observable until around 700 °C. Then, the main peak (G) appears broader again when a weak shoulder becomes visible on the high binding energy side, representing a contribution from the carbon buffer layer. These changes are even more pronounced after heating at higher temperatures, up to 1200 °C, as shown in figure 2(a). Interestingly, although no shift in binding energy of the SiC' component is observed, a reduction in the G/SiC' peak intensity ratio can be observed after heating at these higher temperatures. This indicates that the Al does not leave the interface region completely when a carbon interface buffer layer re-establishes. Similar trends are also observed in recorded Si 2p core level spectra, as shown in figure 2(b). Heating at around 400 °C is also found to be required to induce significant changes in the Si 2p spectrum. Then, the bulk SiC component exhibits a similar shift of 1.3 eV (which is labeled SiC'), as in the C 1s spectrum. Two new additional components (labeled S1 and S2) appear, which are a dominant S1 and a weak S2 component that is barely visible in the spectrum collected at 190 eV. However, when using a photon energy of 150 eV, the shift becomes visible in figure 2(b) and is further illustrated in figure 3(a), which also contains the fitted components. It should be noted that the S1 component also increases in relative intensity at this lower photon energy, indicating that it is surface-related. After heating at higher temperatures, the S1 component decreases in relative intensity while the S2 component does increase, as seen in figure 2(b) and further illustrated in figure 3(b), where the fitted components are included. The relative intensity ratios between these components were extracted and are in the inset in figure 3(b), where they are plotted versus photon energy. The S1/SiC and S2/SiC intensity ratios both decrease with increasing photon energy, which confirms that S1 and S2 are surface/interface-related components. However, the S2/S1 intensity ratio also shows a strong decrease with increasing photon energy, indicating that the S2 component is located more on the surface while the S1 component is located more at the interface. From these results, we suggest that the S1 and S2 components correspond to Si in the outermost bi-layer of the SiC substrate, which has interacted with Al at the interface and, respectively, to the Si that has been pulled/pushed out from the interface region and onto the surface after heating. The S2 component in figure 3(b) is observed to be the strongest after heating to 700 °C, while the S1 component has then decreased in intensity quite dramatically compared to 400 °C. Upon heating at higher temperatures, the S2 component becomes barely detectable while the S1 component remains, but with lower intensity. The Si 2p spectrum becomes quite broad after heating at 800 °C and higher temperatures. This is suggested to reflect that a mixture of different reactions have occurred at the interface/surface region, including a mixture of regions of non-uniform Al concentrations in the layers within the detected area.

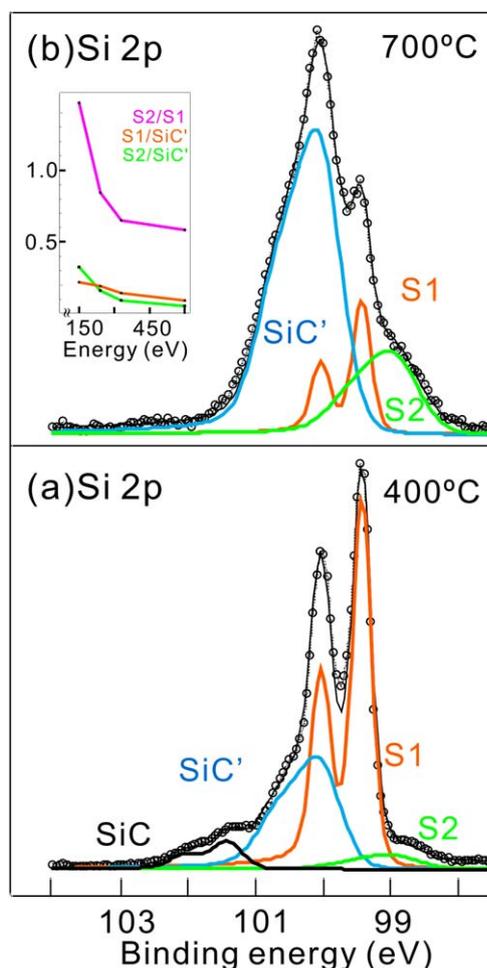


Figure 3. Si 2p spectra recorded using a photon energy of 150 eV after heating at (a) 400 °C and (b) 700 °C. The fitted components are also displayed. The inset in (b) shows how the extracted intensity ratios S2/S1 (red), S1/SiC' (yellow orange) and S2/SiC' (green) vary with selected photon energy, after heating to 700 °C.

Changes in the surface morphology with heating temperature were studied live under the LEEM microscope. The sample appeared quite stable up to a temperature of around 350 °C. A LEEM image collected at a field of view (FOV) of 15 μm after heating the sample at 750 °C is shown in figure 4(a). Areas with different contrasts are clearly observed in the LEEM image and are labeled from (1) to (5). The selected area LEED pattern collected from each of these areas are also displayed in the figure and given the corresponding label (1)–(5). The bright grey areas in figure 4(a) represents areas that are still intercalated, at least partially, with Al since the diffraction pattern from areas (1) and (2) show mainly the (1 \times 1) graphene spots. Weak $6\sqrt{3} \times 6\sqrt{3}$ buffer layer spots are detectable from area (1) around the (1 \times 1) SiC substrate spots, but not from area (2). This illustrates that part of the Al has left the interface at this temperature. Interestingly, (7 \times 7) and (4 \times 4) diffraction patterns are observed from areas (3) and (4), indicating the existence of pure ordered Si or a Si-compound on the surface after heating at this temperature [14]. This observation agrees well with the suggestion for the S2 component observed in recorded Si 2p spectra; that is, it originated from Si on the sample

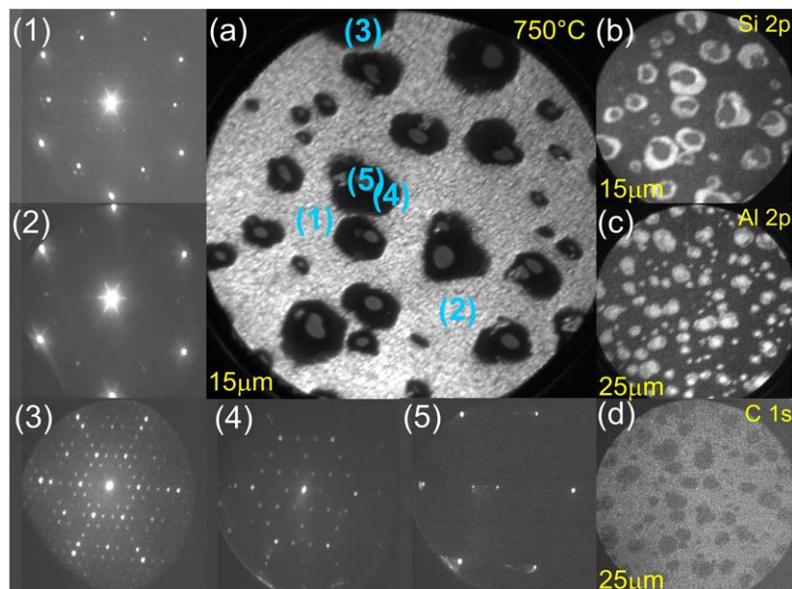


Figure 4. (a) LEEM image recorded after heating at 750 °C, using an energy of 11 eV. (1)–(5) Selected area LEED patterns collected using a probing area of 500 nm from the areas labeled (1)–(5). E_{kin} of 44, 45, 35, 41, and 35 eV were selected, respectively. XPEEM images collected using (b) the Si 2p at a photon energy of 133 eV and electron energy of 29.3 eV, (c) the Al 2p at the same photon energy but electron energy of 55.6 eV, and (d) the C 1s at a photon energy of 330 eV and electron energy of 41.0 eV.

surface. It should be noted that Al droplets appear to remain on the surface at this temperature since selected area LEED from area (5) shows a pattern interpreted to correspond to a (1×1) pattern from Al(111). The presence of islands of ordered Si, Al or Si-Al compound is also verified by the Si 2p, Al 2p, and C 1s XPEEM images shown in figures 4(b)–(d), respectively. In figure 4(b), the brightest areas represent Si-rich regions, such as (3) and (4) which produced (7×7) and (4×4) diffraction patterns. Similarly, the brightest areas in figure 4(c) represent Al-rich regions, such as (5) which showed a (1×1) diffraction pattern from Al(111). The XPEEM image generated using the graphene C 1s signal, in figure 4(d), is quite bright but has darker islands and is interpreted to correspond to graphene partly covered by islands of Si, Al or Si-Al compounds that attenuate the C 1s signal.

After further heating in the SPELEEM at a temperature of 1000 °C, the XPEEM image from secondary electrons displayed in figure 5 was obtained. It shows larger islands of Al or Al-compounds since areas with lower work functions appear brighter than areas with larger work functions. The selected area LEED patterns collected from the areas marked (1) to (3) are shown as insets in figure 5. The bright areas (1) and (2) mainly show a (1×1) pattern from Al while the dark area (3) shows a (1×1) pattern from graphene. These findings agree well with the Al 2p core level spectra in figure 6, which were collected at the PES end-station. A sharp Al 2p doublet (A1), located at a binding energy of 72.7 eV, is observed after deposition⁴. After

⁴ A Spin-orbit splitting of 0.42 eV, a branching ratio of 0.50, a Lorentzian width of 0.07 and an asymmetry parameter value of 0.07 were selected as the fitting parameters for the Al 2p core levels. The Gaussian width was allowed to vary independently for different components. The Gaussian widths of 0.08, 0.1, 0.86 and 0.8 eV were applied to achieve best fitting for A1, A2, A3 and A4 components at a photon energy of 140 eV, respectively.

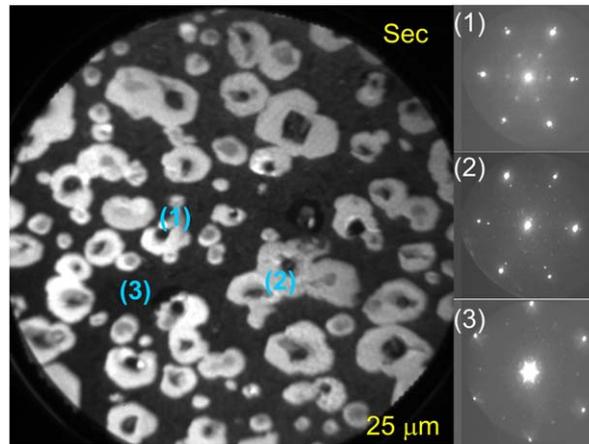


Figure 5. XPEEM image collected from secondary electrons after annealing at 1000 °C using a photon energy of 133 eV and electron energy of -0.28 eV. Selected area LEED patterns collected from the areas labeled (1)–(3) in the XPEEM image. E_{kin} of 40 eV and probing area of 500 nm were utilized.

heating at 400 °C an additional doublet (A2), located at about 0.1 eV lower binding energy, appears. The relative intensity of A2 was larger at higher photon energy and increased with heating temperature up to around 700 °C. We, therefore, suggest this A2 doublet to be a chemically shifted component originating from intercalated Al at the interface region between the SiC substrate and graphene. After heating at temperatures from 700 °C to 1200 °C, two additional very broad peaks labeled A3 and A4 appeared on the high binding energy side of the initial A1 peak. Spectra collected using photon energies from 140 eV to 600 eV showed these two components to be most intense at 140 eV; that is, in the most surface sensitive spectrum. This indicates that these A3 and A4 components originate from compounds formed on the surface. They are probably mainly Al-Si containing compounds since the Si 2p spectrum exhibited one broad peak after heating at temperatures from 800 to 1200 °C, see figure 2(b). No direct interaction between Al and graphene could be detected since no additional component possibly related to Al-C interactions appeared in the C 1s spectrum after heating in the temperature range investigated.

Changes induced by the deposited Al in the electronic band structure of the graphene sample were studied using ARPES. The spectra displayed in figure 7 were recorded around the K point of the graphene Brillouin zone, both before and after Al deposition and after subsequent heating. One single π -band with the Dirac point at ~ 0.45 eV below the Fermi level is commonly observed from epitaxial monolayer graphene grown on a SiC (0001) substrate, as shown in figure 7(a). This has been attributed to electron transfer from the SiC substrate that produces an intrinsic n-doping concentration of about $1.3 \times 10^{13} \text{ cm}^{-2}$ to the as grown monolayer graphene [15]. No significant change can be observed after Al deposition, as illustrated in figure 7(b). However, after heating at 400 °C, a bi-layer like π -band [16] appears and is found to be stable up to a temperature of about 600 °C, as seen in figures 7(c), (d). Further heating at temperatures from 700 °C to 1000 °C transforms this conventionally shaped bi-layer graphene π -band completely, as seen in figures 7(e)–(h). Now essentially two π -bands are resolved with Dirac points located around 1.1 eV and 0.25 eV below the Fermi level, respectively. The LEEM/XPEEM results in figures 4 and 5 showed a quite non-uniform surface composition and

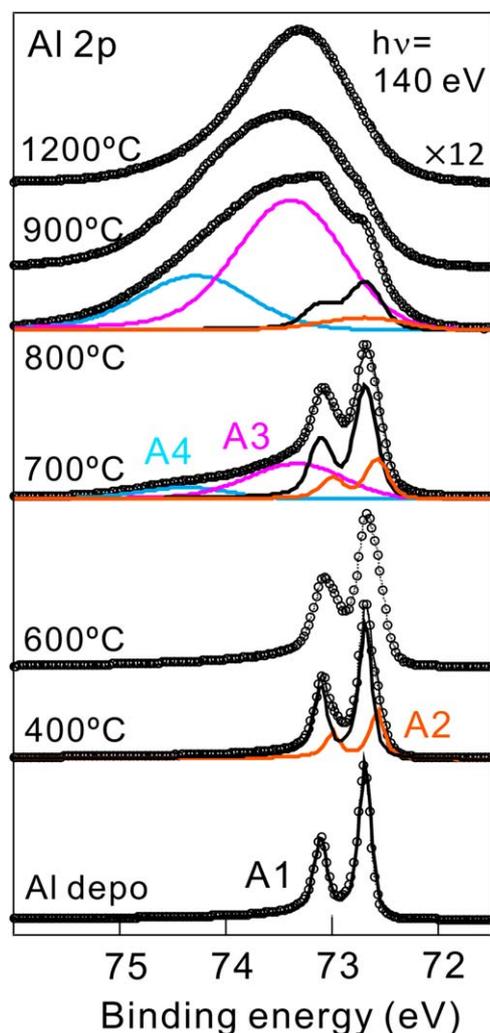


Figure 6. Al 2p spectra recorded at photon energy of 140 eV from a 1 ML graphene sample, after Al deposition and after subsequent heating at different temperatures.

morphology after heating at these temperatures. The formation of islands of different chemical composition and atomic structure was revealed on top of the graphene sample. The core level PES results in figures 2, 3, and 6 show intercalation of Al into the substrate graphene interface region after heating at 400 °C and indicate Al-Si compound formation on the sample surface after heating at temperatures from ca. 700 °C to 1200 °C. We can only speculate that some of the islands formed may produce local strongly n-doped areas that move the Dirac point down to 1.1 eV below the Fermi level, corresponding to a doping concentration of about $7.6 \times 10^{13} \text{ cm}^{-2}$. The areas outside the islands should, in principle, remain to have a bi-layer like electronic π -band structure because the intercalated Al at the interface should at least provide a partial decoupling of the buffer layer. This is not obvious, however, and one needs to keep in mind that the conventional ARPES system used has a probing area size of around $10^5 \mu\text{m}^2$. The ARPES spectrum is thus integrated over graphene areas that are fully and partly Al intercalated, and is also integrated over a large number of islands formed on the surface. Although the ARPES spectrum represents a superposition of the π -bands from these different areas, we cannot sort

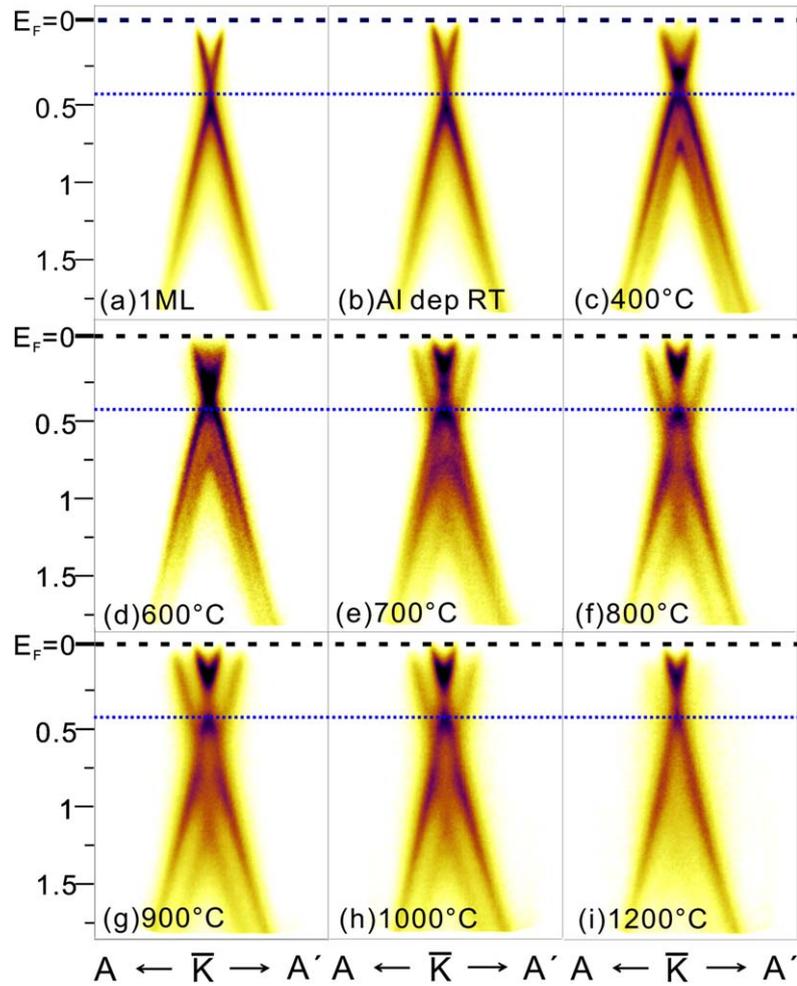


Figure 7. The π -band structure recorded around the K-point, using a photon energy of 33 eV, from (a) the initial 1 ML graphene sample, (b) after Al deposition, and (c)-(i) after subsequent heating at temperatures from 400 °C to 1200 °C.

out the different contributions. Island formation is, in figure 1, seen to occur already after heating at 400 °C and the islands are observed in figure 4(a) and figure 5 to increase in size with increasing heating temperature. After heating at 1200 °C in the ARPES system, one single π -band is again observed but is slightly less n-doped since the Dirac point is now located slightly closer, 100 ± 20 meV, to the Fermi level than for the as prepared sample. This is interesting because the SiC' component is still detectable in both the C 1s and Si 2p spectrum at this temperature, see figure 2, and Al is still present in the sample, see figure 6. This suggests some compound formation at the interface region at this high temperature, which alters the charge transfer between the SiC substrate and the graphene layer, compared to the as prepared graphene sample. Therefore, when selecting Al as a contact material, one has to be aware that the electronic properties can vary from single π -band to bi-layer-like π -bands, or even doped π -bands, within a temperature range of a few hundred degrees.

4. Conclusions

Detailed studies of the interaction of deposited Al on monolayer epitaxial graphene grown on SiC(0001) are reported. The morphology, chemical composition, electronic structure and atomic structure were investigated using LEEM, XPEEM, PES, ARPES, and μ -LEED. Depositions on samples kept at room temperature produced a fairly uniform Al overlayer with no change in the graphene electronic properties and no chemical reaction. Full intercalation of Al into the SiC-graphene interface region occurred after heating at a temperature of ~ 400 °C, as revealed by the appearance of a (1×1) graphene LEED pattern and chemically shifted core level components. The Al remaining on the surface was found to form islands. A bi-layer graphene like π -band electronic structure was observed after intercalation and was found to be stable up to around 600 °C. After further heating at temperatures from 700 to 1000 °C, islands of ordered phases of Al, Si, and Al-Si were observable on the surface producing $(1 \times 1)_{\text{Al}}$, (7×7) , and (4×4) LEED patterns. Outside these islands, the selected area LEED then showed either a (1×1) graphene pattern or a (1×1) pattern with weak $6\sqrt{3} \times 6\sqrt{3}$ superstructure spots. ARPES now did not show a bi-layer graphene-like π -band structure. Instead, essentially two π -bands with Dirac points located around 1.1 eV and 0.25 eV below the Fermi level were resolved. Although heating at 1200 °C restored the single π -band structure, some Al was found to remain in/on the sample, even after this high-temperature annealing.

Acknowledgments

The authors gratefully acknowledge support from the Swedish Research Council #621-2011-4252 and the Linnaeus Grant.

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