Graphene layer number characterization using scanning kelvin probe force microscopy

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As the importance of material surfaces and interfaces for industrial applications is ever increasing, a need for accurate measurement of their properties and functionalities with traceability and reproducibility through unbroken chain of measurements and their reference materials for proficiency testing has become very important. Carbon and its allotropes have several industrial applications and recently graphene which is a two dimensional layered material of carbon has proven to have great potential, and its characterization for layer number has become very important. A need for quantitative measurement apart from existing qualitative techniques is very much required for accurate determination of layer number. Under the aegis of Versailles Project on Advanced Materials and Standards (VAMAS), technical working area (TWA-2) an international round robin test is conducted among 13 laboratories for establishing a protocol for accurate measurement of graphene layer number and generating reference material. CSIR-NPL being NMI of India participated and contributed to the project which got recognition from VAMAS for its participation. Scanning Kelvin Probe Force Microscopy (SKPFM) of graphene layers on $Au/SiO_2/Si$ and SiO_2/Si substrates is performed and their CPD data is compared. Graphene on $Au/SiO_2/Si$ has shown consistent CPD data for different modulation voltages with least uncertainty. From the comparative analysis it is found that SKPFM has potential to be an international standard technique to determine graphene layer number and can generate certified reference material.

Keywords: Metrology, NMI, NPL, BIS, VAMAS, Graphene, AFM, KPFM

1 Introduction

National Quality Infrastructure is needed for any country to become super power with great economy and high standard of living. The Quality infrastructure is determined by unbroken chain of measurements delivered by any instrument under test with those of a calibration standard of known accuracy traceable to SI units. The reliability of the value of a measurement and its associated uncertainty are of crucial importance to manufacturers, operators and investors[1]. In accord with meter convention, International Bureau of weights and measures (BIPM) is formulated and National Metrology institutes (NMI) of all countries being members of the bureau maintain calibration and measurement capabilities (CMC) to disseminate all measurements traceable to SI units through hierarchical procedure of primary standards, secondary standards, reference standards and working standards to measuring instruments of all institutes and industries maintaining quality infrastructure. Pertaining to India, CSIR's National Physical Laboratory (NPL) which is an NMI of India provides traceability and training of measurement, Board of Indian Standards (BIS) formulates all standard protocols and documents for measurement and traceability. On the other hand, National Accreditation Board, NABL provides accreditation to testing and measurement laboratories which have conformity with ISO standards and traceability with respect to NMI measurement and reference standards. Legal metrology under Department of Consumer Affairs ensures public guarantee from the point of security and accuracy of the weights and measurements.

Any research activity to reach the level of commercialization and thereby to industry through technology transfer requires technical feasibility, economic feasibility and sustainability. Carbon and its allotropes are of prime use in industry in several forms like coal, coke, high temperature and high voltage electrodes and high strength materials.

CSIR-NPL is the pioneer of carbon based research and Indian Carbon Society is its offshoot which formulated in 1979. This society is rendering tremendous service to promote the advancement of knowledge of carbon science and technologies dealing with several industrial products by arranging seminar, symposium, discussions and lectures.

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Versailles Project on Advanced Materials and Standards (VAMAS) is an international organization which organizes international collaborative projects aiming at providing technical basis for harmonized measurements, testing, specifications, and standards. Its main objective is to supports world trade in products dependent on advanced materials technologies, Technical Working Area 2 (TWA-2) of VAMAS deals with surface chemical analysis and conducts pre-normative studies helping to ensure that international standards are robust, have inter-operability and are enduring.

The importance of surfaces and interfaces for several applications across a wide range of industrial sectors from drug delivery, imaging of tissue to photo voltaics, nanoparticle catalysts, security applications and aerospace is ever increasing and a need for quantitative measurement of properties and functionalities is on high demand. Authentication of any such measurements needs a standard protocol along with a Bharatiya Nirdeshak Dravya (BND) which is an Indian Certified Reference Material (CRM).

Graphene is one of many crystalline allotropes of carbon which is a perfect thermal conductor, hundred times stronger than steel but yet lighter. It has several applications in the field of optics and electronics. These properties are greatly influenced by the number of layers present and it has become very crucial to determine the exact number of layers. There are several techniques which enable us to determine the layer number, mostly qualitatively. Casiraghi et al. observed few layer graphene and even single layer graphene based on Rayleigh scattering under optical microscope and established the accurate thickness of SiO_2/Si substrates for layer determination[2]. They found that either 300 nm or 110 nm of SiO_2 thickness creates multiple interference constructively to enhance the visibility of graphene and single layer can easily be observed. This is completely qualitative approach but made graphene easily observable and paved the way for understanding its immense properties and for variety of applications. Further our group has worked on making graphene visible on metal substrates. When the metal coating is thin enough to be transparent on SiO_2 it is possible to observe few layer Graphene flakes but is not possible on thick coatings. To enhance the visibility of graphene, the metal film is patterned into regular sub micron disk array. Based on surface plasmon-polaritons scattering of light, the visibility of mono layer graphene even on thick metal substrates can be enhanced[3].

Further graphene can be easily identified by Raman Spectroscopy due to the nature of carbon atoms bonding and their sensitivity to light scattering[4,5]. In case of graphene, Raman spectroscopy is widely used for layer number characterization for $N \leq 4$, albeit qualitative. There are three different ways of characterizing graphene layer number using Raman spectroscopy. First one is G-band position as a function of layer number. The G-band under Raman spectroscopy occurs at 1587 cm^{-1} due to in plane vibrational modes of SP^2 hybridized carbon atoms in graphene. With increase in graphene layer number, the G-band shifts to lower wave number. This shift is highly sensitive and is given by $1581.6 + 11(1+n^{1.6})$. Even though it seems straight forward, the position of G-band is sensitive to other parameters like exciting laser wavelength, strain, defects, doping and temperature. Hence the shift in G-band position could be due to many other factors and lot of uncertainty pertains to layer number characterization. Also G-band intensity increases linearly with increase in graphene layer numbers. Second method is monitoring the D-band also called as defect band which occurs due to ring breathing mode from sp^2 carbon atoms present near the defects. This resonant band has dispersive behavior and is very sensitive to exciting laser wavelength as the position and shape of band can vary significantly with varying laser wavelength. This is generally weak for graphite, pristine graphene and is observed only for defective material. The third method is 2D band which is the result of two phonon lattice vibration. It is not sensitive to defects and is the strong band in graphene ($\sim$2600–2700 cm^{-1}). Unlike D-band method, the 2D band method depends on band position and shape. This method is proven to be effective in determining layer number of graphene between mono layer to that of multi layers of number less than four. To summarize, single layer graphene can be qualitatively identified using Raman Spectroscopy by the ratio of intensities of 2D to G-band. The absence of D-band and the ratio $I_{2D}/I_G = 2$ indicates high quality graphene.

Next to optical imaging techniques, Atomic Force Microscopy techniques are widely used for graphene layer number determination. It has advantage over optical techniques, as it gives direct three dimensional

mapping for topography and size. Even though it is widely practiced worldwide it is highly inaccurate method for graphene layer number determination, especially monolayer graphene whose literature values range from 0.4 – 1.7 nm compared to interplanar spacing of 0.335 nm. The discrepancy from actual thickness ~ 0.4 nm is attributed to several adsorbed layers on SiO_2 like humidity and other atmospheric ions trapped under the graphene sample forming a buffer layer. Along with this tip-surface interactions, image feedback settings and surface chemistry could also affect graphene thickness. Shearer et al have measured accurate thickness of graphene and the role of buffer layer for the measured uncertainty using peak force tapping AFM imaging[6]. It is demonstrated that an optimal force ~ 10 nN during graphene imaging is required to displace the adsorbed layer for accurate thickness measurement of single layer graphene. The adsorbed buffer layer not only affects the physical dimension like thickness but also influences its electronic properties. Joshi et al have demonstrated the effect of buffer layer in shifting the dirac peak which is also called charge neutrality point for graphene based FET and the effect of annealing to minimize this[7].

In the present work, contact potential difference (CPD) measurements on graphene deposited on both gold coated and bare SiO_2/Si (001) substrates using Scanning Kelvin Probe Force Microscopy (SKPFM) are done. This could be an alternative technique to the existing techniques and is carried out to establish a standard protocol through international inter comparison and proficiency testing. This work is carried out as an International Round Robin Test (RRT) study among 13 laboratories across the world under the aegis of VAMAS; TWA 2. This includes NIST USA, NIMS Japan, AIST Japan and NPL UK along with CSIR- NPL India among other laboratories.

Scanning Kelvin Probe Force Microscopy (SKPFM) is a noncontact variant of atomic force microscopy (AFM) for the direct measurement of contact potential difference (CPD) between an AFM tip and a sample surface with nanometer resolution. SKPFM has found diverse applications in material research fields as the surface potential relates to various surface phenomena.

The objective of this RRT is to establish the standard protocol for quantitative CPD measurements and to study the effectiveness of CRM generated through potential calibration.

2 Experimental Section

Two types of graphene samples were supplied for the RRT studies. First sample, sample 1 comprises of graphene layers on gold/SiO_2/Si(001) substrate. Conductive layer under graphene is 5-8 nm gold thin film on 0.5 nm thick titanium layer. Other sample, sample 2 comprises of graphene layers on SiO_2/Si(001) substrate. Both samples were fabricated by mechanical exfoliation of graphite (Graphene Industries Limited, UK). Multimode AFM with Nanoscope V controller (Veeco Ltd, USA) was used for all AFM studies. For scanning Kelvin probe microscopy, co coated tip biased at an ac-amplitude of 1 and 2 V and a modulation frequency ~ 80 kHz was used in interleave potential scan mode with a lift height ~ 50 nm. All the scans were done at ambient conditions of relative humidity ~ 40 % and temperature ~ 24 °C.

3 Results and Discussion

Traceability pyramid established at CSIR-NPL (Fig. 1) shows how all measurements should be traceable to SI units and all manufacturers should maintain unbroken chain of measurements for quality.

The Optical microscope images of mono, bi and tri layer graphene deposited on Au/SiO_2/Si and SiO_2/Si are shown in Fig. 2. Figure 2a shows different layered graphene flakes as numbered and are visible inspite of being deposited on Au film. The visibility of flakes was possible due to thickness of Au film, being very low ~ 5-8 nm. Compared to Fig. 2a, graphene flakes on SiO_2/Si as shown in Fig. 2b are clearly visible. The need for two different samples with graphene layers was for comparison of SKPFM data as it is an electrical characterization technique.

Fig. 1 — (a) Traceability pyramid of measurements and (b) Unbroken chain of measurements for quality.
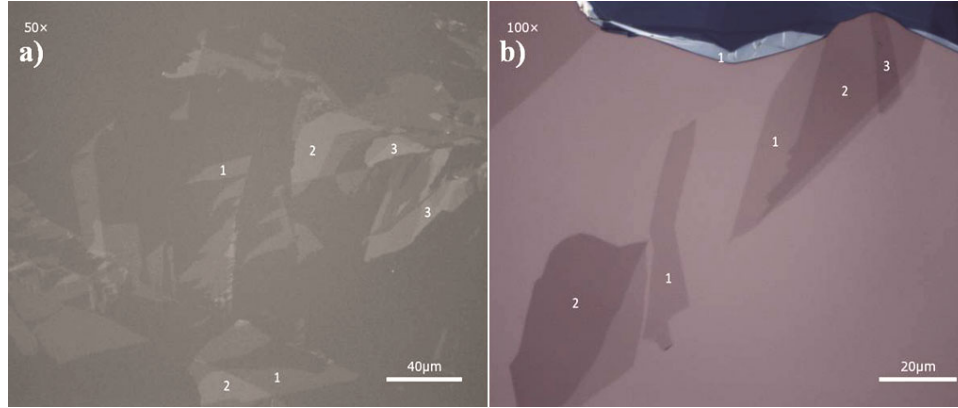*Courtesy: CSIR-NPL*

Fig. 2 — Optical microscope images of (a) Mono-, Bi- and Tri-layer graphene sheets on a Au/SiO$_2$/Si (001) substrate and (b) Mono-, Bi- and Tri-layer graphene sheets on a SiO$_2$/Si (001) substrate.

In SKPFM, the amount of voltage to nullify the electrostatic force generated between AFM tip and sample surface due to their contact potential difference (CPD) which is the difference in work function of two surfaces in contact is estimated based on Fermi level equilibrium model. Measured CPD will also be affected by defects and residual charges present on sample surface[8,9].

The electrostatic force generated between tip and sample due to applied bias is

$$F = \frac{q_s q_t}{4\pi\varepsilon_o z^2} - \frac{1}{2}\frac{\partial C}{\partial z}\left(U^2\right) \qquad \ldots (1)$$

where q_s, q_t are sample and tip charge respectively, ε_o is the permittivity of air, z is the distance of separation, dc/dz is the capacitance variation with separation and U is the applied potential.

The applied potential U is given by

$$U = V_{dc} + V_{cpd} + V_{ac}Sin(\omega t) \qquad \ldots (2)$$

where, V_{dc} is the dc bias and V_{ac} is the modulating ac bias of frequency ω applied to the tip.

In SKPFM several scans with ac bias of different modulation voltage to the tip was done to verify miscellaneous effects due to tip contamination, substrate capacitance and nature of electrical contacts and for consistent measurement. The force/potential required to nullify the contact potential difference is monitored by ac signal when its amplitude reaches zero through counter bias.

For semiconductors, the CPD can be expressed as

$$V_{CPD} = \frac{1}{e}(\phi_m - \chi_s - \Delta E_{fn} - \Delta\phi)^{10} \qquad \ldots (3)$$
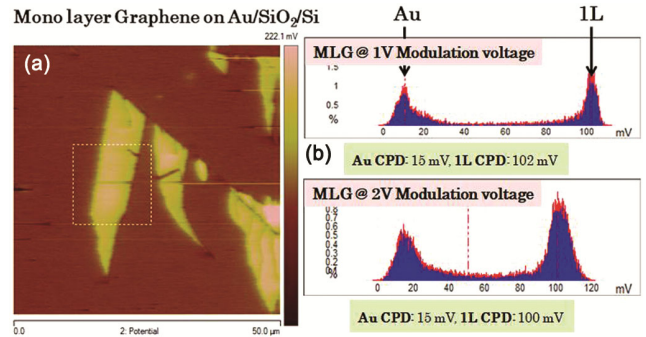

Fig. 3 — Mono layer graphene on Au/SiO$_2$/Si, sample 1 (a) Potential scan for CPD of MLG at 1V modulation voltage and (b) Histogram plots of CPD for Au and MLG at 1V and 2V modulation voltage, respectively.

whereas for metals, the CPD is simply the difference in work functions of tip and sample

$$V_{CPD} = \frac{1}{e}(\phi_m - \phi_s) \qquad \ldots (4)$$

where, ϕ_m is the work function of the tip, ϕ_s is the work function of the metal sample, χ_s is the electron affinity of a semiconductor, ΔE_{fn} is the energy gap of the fermi level to the bottom of the conduction band and $\Delta\phi$ is the band bending due to surface states.

Hence the comparison of SKPFM data with two different substrates will establish the concept and is must for making reference material for graphene layer number characterization using present technique.

Figure 3 shows potential scan of mono layer graphene and their corresponding contact potential difference data for modulation voltages of 1V and 2V, respectively applied at a frequency of 81 kHz. From the potential scan the profile of graphene flake was uniform and rules out any contamination. Also the graphene layer is smooth and uniform. As potential

scan depicts the work function difference between AFM tip and sample surface, taking into consideration the Co tip used whose work function is ~ 5 eV an estimate of the work function of graphene layer can be made. The consistency in the CPD data at two different modulation voltages further confirms that there was no charging effect on the surface due to increased bias. From the histogram plots of CPD in Fig. 2b, calculated CPD values of graphene is around 100 mV with an uncertainty of ±5 mV.

Similar to data in Fig. 3, potential scans for both bi layer and tri layer graphene was done at modulation voltages of 1V and 2V respectively. Figure 4a shows the potential scan data, comprising of mono and bi layer as shown in the rectangular section. The corresponding histogram plots in Fig. 4b points out CPD at 100 ± 5 mV for monolayer and CPD at 170 ± 4 mV for bi layer. As observed the data is consistent and an increase in CPD was observed with increase in layer number. Also the potential scan for tri layer graphene as in Fig. 4c and its corresponding histogram plots on Fig. 4d confirms the behavior of increase in CPD with layer number. The CPD data for tri layer graphene observed were ~ 180 ± 6 mV as shown in Fig. 4d. From the above CPD data and considering the work function of Co AFM tip ~ 5 eV, the work function for mono layer to tri layer graphene ranges from 4.9 ± 0.005 eV to 4.8 ± 0.02eV.

For the sample 2 of graphene on SiO_2/Si, the SKPFM data has yielded completely different effect as shown in Fig. 5. Figure 5a shows potential scan data of mono, bi and tri layer graphene on SiO_2 at 1V modulation voltage. The contrast of graphene layers was poor because of high data scale and due to background SiO_2 which has large potential difference due to electron affinity and fermi energy level difference from conduction band. Figure 5b and 5d showed CPD for several layers of graphene along with SiO_2 for two different modulation voltages. Mono layer graphene has CPD ~ 90 ± 5 mV, bilayer graphene has CPD ~ 118 ± 10 mV and tri layer graphene has CPD ~ 210 ± 4 mV. Inset of Figure 5a and 5b shows CPD from SiO_2 region which has high value ~ 2.5 ± 0.1 V. Also the increase in CPD values for all layers of graphene was observed as compared to CPD values of graphene layers on Au/SiO_2/Si samples. This was due to the charging effect of SiO2 in ambient atmosphere, and can be minimized in vacuum. In ambient atmosphere the capacitance generated on SiO_2 substrate attracted several ions,
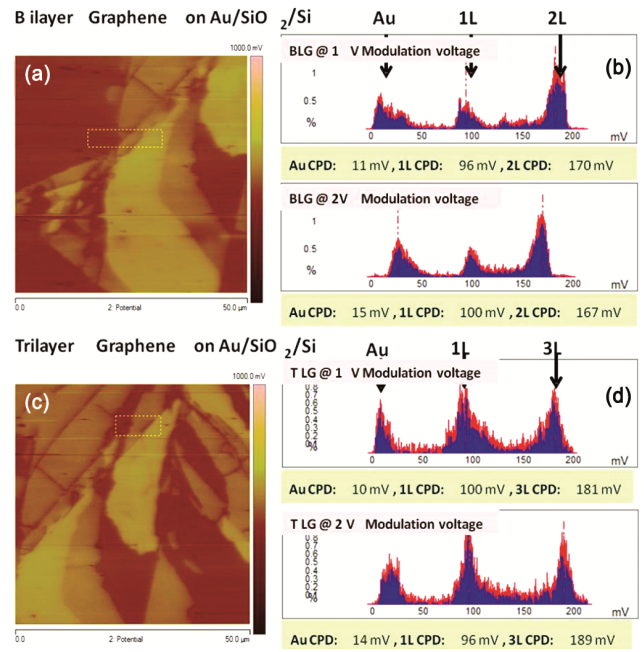

Fig. 4 — Bilayer and tri layer SKPFM data for sample 1 (a & c) Potential scan of BLG and TLG at modulation voltage ~1 V, respectively and (b & d) Histogram plots of CPD for Au , BLG and Au, TLG at 1V and 2V modulation voltage, respectively.
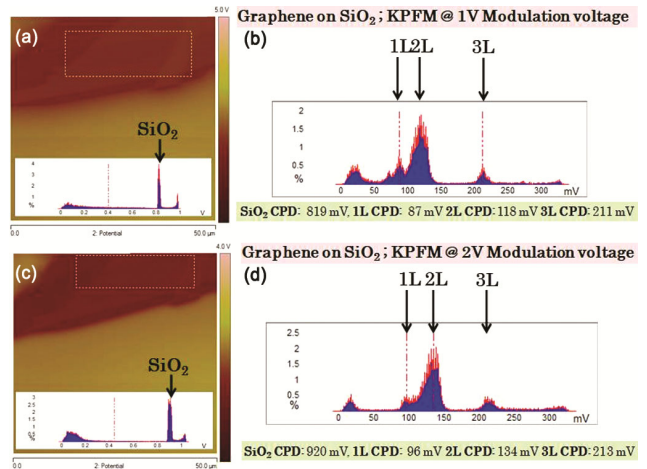

Fig. 5 — SKPFM of mono layer, bi layer and tri layer graphene of sample 2 on SiO_2/Si (a & c) Potential scan of graphene layers at modulation voltage ~1 V and 2V, respectively and (b & d) Histogram plots of CPD for Au, MLG, BLG and TLG at 1V and 2V modulation voltage , respectively.

water vapor and dust particles which would potentially affect the CPD values. Also the electron affinity of SiO2 produced band bending in graphene and increased CPD.

4 Conclusions

In conclusion, SKPFM of graphene layers on Au/SiO_2/Si and SiO_2/Si substrates is done and their

CPD data is compared. Graphene on Au/SiO$_2$/Si has shown consistent CPD data for different modulation voltages with least uncertainty. An increase in CPD is observed with increase in graphene layer number. Sample 2 with graphene on SiO$_2$/Si has shown CPD data with large uncertainty in comparison to sample 1. Also a large CPD value for SiO$_2$ observed is due to high electron affinity. Increase in uncertainty of CPD data is attributed to ambient conditions and charging effects. Also there is an effect of band bending on CPD values of graphene layers due to capacitance from bottom SiO$_2$. From the comparative analysis it is found that sample 1 with graphene layers on Au/SiO$_2$/Si has potential to be a standard reference sample or BND for graphene layer number characterization using SKPFM.

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