Current methods of hydrogen storage are expensive, with difficulties found in storage and transport. In gas form, high pressures are necessary to store sufficient amounts of hydrogen due to its low energy density. In liquid form, energy density of hydrogen is improved, but must be stored at cryogenic temperatures (−253 °C) to prevent loss of hydrogen due to boil-off. Conversely, hydrogen can be stored using solid state materials such as metal hydrides and nanostructures such as graphene to serve as a scaffold for hydrogen incorporation via chemical reaction and adsorption, providing a stable and reversible storage medium while substantially lowering cost. Graphene is an ideal scaffold for hydrogen storage with a storage capacity of 7.7%wt.2

Hydrogenated graphene, known as graphane, is an ideal material for hydrogen storage due to graphene’s exceptionally high surface area of 2630 m² g⁻¹, with every atom in the layer capable of incorporating atomic hydrogen via its p-orbitals.2 Hydrogenation of sp² bound semi-metal graphene forms, when fully hydrogenated, sp³ bound insulating graphene akin to diamond. A material that would allow for traditional semiconductor device fabrication. Graphene was theoretically predicted in 20072 and later synthesized in 2009, with the difficulty in synthesis being the need for atomic hydrogen, as hydrogen gas (H₂) does not directly react with carbon.4-6 Techniques implemented by others to synthesize graphene involve development of atomic hydrogen by plasma-assistance that can cause lattice damage due to energetic ions, rotation of hot filaments using high temperature/energy to break the H-H bonds in hydrogen gas,6 and electron-induced dissociation of adsorbates using an electron beam to break the H-H bonds of adsorbed molecules.1,9 The in situ or cumbrous nature of these techniques has led to an ex situ electrochemical means of graphene fabrication.10-12

Electrochemical hydrogenation of graphene was first demonstrated in 2012 where free H⁺ cations from an acidic electrolyte reacts with negatively biased graphene forming thermally reversible hydrogenated graphene. Since EG is negatively biased, only hydrogen ions, which are positively charged, are attracted to the surface, excluding any possibility for adsorption of other functional groups.12 Hydrogenation was also determined to be electrochemically reversible by applying a positive bias to the graphene.12 Hydrogen adsorption via electrochemistry offers superior controllability of hydrogen incorporation, reversible thermally and electrochemically with direct applications in hydrogen storage.12 Degree of hydrogenation was first suspected then confirmed to be dependent on the starting defect density of graphene via a detailed cyclic voltammetry and electrochemical impedance spectroscopy study on graphene with varying defect densities.11 Hydrogen incorporation in graphene with low defect density was shown to be around 33% compared to 50% in graphene with higher defect density. The goal of this work is to try and improve hydrogen incorporation in low defect epitaxial graphene to match or exceed that observed with defective epitaxial graphene by addition of catalytic metals.

Traditional hydrogenation of alkenes by molecular hydrogen gas to form alkanes requires catalysis by precious transition metals, such as Pt, sometimes at high temperatures and pressures.12,14 These catalytic transition metals decrease the activation energy, and thus increase the rate of C-H bond formation. Platinum-group transition metals offer a facile pathway for hydrogen to adsorb and dissociate, and the resulting H atoms can then transfer directly to the alkenes adsorbed on the metal surface.15 Edges, corners and basal planes of all metals have different catalytic activity.16-18 As such, the effectiveness of these metals as catalysts depends directly on the size and shape of the particles.16,17 Smaller particles result in more adsorption sites for hydrogen to be adsorbed due to increase in surface area.16,17,19

Platinum and gold were chosen as catalyst to increase hydrogenation of low defect epitaxial graphene. Despite its high cost, platinum is one of the most commonly used catalysts for hydrogenation of carbon.17,20 Reducing the size of the Pt nano-clusters reduces cost and results in higher catalytic activity with more atoms exposed to reactants, of which are catalytically active according to first principle calculations of 10 atom clusters of Pt.16 From an electronic point of view, Pt reaction speed as a catalyst is governed by its electron configuration. Pt, with the smallest number of vacant d-orbitals, has more available electrons and holes assisting in adsorption to easily form, in this case, metal-hydrde bonds, making it a superior catalyst.21 As Pt easily forms bonds with most molecules, adsorption selectivity is an issue in systems with multiple species, where hydrogen may not be the only adsorbed species resulting in undesired products.22 For this reason, gold, which is less reactive than platinum, was also investigated.

Bulk gold (i.e., large Au particles) has been shown to be much less active (by two orders of magnitude) in dissociating hydrogen, due to the Au (111) surface being intrinsically inactive for this reaction.16,20 In small clusters, however, Au has demonstrated reactivity to hydrogen in edge Au (200) and corner Au (311).19,20,23 With decreasing particle

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size, Au shows tunable hydrogenation with increasing edge and corner sites compared to bulk Au. The H$_2$ dissociation rate on Au is limited by the inability of molecular hydrogen to adsorb. However, when Au is readily supplied with H atoms or ions from other transition metal spillover or acidic solutions, respectively, hydrogen atoms easily chemisorb on Au.

As precious metals are used to increase hydrogenation of alkenes in traditional thermal catalytic hydrogenation, deposition of catalytic transition metals on EG should increase electrochemical hydrogenation. Most work on hydrogenation being performed on carbon and oxides therefore the observed chemistries on carbon/semiconductor scaffolds could vary. In this study, enhanced electrochemical hydrogenation of low defect EG by deposition of catalytic transition metals is demonstrated.

**Experimental**

To see the effect of these catalytic transition metals on the functionalization of graphene, ten (10) 10 × 10 mm$^2$ 6H SiC semi-insulating samples were chosen from the same wafer, a nominally on-axis wafer, 0.5° in the 11–20 direction, obtained from II-IV, Inc. The Si-face was chemical-mechanical polished (CMP) and thoroughly cleaned using standard RCA clean (Trichloroethylene [TCE], acetone, methanol) and HF to remove any native oxide. Epitaxial graphene (EG) grown on the Si-face of SiC by thermal decomposition of a SiC substrate in vacuum, 26 × 10$^{-5}$ Torr, using a home built RF furnace. Chemically derived Pt nanoparticles were formed on four samples (C.Pt 1–4) of EG by deposition from an aqueous H$_2$PtCl$_6$ solution, dried in vacuum, and treatment with hydrogen (H$_2$ unreactive to graphene) at 200°C. To deposit metal in a more controlled fashion 20 nm of Pt or Au were evaporated on four samples total (E.Pt 1–2 and E.Au 1–2) by E-beam evaporation to act as catalysts and enhance the reactivity of graphene in a more controlled manner. The E-beam evaporator was pumped down to > 1 × 10$^{-6}$ and metal was deposited at a rate of 2 Å/second. A set of two samples (Pristine EG 1–2) were functionalized to act as reference point An atomic force E-beam evaporator was pumped down to 2.5 −2) were functionalized to act as reference point An atomic force microscope (AFM) analysis was performed using a Vecco Dimension 3000 Atomic Force Microscope to determine the surface morphology changes of EG with catalytic metals and the functionalized EG. The images were acquired in tapping mode at a scan rate of 0.6 Hz over a 2.5 μm$^2$ area.

Atomic hydrogen was generated using a home-built electrochemical setup, with current applied through a 10% H$_2$SO$_4$ acid solution. The H$_2$ dissociation rate on Au is limited by the inability of molecular hydrogen to adsorb. However, when Au is readily supplied with H atoms or ions from other transition metal spillover or acidic solutions, respectively, hydrogen atoms easily chemisorb on Au.

According to Casiraghi, three parameters should be taken into account when interpreting Raman of hydrogenated carbon using a single wavelength source. Broadening of FWHM (G) is due to chemical bonding and is evidence of C-C sp$^3$ content, I(D)/I(G) ratio indicates the amount and size of ring-like sp$^2$ clusters, and photoluminescence background can be used to extract the H-content. Hydrogen functionalized graphene is a direct bandgap material, resulting in a fluorescence background being observed in the Raman spectra. The presence of fluorescence could be due to defect induced midgap states or band-to-band recombination, although it is unclear which mechanism is responsible. However, either mechanism indicates the presence of a bandgap. This fluorescence background can be quantified by the fluorescence slope, m, normalized to G-peak intensity, normalized slope, and defined as the photoluminescence background present in samples as a result of hydrogenation. This is further quantified as a percentage of hydrogen atoms per carbon atoms was calculated by Equation 1.

\[
H\% = 21.7 + 16.6 \times \log \left( \frac{m}{I(G)} \right)
\]

The gravimetric density of hydrogenated graphene was then extrapolated from the theoretical gravimetric density of fully hydrogenated graphene, graphene, of 7.7 wt%.

**Results**

The results are broken up into three sections; electrochemical hydrogenation of EG with chemically deposited platinum, electrochemical hydrogenation of EG with E-beam evaporated platinum and gold, and a discussion on the mechanisms taking place between the nanoparticles, hydrogen and graphene. Chemically deposited platinum on four (4) EG samples were electrochemically hydrogenated revealing wide variability in extent of hydrogenation. Two (2) samples showed little to no hydrogenation, increase in sp$^3$ content, based on I(D)/I(G) ratio, increasing to 0.17 and 0.44 from starting I(D)/I(G) ratio of 0.14. The other two (2) samples showed promising prominent increases in sp$^3$ content with increases in I(D)/I(G) ratio of 1.1 and as shown in Figure 1, 5.01. The Raman spectra of the functionalized Pt nanoparticle catalyzed graphene revealed a very large I(D)/I(G), 5.01, and a narrow FWHM of 33 cm$^{-1}$ FWHM, showing an extremely high sp$^3$ content present in the material, and the lack of damage to the graphene and functionalized graphene peaks.5,28 All the spectra shown are difference Raman spectra obtained in this manner. There are three peaks associated with graphene: The D peak (∼1345 cm$^{-1}$) corresponds to the disorder and diamond like sp$^3$ content in the material, The G peak (∼1595 cm$^{-1}$) corresponds to the in plane vibration of the graphene lattice and the 2D peak due to double resonance.

Figure 1. Raman spectra revealing an atypical before and after hydrogenation with chemically deposited platinum nanoparticles. An I(D)/I(G) ratio of 5:1 was observed with a prominent D’ shoulder peak and C-H bond peak showing hydrogenation of EG and high sp$^3$ content.
graphene surface. The D and 2D peak red shifted, caused by the formation of sp³ bonds. The G and 2D peak full width half maximum (FWHM) broadens, further supporting the sp³ hybridization of graphene and the C-H bond peak at ~2930 cm⁻¹ further supports successful functionalization.⁵ A very prominent D' prime shoulder peak on the G peak indicating distortion of the ideal graphene lattice further shows that changes in the C-C bond length have taken place.² While this method of catalyst preparation as evident by the sample in Figure 1 is promising, it lacks reproducibility and uniformity due to changes in conductivity and reactivity of graphene (doped p-type by the water in the aqueous catalyst solution), and clustering of the nanoparticles on graphene (poor adhesion) causing a large variability between the four samples hydrogenated.

Raman confirmed that no damage occurred to the graphene during aqueous catalyst deposition and that the material was electrochemically functionalized successfully. However, a more controlled, non-aqueous deposition of catalytic metals was needed to make this functionalization more reproducible, since aqueous based solutions can change the doping of graphene. Similar to water reactions observed with single wall carbon nanotubes (SWCNT), water results in functionalization, more so with evaporated Pt than with Au, according to AFM with RMS roughness of 4.2 nm and 2.6 nm for Au and Pt respectively with areas in the Pt deposited sample showing the underlying graphene with an RMS roughness of 0.4 nm. This could change the concentration and overall geometry of the catalyst, affecting reactivity. Despite the lower reactivity of Au, the enhanced hydrogenation seen with this metal could simply be more metal remaining during electrochemical hydrogenation and more hydrogen adsorbing due to the higher concentration of adsorption sites compared to Pt. It may also be due to the fact that no H₂ dissociation is required (H⁺ is already present), a situation in which Au has previously shown similar high catalytic activity.²⁵ At the end of hydrogenation, the metals are seen to remain in clusters ~50–100 nm in size, at metal cluster densities 10 × 10⁶–50 × 10⁶ cm⁻², clusters we argue later are responsible for initiating hydrogenation, with hydrogen spillover to graphene resulting in increased hydrogenation from pristine graphene. The adhesion of metal to graphene, and its consequent clustering, bear further investigation as changes in geometry during functionalization affect the reactivity and overall effectiveness of the catalytic metal.

Functionalization of metal catalyzed EG revealed increases in functionalization as evident by marked increases in I(D)/I(G) ratio, shifts in D, G and 2D peaks (lines represent peak position of unfunctionalized EG) and emergence of C-H peaks for typical Au and Pt enhanced EG with data shown in Figure 3 and Table I. Figure 4 shows gravimetric density of electrochemically hydrogenated graphene vs. hydrogen cluster density, where gravimetric density extracted from I(D)/I(G),³³,³⁶ of the ten (10) samples after to provide uniform coverage and dispersion according to AFM before electrochemical hydrogenation.

However, after hydrogenation, the metal particles appear to agglomerate together, exposing the underlying steps of the graphene surface. These metals also appear to partially lift off during functionalization, more so with evaporated Pt than with Au, according to AFM with RMS roughness of 4.2 nm and 2.6 nm for Au and Pt respectively with areas in the Pt deposited sample showing the underlying graphene with an RMS roughness of 0.4 nm. This could change the concentration and overall geometry of the catalyst, affecting reactivity. Despite the lower reactivity of Au, the enhanced hydrogenation seen with this metal could simply be more metal remaining during electrochemical hydrogenation and more hydrogen adsorbing due to the higher concentration of adsorption sites compared to Pt. It may also be due to the fact that no H₂ dissociation is required (H⁺ is already present), a situation in which Au has previously shown similar high catalytic activity.²⁵ At the end of hydrogenation, the metals are seen to remain in clusters ~50–100 nm in size, at metal cluster densities 10 × 10⁶–50 × 10⁶ cm⁻², clusters we argue later are responsible for initiating hydrogenation, with hydrogen spillover to graphene resulting in increased hydrogenation from pristine graphene. The adhesion of metal to graphene, and its consequent clustering, bear further investigation as changes in geometry during functionalization affect the reactivity and overall effectiveness of the catalytic metal.

Table I. Average Raman parameters and calculated gravimetric densities with standard deviation of electrochemical hydrogenation with and without metal catalyst.

| Sample       | D Position Before (cm⁻¹) | D Position After (cm⁻¹) | I(D)/I(G) Ratio Before | I(D)/I(G) Ratio After | Slope (m)/I(G) After (μm) | Calculated H Content (%) | Calculated Gravimetric Density (% wt) |
|--------------|-------------------------|-------------------------|------------------------|----------------------|---------------------------|--------------------------|--------------------------------------|
| Avg w/o Cat | 1347 ± 0                | 1328 ± 4                | 0.13 ± 0.08            | 0.81 ± 0.19          | 4.9 ± 0.2                 | 33 ± 0.5                 | 2.55 ± 0.02                          |
| Avg w/E-Pt  | 1342 ± 2                | 1330 ± 0.6              | 0.22 ± 0.01            | 1.05 ± 0.01          | 7.9 ± 0.4                 | 37 ± 1.1                 | 2.81 ± 0.03                          |
| Avg w/E-Au  | 1364 ± 4.5              | 1330 ± 3.5              | 0.09 ± 0.01            | 1.24 ± 0.17          | 17.7 ± 6.6                | 42 ± 2.3                 | 3.23 ± 0.22                          |
| Avg w/C-Pt  | 1345 ± 5.6              | 1330 ± 3.0              | 0.14 ± 0.03            | 1.68 ± 1.74          | 9.1 ± 6.0                 | 38 ± 4.8                 | 2.79 ± 0.3                           |
hydrogenation. In this analysis, we assume that each cluster is small enough (much smaller than the Raman probe wavelength) that it registers as a single Raman active D-peak site during the Raman measurement. The EG samples before hydrogenation are of good quality (Fig. 4) with $I(D)/I(G) < 0.22$ and fluorescence background ($m/I(G) < 5$ um) below the noise threshold of the Raman spectra indicating zero H-content. Samples functionalized with no catalyst showed an increase in the $I(D)/I(G)$ ratio and an increase in fluorescence background greater than the noise threshold indicating an increase in sp$^3$ content as well as hydrogen content. The average hydrogen cluster density observed, $0.7–1.6 \times 10^{11}$, is comparable to the average electron/hole puddle density from charge impurities ($\sim 1–3 \times 10^{11}$) and pre-hydrogenation defect density ($\sim 10^{10}$) from Raman, suggesting that these sites may play a role in hydrogen adsorption on epitaxial graphene.

The hydrogen cluster size, estimated by dividing the total surface hydrogen concentration by the number of clusters from Raman, was found to be $\sim 28.5$ nm with $\sim 10^{12}$ hydrogen atoms per cluster, assuming circular clusters for simplicity. Space between hydrogenated clusters was estimated to be $< 30$ nm, increasing with decreasing density of hydrogenated clusters, assuming a uniform distribution of H-clusters across the EG surface. The presence of H-clusters is consistent with previous measurements of electrochemical hydrogenation of EG, where localized H-induced states were observed by scanning tunneling spectroscopy (STS), rather than uniformly distributed H, which would have led to the observation of a bandgap.

Figure 5 illustrates this geometrical distribution of H-clusters across the EG surface. As shown above in the AFM images in Fig. 2, metal clusters $\sim 10^{10}$ cm$^{-2}$ are present, and led to an increase in hydrogenation of the EG surface due to the demonstrated catalytic activity (Figs. 1, 3). Such catalytic behavior has also been observed in H-spillover from catalyst metal to substrate. However, this metal cluster density is not sufficient to explain the total number of H-clusters observed. Therefore, we post that pre-hydrogenation defects are responsible for seeding these H-clusters as well, a hypothesis that has been validated in greater detail in a recent article on defect-engineered EG. The observed defect density $\sim 10^{10–11}$ cm$^{-2}$ (from Raman) is consistent with the discrepancy between the observed metal cluster density and H-cluster density. In other words, the role of defects and metal nanoparticle/cluster formation must be thoroughly understood to be able to engineer the H-functionalization of the EG surface. Also noteworthy is the fact that EG-defects and catalysts have similar behavior, suggesting possible application of EG defects in catalysis.

As shown in Table I, functionalization with catalytic metals shows improvements in hydrogenation compared to EG without catalyst. However, counter to what the literature suggests, hydrogen content on average was shown to be higher in Au enhanced hydrogenation than Pt. This is most likely due to the fact that in most hydrogen catalysis reactions, H$_2$-dissociation is the bottleneck, and Pt include: i) Cluster density geometry favoring Au more than Pt with the presence of more edges in metal clusters allowing for greater hydrogenation; ii) Au has greater selectivity to adsorbed species than Pt, particularly with H. The different dispersions observed of Pt and Au as shown by AFM (Fig. 3) make it impossible to determine if these secondary effects are directly involved in the observed enhanced hydrogenation in graphene using Au.

Conclusions

The present study shows enhanced electrochemical hydrogenation of EG by chemically deposited and evaporated metals to improve hydrogen incorporation. The introduction of catalytic metals has shown to improve electrochemical hydrogenation of EG, from 2.55%wt average observed in low defect epitaxial graphene without metal catalyst to 3.23%wt average seen in Au catalyzed EG. Hydrogenation was observed to be seeded from metal catalyst clusters, as well as intrinsic defects in the as-grown EG. This opens up potential for defect engineered composite carbon-based catalysts on semiconductor scaffolds, as well as electrodes in fuel cells for electricity generation. Contrary to what is typically observed in literature, Au on EG demonstrated higher catalytic activity than platinum, an observation we attribute to
the fact that H\(^+\) is readily available, and H\(_2\) dissociation is not the bottleneck to hydrogenation, as is commonly the case.

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