Uncovering the Secrets Governing the Chemical Vapor Deposition of Graphene with Rapid Raman Imaging

Mark H. Wall, Thermo Fisher Scientific, Madison, WI, USA
Robert M. Jacobberger, Dept. of Material Science and Engineering, University of Wisconsin, Madison, WI, USA
Elena Polyakova, Graphene Laboratories, Ronkonkoma, NY, USA

Key Words

DXRxi Raman Imaging Microscope, Copper Substrate, Chemical Vapor Deposition, CVD, Graphene Synthesis, Partial Growth Studies, Single Layer Graphene Films

Introduction

Since its first isolation in 2004, graphene has received an enormous amount of interest due to its unique mechanical, electronic, thermal, and optical properties. A variety of techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and Raman microscopy have been used to characterize graphene, uncovering an immense amount of information.

Raman microscopy, in particular, has had a profound impact on the understanding of graphene. This information-rich spectroscopy can be utilized to gain insight about graphene on the molecular level. For example, the Raman spectrum of graphene can be used to simply and accurately determine the number of layers present, from a single-layer sample to a sample with up to twenty layers. The Raman spectrum can also be used to determine the overall quality and uniformity of graphene films. A previous application note is available illustrating these results *Thermo Scientific Application Note (AN) 52252: The Raman Spectroscopy of Graphene and the Determination of Layer Thickness.*

One major challenge currently facing the graphene industry is the difficulty in controlling the quality of graphene sheets when produced over large areas using industrial scale techniques. The key to solving this challenge lies in gaining a thorough understanding of the synthetic methods used to fabricate macro-sized single-layer graphene films.

In this work, we show how Raman imaging can be used to gain important insight with respect to critical parameters and mechanisms that govern the nucleation and growth of graphene via chemical vapor deposition (CVD). We use this knowledge to develop scalable techniques to engineer high-quality graphene samples with superior properties. Additionally, this application note introduces the latest tool available to elucidate the growth of graphene through CVD synthesis, the Thermo Scientific™ DXR™xi Raman imaging microscope.

DXRxi Raman Imaging Microscope

Thermo
SCIENTIFIC

Graphene Synthesis, Partial Growth Studies, and Raman Imaging Microscopy

There are two synthetic pathways to produce single-layer graphene. One route, the top-down approach, starts with graphite (highly oriented pyrolytic graphite or HOPG) and through either mechanical or chemical exfoliation, single-layer graphene is obtained. This method yields high-quality graphene but the number of graphene layers cannot be controlled and the sample size is limited to tens of microns, making its scalability unfeasible. The other approach, which includes CVD, relies on bottom-up, chemical methods to synthesize single-layer graphene sheets.

In the CVD process, carbon precursors are converted into graphene on a catalyst surface. In this work, methane is used as the precursor and copper is used as the catalyst. The CVD reaction typically occurs at high temperatures around 1000 °C. During CVD, the carbon precursors adsorb on the catalyst surface and are subsequently decomposed to form different carbon species that serve as the fundamental building blocks during the graphene growth. These carbon species diffuse on the catalyst surface until they eventually react with each other to form small carbon clusters. Once the carbon clusters exceed a critical size, graphene crystals nucleate. As the deposition progresses, carbon species continue to add to the edges of the graphene islands, eventually resulting in a continuous, single layer of graphene. Once a complete monolayer has formed, additional layers typically do not grow due to the low reactivity of the graphene surface compared with that of the catalyst. The nucleation and growth are highly dependent on the synthesis conditions, including the growth temperature, pressure, and precursor flux and composition, and the catalyst properties, including the crystallinity, composition, crystal facet, and surface roughness.

The deposition can be stopped prematurely before the individual graphene islands have merged together to obtain information about the crystal growth. These partial growth studies allow us to understand how the synthesis parameters listed above affect the graphene crystal shape, orientation, crystallinity, nucleation density, defect density, and evolution (Jacobberger, R. M.; Arnold, M. S. Chem. Mater., 2013, 25, 871–877). For example, in the low pressure regime, the vertices of the graphene islands extend along specific copper crystallographic directions, resulting in shapes that reflect the underlying copper lattice [squares on Cu(100), rectangles on Cu(110), and hexagons on Cu(111)]. On the other hand, in the atmospheric pressure regime, the islands are hexagonally-faceted on all surfaces, indicating that the crystal morphology is independent of the underlying copper orientation. In addition, increasing the hydrogen-to-methane flux ratio results in a dendritic-to-planar transition, resulting in more planar, thermodynamically-favored crystal shapes with smoother,

less defective edges. Figure 1 is a scanning electron microscopy image showing dendritic growth of graphene synthesized in the low pressure regime on Cu(111) with low hydrogen-to-methane flux ratio.

Figure 1: SEM image of dendritic graphene growth on Cu(111) that was synthesized using low pressure CVD with low hydrogen-to-methane flux ratio.

SEM illustrates the morphological characteristics that result from particular CVD deposition conditions; however, other techniques are required to get deeper insight into the deposited graphene. Raman spectroscopy, in particular rapid Raman imaging, provides a wealth of information about these partial growth samples. For example, the Raman spectrum of graphene allows determination of the number of graphene layers and provides information about the density of defects incorporated into the graphene lattice during growth. Furthermore, spatial mapping reveals the graphene coverage, nucleation density, and island morphology. This information can be used to understand the critical synthesis parameters and mechanisms that govern the growth and nucleation of graphene and can be used as feedback to optimize growth conditions to minimize the defect density in these graphene films.

Rapid Raman imaging is a relatively new technique that has been made accessible only recently through improvements in detectors, automated stages, data acquisition, and transfer technologies. The instrument used in this application note is the DXRxi Raman imaging microscope. It utilizes the latest technologies in CCD detectors, automated xyz stages, software, and data acquisition and control. Integration of these technologies translates into a system capable of extremely fast imaging with rates of up to 600 spectra/sec over areas as large as 4 × 3 inches at sub-micron spatial resolution. With increased speed of acquisition and larger area imaging capabilities, the DXRxi Raman imaging microscope opens new avenues of study that were not feasible until now. Fast data acquisition, confocal optics, and precise stage movement make this instrument extremely relevant for studying the graphene growth dynamics.

Figure 2 shows a Raman chemical image of partial graphene growth on Cu that has been transferred to SiO$_2$/Si. The Raman image was collected using 532 nm excitation and represents a total of 10,000 spectra over a 50 × 50 micron area. This image was collected in under 17 minutes. With these specific growth conditions, the graphene nucleation is inhomogeneous and the island shape is non-uniform.

The DXRxi Raman imaging microscope comes complete with a comprehensive set of data analysis tools, generating different views or profiles of the data to provide detailed insight into the sample under investigation. This set of tools allows different views or perspectives of the image including: correlation, which is intensity scaling against a known reference spectrum or a spectrum within the data acquired; intensity based on a peak height or area; intensity based on the peak height or area ratio of two peaks; intensity based on peak position; and the statistical method Multivariate Curve Resolution (MCR). The MCR calculation identifies the principal, unique spectral components in the data set. Once the principal components have been identified, a color is assigned to each component, and the image is reprocessed to show the distribution of the color-coded principal components.

The chemical image in Figure 2 was generated using the peak-height-ratio of two peaks in the spectrum of graphene, the 2D peak centered between 2700 and 2800 cm^{-1}, and the G peak centered between 1580 and 1590 cm^{-1}. The color intensity image of the area ratio of the I$_{2D}$ to I$_G$ is approximately 2, which is indicative of the growth progressing uniformly as a single layer without any simultaneous multilayer growth. The image also gives other useful information such as the nucleation density and rate, which is unique to the chosen synthesis conditions.
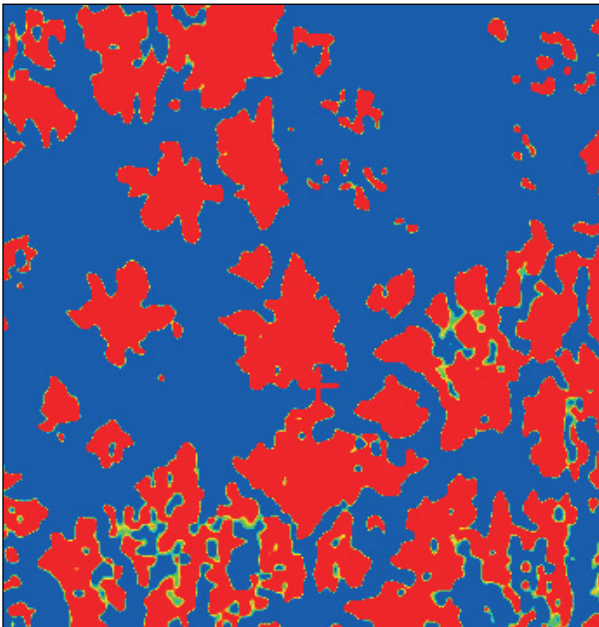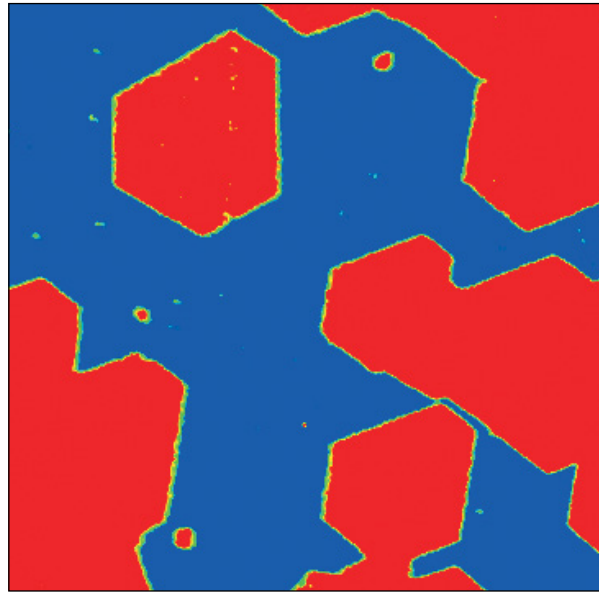

Figure 3: Chemical image of hexagonal graphene islands that has been transferred to SiO$_2$/Si. This image was obtained with 532 nm excitation within a 175 × 175 micron area and 0.5 micron data point spacing. 122,000 spectra were obtained at a rate of 100 spectra/sec., with 10 co-addition scans. The red regions are single-layer graphene and the blue regions are SiO$_2$/Si.

When investigating graphene growth via CVD, it is important that numerous nucleation sites are analyzed. This requires not only fine stage movement for each successive spectrum acquisition but also, in many cases, the ability to acquire a Raman chemical image over large areas. The graphene nucleation sites shown in Figure 2 are relatively small, and thus, a relatively small area can be imaged to investigate a population of sites that is large enough to draw statistically definitive conclusions about the CVD growth dynamics. The ability to spatially map over larger areas becomes important when the nucleation density is small, which is especially true for the study of CVD graphene growth dynamics because one of the main goals is to obtain larger single crystal domains. Figure 3 shows hexagonal growth that originated from conditions leading to a lower nucleation density. MCR was applied and two components were identified namely, single layer graphene, shown in red, and Si, shown in blue.

The larger graphene islands in Figure 3, relative to Figure 2, require a much larger imaging area, and consequently a large number of spectra to be collected to provide the same level of detailed information. The number of spectra acquired in Figures 2 was 10,000 and in Figure 3 was 122,000, were collected over a time of 16.7 minutes and 3.4 hours, respectively. Acquisition of these spectra on a conventional non-rapid imaging Raman microscope would have taken more than 6 hours and 68 hours respectively. Therefore, the DXRxi productivity advantage for these large, detailed area image acquisitions is clear.

Figure 2: Raman chemical image of island growth of monolayer graphene grown on Cu and transferred to SiO$_2$/Si. The image, containing 10,000 spectra over a 50 × 50 micron area, was measured using 532 nm excitation at 3 mW with a collection rate of 100 spectra/sec and 10 co-addition scans. The total collection time was 16.7 minutes.

The samples in Figures 2 and 3 were transferred to a Si/SiO_2 substrate to avoid the fluorescence interference due to the Cu substrate when 532 nm excitation is used for analysis. The steps for transfer of the CVD grown graphene from Cu to Si/SiO_2 involve applying a polymer (PMMA) layer over the graphene, etching away the Cu, transferring the graphene/PMMA membrane to SiO_2/Si, and dissolving the PMMA with acetone. This process is labor intensive and is a possible source of sample contamination and defect creation in the graphene film.

An alternative to this transfer is to directly measure the CVD grown graphene on the Cu substrate using a higher energy laser excitation source, such as a 455 nm laser, which yields a fluorescence-free spectrum. The DXRxi imaging microscope can be configured with a 455 nm laser. As compared to other less energetic, commonly-used excitation sources such as 514, 532, 633 and 785 nm, the 455 nm source does not generate fluorescence from the underlying Cu substrate, thus eliminating the need to transfer graphene to another substrate. This saves considerable time and avoids complications, such as contamination and defects in the graphene lattice, that arise from the transfer process. Additionally, the Raman scattering intensity, which has a $1/\lambda4$ dependence on the laser wavelength, is greater for 455 nm excitation than less energetic laser excitations.

A Raman chemical image of a graphene on Cu(111) samples using 455 nm excitation wavelength is shown in Figure 4. The MCR results reveal three distinct principal components; the bare Cu substrate in blue, single-layer graphene in red, and unexpectedly, oxidized Cu in yellow. The Cu oxidation is due to the sample being stored in ambient conditions. The image reveals preferential oxidation of the Cu substrate at the periphery of the dendritic graphene island relative to bare Cu and the Cu that is underneath the interior of the graphene island. The exact mechanism for this enhanced reactivity towards oxidation at the graphene edges is currently being researched is the subject of a future application note.

Conclusion

This application note highlights the effectiveness of rapid Raman imaging applied to the field of graphene CVD growth dynamics. The integration of a 455 nm laser excitation eliminates the time-consuming and labor-intensive effort of transferring the CVD grown graphene from Cu to a different substrate on which the Raman signal is enhanced and the fluorescence is minimized, such as SiO_2/Si. The detailed insight into the growth process using the Thermo Scientific DXRxi Raman imaging microscope assists in monitoring factors affecting CVD growth. In addition, rapid Raman imaging provides key information in developing CVD methods for single-layer graphene films with lower defect density, and thus, superior properties.
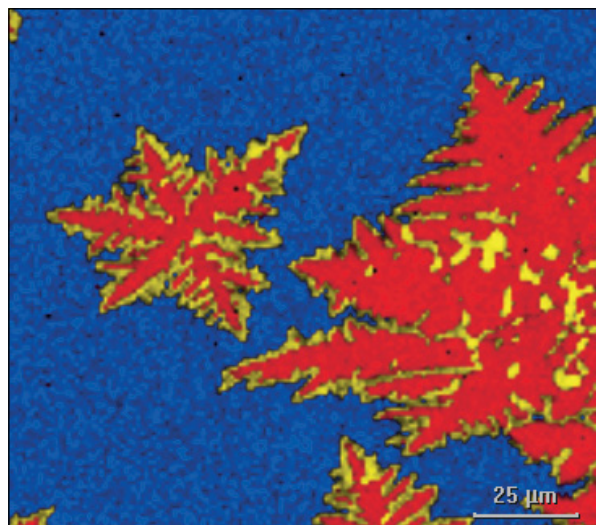

Figure 4: Raman chemical image of dendritic graphene growth on Cu(111). The image represents the results of applying Multivariate Curve Resolution (MCR) to the collected Raman image. The MCR results show that there are three components present, Cu shown in blue, single-layer graphene shown in red, and CuO shown in yellow. As seen here, exposed graphene edges promote Cu oxidation. This image was collected using 455 nm excitation and contains 90,000 spectra over an area of 150×150 micron area.

Africa +43 1 333 50 34 0	**Denmark** +45 70 23 62 60	**India** +91 22 6742 9494	**New Zealand** +64 9 980 6700
Australia +61 3 9757 4300	**Europe-Other** +43 1 333 50 34 0	**Italy** +39 02 950 591	**Russia/CIS** +43 1 333 50 34 0
Austria +43 810 282 206	**Finland/Norway/Sweden**	**Japan** +81 45 453 9100	**Spain** +34 914 845 965
Belgium +32 53 73 42 41	+46 8 556 468 00	**Latin America** +1 561 688 8700	**Switzerland** +41 61 716 77 00
Canada +1 800 530 8447	**France** +33 1 60 92 48 00	**Middle East** +43 1 333 50 34 0	**UK** +44 1442 233555
China +86 21 6865 4588	**Germany** +49 6103 408 1014	**Netherlands** +31 76 579 55 55	**USA** +1 800 532 4752

Thermo SCIENTIFIC

A Thermo Fisher Scientific Brand