

Growth of Graphene on Stainless Steel by Thermal Chemical Vapor Deposition

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Abstract

Graphene is a 2-dimensional material of sp^2 bonded carbon atoms which has many exotic properties such as hydrophobia, great electronic and mechanical properties. Stainless steel is an iron alloy which is widely utilized. Coating graphene on stainless steel surface can improve the surface properties of stainless steel for example electronic properties, strength and resistance of corrosion. In this report, we have demonstrated the growth of graphene on stainless steel 304 by thermal chemical vapor deposition. After carburization process, we found that the color at graphene region is black. Inside the graphene region, Raman spectra show D, G and 2G peak signals, confirming the appearance of graphene. Although the optic image shows large graphene area, high intensity of D peak reveals graphene grain size is very small and discontinuous. In addition, the position of G peak implies that this graphene has no stress like free-standing graphene monolayer.

Keywords: Graphene: Stainless steel: Raman

Introduction

Stainless steel is an iron alloy consisting with a minimum of 10.5% chromium and many other elements such as nickel, sulphur, molybdenum and so on. The additional elements are added to enhance its properties for example formability, strength and cryogenic toughness. Stainless steel is widely utilized because it has resistance of corrosion, rust or stain more than general iron. However, stainless steel can still be corroded in some environments such as corrosive fluids which contain halide ions. In addition, the surface hardness of stainless steel is low. These disadvantages limit the engineering application of stainless steel from wide range to some range [1].

Graphene is an allotrope of carbon created by arrangement of carbon atoms in a two-dimensional

honeycomb lattice. Graphene structure is tightly packed by sp^2 bonded carbon atoms. Graphene has many exotic properties such as hydrophobia, great electronic and mechanical properties. In the electronic band structure, graphene has remarkable electronic properties such as high mobility ($\sim 250000 \text{ cm}^2/\text{Vs}$ for calculation and $5000 \text{ cm}^2/\text{Vs}$ in the case of experiment [2]) and linear dispersion (Dirac cone) at the K-point in the Brillouin zone [3]. For the mechanical properties, graphene is the strongest material ever tested i.e. high in-plane stiffness (1 TPa) and superior strength (130 GPa) [4]. These excellent mechanical properties imply that graphene has potential to enhance the strength of composites.

Graphene can be fabricated in many ways, such as mechanical exfoliation of graphite [5], chemical

vapor deposition (CVD) of carbon bearing gases on the surface of copper films [6] and annealing of SiC substrates [7-9]. For coating graphene on stainless steel, CVD is a suitable method because it can produce large area graphene on the stainless steel.

In recent years, researchers invent new technologies like ion implantation [11], electron beams [12], laser beams [13], to improve surface of stainless steel. Graphene coatings on stainless steel are a new technology for modification of stainless steel surface. The surface properties of stainless steel after coating graphene on top are expected to have hydrophobia, higher strength and better electronic property.

In this report, we study the growth of graphene by thermal chemical vapor deposition on stainless steel 304 which is widely used in commerce. The appearance of graphene is confirmed by Raman spectroscopy.

Materials and Methods

0.4 mm thick sheet of stainless steel 304 was pre-cleaned by ultrasonic in acetone for about 6 min. After the acetone evaporated, the stainless steel sheet was inserted into a quartz tube of CVD furnace. The quartz tube was first evacuated until the base pressure reaches $\sim 10^{-3}$ Torr and then heated to $950\text{ }^{\circ}\text{C}$ with Hydrogen gas flow. The heating rate and flow rate are $38\text{ }^{\circ}\text{C}$ per min and 560 Sccm. When the annealing temperature was more than $700\text{ }^{\circ}\text{C}$, methane gas (4700 Sccm) was introduced into the quartz tube. The stainless steel sheet was annealed at $950\text{ }^{\circ}\text{C}$ for 10 min under a pressure of 5×10^2 Torr. After that the furnace was cooled down to $800\text{ }^{\circ}\text{C}$ with the cooling rate of $10\text{ }^{\circ}\text{C}$ per min. Methane gas flow only was stopped at $800\text{ }^{\circ}\text{C}$.

Raman measurements were carried out at room temperature using a Renishaw spectrometer with a 50x objective and a 532 nm laser. The laser beam size is $1\text{ }\mu\text{m}$ diameter.

Results and Discussion

After the graphene growth process, the stainless steel sample was put in Renishaw spectrometer for photographing and Raman measurement. Figure 1 shows optical image of Stainless steel before and after graphene growth process. Initial stainless steel (Figure 1(a)) contains only gray and black colors but the optical image of the stainless steel which underwent CVD process is colorful. It may be attributed to reflection of small carbon domains. We also found that the color of graphene area is black as shown in Figure 1(b).

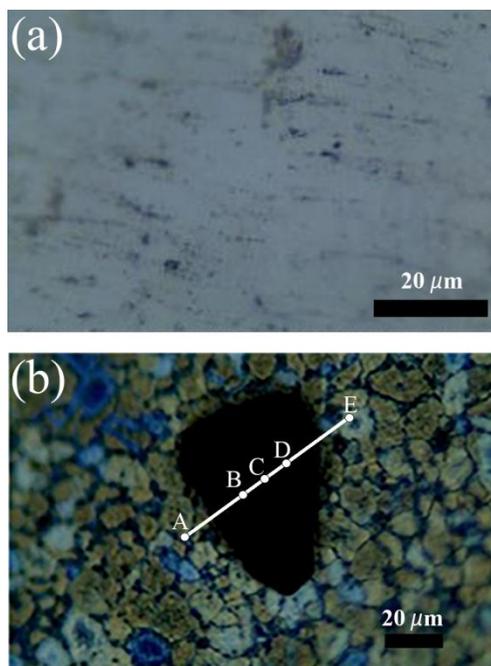


Figure 1 Optical image of stainless steel (a) before and (b) after graphene growth process

Figure 2 shows Raman spectra inside and outside the black region in Figure 1(b). The Raman spectra inside the black region (at point B, C and D) reveal that there are 3 peaks at 1350 cm^{-1} (D peak), 1580 cm^{-1} (G peak) and 2690 cm^{-1} (2D peak) while there is no peak on ordinary stainless steel. The position of G peak of this sample is same as that of free-standing graphene monolayer implying that there

is no stress for this graphene [14]. However, the intensity of D peak at this graphene region is high. It reveals that grain size of graphene in this region is very small (smaller than layer beam size). Therefore, the large graphene area in Figure 1(b) (~2000 μm) does not contain 1 continuous graphene sheet but it contains many small sized graphene grains.

For outside the black area (point A and E), there is no 2D peak in the Raman spectra indicating that there is no graphene. The small G peak at point A indicates very small and discontinuous graphitic domains [15].

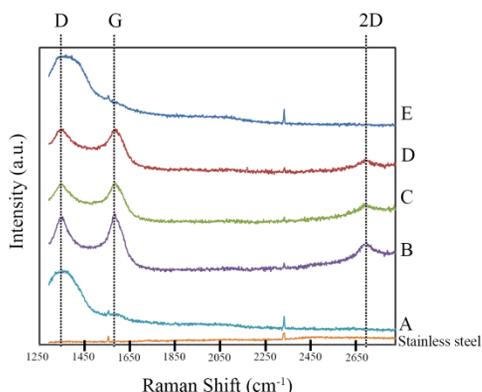


Figure 2 Raman spectra of ordinary stainless steel and at point A-E in Figure 1(b)

Conclusions

In this report, we demonstrate the growth of graphene on stainless steel by thermal chemical vapor deposition. After Carburization process, the Color of graphene region on the stainless steel is black. Graphene on the stainless steel has no stress but very small grain size.

Acknowledgement

The authors gratefully acknowledge the financial support provided by Thai Government Research Fund and department of physics, Thammasat University.

References

- [1] Cui, C.Y. et al. (2011). Microstructure and corrosion behavior of the AISI 304 stainless steel after Nd:YAG pulsed laser surface melting. *Surf. Coat. Technol.*, 206, 1146–1154.
- [2] Hass, J., et al. (2008). The growth and morphology of epitaxial multilayer graphene. *J. Phys: Condens. Matter*, 20, 323202.
- [3] Ruammaitree, A., et al. (2013). Determination of non-uniform graphene thickness on SiC (0001) by X-ray diffraction. *Applied Surface Science*, 282, 297-301.
- [4] Lee, C., et al. (2008). Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, *Science*, 321, 385.
- [5] Novoselov, K. S., et al. (2004). Electric Field Effect in Atomically Thin Carbon Films. *Science*, 306, 666-669.
- [6] Ismach, A., et al. (2010). Direct Chemical Vapor Deposition of Graphene on Dielectric Surfaces. *Nano Lett.*, 10, 1542-1548.
- [7] Hu, H., et al. (2011). Few-layer epitaxial graphene with large domains on C-terminated 6H-SiC. *Surf. Interface Anal.*, 44, 793–796.
- [8] Ruammaitree, A., Nakahara, H. and Saito, Y. (2014). Growth of non-concentric graphene ring on 6H-SiC (0001) surface. *Applied Surface Science*, 307, 136–141.
- [9] Ruammaitree, A., et al. (2014). Growth of Embedded and Protrusive Striped Graphene on 6H-SiC (0001). *International Journal of Engineering and Innovative Technology*, 3, 34-38.
- [10] Ruammaitree, A., Nakahara, H. and Saito, Y. (2014). Growth of protrusive graphene rings on Si terminated 6H-SiC (0001). *Surf. Interface Anal.*, 46, 1156–1159.

- [11]Thanigaiarul, K., et al. (2013). Surface modification of nanocrystalline calcium phosphate bioceramic by low energy nitrogen ion implantation. *Ceram. Int.*, 39, 3027–3034.
- [12]Koleva, E.G., et al. (2014). Signal emitted from plasma during electron-beam welding with deflection oscillations of the beam. *J. Mater. Proc. Tech.*, 214, 1812–1819.
- [13]Pariona, M.M., et al. (2012). Yb-fiber laser beam effects on the surface modification of Al–Fe aerospace alloy obtaining weld fillet structures, low fine porosity and corrosion resistance. *Surf. Coat. Technol.*, 206, 2293–2301.
- [14]Berciaud, S., et al. (2009). Probing the intrinsic properties of exfoliated graphene: Raman spectroscopy of free-standing monolayers, *Nano Lett.*, 9, 346-352.
- [15]Gullapalli, H., et al. (2011). Graphene Growth via Carburization of Stainless Steel and Application in Energy Storage. *Small*, 7, 1697-1700.