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High thermal stability quasi-free-standing bilayer graphene formed on 4H–SiC(0001) via platinum intercalation

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ABSTRACT
Influences on electronic structure induced by platinum (Pt) deposited on monolayer graphene grown on SiC(0001) are investigated by photoelectron spectroscopy (PES), selected area low energy electron diffraction (μ-LEED) and angle resolved photoelectron spectroscopy (ARPES) techniques at the MAX Laboratory. Stable monolayer graphene electronic properties are observed after Pt deposition and after annealing at temperatures below 600 °C. At >600 °C platinum silicide forms at the graphene/SiC interface. Annealing at 900 °C results in an efficient decoupling of the carbon buffer layer from the SiC substrate and transformation into a second graphene layer. At this stage a quasi-free standing bi-layer graphene sample is obtained. The new superstructure spots then appearing in μ-LEED pattern suggest formation of an ordered platinum silicide at the interface. This silicide is found to be stable even after annealing at temperature up to 1200 °C.

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1. Introduction
As one of the most promising candidate materials for a new generation of electronic devices, graphene has demonstrated its outstanding electronic and mechanical properties [1,2]. Among the methods to grow graphene, epitaxial growth on silicon carbide (SiC) substrates by thermal graphitization provides a potential solution for wafer-scale production of graphene based electronic devices operating at high frequencies, temperatures and voltages. Continuous and homogeneous graphene layers over large surface areas have been achieved using this method [3,4].

The low charge carrier mobility of graphene grown on Si-face SiC is, however, a major obstacle for graphene based electronic devices, since the mobility is substantially deteriorated due to the first carbon layer formed on Si-face SiC. This so called carbon buffer layer [5] does not exhibit a graphene π-band. One effective way to eliminate this buffer layer is to intercalate atoms at the interface, which converts this carbon layer into a quasi-free-standing graphene layer. Elements such as H, F, O [6–10] have been reported to eliminate, i.e. fully intercalate, the buffer layer. Moreover, the mobility was found to increase dramatically after intercalation [11]. However, so far none of quasi-free-standing graphene achieved by intercalation is thermally stable above ca. 800 °C which will limit operation temperature of the graphene based SiC device. Those intercalated atoms mentioned above will leave the interface after annealing above ca. 800 °C.

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A suitable intercalation element with high melting point could provide the possibility to endure high temperature. Therefore, platinum (Pt) can be a good candidate for this purpose. Theoretical studies predict that Pt functionalized graphene can increase the adsorbability of hydrogen, CO and H2S gases [12,13] which can be exploited for hydrogen storage [14] and gas sensor applications. Hydrogen and ammonia sensors with enhanced performance compared to bare graphene have been experimentally realized [15,16]. No study of the electronic structure or the chemical and thermal stability of Pt decorated graphene has previously been reported, however. We therefore carried out detailed studies of the effects on the electronic structure and chemical composition induced by Pt deposited on epitaxial graphene on Si-face SiC, and after subsequent annealing at different temperatures. We find that the deposited Pt wets the graphene surface very well and provides a homogeneous layer on the surface. No intercalation of the Pt or chemical reaction is observed to occur until after annealing the sample at 600 °C. The electronic band structure is observed to change at around 700 °C from the initial single layer to bi-layer like graphene electronic properties, with significantly reduced electron doping of the graphene layers. These electronic properties are stable up to 1200 °C, i.e. the highest temperature investigated. In this high temperature range a new ordered phase due to silicide formation is more prominent.

These electronic properties are stable up to 1200 °C, i.e. the highest temperature investigated. In this high temperature range a new ordered phase due to silicide formation is moreover observed.

2. Experimental

2.1. Sample preparation

N-type nominally on-axis 4H–SiC(0001) substrates with a misorientation error within 0.05°, purchased from SiCrystal, were utilized. The substrates were chemically and mechanically polished on the Si face and cleaned using the RCA method and HF etching in order to remove surface contaminations and oxides. Monolayer graphene was prepared by heating a 4H–SiC(0001) substrate at a temperature of 1300 °C for a few minutes under a pressure of about 5 × 10−7 Torr. Pt was then deposited, using an electron beam evaporator, on the sample kept at room temperature. The amount of Pt deposited was found to vary from ~1 to ~3 Å, due to the different geometries of the different end-stations used. Changes induced in the electronic and atomic structure and in surface morphology and chemical composition were investigated after Pt deposition and subsequent annealing, for 2 min, at different selected temperatures.

2.2. Characterization

The experiments were performed at beamlines I311 and I4 at the MAX-lab. Beamline I311 is equipped with a modified SX-700 monochromator, which provides light for two end-stations. The first station is equipped with a large hemispherical Scienta electron analyzer where high resolution photoelectron spectroscopy (PES) studies of the C 1s, Si 2p and Pt 4f core levels were performed. There a total energy resolution, determined by the operating parameters, of <10–100 meV at a photon energy from 33 to 450 eV and of <300 meV at a photon energy from 600 to 750 eV was utilized. The second end-station is equipped with a spectroscopic photoemission and low-energy electron microscope (SPELEEM) instrument. This microscope has a spatial resolution better than 10 nm in the LEEM mode. In this instrument also selected area low energy electron diffraction (micro-LEED) and selected area PES (micro-PES) data were collected. Angle resolved photoemission (ARPES) was performed at beamline I4 which is equipped with a SGM monochromator and a PHOIBOS 100 2D CCD Specs energy analyzer. The low angular dispersion (LAD) lens mode with an acceptant angle of ±7° was utilized. The base pressure was about 1 × 10−10 mbar in all three end-stations used.

3. Results and discussion

High-resolution core level photoemission spectra were acquired before and after Pt deposition and also after subsequent annealing at different temperatures. A series of C 1s spectra collected at a photon energy of 600 eV are presented in Fig. 1(a). The bottom spectrum is from the as-prepared monolayer graphene sample and show the three commonly observed components, labeled B, G and SiC that correspond to carbon buffer layer, graphene, and SiC substrate, respectively. The G/SiC and G/B intensity ratios indicate a graphene layer thickness of ~1 ML [3]. No significant changes in the C 1s spectrum are observed after Pt deposition, or after subsequent annealing at temperatures below 600 °C (therefore not shown). Annealing at 600 °C results in an additional C 1s component shifted ~0.9 eV to lower binding energy than the initial bulk SiC substrate component (labeled SiC′ and position indicated by a red arrow). This component is seen to increase in intensity after annealing at higher temperatures while on the other hand the initial substrate SiC and the carbon buffer layer components are seen to decrease. A similar effect in the C 1s spectra has been reported earlier upon intercalation of Li [17] and Si [18], although with slightly different shifts of the SiC′ component. The shift of the substrate component was
then interpreted as induced by a change in the dipole layer formed at the graphene–SiC interface. Thus, in this case it suggests that Pt has reached the interface region and interacted with the SiC substrate and created a different coulomb charge environment. This started at 600 °C and after heating at 900 °C, no signals from the initial SiC and buffer layer components can be detected. The G/SiC’ intensity ratio is at 900 °C more than two times larger than the G/SiC ratio from the initial clean graphene sample. This indicates that full intercalation is obtained, i.e. that the carbon buffer layer has been fully decoupled from the SiC substrate and transformed into an additional graphene layer. No significant changes are observed in the temperature range 900–1200 °C.

Similar trends are observed in the Si 2p core level spectra after Pt deposition and subsequent annealing, as illustrated in Fig. 1(b). For the initial 1 ML graphene sample, the Si 2p spectrum is dominant by a bulk SiC substrate component, labeled SiC, but can also contain a very weak additional component shifted ca. 0.8 eV to lower binding energy, as the one labeled S0 in Fig. 1(b). This component may correspond to Si clusters or defects formed at the interface and is not always detectable on the epitaxial graphene samples prepared. After Pt deposition, no significant changes are observed in the Si 2p spectrum until after annealing at 600 °C, when a weak shoulder on the low binding energy side is visible. After annealing at 700 °C the shifted components are more pronounced and at 800 °C and higher temperatures the signal from the substrate is dominated by a SiC’, component shifted ~0.9 eV to lower binding energy. This is similar as in the C 1s spectra and confirms the proposed change in the dipole layer at the interface. The result of a fit to the 900 °C spectrum show three components labeled SiC’, S1 and S2. The S1 and S2 components, located at respectively 0.7 and 1.1 eV lower binding energy than the SiC’ peak, are suggested to originate from silicide formation at the interface, i.e. silicide formation in the uppermost Si-C bilayer of the SiC substrate. That both components originate from the interface is supported by the variation obtained in the relative intensity ratios extracted between the S1, S2 and SiC’ components, from spectra collected at photon energies from 150 to 600 eV. Since the S2/S1 intensity ratio is found to increase somewhat with decreasing photon energy, the S2 component appears to originate from atoms located closer to the surface than for the S1 component. Both components are found to be stable up to the highest annealing temperature of 1200 °C investigated.

Pt 4f core level spectra recorded after deposition and subsequent annealing are displayed in Fig. 2(a). The Pt deposited on the graphene sample exhibits a 4f doublet, labeled P1, where the 4f(7/2) component is determined to be located at a binding energy of 71.2 eV, using a curve fit procedure [19]. An additional 4f doublet, labeled P2 and shifted 1.1 eV to higher binding energy, appears after annealing at 600 °C and becomes at 800 °C the dominant spectral feature. The intensity ratio P2/P1 does increase quite significantly with increasing photon energy, as illustrated in Fig. 2(b) by spectra recorded after annealing at 700 °C. This indicates that the P2 component originates from Pt atoms located not only underneath the metallic Pt layer on the surface, P1, but also underneath the graphene layers so they are located at the interface. The P2 doublet is therefore suggested to originate from platinum compound formation at the interface. That only chemically shifted core level components from atoms at the interface appeared in the Si 2p spectrum, but not the C 1s spectrum, in this temperature range, 600–1200 °C, indicate platinum silicide formation. The intensity of the P1 doublet, from Pt atoms on the surface, is dramatically reduced after annealing at 800 °C and becomes essentially undetectable at 900 °C.

Data collected at the SPELEEM end-station by X-ray photoelectron emission microscopy (XPEEM) and reflectivity (I–V) curves extracted from low-energy electron microscopy (LEEM) pictures look similar all over the sample both for the initial sample as well as after Pt deposition and subsequent annealing, indicating a fairly homogenous sample. Therefore such data are not shown, while distinct changes appear in the micro-LEED patterns, as displayed in Fig. 3. The typical diffraction pattern of monolayer graphene grown on Si-face SiC is shown in Fig. 3(a). This diffraction pattern contain contributions from the ordered graphene layer (the six brightest outer spots), the SiC substrate (the six somewhat weaker spots rotated 30° relative to the graphene spots) and also from the (6√3 × 6√3) R30° reconstructed ordered carbon buffer layer (the rest of the spots, where six spots around the graphene and SiC spots are most clearly visible). After Pt deposition, Fig. 3(b), only a pronounced decrease in overall intensity of the diffraction pattern is observed. The substrate and also the buffer layer spots (see inset (1)) are still detectable. After annealing at 700 °C, Fig. 3(c), six additional superstructure spots appear around the (0, 0) spot and inside the six buffer layer spots, see inset (2) and yellow circle. The six outer spots enclosed by the blue circle correspond to those in inset (1) that was collected at a lower electron kinetic energy. After annealing to 900 °C, only the graphene diffraction pattern and the new additional superstructure spots are visible, see Fig. 3(d) and inset (3). These new superstructure spots, which are rotated 30° relative to the buffer layer spots, indicate formation of a new ordered structure. From the core level results presented above Pt was found to be fully intercalated after...
annealing at 900 °C and to have formed a platinum silicide at the interface. Therefore we suggest that this new ordered structure is related to a platinum silicide phase formed at the interface. This also results in a decoupling of the buffer layer from the SiC substrate, transforming it into a second graphene layer, which is consistent with the observed twofold increase in the intensity of the graphene component in the C1s spectrum.

ARPES was utilized to investigate changes induced in the electronic band structure after Pt deposition and subsequent annealing. The electronic $p$-band structure was investigated close to the K point of the graphene Brillouin zone using a photon energy of 33 eV. The initial monolayer graphene sample shows a single $p$-band with a linear dispersion and a Dirac point located at $-0.4$ eV below the Fermi level, as illustrated in Fig. 4(a). Electron transfer from the buffer layer and SiC substrate produces an electron doping concentration of $\sim 1 \times 10^{13}$ cm$^{-2}$ to the as grown monolayer graphene [20]. After Pt deposition, Fig. 4(b), a more diffuse $p$-band and high background intensity, presumably from Pt 5d states, but no shift of the Dirac point are observed. Annealing at 700 °C induces no significant changes except a considerable reduction of the background intensity, see Fig. 4(c). After annealing at temperatures from 800 °C to 1200 °C a bi-layer like $p$-band structure is clearly detected. The $p$-bands become sharper with increasing annealing temperature. The charge transfer from the substrate decreases on the other hand with increasing temperature and results in that the Dirac point shifts towards Fermi level, see Fig. 4(d)-(f). After annealing at 1200 °C the Dirac point is located about 0.15 eV below the Fermi level which corresponds to an electron doping concentration of $\sim 1.4 \times 10^{12}$ cm$^{-2}$. This result disagrees however with earlier theoretical results [21] which predict the Dirac point to be located 0.685 eV below the Fermi level for a similar amount of platinum.

Our ARPES results confirm that the platinum silicide formed at the interface decoupled the buffer layer from the SiC substrate. The buffer layer was transformed into a second graphene layer, since a bi-layer like electronic $p$-band structure was obtained. It deserves to be noticed that the amount of Pt deposited varied, from 1 to 3 Å or about 0.3 to 1 ML,
among the three different end-stations used. However, an efficient decoupling of the carbon buffer occurred in all three cases when the Pt-silicide had fully formed at the interface after annealing at a temperature of \( \sim 900 \) °C.

Worth mentioning is also that an intense bi-layer like \( \pi \)-band structure has not been reported earlier after intercalation and annealing at such a high temperature as 1200 °C. In most cases the bi-layer like properties are transformed back to single layer electronic properties after annealing at temperature of 800 °C and higher [7,10,18,22–24] due to de-intercalation processes. For this reason platinum intercalated graphene on Si-face SiC can be a good choice to produce buffer layer free graphene devices for higher temperature applications.

4. Conclusion

Detailed high resolution PES, ARPES and micro-LEED studies of changes induced by Pt deposited on epitaxial monolayer graphene grown on SiC(0001) and after subsequent annealing at different temperatures are reported. Annealing at a temperature of \( \sim 600 \) °C is found to be required in order for Pt to start to intercalate and form a platinum silicide at the graphene/SiC interface. A full decoupling of the buffer layer is achieved after annealing at 900 °C when the amount of Pt deposited varied from 0.3 to 1 ML. Superstructure spots appearing in micro-LEED patterns recorded after intercalation indicate formation of an ordered platinum silicide phase at the interface. The monolayer graphene electronic properties of the initial sample transformed into bi-layer like graphene electronic properties after intercalation. The quasi-free-standing bilayer graphene formed is shown to be of high quality and stable up to an annealing temperature of 1200 °C.

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References

[19] The parameters utilized for Pt 4f spectra were a spin orbit parameter of 0.15 and a Gaussian and a Lorentzian widths of 0.88 eV and 0.15 eV respectively. n.d.