

Graphene as a Corrosion Inhibitor

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Abstract

Corrosion of metal components presents a problem for all electronic devices that may be exposed to hostile conditions during use. Microelectronics are particularly susceptible to the effects of corrosion due to their small size, and even minor corrosion can lead to device failure. Physical barriers, like paints and other coatings, are a common and effective method to protect materials from corrosion, but the thickness required to effectively protect a material is impractical on the micro scale. Graphene is an atomically thin material that has been proven to be an effective barrier against corrosion. This project aimed to investigate the effect of graphene quality on its ability to act as a corrosion inhibitor by varying the defect density of graphene. Graphene was grown directly on copper foil and ozone treatment was used to induce point defects in the graphene. From the results of Raman spectroscopy, SEM, and XPS analysis of the samples, it was determined that (1) ozone exposure induces defects in graphene and (2) as the defect density of graphene increases, the graphene's ability to protect against thermal corrosion decreases.

Introduction

Graphene is a 2D material composed of sp^2 carbons in a hexagonal crystal lattice, making it extremely impermeable [1,2]. While initial studies have shown that graphene can act as an effective physical barrier against corrosion, little work has been done to evaluate how the quality of graphene affects its ability to protect metal from corrosion. In our experiments, graphene was grown via chemical vapor deposition (CVD) and then subjected to ozone in order to induce point defects in the sample and effectively decrease the quality of the graphene. This exposure forms epoxide complexes as graphene reacts with ozone, creating point defects [3]. The corrosion inhibition performance of a pristine graphene coating was compared with that of an ozone-exposed, defective graphene coating.

Methods

Graphene was grown via CVD, with ozone treatment of samples immediately following removal from the growth furnace. Coating 1 was not exposed to ozone and remained pristine graphene, while Coating 2 was exposed to ozone for 5 minutes to induce graphene defects. Transfers of each graphene coating were made from the copper foil onto SiO_2 wafers for use in Raman spectroscopy analysis. Average peak ratios were determined from maps and used to calculate the defect density in each coating. In order to test the corrosion

inhibiting ability of each coating, thermal corrosion experiments were performed on the graphene-coated copper. Annealed copper with no graphene was used as a control. Foil samples were placed on a hot plate and heated at 250°C in air. An infrared thermometer was used to confirm that temperature was consistent throughout the samples. Both coatings and the control were heated for 0, 2, and 10 minutes. Coating 1 was also heated for 30 minutes in order to fully corrode the sample to a degree similar to that of Coating 2. All samples were characterized through scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy was performed on each sample.

Results

Each graphene transfer was analyzed through Raman spectroscopy to determine defect densities in the coatings. Specifically, the characteristic graphene peaks, D, G, and 2D, were analyzed. The presence of a D peak at 1350 cm^{-1} is indicative of defective graphene, and the dramatic increase in magnitude of the D peak between Coating 1 and Coating 2 indicated that ozone exposure did induce defects (see Figure 1). A decrease in the 2D peak can also be observed in the coating exposed to ozone. This occurs due to oxygen doping during ozone exposure [4]. The average D to G ratio of each coating was analyzed to determine defect density. Coating 1 was found to have an average defect density of 284 defects per μm^2 , while Coating 2 had 7665 defects per μm^2 on average.

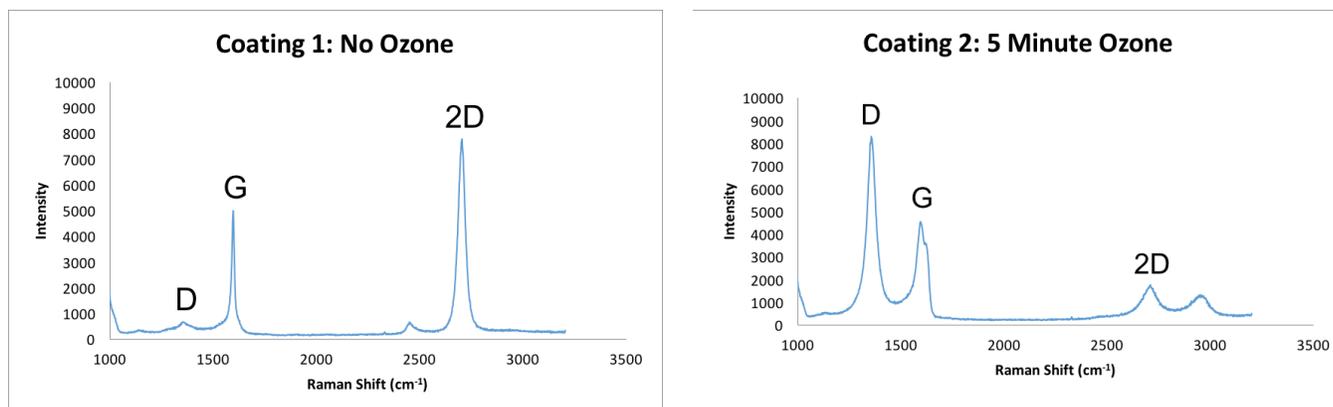


Figure 1: Raman spectra representing the average peak heights of each coating.

XPS and SEM were used in conjunction to evaluate oxide formation during thermal corrosion experiments. The progression of corrosion through each coating can be seen in Figure 2. Before heat exposure, both coatings only showed copper metal in, and no oxide was visible in the SEM images. After 2 minutes of heating, Coating 1 had thin lines of oxides visible in, though the XPS spectra was still dominated by copper metal. After 10 minutes, the amount of visible oxide varied greatly between copper grains in SEM images, as seen in Figure 2c. Similar results were reflected in XPS, with some areas producing spectra with only copper metal peaks and others showing only copper oxides. After 30 minutes, SEM showed that the copper sample was completely covered in oxide and XPS spectra of copper scans showed that only copper oxide was present within penetration depth.

The progression of corrosion in samples protected by Coating 2 occurred notably faster than Coating 1. SEM showed more corrosion on the sample after just 2 minutes of heating than samples protected by

Coating 1 showed after 10 minutes. XPS scans of the same sample reflected similar results, showing that only copper oxide was detected. After 10 minutes of exposure, the oxide layer was similar in appearance to that of Coating 1 after 30 minutes (see Figures 2d and 2g).

It is interesting to note the dark spots in Figures 2d, 2f, and 2g appear to be holes in the oxide layer where corrosion did not occur. It is currently hypothesized that these holes are caused by small multilayer grains of graphene that protect against corrosion dramatically better than single layer graphene.

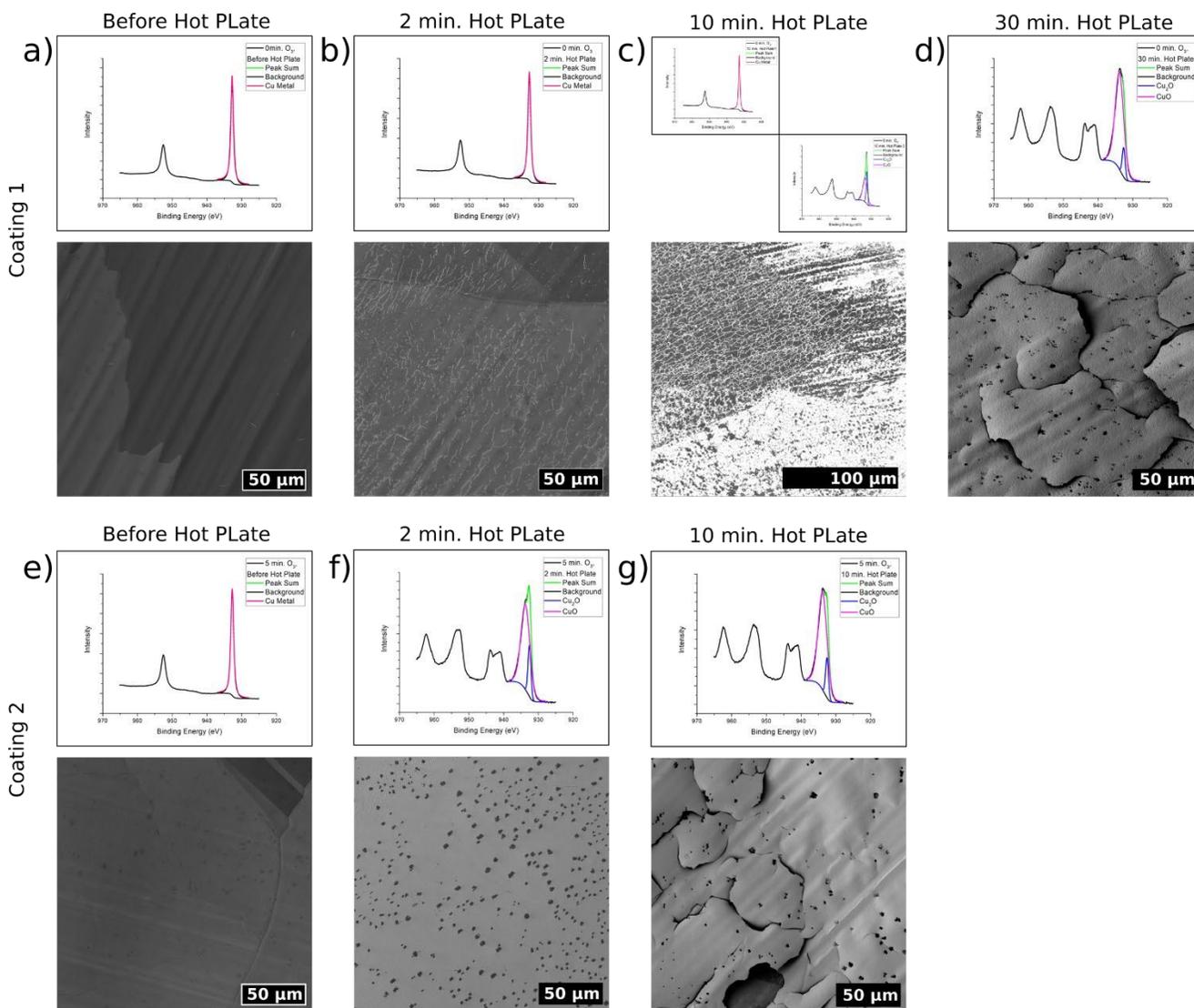


Figure 2: X-ray photoelectron spectroscopy copper 2p scans and scanning electron microscopy results from corrosion experiments.

Conclusions and Future Work

Exposing graphene to ozone induced point defects and increased the defect density in graphene. As defect density in a graphene coating was increased and graphene quality decreased, the ability of the coating to resist thermal corrosion was decreased. Further investigation is needed to determine if the visible holes in the oxide layers are due to regions of multilayer graphene. Work will continue on this project through electrochemistry experiments to determine quantitative corrosion rates as well as testing the corrosion inhibiting characteristics of other 2D materials.

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