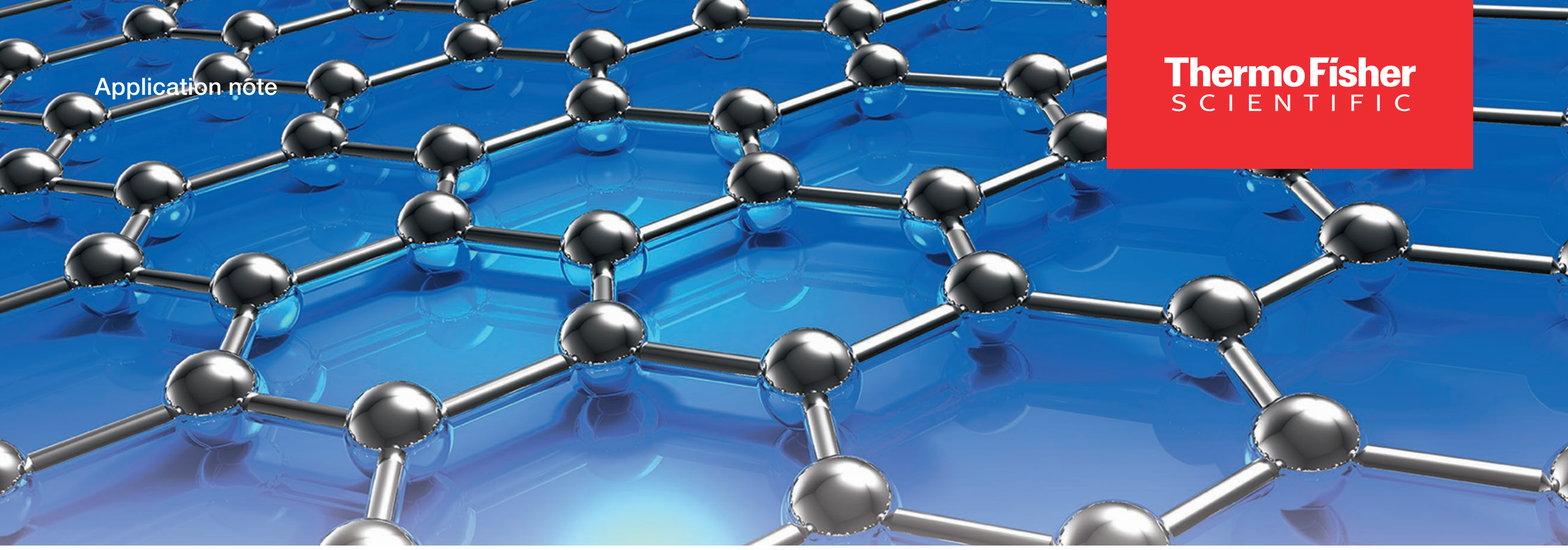


Graphene protective coating capabilities investigated by Raman rapid chemical imaging

Authors

Mark H. Wall, Thermo Fisher Scientific, Madison, WI, U.S.A.

Susmit Roy, Department of Materials Science and Engineering, University of Wisconsin, Madison, WI, U.S.A.

Keywords

DXR3xi Raman Imaging Microscope, chemical vapor deposition, copper oxide, graphene, high spatial resolution, rapid imaging

Introduction

Graphene holds great potential for use in a variety important areas that include electronics, energy storage, high strength composites and sensing technologies, to name a few. Graphene has demonstrated exceptional barrier properties, being impenetrable to even helium. Coupled with the fact that the material is also optically transparent this behavior has attracted intense interest in the material science area towards using graphene as a barrier layer in a variety of applications. This application note presents preliminary work investigating the protective capabilities of graphene employing the use of rapid Raman imaging.

Raman spectroscopy is a laser based scattering spectroscopy providing detailed molecular information that can be used to identify the chemical nature of a material. Raman is ideally suited for graphene due to the structure and bonding found in the material. Single layer graphene is a two-dimensional material composed exclusively of sp^2 bonded carbon. The sp^2 bonded carbon gives an extended network of highly polarizable π bonds which results in an extremely intense Raman signal.

Experimental

Sample preparation, Raman spectroscopy of graphene and Raman instrumentation

The material was a fresh layer of graphene on copper (Cu), obtained via chemical vapor deposition (CVD). The sample was annealed in air at 200 °C for one hour prior to measurement. Before annealing, the sample had a bright, shiny copper appearance. After annealing, the sample contained dark point and line features. The graphene sample used in this study is shown in Figure 1.

Figure 2 shows the Raman spectrum (red) of single layer graphene. The spectrum is composed of three major bands: the G band appearing at 1580 cm^{-1} which arises from the extensive sp^2 bonded carbon; the D band occurring at 1370 cm^{-1}, present when there are defects in the sp^2 bonded network (such as broken bonds or the presence of sp^3 bonded carbon); and the 2D band, an overtone band of the D band, occurring at twice the frequency of the D band. This band is present whether or not there are defects. Raman spectroscopy is also very sensitive in the detection and identification of metal oxides, in this case Cu oxides.

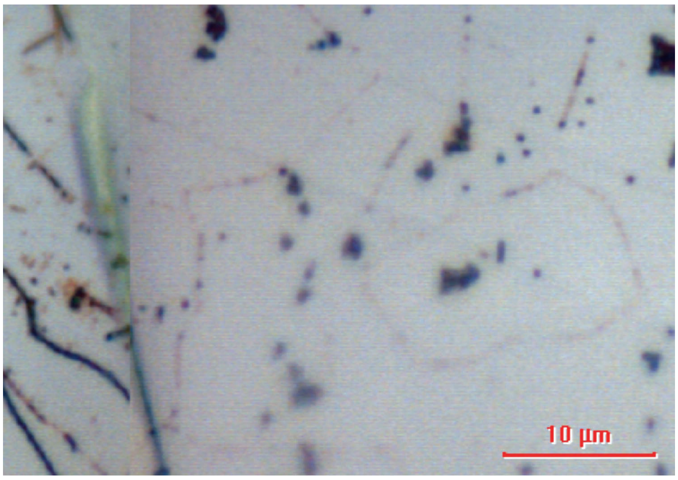


Figure 1. Optical image of single layer graphene coated Cu.

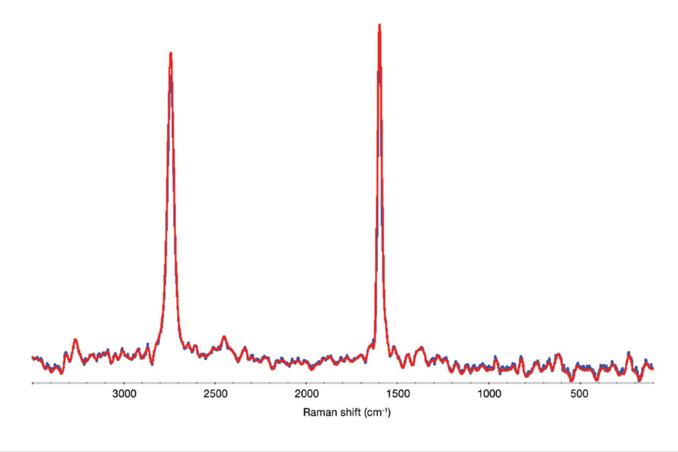


Figure 2. Spectra taken at two points of a sample of defect free, single layer graphene showing the G and 2D bands

One intense band occurs at 685 cm^{-1} and can be used to determine whether oxidation of the Cu substrate has occurred on its surface. Raman imaging can investigate microscopic features with sub-micron resolution. Raman instrumentation can be configured with a light microscope, an automated stage and suitable detector to generate high spatially resolved chemical images based upon the Raman response from the sample. The instrument used in this application note is the Thermo Scientific™ DXRxi Raman imaging microscope, capable of being configured with four laser excitation wavelengths (455, 532, 633, and 780 nm), a high precision x, y, z automated stage, high efficiency spectrograph and an EMCCD detector.

Results and discussion

A 10,000 spectra Raman chemical image, shown in Figure 3, was obtained in 50 minutes, from the annealed sample shown in Figure 1, using 2mW 455 nm excitation and a 100× objective. 455 nm laser excitation is ideal for graphene samples that have been deposited on to Cu as it does not exhibit the fluorescence that is observed for Raman measurements using 532, 514.5 or 633 nm excitation. The absence of fluorescence greatly simplifies the interpretation of the Raman results.

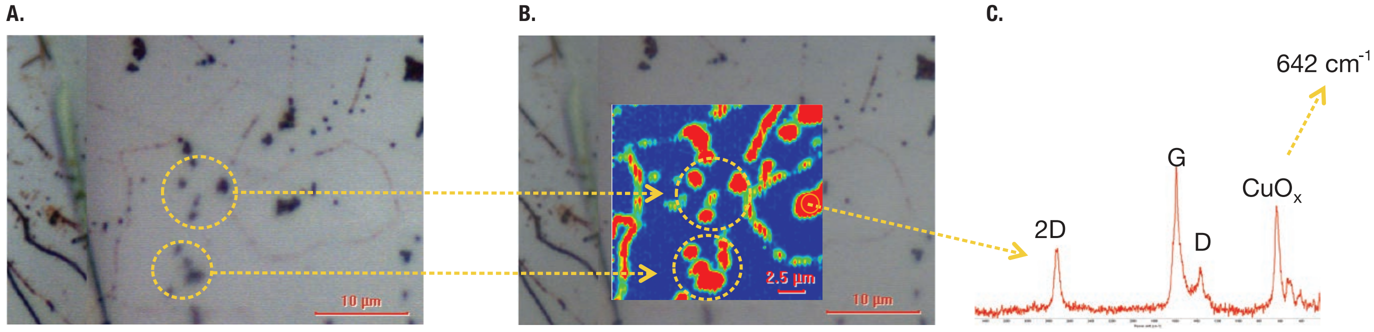
Each pixel in the chemical image represents the Raman intensity integrated over 250 nm of stage movement. In Figure 3 the optical image, Raman chemical image overlay, and points in the Raman spectrum are presented for the point-like and line-like dark features. The Raman chemical images are based upon a color intensity scale where blue represents low Raman intensity and red represents high Raman intensity. The Thermo Scientific™ OMNIC™xi Raman imaging software allows for a number of ways to view the chemical image. In this case, the color intensity image is based upon the peak height of the band occurring at 685 cm^{-1}. This band location in the chemical image coincides with the dark feature and thus identifies them as oxidized Cu.

For oxidation to occur on graphene coated Cu, as in this sample, oxygen must penetrate the graphene film barrier. Since oxygen would be too large to permeate through graphene it is reasonable to assume that it must be coming into contact with the Cu substrate at point defects or tears in the graphene.

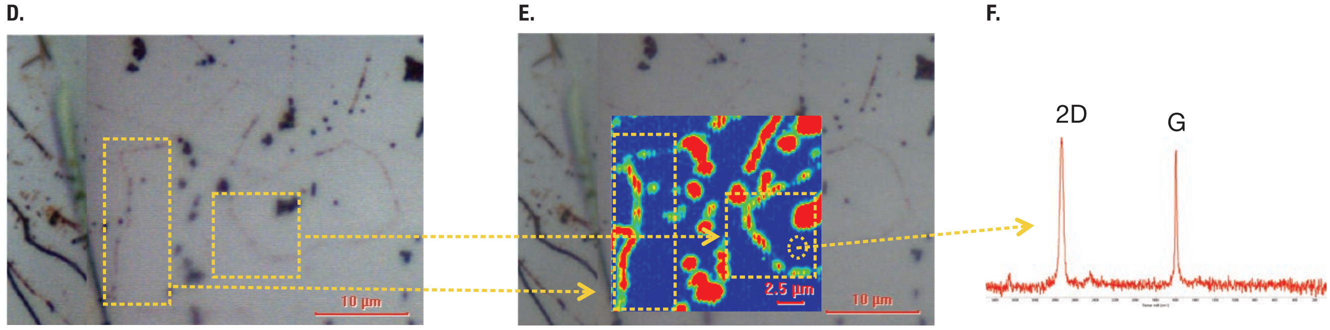
To verify this, the Raman chemical images have been re-analyzed so as to base the color scale on the D band of graphene. The D band will show appreciable intensity when defects are present that disrupts the sp^2 network of bonds and can allow a route for oxygen to permeate across the barrier to cause Cu oxidation. The chemical images shown in Figure 3 have been re-analyzed to display the image intensity color scale as based upon the intensity of the D band of graphene and are presented in Figure 4. It can be seen in Figure 4 that the D band intensity also coincides with the dark features in the optical image just as it does for the Cu oxide band in Figure 3. The D band intensity occurs at point defects, tears, or grain boundaries of graphene which is consistent with oxygen making its way across the graphene via these channels.

A closer look at the two sets of chemical images in Figures 3 and 4 reveals that the D band based features are smaller (i.e. narrower) than the Cu oxide band features. This broadening of the oxidation beyond the D band is most likely the result of oxygen migrating underneath the surface of the graphene once it has made its way across the graphene via the point defects, tears, or at grain boundaries. This work questions whether the heating process or the heating in air caused the defects and thus, the route of oxidation. Future studies will be pursued to address the important issue of the temperature stability graphene coatings.

Figure 3.

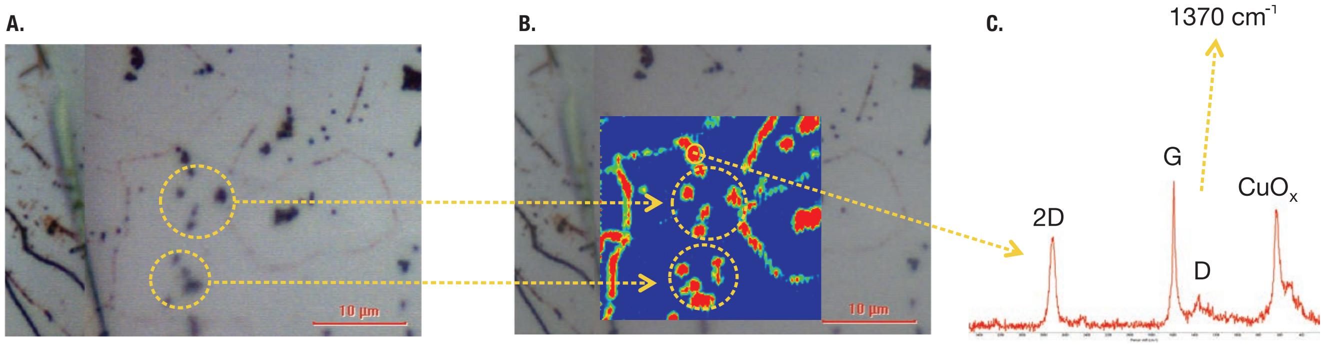


A. Optical image of point-like features in the annealed single layer graphene on Cu substrate
B. Raman chemical image overlaid on top of the optical image
C. The spectrum observed at the point identified in the chemical image (pure red) shows considerable intensity of this CuO$_x$ band. The chemical image is based on color contour intensity scale associated with the 642 cm^{-1} band of CuO$_x$.

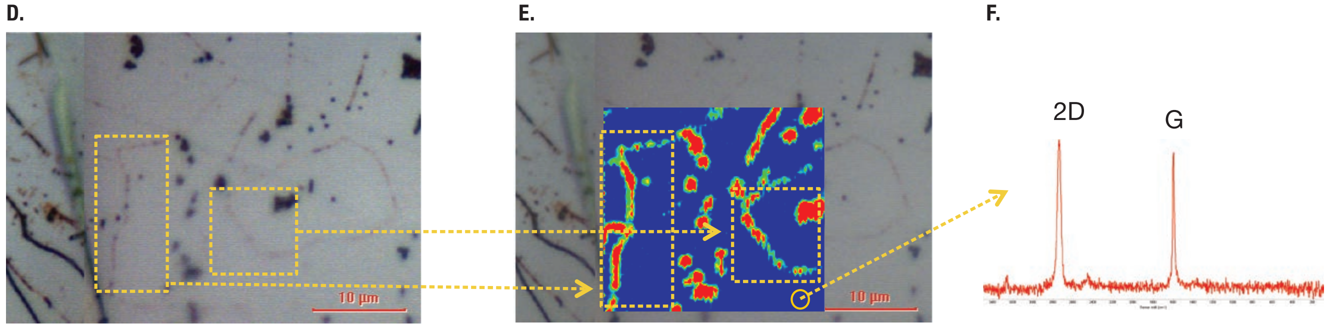


D. Optical image of the line-like features in the annealed single layer graphene on Cu substrate
E. Raman chemical image overlaid on top of the optical image
F. The spectrum was taken at a position that is not associated with the dark feature (i.e. an area where the Cu substrate did not exhibit oxidation)

Figure 4.



A. Optical image of point-like features in the annealed single layer graphene on Cu substrate
B. Raman chemical image overlaid on top of the optical image
C. The spectrum observed at the point identified in the chemical image (pure red) shows the chemical image is based on color contour intensity scale associated with the D band of graphene occurring at 1370 cm^{-1} the spectrum displayed exhibits significant D band intensity



D. Optical image of the line-like features in the annealed single layer graphene on Cu substrate
E. Raman chemical image overlaid on top of the optical image
F. The spectrum was taken at a position not associated with the dark feature (i.e. an area where there is not an appreciable D band)

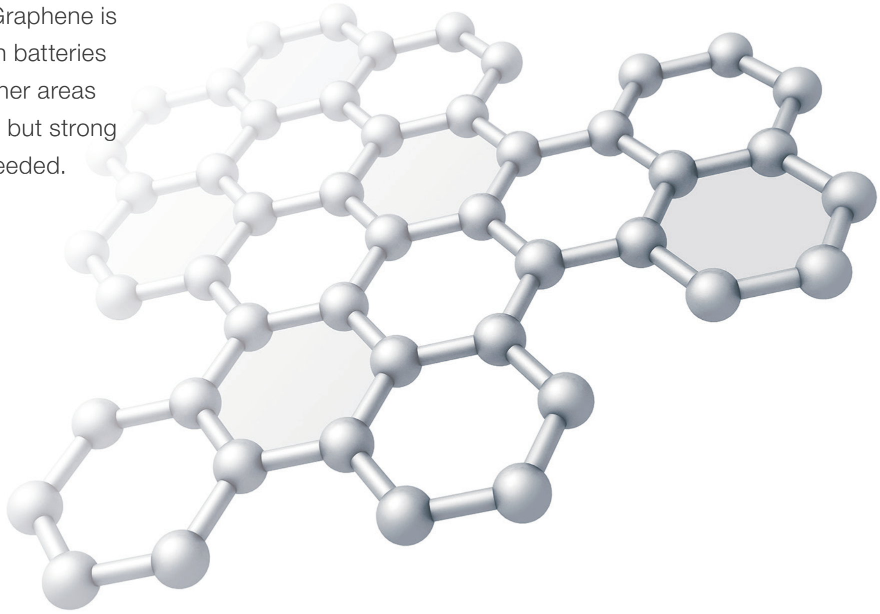
The Thermo Scientific DXR3xi Raman Imaging Microscope used in this study.

Conclusions

Rapid Raman imaging was used to investigate the protective capabilities of single layer graphene. It was shown that Raman imaging can be used to investigate failure points in the protective barriers that were induced with high temperature annealing of single layer graphene coated Cu. In this study Raman imaging revealed the chemical nature of the discoloration and insight into the mechanism underlying the behavior.

The data were collected using an older model instrument DXRxi Raman Imaging Microscope. Currently, Thermo Fisher Scientific offers an improved model, the DXR3xi Raman Imaging microscope, which offers superior speed and performance over its predecessor model.

This is a graphical representation of graphene. Graphene is one of the major constituents for making modern batteries more powerful. However, graphene is used in other areas as well - other electronics, and items where light but strong (sometimes as strong as metals) materials are needed.



Learn more at **thermofisher.com/energy**