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Low Temperature Graphene-Like Film Growth By Microwave Plasma Enhance Chemical Vapor Deposition Technique

Atul Bisht[1], S. Chockalingam[2], O. S. Panwar[3],

1. Deptt. of Physics, Uttaranchal University
2. Polymorphic Carbon Thin Films Group,
3. CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi -110012 (India).

***Corresponding author's :** atul.bisht88@gmail.com

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Abstract: Multilayer graphene like (MLG) film were grown on copper substrates by the microwave plasma enhanced chemical vapor deposition (MW PECVD) technique at low pressure of ~ 5.5 x 10^{-2} Torr. Copper has been used as catalyst substrate for deposition. The growth temperature was found to be 750 ºC. The precursor gas methane was found to dissociate at low temperature with assist of plasma. The MLG films were removed from copper with the help of ferric chloride solution and were transferred to glass substrate. The appearance of 2D band in Raman spectra confirms the growth of graphene film. The highest I_{2D}/I_G ratio was found to be 0.70, which confirms few layer graphene.

Keywords: Multi layer graphene, MWPECVD, low temperature deposition, Raman spectra.

INTRODUCTION

Graphene has attracted significant attention due to its remarkable thermal, electrical, optical and mechanical properties. Graphene is a crystalline monolayer of sp^2-bonded carbon atoms arranged in a regular hexagonal pattern. Optical transparence of up to 97% and electron mobility above 15000 cm^2/Vs has been reported with theoretically potential limits as high as 200.000 cm^2/Vs for free-standing graphene limited by the scattering of graphene's acoustic phonons (Woehrl et al 2014). However, these values are limited by the quality of the graphene itself and the type of substrate. Graphene may be single layer, double layer or multilayer. Graphene with multi layers may be termed as graphene like film (Novoselov et. al 2004). Due to these properties graphene is getting much attention from fundamental as well as applied science and technology. Among various methods, chemical vapor method is considered as best method to grow single layer graphene. It has disadvantage of high temperature and pressure process. Plasma enhances chemical vapor deposition (PECVD) technique has already proved itself as low temperature process to deposit material. Microwave PECVD has its advantages e.g., high ionization, cathode less deposition, high deposition rate. One of the measure problems related to deposition and application of graphene is large area with low temperature deposition. Chemical vapor deposition is prominent technique to deposit high quality grapheme (Wang et al 2010). High temperature deposition is the main problem related to CVD deposition. Plasma enhanced deposition may be substitution to CVD due to low temperature and high deposition area technique (Bisht et al 2015). Surface wave plasma in MW PECVD reduces the temperature to synthesize graphene at low temperatures in the range of 300 ºC to 400 ºC on large area conductive electrode (Kim et al 2011). The necessity of catalytic substrate is also not applicable to PECVD technique. A radio frequency PECVD system was used to synthesize graphene on a variety of substrates (Si, W, Mo, Zr, Ti, Hf, Nb, Ta, Cr, 304 stainless steel, SiO_2, Al_2O_3), without any special surface preparation operation or catalytic deposition . The resulting graphene like carbon structures grown by PECVD technique, often lack of quality being FLG with considerable amount of defects due to continuous bombardment of high energy species presented in plasma (Woehrl et al 2014).

In this study we have grown graphene like film on Cu substrate at low temperature of 750 ºC and low pressure of 5 x 10^{-2} Torr pressure.

Experimental Details

Graphene like film were grown on Cu substrate by MW PECVD system. MW PECVD system consists of 1.2 kW generator, tuner, waveguide and deposition chamber. The deposition chamber is separated with microwave component by a quartz window. The deposition chamber has been equipped with a turbo and rotary pump and vacuum up to 2 x 10^{-7} Torr was achieved with the help of molecular and rotary pump. C_2H_2 gas was used as a carbon precursor, with hydrogen and argon as carrier gas. The substrate was cleaned by plasma treatment at high temperature. The deposition time was varied from 30 s to 2 min. The cu substrate was etched with help of ferric chloride solution and the film was transferred to glass substrate. Due to the multilayer, graphene sustained the transferred process, whereas the single layer graphene is too fragile that it cannot be transferred without the PMMA coating. The film was characterized by the Raman spectroscopy and scanning electron microscopy (SEM). The structure and bonding information of the samples were studied by Raman spectroscopy (Renishaw, micro-Raman model in Via Reflex) with 514 nm laser excitation at room temperature.

RESULTS AND DISCUSSION

Fig. 1 shows the optical image of MLG film grown on the copper substrate. The optical image of MLG film on copper for etching in $FeCl_3$ solution and subsequently transferred to the DI water is also shown in Fig. 2.

Fig. 1 Optical image of MLG

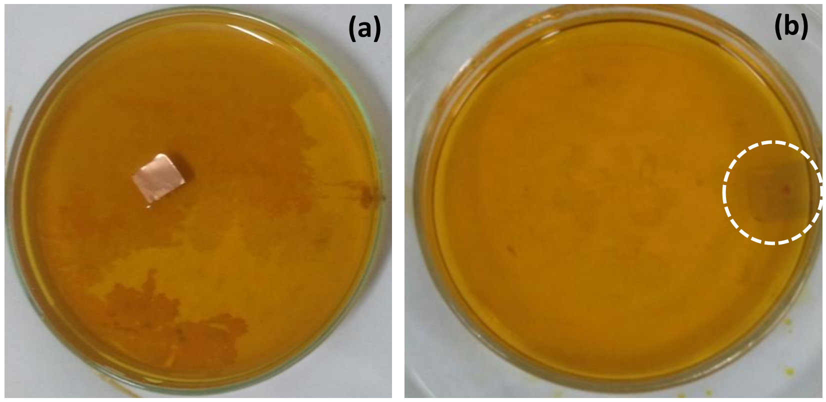

Fig. 2 Optical image of MLG film transferred to a Si wafer

The growth of graphene in the PECVD technique is a competitive process in which there is a competition between the growth by carbon radicals and etching of amorphous or disordered carbon by the atomic carbon (Boyd et al 2015). Kalita et al. 2012 have proposed that during the growth of graphene in the PECVD technique, carbon radicals present in the plasma are continuously absorbed on the Cu surface and bind together in sp^2 bonded graphene film by the diffusion process. In contrast to Ni and Co, the temperature required to dissolve carbon on the Cu lattice is very high~ 2700 °C. This temperature is very low compared to the maximum temperature needed for the growth of graphene on Cu at ~1000 °C. Cu has the lowest carbon affinity to form a carbide phase (0.001-0.008 % wt. at 1084 °C) (Mattevi et al 2011). The absorption-decomposition mechanism is responsible for the graphene growth on Cu lattice rather than the dissolution-precipitation mechanism in Ni and Co metal (Peng et al 2013). Cu is an important substrate for a single layer graphene deposition by the CVD technique as copper acts as a catalyst for the hydrocarbon dissociation. The MLG growth is possible in the plasma based technique as the carbon radicals are generated by the plasma and have no much effect of the substrate. The carbon radicals with hydrogen detachment induced by the microwave plasma formed sp^2 carbon film on the copper substrate (Kalita et al 2012). The low temperature growth of MLG even at 240 °C is possible in the plasma based techniques as carbon atoms or radicals are supplied by the plasma, and there is not much effect of the substrate (Thouti et al 2013). The Ar assisted smooth, uniform plasma and high carbon radical density induced by the microwave provides MW-PECVD as a rapid growth process.

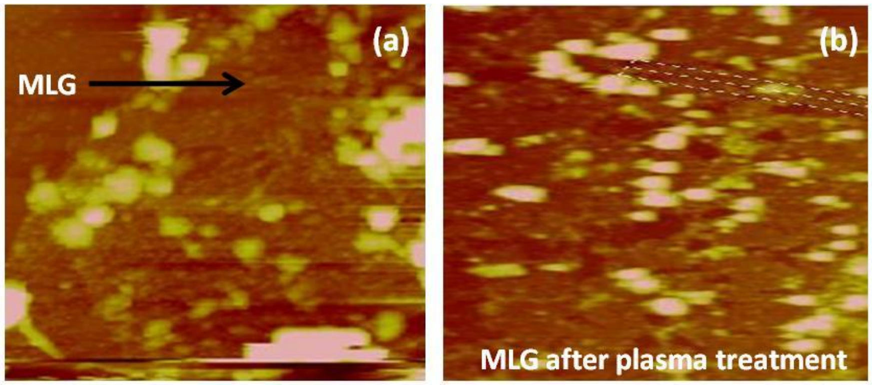

Fig. 3 AFM image of MLG film without plasma treatment and plasma treatment.

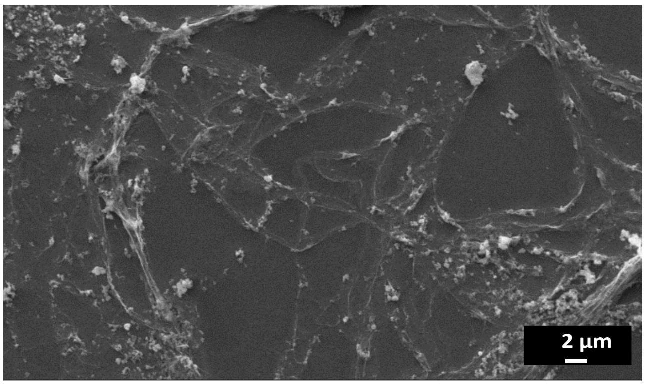

Fig. 4 MLG film transferred to a Si wafer.

Fig. 3 depicts the AFM image of MLG film transferred to the Si wafer. The sheet is clearly visible in image. The SEM micrograph in Fig. 4 show, during deposition at high temperature and in the presence of plasma, the MLG film is sustained during the deposition process.

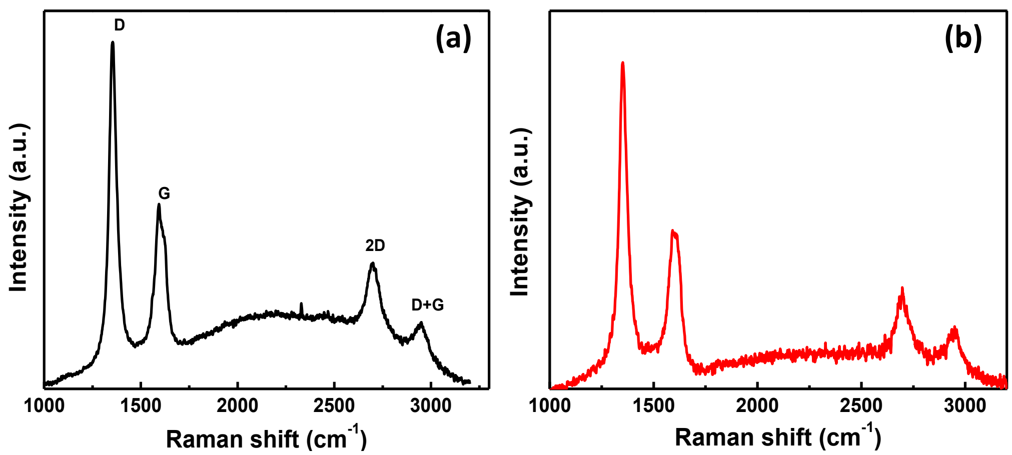

Fig. 5 Raman spectra of MLG film grown on copper

Fig. 5 shows the Raman spectra of MLG film on the copper deposited for different times.

All the samples show a disorder induced D band at around 1350 cm^{-1} due to the phonon scattering at the defective site and impurities. The band is generally absent or weak in graphite or high quality graphene. The G band with a peak position varying from ~1590 to 1600 cm^{-1} originates due to E_{2g} in plane vibration of the sp^2 carbon atoms. A second order band 2D with position varying from 2690 to 2697.9 cm^{-1} and D+G band occurs at ~ 2940 cm^{-1}. The difference between the Raman spectra of MLG and graphite is the shape of the 2D band. In the MLG, the 2D band is symmetric, whereas, in graphite the 2D band is non-symmetric with a shoulder appearing in the left. The D peak is prominent in all the samples which may be correlated to the non-coalescence of the graphene domains as D band is associated with the edge defects and the direct expose to the plasma also affects adversely the graphene film (Woehrl et al 2014). The quality of Cu substrate also affects the graphene film growth as it is preferably a defect free and smooth Cu substrate, which is achieved in multi-steps e.g. electroplating, annealing, etc. This may also be the reason for the prominent D peak as the MLG film is grown in a single step. Such type of Raman spectra with the prominent D peak is an important spectral feature of the graphene film grown by the PECVD technique at low temperature (Woehrl et al 2014). The high amount of defect density in the PECVD grown graphene is due to the energetic particle from the plasma interacting with the growing graphene surface. The I_D/I_G ratio has been found to be 1.9, 2, 1.7 and 1.3 for the sample deposited at different times, respectively. The number of graphene layer can be calculated from the intensity ratio of 2D and G band. The I_{2D}/I_G ratio is varying from 0.70 to 0.45 with the increase of deposition time from 30 s to 2 min. D+G band is also due to the defects in sp^2 sites and graphene domain edge in the MLG film (Kalita et al 2012). The I_{2D}/I_G ratio is showing that the numbers of layers are varying in the range of 6-10. Origin of the similar D+G band is a feature of the Raman spectra of MLG film deposited by the plasma based techniques. Although high intensity of D peak shows that the quality of graphene film is not so good compared to the CVD grown graphene but Kim et al. 2011 have demonstrated capacitive touch panel cab be realized with similar graphene film.

CONCLUSIONS

We have demonstrated a synthesis of MLG on copper by MW PECVD technique at low pressure. Optical image and SEM micrographs are confirming the transmittance of the MLG film deposited at different times, which has been found to vary from 82 to 91.8 %. The low temperature process may find applications in semiconductor industry.

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