Low temperature synthesis of graphite on Ni films using inductively coupled plasma enhanced CVD†

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Controlled synthesis of graphite at low temperatures is a desirable process for a number of applications. Here, we present a study on the growth of thin graphite films on polycrystalline Ni films at low temperatures, about 380 °C, using inductively coupled plasma enhanced chemical vapor deposition. Raman analysis shows that the grown graphite films are of good quality as determined by a low \( I_G/I_D \) ratio, ~0.43, for thicknesses ranging from a few layers of graphene to several nanometer thick graphitic films. The growth of graphite films was also studied as a function of time, precursor gas pressure, hydrogen concentration, substrate temperature and plasma power. We found that graphitic films can be synthesized on polycrystalline thin Ni films on SiO\(_2\)/Si substrates after only 10 seconds at a substrate temperature as low as 200 °C. The amount of hydrogen radicals, adjusted by changing the hydrogen to methane gas ratio and pressure, was found to dramatically affect the quality of graphite films due to their dual role as a catalyst and an etchant. We also find that a plasma power of about 50 W is preferred in order to minimize plasma induced graphite degradation.

1. Introduction

Nanostructured carbon materials (carbon nanotubes (CNTs) and graphene) are being studied as alternatives for future devices and interconnect applications because of their unique properties.1–7 Recent studies of interconnects in integrated circuits fabricated using CNTs8,9 and graphene10 have demonstrated a high breakdown current density of up to \( 10^9 \) A cm\(^{-2}\), which is about three orders of magnitude higher than Cu wire interconnects. This along with their high resistance to electron migration makes sp\(^2\) carbons appealing for device applications.

Commercial graphite is largely produced by thermal annealing of petroleum cokes and coal tar pitches in furnaces at very high temperatures of up to 3000 °C.11 Over the past 10 years in an effort to grow graphene, graphitic film growth at temperatures as high as 1300 °C has been rediscovered.12 The process takes place by a thermal dissociation of hydrocarbons on transition metal substrates followed by dissolution of carbon in the metal at high temperature13–17 followed by segregation and precipitation of the supersaturated carbon upon cooling to form large area and high quality graphitic films. However, the typical temperature at which graphite is formed is not compatible with silicon BEOL thermal budgets. Recently, there have been many reports on the growth of graphite films at reduced temperature using plasma enhanced chemical vapor deposition (PECVD)18–22 where plasma, instead of heat, is used to dissociate the hydrocarbon sources. PECVD synthesis of large area, high quality graphene and few layer graphene films has been reported at ~700 °C on metal substrates such as Cu,23,24 Ni25–27 and Co.28 However, for some applications, lower growth temperatures are desired in order to integrate sp\(^2\) carbons directly into device flows rather than transferring the films as is currently done for graphene films.

In this work, we present a detailed study on the growth behavior of graphitic films on polycrystalline Ni substrates using inductively coupled plasma enhanced chemical vapor deposition (IC-PECVD). The growth temperature in our work is lower than 475 °C, a temperature range outside of what is reported to be necessary to promote graphitic film growth on Ni by precipitation.29 Our results strongly suggest that good quality, thick graphite films of several nanometers can be obtained at temperatures as low as 380 °C and growth of sp\(^2\) carbon as observed at temperatures as low as 200 °C. We also studied the influence of the growth conditions, namely growth time,
temperature, plasma power and precursor composition on the quality of graphite. The as-grown graphitic films were then characterized using Raman spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

2. Experimental

The graphite films were grown on sputtered Ni polycrystalline films (~500 nm) on the SiO₂ (200 nm)/Si substrate in a commercial PECVD chamber. As schematically shown in Fig. 1, the plasma setup is an ICP generator operating at 13.56 MHz and is mounted on a high vacuum stainless steel chamber, 16 cm above the sample heater. The growth chamber is evacuated using a turbo pump to maintain high vacuum conditions at around ~10⁻⁸ Torr and the substrate is placed directly on the heater. Growth of the graphite films was performed as follows: (1) the Ni film was annealed at 380 °C in a hydrogen and argon gas environment with a flow ratio of 40:40 standard cubic centimeters per minute (sccm) for 1 hour to clean the Ni surface and to stabilize the Ni microstructure; (2) the Ni surface was then exposed to a mixture of H₂ and Ar plasma for 2 minutes with a plasma power of 50 W and an Ar/H₂ flow rate ratio of 40:40 sccm at a total pressure of 20 mTorr; (3) graphite was then grown according to the prescribed recipes. The graphite growth conditions such as sample temperature are varied from 200–800 °C; the gas mixture ratio and flow of argon (Ar), hydrogen (H₂) and methane (CH₄) were 40:30:10 or 70:0:10 sccm (the Ar carrier gas is used to dilute the hydrocarbon gas source and stabilize the plasma); and the growth time was varied from 10 s to 2 h. Note that all temperatures mentioned in this work are the actual growth temperature calibrated using the thermocouple to ensure the accuracy of the growth temperature for every growth run. After deposition, the samples were cooled down to room temperature over a period of 30 minutes under a 100 sccm continuous flow of Ar. The structure of the graphite films was then analyzed using a Renishaw confocal Raman spectroscopic system with a laser excitation energy of 532 nm in an inVia Reflex spectrometer. The laser power was maintained at ~1.5 mW to avoid local laser overheating. For each sample, Raman spectra of at least three random points (spot size: ~500 nm) were collected. Raman mapping images were recorded at a spot step size of 100 nm over a 10 × 10 μm area with a spatial resolution of 200–300 nm. The film composition was also studied by X-ray photoelectron spectroscopy (XPS) using a monochromatic Al Kα (hv = 1486.7 eV) X-ray source equipped with a 7 channel analyzer using a pass energy of 15.0 eV with all scans taken at 45° and a spot size of 100 × 100 μm² with respect to the sample.

3. Results and discussion

3.1. Effect of deposition time

Fig. 2a shows the Raman spectra of graphite films on a polycrystalline Ni surface as a function of growth time at a growth temperature of 380 °C. The graphite films are deposited using methane diluted in Ar at a flow rate ratio of 70:10 sccm and a plasma power of 50 W. After a 10 s deposition time, the deposited films show both D and G Raman peaks at ~1342 cm⁻¹ and ~1596 cm⁻¹, respectively. The D peak is considered as a signature of structural defects present in graphene films while the G peak is associated with the formation of the sp² hybridized carbon network and originates from the doubly degenerated phonon vibrations at the Brillouin zone center. Hence, for a very short deposition time, the Raman results show the formation of defective graphitic carbon on the Ni surface. For longer growth times the 2D peak, observed at ~2705 cm⁻¹, starts to appear.
and becomes stronger. This 2D peak is generated by second-order zone boundary phonon scattering and is sensitive to the c-axis stacking of graphene layers.\textsuperscript{34,35} The appearance of a 2D Raman peak accompanied by a red shift of the G peak at \( \sim 1582 \text{ cm}^{-1} \) after 300 s deposition points towards the formation of Bernal stacked few layer graphene films. Furthermore, the decrease of the D peak and the increase of the G peak intensity suggest that the growing film quality improves with growth time. Increasing the deposition time up to 2 h causes no distinctive changes in the relative intensity between D and G bands, but the 2D band broadens and changes its shape from symmetric to asymmetric with the FWHM increasing from \( \sim 80 \) to \( \sim 94 \text{ cm}^{-1} \), which implies the formation of multilayer graphene films. A similar transition of the initial highly defective graphitic structure to good quality of graphite films has also been observed by other groups at \( \sim 800 \text{ °C} \),\textsuperscript{31,24,26} in which the continuous adsorption of incoming carbon radicals on highly reactive carbon defects, such as grain boundaries or dangling bonds, and graphite edges contributes to the increase of graphite domain size and film thickness.

Fig. 2b and c present the change in the relative intensity ratios of the D\(_r\), G- and 2D-bands, \( I_{D}/I_G \) and \( I_{2D}/I_{G} \), and their respective FWHM as a function of deposition time. The \( I_{D}/I_G \) peak ratio continuously decreases from \( \sim 1.2 \) to \( \sim 0.42 \) as the deposition time is increased from 10 s to 300 s; concurrently, the peak linewidths of the D- and G-bands become narrower from \( \sim 80 \) to \( \sim 53 \text{ cm}^{-1} \) and \( \sim 85 \) to \( \sim 46 \text{ cm}^{-1} \), respectively; an indication of larger graphite domain size and better structural quality. However, our observation on the evolution of the \( I_{D}/I_G \) ratio as a function of deposition time is opposite to that claimed by Peng \textit{et al.}\textsuperscript{29} where extended plasma exposure was found to degrade the graphite film quality at 475 °C. The principal difference that could explain our results from Peng's\textsuperscript{29} chamber geometry as it is related to the plasma source. In our case, the use of the IC plasma setup isolates the substrate from direct plasma contact, thereby reducing damage because of the decrease of Ar ion bombarding energy.\textsuperscript{36}

To confirm the uniformity of the deposited graphite films on the Ni substrate, we performed Raman mapping of the graphite films grown for a period of 300 s at a growth temperature of 380 °C. Fig. 3a shows the G peak intensity map across an area of \( 10 \times 10 \mu \text{m} \). Fig. 3b shows a HR-TEM cross-section image of a graphite film having a thickness of several tens of nanometers.

3.2. Effect of gas mixture pressure

Hydrogen has been reported to play a role in thermal CVD synthesis of graphene.\textsuperscript{37} We find that the same is true in PECVD; Fig. 4 shows the effect of gas source pressure on graphite quality in a hydrogen-free and -rich environment at 380 °C for the same plasma power of 50 W and a growth time of 300 s. The gas pressure is adjusted by using a downstream pressure control under different gas flow rates. Fig. 4a shows the Raman spectra of graphite films deposited using an Ar : CH\(_4\) gas mixture (hydrogen-free) at a flow rate ratio of 70 : 10 sccm. Three Raman peaks, at \( \sim 1346, \sim 1586 \) and \( \sim 2702 \text{ cm}^{-1} \), are observed after 300 s of plasma exposure at 10 mTorr, along with a low intensity peak at \( \sim 2940 \text{ cm}^{-1} \), referred to as the D + G peak, which is believed to be associated with the presence of defective sp\(^2\) sites.\textsuperscript{32} Under these conditions, both D and G peaks are broad and exhibit similar intensities indicative of the formation of a defective graphite film. Upon increasing the gas pressure to 20 and 50 mTorr, the D peak intensity is reduced, accompanied by the disappearance of the D + G peak. As indicated by the Raman spectra, the corresponding D and G peak intensity ratio \( I_{D}/I_G \) also shows a significant reduction, from \( \sim 1.1 \) to \( \sim 0.33 \), upon increasing gas pressure to 50 mTorr from 20 mTorr, as shown in Fig. 4b–d. The FWHM of the G peak also decreases from \( \sim 62 \text{ cm}^{-1} \) to \( \sim 40 \text{ cm}^{-1} \), presumably as a result of improved lattice ordering of graphitic film. This suggests that the graphite quality improves in the absence of hydrogen presumably as a result of a decrease in graphite etching by hydrogen ions.

![Fig. 3](image-url) Fig. 3 (a) Raman mapping of the G peak intensity of graphite films after 300 s deposition time using Ar : CH\(_4\) (70 : 10 sccm) gas sources at a plasma power of 50 W and a growth temperature of 380 °C; (b) HR-TEM image of the graphite film after 2 h growth time under the same deposition conditions as (a) showing thick films up to \( \sim 40 \text{ nm} \).

![Fig. 4](image-url) Fig. 4 (a) Raman spectra of graphite films grown at various plasma pressures using (a) Ar : CH\(_4\) ratio of 70 : 10 sccm; (c) Ar : H\(_2\) : CH\(_4\) ratio of 30 : 40 : 10 sccm at 380 °C and a plasma power of 50 W. (b) Intensity ratio of D to G bands (\( I_{D}/I_G \)), and (d) FWHM of the G band for hydrogen-free and -rich conditions as a function of total gas pressure.
In contrast, when hydrogen is introduced using a gas mixture of Ar–H2–CH4 (hydrogen-rich) at a flow rate ratio of 30 : 40 : 10 sccm, as shown in Fig. 4c, the Raman spectra of the graphite films display an opposite trend in the corresponding D and G peak intensities in reference to those deposited from a hydrogen-free gas source. The increase of the deposition pressure from 10 to 50 mTorr leads to a higher intensity D peak and a lower intensity G peak. Accordingly, in Fig. 4b–d, the I_D/I_G increases from ~0.45 to ~1.05, accompanied by a broadening of the FWHM of the G peak from ~38 cm⁻¹ to ~79 cm⁻¹. This opposite trend in the I_D/I_G, as a function of deposition pressures, is believed to be caused by the variations in the amount of hydrogen species generated in both hydrogen-free and -rich deposition environments. Previous studies have demonstrated that hydrogen can play several complicated roles in the growth of graphene by CVD, such as co-catalyst creating active sites for carbon species, e.g. CHx, surface binding and dehydrogenation, passivation of defects and gain boundaries, C-etching, etc. However, during graphite/graphene growth by PECVD, hydrogen species can be effectively supplied by decomposition of the methane molecule using plasma,29,39 and the amount of these hydrogen species generated for graphite deposition can increase gradually when the gas source pressure increases under hydrogen-free conditions, which leads to the formation of graphite films with large grain size at higher gas pressure. Nevertheless, by adding hydrogen molecules to the gas source, the relative ratio of carbon and hydrogen species can be dramatically increased which can contribute to the formation of hybridized sp³ CHx species and passivation of the carbon active site for continuous graphene growth. Our Raman results show that at 10 mTorr, the I_D/I_G of films grown under hydrogen-free gas sources is lower than that under hydrogen-rich conditions due to the increase in etching of the graphite because of a higher concentration of hydrogen species. These findings suggest that optimizing the hydrogen species concentration is crucial for the synthesis of good quality graphite films.

3.3. Effect of deposition temperature

The effect of the growth temperature on the carbon deposition rate under Ar–CH4 and Ar–H₂–CH4 conditions was also studied as a function of temperature in the range of 200 to 800 °C. A plasma power of 50 W was used to generate the carbon radicals and the deposition time was kept constant at 300 s. Fig. 5a–b shows the Raman spectra of the deposited graphite films. At low growth temperatures, the Raman spectra of the samples grown at 200, 250 and 300 °C show relatively strong and broad D and G bands at ~1355 cm⁻¹ and ~1596 cm⁻¹, respectively, along with a weak 2D band at ~2702 cm⁻¹ and the intensity ratios of D to G bands, I_D/I_G, are found to be above ~1.0. The presence of a very weak 2D peak and high I_D/I_G values is related to the formation of highly defective and small graphitic nanostructures. At low growth temperatures, the mobility of reactive carbon species is relatively low, which could restrict carbon species from forming large sp² networks. At temperatures above 380 °C, the Raman D-band shifts towards ~1584 cm⁻¹, and the band intensity decreases, causing the corresponding I_D/I_G ratio to gradually decrease from ~0.45 to nearly ~0.002 as the growth temperature is increased to 800 °C. In addition, the FWHM of the G band becomes narrower, from ~64 to ~30 cm⁻¹, close to that of graphite;40 and evidences that the crystallinity of the growing film improves with increasing growth temperature. The Raman data of the multilayer graphene films grown at ~500 °C agree well with those reported in other studies,41,42 conducted at similar temperatures. It is worth noting that our demonstration on the successful growth of graphitic films at temperature as low as 200 °C is in contrast to what was reported by Peng’s group, who claimed that graphene layers fail to deposit on the Ni surface due to the negligible carbon dissolution below 475 °C. Jayeeta et al. suggested that the NiC carbide phase formed favorably at low carbon concentration below 480 °C, which impedes the nucleation and growth of single layer graphene on the Ni crystal surface.43 The results presented in this paper suggest that a different growth mechanism is operative and it is not dissolution and precipitation mechanisms as is the case in thermal growth of graphene on Ni reported to date, in which the relatively high carbon solubility of ~2.7 at% at a temperature of ~1000 °C serves as the main driving force for graphene precipitation. At temperatures below 450 °C, the carbon solubility drops to 0 at%, close to the value of ~0.001 at% reported for Cu at 1084 °C,47 and thus the growth mechanism, once a nucleus is formed, is by nucleation and growth of incoming carbon radicals at graphene edges and defects without carbon diffusion from the bulk Ni substrate. The quality of the multilayer graphene films grown at a temperature as low as 380 °C is comparable to films deposited at ~500–600 °C by PECVD.21,41 Unlike the thermal CVD process of Cu where dehydrogenation of hydrocarbon stops due to the poisoning of the catalyst, a continuous supply of CHx species is realized by the plasma and these active carbon species can attach to graphene edges (defects) and gain boundaries, leading to the formation of multilayer graphene films.20,24,41,48 Our results suggest that the deposition of graphitic structure using
IC-PECVD methods is not limited to metal surfaces like Ni but perhaps also on other materials, e.g. hexagonal 2D materials.

The growth of graphitic films on Ni as a function of temperature was also performed using Ar–H2–CH4 gas sources in a hydrogen-rich environment for a plasma excitation power of 50 W and a growth time of 300 s. The Raman spectra are shown in the ESI† Fig. S1. Even though the Raman spectra of these samples demonstrate a similar trend to films grown without hydrogen, the related intensity ratios of D to G bands, I_D/I_G, and the FWHM of the G band are slightly higher. In addition, the etching effect of hydrogen is not obvious at temperatures above 500 °C whereof the graphitic film growth mechanism is dominated by segregation and precipitation mechanisms.14,44,45

To further verify the growth of sp² carbon in the temperature range of 200 °C to 800 °C, the composition of these films was characterized using XPS as shown in Fig. 6a. The XPS spectra of C1s for the films grown at 200, 380 and 800 °C appear to be nearly identical, suggesting that the main components of the carbon films are C bonding sp² structures. However, the Raman spectra, that are more sensitive to structure than XPS, shown in Fig. 6b, indicate that while the films grown at high temperature show a very small D-band and a well-defined 2D band, the films grown at low temperature show a very high D-band and a less developed 2D-band. The microstructure of Ni, shown in Fig. S2 (ESI†), may not have a large effect on the quality of the growing graphite and the Raman spectra of films grown at different temperatures are shown in the ESI,† Fig. S1 and Fig. 5.

3.4. Effect of deposition plasma power

Fig. 7a shows the Raman spectra of graphite films grown for 2 h as a function of plasma power at a growth temperature of 380 °C under hydrogen-free conditions. The intensities and FWHMs of the D, G and 2D peaks of graphene films, found at ~1351, ~1581 and ~2703 cm⁻¹, respectively, degraded when the plasma power is increased from 50 to 150 W. At a low plasma power, below 100 W, low defect density graphitic films are observed as evident from the low ratio of D to G peaks, I_D/I_G, of ~0.45, Fig. 7b. This ratio increases to ~1.0 when the plasma power is increased to 150 W, implying that structural defects are induced by the effects of the plasma, probably hydrogen ion etching, and consequently, the FWHMs of the G band broaden from ~37 to ~83 cm⁻¹. The Raman behavior of graphite films grown as a function of plasma power is in agreement with the results reported by Kim et al.39 The plasma power can influence the graphite grain size by controlling the amount of the active species, in particular, the hydrogen ions generated by plasma. Increasing the plasma power can increase the graphene grain size by increasing the carbon species concentration, however, higher plasma powers can impact the graphite quality in a negative way because of hydrogen ion etching effects. In addition, Lim’s study has shown that the Ar ion density can be increased to about one order of magnitude upon increasing plasma power to 150 W.36 Therefore, as the Raman data suggest, plasma powers below 100 W are more desirable for the growth of good quality graphite. The higher defects observed in graphite films deposited at 150 W could be a result of two potential mechanisms: (1) physical damage from energetic ions, e.g. Ar ion bombardment;36 (2) the etching effect caused by hydrogen ions generated by the higher plasma power. As with previous reports,26,39 it is believed that low plasma power is preferable in PECVD synthesis of graphite films.

4. Conclusions

In summary, we have demonstrated the synthesis of graphite films on polycrystalline Ni surfaces by IC-PECVD at a low temperature of ~380 °C. The graphite films grown in this work show a lower Raman I_D/I_G ratio, ~0.43, compared to those reported by other groups using PECVD at higher temperatures. The Raman studies suggest that graphitic nanostructures can be synthesized on Ni after only 10 s and longer growth times lead to the uniform formation and less defective graphite films with thickness of a few nanometers. Hydrogen was found to play a key role in the quality of graphite. In the case of hydrogen-free conditions, a higher total gas pressure is needed to grow graphitic films with a low I_D/I_G ratio, while lower gas pressure is preferred to deposit graphite of similar quality under hydrogen-rich conditions. The difference between the
two processes is associated with the etching effect caused by excessive hydrogen ions generated by the plasma in the case of the hydrogen-rich process in comparison to the hydrogen-free process. In addition to the graphite films obtained at 380 °C, graphitic nanostructures as determined by XPS and Raman are observed at a temperature as low as 200 °C. The observation of graphitic films at such low temperature, where there is a close to zero carbon dissolubility in Ni, indicates that it is unlikely that the diffusion, segregation and precipitation growth mechanism observed at high temperature is the operating mechanism, rather the growth process proceeds by a nucleation and growth by an edge attachment process. Finally, low plasma power, about 50 W, is preferable in order to minimize the etching effect of hydrogen on the growing graphite film.

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**References**

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