Hydrogen etch resistance of aluminium oxide passivated graphitic layers

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Abstract
Graphene inherently possesses defect sites and grain boundaries that are vulnerable to chemical etching by hydrogen radicals. In this study, an etch-mitigation method is presented to selectively passivate these sites using atomic layer deposition (ALD) of a H etch-resistant material. First, as a reference experiment, pristine exfoliated graphitic layers are exposed to H radicals to determine the lateral etch rate from defect sites. Next, these samples are compared to graphitic layers in which the defects are selectively passivated by Al2O3, in the same exposure conditions, using atomic force microscopy at every step in the experiment. The results show that etching is slowed down by local deposition of Al2O3 ALD at sites vulnerable to H radical etching.

Keywords: graphene, HOPG, hydrogen radical, ALD, etching, Al2O3

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene is an exceptional material, owing to its marvellous electronic properties, high optical transparency, thermal conductivity, and theoretical mechanical strength [1–4]. Recently, free-standing graphene layers have been considered for various applications, including energy storage device applications [5] and particle filtering membranes inserted into optical beam paths for e.g. light element x-ray transmission windows [6] and extreme ultraviolet (EUV) lithography pellicles [7].

The application of graphene as a particle filter in high energy radiation environments requires stability under these radiation fields and specific environmental conditions, such as H radicals/ions in the case of EUV pellicles [8]. Simulations by Despiau-Pujo et al suggest that chemical-etching mechanisms of defect-free graphene by H ions start to play a role for ion energies of 5 eV and higher [9]. Defective graphene, however, already degrades in H radical environments starting from its structural defects, such as grain boundaries and point defects [10], which are vulnerable sites for etching due to their enhanced reactivity towards H radicals [11–14].

One way to improve the resistance of realistic defective graphene to chemical etching by H radicals is to deposit a uniform etch-resistant layer on top of graphene. The disadvantage of this solution is the increase of EUV absorption of this stack, which is a key property for EUV pellicles. We present a method to selectively passivate the structural defects of graphene using a H etch-resistant material, thereby drastically reducing the loss of (EUV) transmission compared to a uniformly deposited layer. For this, atomic layer deposition (ALD) is used, an appealing method due to the possibility to initiate growth in particular at the chemically more active defect sites [15]. Thermal ALD does not introduce new defect
sites, as evidenced by Vervuurt et al with Raman measurements [16]. As a H etch-resistant material, Al₂O₃ is an excellent candidate [17]. In addition, ALD of Al₂O₃ on graphene surfaces has been widely studied [18–23].

In this paper, we demonstrate the passivation of defect sites in exfoliated highly oriented pyrolytic graphite (HOPG) by selective ALD at these relatively more chemically active sites. Exposure of HOPG flakes passivated by ALD Al₂O₃ shows a strongly increased resistance to H radical etching when compared to reference HOPG flakes prepared without ALD. The results show that selective passivation of HOPG from defect sites is a viable method to protect graphene in chemically active environments.

1.1. Graphene etching by H radicals with and without ALD etch mitigation

H radical adsorption to the graphene basal plane requires minimum energies of about 0.4 eV [13]. We estimate this cannot be overcome by thermal H radicals. On the other hand, H adsorption is known to have no energy barrier at defect sites and free edges of the graphene where dangling bonds are expected to be present, as given schematically in figures 1(a) and (b) [13, 17]. H uptake at these sites results in C–C bond breaking and the formation of volatile compounds [12, 13]. It is also demonstrated experimentally that H radicals start to etch graphene from pre-existing defect sites and, subsequently, etching propagates laterally, [11, 12] as also sketched in figure 1(c). We hypothesize that passivation of structural defects prevents H adsorption at these sites, and strongly reduces etching.

To verify this, the proposed method is to use selective ALD for passivation of the defect sites, as visualized in figures 1(d) and (e). Similar to H etching, chemisorption of ALD precursors also occurs selectively on the reactive defect sites where dangling bonds or functional groups are present in the graphene, in contrast to the inert basal plane [24–27]. In our experiments, we expect that these reactive sites show a similar chemical affinity towards both H radicals and Al₂O₃ ALD precursors, and therefore chemisorbed ALD Al₂O₃ is expected to reduce the H etching significantly at these sites.

2. Experimental methods

In this work, commercially available HOPG was used as a model system for graphene with a lower defect density than chemical vapor deposition (CVD)-grown graphene. This is important to demonstrate the graphene etching specifically at defect sites, as well as selective passivation via ALD [28]. HOPG flakes were deposited onto a thermally oxidized wafer (approximately 300 nm SiO₂ layer on Si), using a deterministic dry transfer method based on Castellanos-Gomez et al [29]. HOPG flakes were exfoliated by a polydimethylsiloxane (PDMS) gel film (Gel-Pak) using 3M Scotch Magic Tape. The PDMS gel film was placed on top of a PDMS block, which was bonded to a glass microscope slide. The HOPG flakes were transferred at a substrate temperature of 45 °C. The thickness of the HOPG flakes were measured to be around 5–8 nm using atomic force microscopy (AFM).

The ALD process for Al₂O₃ was performed on prepared HOPG samples. Prior to the ALD, the sample was annealed at 400 °C in an Ar/H₂ environment for 1 h using the same conditions reported in the literature for removing possible residuals from the HOPG transfer process [18]. Trimethylaluminium (TMA) and H₂O were selected as ALD precursors since they have been widely studied in the literature and are known not to damage the graphene structure in thermal ALD processes [16, 25]. A 100 cycle ALD process was performed at 200 °C, whereby typically for each cycle approximately 0.1 nm deposition was expected [22].

In this study, the HOPG flakes with and without ALD passivation were exposed to H radicals generated by a thermal cracking process in order to avoid additional plasma-induced defects. H radicals were created using a tungsten filament at roughly 2000 °C, and H₂ gas was supplied with 100 standard cubic centimetre per minute (sccm) flow resulting in a pressure of 1.6 × 10⁻² mbar. The sample was placed 3 cm from the radicals source and prior to exposure heated to 450 °C. Based on literature data, a maximum graphene etching rate was expected at this temperature [12]. The minimum H flux of about 10¹⁶ H cm⁻² s⁻¹ was calculated by an amorphous
3. Results and discussion

In this section, the resistance of HOPG flakes (stacked graphene layers) towards H radicals is investigated in three steps. First, a reference experiment without ALD was carried out to demonstrate the H radical etching from defect sites, and the etch rate was determined. Then, Al₂O₃ ALD was performed on HOPG flakes to selectively passivate the defect sites. Finally, the Al₂O₃ ALD decorated HOPG was exposed to H radicals to test the extent to which ALD passivation of defects reduces the etch rate.

3.1. H radical exposure of HOPG flakes

Figure 2 shows AFM data after sequential exposure of the same HOPG flake to increasing doses of H radicals. The data reveals that the radical exposures lead to etching of the graphene along the grain boundaries and hexagonal etch pits (the latter originating from point defects). The observed defect sites are clearly visible and confirm a low number of defects in the HOPG flakes (figures 2(b)–(d)). The AFM results shown here are in line with previous observations of H radical etching of exfoliated HOPG, where grain boundaries and hexagonal etch pits are typically observed defects [12].

Figures 2(b)–(d) also show that etching progressively continues from pre-existing defect sites, as also stated in earlier reports [12]. By increasing exposure time, the size of the grain boundary openings and hexagonal etch pits increase at a constant rate of 0.4 nm min⁻¹ (figures 2(e) and (f)), whereas no change is observed on the basal plane. These results confirm that HOPG is being etched exclusively at the defect sites and grain boundaries (assumed to mainly consist of sp³ carbon) and not at the defect-free basal plane.
Figure 3. AFM data of (a) HOPG before ALD and (b) after Al$_2$O$_3$ ALD. (c) Line profile analysis of AFM data given in (b) for three specific locations indicated by blue, red, and green.

To further study the reactivity towards sp$^3$ carbon etching, sputtered a-C layers, which are expected to consist predominantly of sp$^3$ carbon, were exposed to H radicals. A decrease in thickness of 0.4 nm min$^{-1}$ is observed for a-C layers, tested at identical conditions as used for the HOPG experiments before, showing a similar behavior as the graphene lateral etching from defect sites.

3.2. ALD of Al$_2$O$_3$

To investigate the process of selective ALD of Al$_2$O$_3$ on HOPG, AFM measurements were performed. Figure 3 shows AFM data of HOPG before (a) and after (b) the ALD process, clearly showing localized Al$_2$O$_3$ deposition, with a height of approximately 10 nm as extracted from the AFM line profiles (figure 3(c)). For a 100-cycle ALD process, this height corresponds to ~0.1 nm growth per ALD cycle, in agreement with earlier reports in the literature on Al$_2$O$_3$ growth also at 200 °C [26]. The result shows that there is a selectivity of the deposition at specific locations, which could be explained by the chemisorption of precursor materials (TMA, H$_2$O) selectively at defect sites that are more energetically favourable for ALD [32], but not at the defect-free basal plane due to a lack of functional groups where a few eV are required for chemisorption [25, 32].

Considering the observed defect density of exfoliated HOPG flakes, as can be seen in the H radical etching section, additional Al$_2$O$_3$ ALD could be explained by physisorbed species at non-defective sites (figure 3(b)). Several studies have shown that a small amount of physisorbed species can result from ALD at the basal plane, which might be caused by insufficient removal of organic residues from the transfer process and/or the presence of water species adsorbed at the basal plane [33].

3.3. H radical exposure of Al$_2$O$_3$ coated HOPG

To test the impact of H radicals on the Al$_2$O$_3$ passivated HOPG flakes, AFM measurements (shown in figure 4) were performed after radical exposure for a series of durations, and the results for passivated HOPG were compared with the results for HOPG without ALD. Figures 4(d)–(g) clearly indicate the absence of a strong development of etch pits or grain boundary widening by H exposure, as observed earlier for pristine
HOPG (figure 4(b)). In addition, the impact of H radicals on graphene underneath Al₂O₃ was evaluated by removing the Al₂O₃ from the graphene after the H radical exposure. While figure 4(h) shows some residual damage to graphene after the ALD layer was removed by wet chemical etching, the extent of this damage is reduced by 87% compared to the case of pristine, not passivated HOPG after H radical exposure (figure 4(b)). The percentage of etched areas (excluding flake edges) were further calculated from $10 \times 10 \, \mu\text{m}$ AFM scans of these 18 h etched samples, showing that the ratio of the etched area to the total area is 28.5% for samples not passivated by ALD, while this ratio amounts to 3.7% for passivated samples. This indicates that the process of Al₂O₃ defect decoration is capable of protecting defects in graphene from H radical etching.

Further research will be needed to understand and mitigate the mechanism leading to the residual etching of some locations of the HOPG, despite passivation by Al₂O₃, as shown in figures 4(f)–(h). A potential cause of the observed residual etching of the Al₂O₃ coated HOPG could be the presence of polymer/water residues leading to a (partly) physisorbed ALD coating, rather than chemisorbed. Such a physisorbed ALD coating can detach relatively easily from HOPG due to insufficient adhesion. Another reason could be the accumulation of local stress at the Al₂O₃–HOPG interface. The etching process requires cyclic heating up and cooling down steps, where the differences in thermal expansion coefficients of graphene and Al₂O₃ might lead to detachment of the Al₂O₃. Moreover, it is known from the literature that the areal density of graphene wrinkles changes upon cyclic heating up and cooling down to release the built-up stress [34], which can potentially assist this detachment.

The results shown here are promising for slowing down the etching of the graphene layers in a H radical environment, which is a solution that can potentially also be extended to other two-dimensional (2D) materials such as MoSe₂, MoS₂, and WSe₂ [35]. This can be further improved by reducing the physisorption via optimization of cleaning and/or
change of the transfer process. This method could also be used in applications where low energy H ion (<5 eV) (cleaning) processes are required since the demonstrated method is in principle valid for ion-energies below 5 eV [9]. In addition, blocking of H radicals and ions can be easier at higher temperatures due to the increased desorption rate from graphitic surfaces, where Al₂O₃ is known to be a high-temperature resistant material. It should be noted that, in this work, a ~10 nm Al₂O₃ was applied as a H resistant material to demonstrate the potential of localized protection of graphene, but future work should evaluate if thinner Al₂O₃ layers also serve as a protective layer for the graphene layers and thereby reduce the transmission loss for EUV pellicles.

4. Conclusion

We have shown that etching of graphene occurs at defect sites present in the basal plane and at grain boundaries. HOPG flakes exposed to H radicals at an elevated temperature of 450 °C show a lateral etch rate of 0.4 nm min⁻¹, taking place at exposed reactive sites (structural defects). The etching of graphene at defect sites is strongly reduced by the presence of ALD Al₂O₃ locally chemisorbed at defect sites. This can be explained by the effective blocking of H radicals at such protected defect sites. The passivation process demonstrated here, and the resulting resistance of graphene against H radicals, is promising for etch retardation of, for example, graphene pellicles in EUV lithography, but may also be effective to protect graphene in environments containing low energy H ions (<5 eV) (e.g. present in plasmas).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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