Abstract

We explore a number of different electrochemical, wet chemical and gas phase approaches to study intercalation and oxidation at the buried graphene-Ge interface. While previous literature focussed on the passivation of the Ge surface by chemical vapour deposited graphene, we show that particularly via electrochemical intercalation in a 0.25 N solution of anhydrous sodium acetate in glacial acetic acid this passivation can be overcome to grow GeO$_2$ under graphene. Angle resolved photoemission spectroscopy, Raman spectroscopy, He ion microscopy and time-of-flight secondary ion mass spectrometry show that the mono-layer graphene remains undamaged and its intrinsic strain is released by the interface oxidation. Graphene acts as a protection layer for the as-grown Ge oxide, and we discuss how these insights can be utilised for new processing approaches.
Heterogeneous materials integration and interface control are key challenges for integrated device technology. 2D layered materials such as graphene offer a versatile platform to create a wide range of new heterostructures, as highlighted by the recent literature on so called van der Waals heterostructures.\textsuperscript{1–3} The importance of interface effects between 2D and 3D materials is only starting to emerge. Examples in the context of 2D material manufacturing include the growth by scalable chemical vapour deposition (CVD),\textsuperscript{4–8} transfer,\textsuperscript{9–12} contacts,\textsuperscript{13} encapsulation of 2D device channels\textsuperscript{14–17} or the wettability,\textsuperscript{18–20} remote epitaxy\textsuperscript{21} and surface and corrosion protection effects that 2D materials can provide for 3D materials.\textsuperscript{22,23} Intercalation at the graphene-metal interface has been widely studied as a means of tuning interaction strength, and the selective oxidation of the metal surface beneath graphene has been introduced as a route to facilitate graphene transfer.\textsuperscript{10,24–26} It has been recently shown that direct CVD of graphene is possible on Ge (100), (111) and (110) surfaces.\textsuperscript{27–32} This offers a route for metal-contamination free graphene CVD, alike to graphene growth on SiC substrates.\textsuperscript{33–37} As-grown mono-layer graphene has been reported to provide stabilisation and passivation of the Ge surfaces.\textsuperscript{38,39} In contrast to the native oxide of Si which forms an excellent interface with Si and provides good passivation, GeO\textsubscript{2}, the native oxide of Ge, is water soluble, i.e. offers poor protection, and forms a poor interface with Ge.\textsuperscript{40–43} Analogous to prior work on SiC based graphene growth, hydrogen intercalation at the graphene-Ge interface has been studied.\textsuperscript{36,44–46} The motivation being to preserve and tune the graphene-Ge interface for use in processes and devices where graphene directly supported on Ge is desired. However, for many applications the opposite is of interest, i.e. the complete decoupling or removal of graphene from Ge, particularly via the formation of a new layer at the buried graphene-Ge interface. This remains largely unexplored.

Here, we study oxidation at the buried graphene-Ge interface as a simple model reaction to explore the effect of mono-layer graphene coverage on the Ge. It is well known that an uncovered Ge surface can be oxidised by immersion in nitric acid (HNO\textsubscript{3})\textsuperscript{42,47–50} or hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}).\textsuperscript{51} However, the water present in aqueous solutions of nitric acid and hydrogen peroxide leads to the simultaneous dissolution of the GeO\textsubscript{2}.\textsuperscript{41,47} The Pourbaix diagram of Ge, which maps out possible stable (equilibrium) phases of an aqueous electrochemical system, highlights only a very narrow stable region where Ge oxides are stable (as GeO) which lies entirely outside of the electrochemical stability window of water.\textsuperscript{41} Thus, the oxidation of pristine Ge through immersion in aqueous liquids is accompanied by simultaneously dissolution of the Ge oxide.\textsuperscript{52} Non-aqueous Ge oxidation is possible by electrochemical oxidation with the formation of Ge oxide layers demonstrated using glacial acetic acid and anhydrous sodium acetate as electrolyte.\textsuperscript{53} We show here how the result of such reactions can change in the presence of a mono-layer of graphene. Through intercalation mediated reactive interface oxidation even wet chemical approaches can be used to grow thick Ge oxide layers at the buried interface protected by graphene. Graphene acts as an ultra-thin capping layer in analogy to previous reported use of thicker capping layers and oxidation at capped Ge oxide interfaces.\textsuperscript{54–56} We explore
a number of different electrochemical, wet chemical and gas phase approaches to oxidation and also nitridation. Using an electrochemical oxidation approach, the graphene mono-layer remains undamaged while a thick Ge oxide layer can be grown at the buried interface. The roughness of this oxide leaves the graphene layer partly free-standing and the CVD induced strain in the graphene layer is released. We show detailed characterisation of this via angle resolved photoemission spectroscopy (ARPES), Raman spectroscopy, He ion microscopy and time-of-flight secondary ion mass spectrometry (ToF-SIMS), and discuss how this knowledge can be utilised for new processing approaches.

**Results and Discussion**

Figure 1 schematically shows the process flow and the separate reaction pathways that we focus on. We use CVD to directly grow mono-layer graphene on Ge wafers (see SI for further details). As a model system we specifically focus on the Ge(110) orientation, motivated by prior literature reporting the lowest graphene defect density for this orientation.\(^{32,57}\) Our CVD conditions result in an average graphene domain size of the order of few \(\mu\text{m}\) (see SI, Figure S1), and transmission electron microscopy (TEM) analysis indicates that there are predominantly two graphene domain orientations present, rotated by 30° with respect to each other, consistent with previous literature.\(^{31,32,57–59}\) For Ge it is established that the difference in oxidation rates for different surface orientations is relatively small,\(^{60,61}\) hence we expect the oxidation results on other Ge surfaces to be similar. As we show below, our CVD-grown mono-layer graphene film inhibits Ge oxidation in ambient air, in line with previous reports.\(^{38,39}\) The question we focus on here is if this passivation can be overcome without damaging the graphene layer. For this we consider three separate pathways to interface oxidation (see Figure 1): gas phase, wet chemical, and electrochemical.

Gas phase approaches, where the graphene/Ge sample was exposed to oxygen or ammonia containing atmospheres at 400 – 750 °C were performed (more information in SI section 3), but the high temperatures required, and reactive gas species resulted in graphene damage or complete graphene removal without intercalation. Wet chemical processes using nitric acid condensation or hydrogen peroxide floating for 2 h are successful in growing interfacial oxides (see SI section 3), but obtaining homogenous coverage over large areas is challenging because of the instability of the Ge oxide in aqueous liquids. Thus, we focus here on the electrochemical approach in a non-aqueous solution, which overcomes the problem of Ge oxide instability while providing the electrochemical potential to drive intercalation and interface oxidation. Our results regarding gas phase and wet chemical reactive intercalation are shown in the supplementary information.
Figure 1: Process flow overview: Continuous, mono-layer graphene is grown by CVD on untreated Ge wafers and intercalation/interface oxidation is explored via gas phase, wet chemical and electrochemical processes.

Electrochemical intercalation is performed in a simple voltaic cell. The graphene-Ge sample was immersed in a non-aqueous solution of acetic acid and sodium acetate at 1 V for 6-24 h (see Methods). We employ nano-resolution angle resolved photoemission spectroscopy (nanoARPES) to probe the electronic structure of graphene and gain insights into the interaction of the graphene layer with Ge(110) and with the electrochemically grown interfacial oxide. NanoARPES further allows us to locally probe the photoemission spectrum of Ge, i.e. to probe the oxidation state of Ge under graphene. Intercalation can result in electronic decoupling of graphene from the substrate, as is the case for strongly interacting substrates (e.g. SiC, Ni, Ru, etc.)\textsuperscript{36,62,63} where graphene’s linear dispersion near the K-point can be recovered, or for more weakly interacting substrates where charge-transfer from the substrate may be reduced (e.g. Pt, Cu).\textsuperscript{64,65} On the other hand, charge transfer from intercalated oxygen species can cause a shift in the graphene Fermi level.\textsuperscript{22,65,66} The ARPES spectra of as-grown graphene on Ge(110) (Fig. 2a) exhibits a linear dispersion near the Dirac points with a Fermi level shift of -50 +/- 25 meV, corresponding to graphene with very weak p-type doping. Note, all grown and intercalated samples were stored in air for several weeks before measurement and \textit{in-situ} annealed in the ARPES chamber (see methods). At the same location the photoemission spectrum in the binding energy range of 28 to 34 eV shows two peaks corresponding to the Ge3d\textsubscript{5/2} (29.3 eV) and Ge3d\textsubscript{3/2} (29.8 eV)\textsuperscript{67} core levels (Fig. 2c). The spectrum shows no contributions of GeO or GeO\textsubscript{2} peaks, highlighting the passivating effect of the graphene mono-layer at ambient conditions in line with previous literature.\textsuperscript{38,39} After electrochemical intercalation for 6 h the graphene ARPES spectra is almost unchanged (Fig. 2b). We only observe a small shift in the graphene Femi level to -80 +/- 25 meV, corresponding to weak p-type doping. However, after electrochemical intercalation the photoemission spectrum shows a significant change and the emergence of additional peaks at 30.9 eV and 32.5 eV corresponding to GeO and GeO\textsubscript{2}, respectively (Fig. 2c).\textsuperscript{67} This confirms the successful
growth of an interfacial oxide layer whilst largely preserving the electronic structure of the graphene.

Figure 2: NanoARPES analysis of (a) graphene as-grown on Ge(110) and (b) after electrochemical intercalation for 6 h at 1 V. (c) Photoemission spectra corresponding to (a) and (b).

Figure 3 shows the Raman spectra before and after such electrochemical Ge oxidation. Following intercalation, the intensities of the graphene 2D and G peaks increase by ~45 and ~30 times, respectively (Fig. 3a). The 2D peak shifts by approximately 20 cm\(^{-1}\), from ~2700 cm\(^{-1}\) to ~2680 cm\(^{-1}\) after electrochemical intercalation. A Raman peak at 444 cm\(^{-1}\) is observed after intercalation (Fig. 3c), which we assign to trigonal GeO\(_2\).\(^{58}\) Raman mapping confirms that such intercalation does not result in a significant increase in the graphene D peak (see SI Figure S4).

The Raman signal intensity of as-grown monolayer graphene on Ge(110) is comparatively weak and long accumulation times are required to resolve the Raman signature (see SI Figure S5). Reactive intercalation and dielectric formation result in a marked increase in the graphene Raman intensity and we suggest that this is mainly due to two effects.
Firstly, interface interactions between the Ge substrate. Very strong coupling between graphene and the substrate can result in a hybridisation of the graphene electronic bands (e.g. Ru$^{69}$, Ni$^{70}$) and consequently a loss of the resonant condition for Raman scattering.$^{71}$ Our ARPES data shows no such perturbation of the graphene Dirac cone near the Fermi level (Fig. 2a). However, if the graphene and substrate layer are in close contact electronic screening has also been shown to reduce the graphene Raman signal intensity$^{72}$ and e.g. in the case of Pt a significant Raman enhancement was observed upon intercalation.$^{73}$ Secondly, it is well known that the interference on a Si/SiO$_2$ stack can enhance not only the optical contrast of graphene$^{74}$ but also the graphene Raman signal intensity.$^{75,76}$ Thus, also upon formation of an interfacial Ge oxide layer a graphene Raman signal enhancement (compared to the as-grown case of graphene on Ge) can be expected.$^{25,77}$

![Figure 3](image)

Figure 3: Raman analysis of graphene on Ge(110) before and after electrochemical intercalation. (a) Graphene Raman peaks and (c) Ge oxide Raman signature. (b) And (d) scatter plots of the graphene Raman G peak position ($\omega_G$) and 2D peak position ($\omega_{2D}$) and full width half maximum (FWHM) of the 2D peak, where (b) was acquired on as-grown graphene on Ge(110) and (d) after electrochemical intercalation for 24 h.

Figure 3(b,d) shows the Raman G-peak position ($\omega_G$) vs. 2D-peak position ($\omega_{2D}$) for multiple locations across the sample to highlight the strain ($\epsilon$) and charge transfer doping$^{17,78-80}$ (|n|) before and after electrochemical intercalation (see also SI Fig. S8-S9). Raman mapping on as-grown graphene on Ge(110) shows that graphene is under compressive strain with a large strain variation throughout the sample as highlighted by an average $\omega_{2D}$ = 2697 +/- 12 cm$^{-1}$ and $\omega_G$ = 1587 +/- 5 cm$^{-1}$, in line with previous literature.$^{32}$ This compressive strain is relaxed after intercalation, indicated by a shift of $\omega_{2D}$ by approximately 20 cm$^{-1}$ to $\omega_{2D}$ = 2680 +/- 3 cm$^{-1}$. Furthermore, Figure 3(b) shows that as-grown graphene on Ge(110) is practically undoped, whereas for electrochemical intercalation approaches the Raman signal indicates very low doping concentrations ($\omega_G$
=1583 +/- 1.6 cm$^{-1}$). This is consistent with the ARPES measurements above, that indicated slightly increased p-type doping.

To understand the origin of this very low substrate induced doping and residual strain we probe the structural interface between graphene and Ge oxide with helium ion microscopy (HIM) and atomic force microscopy (AFM). In comparison to SEM, HIM offers higher surface sensitivity combined with higher material contrast and resolution, as well as reduced imaging artefacts due to charging. Figure 4(a) shows HIM analysis of a sample area only partly covered by graphene so that the graphene/Ge oxide interface is revealed (highlighted by white arrows). The Ge oxide exhibits a regular pattern of nano-scale roughness. The graphene layer on top does not fully conform to this pattern and hence is partially free-standing. AFM allows us to resolve this surface topography more quantitatively. We find a Ge oxide surface roughness with graphene of approximately $R_{RMS} = 6$ nm (measured by AFM over an area of $1.5 \times 1.5 \mu m^2$). Such surface roughening has been previously reported and arises due to the crystal structure of GeO$_2$ and oxide growth from nucleation sites with random orientation.$^{42,47}$ Oxide nucleation and growth can be observed in situ as shown in Figure S10. The onset of oxide growth is delayed (Fig. S10a,b) when comparing graphene covered to graphene uncovered regions due to the time required for the reactive species to intercalate. After intercalation, graphene covered regions oxidise more uniformly highlighted by a more homogeneous colour contrast (Fig. S10 c,f) compared to uncovered regions where the oxide thickness varies throughout the sample.
Figure 4: (a) Helium ion microscope (HIM) image of a graphene layer on Ge oxide. White arrows indicate the edge of a tear in the graphene layer that leaves an uncovered Ge oxide area. (b) Atomic force microscope (AFM) image of graphene on Ge oxide (different region to a).

ToF-SIMS was performed on the graphene grown on Ge(110) after electrochemical intercalation for 24 h to grow a thick Ge oxide layer (Fig. 5). 10 keV Cs\(^+\) ion sputtering was used for depth profiling, over an extended period of time (10000 s). The SIMS data shows that there is an approximately 350 nm thick Ge oxide layer at the graphene-Ge interface for the given conditions (see section 4 in SI). The depth profile (SI Figure S16) was averaged over an area of 150 x 150 µm\(^2\). We do not observe a sharp interface between the Ge oxide and Ge in the depth profile. This can be explained by the microcrystalline structure of the Ge oxide, causing differences in oxide thicknesses across the sample as observed in the 3D depth profile image in Figure 5(c) for the CsGeO\(^+\) signal, as well as different crystal orientations that will have different sputter rates. The presence of graphene on the thick Ge oxide layer is confirmed by the C\(_2^-\) ion image during more surface sensitive Ar cluster depth profiling from this sample, shown in Figure S17.
Figure 5: 3D ToF-SIMS images of graphene on Ge (110) after electrochemical intercalation for 24 h using 10 keV Cs⁺ ion depth profiling. The x and y dimensions of the 3D plot are 150 x 150 µm² and the z dimension is 3000 nm. Plot (a) shows the combined signal whereas (b) shows C₃H₅⁺ signal, (c) the CsGeO⁺ signal, and (d) the CsGe⁺ signal, representative of graphene, Ge oxide, and Ge substrate respectively.

Our results of electrochemical intercalation of graphene on Ge can be understood in the context of the electrochemical intercalation of graphite, where in contrast to other intercalation approaches the electrochemical methodology can be performed at milder conditions. Furthermore, the electric field provides an additional driving force for molecules to intercalate, thereby significantly accelerating the process. For graphene on Cu, mechanical decoupling of graphene from the catalyst substrate by oxidation has been shown to be a vital step for high quality, large area transfer from graphene on Cu. As in the case of other graphene/metal interfaces the graphene uncovered sample edge as well as defects in the graphene film can act as pathways for intercalants to diffuse into the graphene/Ge interface. Our oxidation approach would allow the translation of such transfer approaches to a Ge platform with the added advantage of being Cu free, which is crucial for CMOS integration. Since epitaxial Ge films on Si wafers can be used, this is scalable to current Si wafer sizes. Importantly, creation of a dielectric at the interface between Ge and graphene, as we have shown here may also open the possibility for a transfer free graphene integration on a Si platform, where the intercalated dielectric is used as a gate dielectric. Furthermore, recent attempts to find a suitable dielectric layer for Ge based CMOS have investigated GeO₂ with a dielectric capping layer as protection. Thus, the graphene layer on interface oxidised Ge could act as an atomically thin capping layer stabilising the Ge oxide.

**Conclusion**

We have shown that by an electrochemical approach graphene directly grown on Ge can be intercalated in a 0.25 N solution of anhydrous sodium acetate in glacial acetic acid at 1 V for 24 h and a 350 nm thick Ge oxide can be formed at the interface without damage to the graphene. This is despite the passivating nature of graphene on Ge in ambient
conditions. The graphene defect density does not increase during electrochemical intercalation and our ARPES and Raman measurements in fact show that the CVD induced strain in the graphene layer can be released as graphene is decoupled from the Ge substrate.

Methods

If not otherwise stated graphene was synthesised on undoped (>50 Ωcm) single crystal Ge(110) substrates (0.5 mm thickness, Pi Kem Ltd.) in a commercial Aixtron Black Magic Pro Reactor (base pressure 5 × 10⁻² mbar). The as-received Ge substrates were loaded into the CVD reactor without further treatment. The temperature was ramped to approx. 900 °C (as measured by a pyrometer against a graphite plate) at a rate of 100 °C /min in a H₂ atmosphere. The substrates were annealed for 90 min at 900 °C, followed by CH₄ injection (H₂:CH₄ flow rate ratio was 26:1 sccm) for a time period (t₉) of 120 min. After the growth the chamber was cooled in a H₂ atmosphere. The chamber pressure during all stages was 50 mbar.

Electrochemical graphene intercalation was performed in a 0.25 N solution of anhydrous sodium acetate in glacial acetic acid using Pt wire as cathode and the Ge/graphene substrate as anode with a 1 V potential difference for a time of 6-24 h and subsequent rinsing in glacial acetic acid, blow drying with N₂ and heating at 150 °C on a hotplate for 1 h.

Nano resolution angle-resolved photoelectron spectroscopy (nanoARPES) was carried out at the IO5-ARPES beamline of Diamond Light Source (Didcot, UK). Spatial resolution is achieved by focusing the photon beam into a spot with diameter of 600 nm. The Fermi level reference was measured on a film of polycrystalline gold. Before ARPES all samples were annealed in ultra-high vacuum (below 1 × 10⁻⁹ mbar) for 2 h at 150 °C and ARPES measurements were performed at a temperature of 30 K (-243 °C). Helium Ion Microscopy (HIM) was performed using a Zeiss Orion NanoFab. Secondary electron images were collected using a scanning focused beam of 25 keV He⁺ ions with the sample tilted at 45°. Scanning electron microscopy (SEM) pictures were taken with a Carl Zeiss SIGMA VP at an acceleration voltage of 2 kV.

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