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Microwave plasma deposition of diamond like carbon coatings

D S PATIL, K RAMACHANDRAN, N VENKATRAMANI, M PANDEY* and R D'CUNHA*
Laser and Plasma Technology Division, *Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

Abstract. The promising applications of the microwave plasmas have been appearing in the fields of chemical processes and semiconductor manufacturing. Applications include surface deposition of all types including diamond/diamond like carbon (DLC) coatings, etching of semiconductors, promotion of organic reactions, etching of polymers to improve bonding of the other materials etc. With a 2.45 GHz, 700 W, microwave induced plasma chemical vapor deposition (CVD) system set up in our laboratory we have deposited diamond like carbon coatings. The microwave plasma generation was effected using a wave guide single mode applicator. We have deposited DLC coatings on the substrates like stainless steel, Cu–Be, Cu and Si. The deposited coatings have been characterized by FTIR, Raman spectroscopy and ellipsometric techniques. The results show that we have achieved depositing ∼95% sp^3 bonded carbon in the films. The films are uniform with golden yellow color. The films are found to be excellent insulators. The ellipsometric measurements of optical constant on silicon substrates indicate that the films are transparent above 900 nm.

Keywords. Microwave; diamond like carbon; chemical vapour deposition.

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1. Introduction

Plasma chemical vapor deposition also known as plasma enhanced CVD is a major process for the deposition of coatings/thin films. In this process the chemical reaction takes place in a plasma where ionization of the carrier gas takes place causing atoms to assume electrical charge. The ionized gas requires much less energy to react, which means that less thermal energy is necessary. As a result, deposition temperatures are lower than those for standard CVD and are usually in the 300–350°C range. Ionization energy is generally provided by a high frequency field. At low plasma densities, the high electric fields obtainable in a resonant microwave cavity as in a wave guide single mode applicator with Q approaching ∼1000, it is possible to effect the breakdown of low pressure gas and sustain the microwave discharge required for CVD applications. For good field penetration in the absence of the magnetic field, $\omega_p \ll \omega$, which sets a critical density limit $n_e < \omega^2 \varepsilon_0$ m/e^2. It is evident that plasma electron and ion densities in a microwave discharge are limited to less than a critical density given by $n_e(m^{-3}) = 1.2 \times 10^{-2} \times f^2$, where f is the excitation frequency of the waves in hertz [1]. For a 2.45 GHz frequency such discharges are having the plasma density $n_e \sim 10^{10}$ /cm^3.

Diamond like carbon material (also known as a-C:H) possesses a unique combination of useful properties. Some of these properties include excellent hardness, optical transparency over a wide range of wavelength, high thermal conductivity, high electrical resistivity, good wear resistance, resistance against chemical attack (both acids and alkalis) and lack of magnetic response. Diamond like carbon consists of an amorphous form of the carbon containing both graphitic type bonding (sp^2) and diamond type tetragonal bonding (sp^3). The properties of this non crystalline material cover a wide range and are intermediate between the properties of diamond, graphite and hydrocarbon polymers. The properties depend on the experimental parameters. Under appropriate deposition condition very hard, chemically inert and optically transparent films can be prepared. As the hardness of this material approaches that of diamond it can be used as a protective layer for delicate IR windows where it can act as a chemical and abrasion resistant coating while also providing an anti reflection layer. Because of these useful properties, the thin films of this material are also finding applications as corrosion resistant coating, anti reflection and scratch proof coating on germanium and silicon optics [2]. Another important application of these coatings is for bearings because of their low sliding friction on the metals.

The preparation of a-C:H films with diamond like properties requires non thermal equilibrium growth conditions. Most important is growth under ion bombardment at low substrate temperature ($<200^\circ$C). For the deposition of a-C:H films, several techniques which provide energy deposition to the growing a-C:H films are appropriate e.g. chemical vapour deposition (CVD), physical vapour deposition (PVD), laser CVD, direct ion beam deposition, dual ion beam sputtering, rf and dc glow discharges [3,4] or microwave discharge [5]. For this deposition condensation of energetic hydrocarbon ions is required; this can be achieved by direct ion beam deposition, or more easily by deposition from hydrocarbon glow discharges onto bias substrate [6]. When hydrocarbon gases are decomposed in a discharge operated at frequencies in the range from dc to GHz, a hydrogenated form of amorphous carbon is produced [7,8]. Microwave discharges have an advantage over dc and rf due to their inherent superiority in terms of quality of discharge. Microwave plasma CVD using methane has been used earlier to deposit crystalline diamonds [9] and DLC deposition from methane or methane-Argon mixture in a dual microwave-rf plasma is reported by Martinu *et al* [5]. The development of low pressure vapor deposition techniques including microwave plasma CVD has increased the prospects for practical use of diamond like carbon films in various technological applications. The properties of the deposited thin films are quite dependent on preparation conditions and they range in hardness from soft polymeric to quite hard coatings. The objective of this work is to optimize the deposition parameters to obtain hard films using microwave plasma CVD process.

Among the various techniques for the characterization of these films [10], Raman and Fourier transform infra red (FTIR) spectroscopic techniques are used extensively for this purpose [11,12].

Carbon atoms occur tetragonally, trigonally or in linearly bonded forms. The free bonds are saturated by hydrogen atoms. Depending upon the deposition method and experimental parameters, the film can contain upto 50 atomic % hydrogen. Hydrogen influences essentially the bonding and network structure of these films. Analysis of the chemical bonds can be performed using FTIR in the spectral region 2700–3100 cm^{-1} wave numbers. The FTIR spectrum shows C–H stretch bands, 3100 cm^{-1} to 2970 cm^{-1} representing sp^2 bonded carbon and 2960 to 2800 cm^{-1} arising from sp^3 carbon bonds [13].

2. Experimental

There has been considerable interest in the microwave induced plasma processing of materials during the last decade because of various advantages over dc and low frequency plasmas. Some of the advantages of the microwave excited plasmas are: higher degree of ionization, wide operating pressure range, high electron to gas temperature ratio and absence of electrodes.

The microwave plasma processing facility (2.45 GHz, 700 W) set up in our laboratory is used for deposition of DLC films. It uses a 2.45 GHz magnetron source powered by a dc power supply. The microwave energy is launched into the wave guide WR284 from the magnetron source. The predominant mode for transmission is TE_{10}. In the circuit there are other components like three port circulator (GL 401 A, Gerling laboratory, USA) and a water cooled dummy load (GL 402 A), cross coupler to extract the signals for measurements of the forward and reflected power (M/S SAIREM, France), a four stub tuner for matching the load impedence (each stub is $\lambda_g/4$ wavelength apart to be able to generate an impedance of any value at any phase), a plasma cavity designed to bring the microwave leakage within the acceptable limit and a sliding short circuit for providing the reflecting surface for the incident microwave radiations so that the Q of the plasma cavity can be increased to get the gas breakdown by the movement of the sliding short.

The plasma generation chamber is a quartz tube which is inserted in the plasma cavity and from the top the processing gases are fed into the tube. The bottom of the tube is connected to a vacuum system (Hind high vacuum company model VS 114, diffusion pump ($\sim$100 mm dia)-rotary pump combination (300 lpm capacity)). There is an arrangement for loading the substrate from the bottom of the quartz tube.

After evacuating the quartz tube to an initial pressure of 10^{-5} torr, microwave plasma was generated using argon as a carrier gas (100 ccs/min) with the application of $\sim$150 watts of microwave power. After stabilization of the plasma, methane (precursor gas 10–15 ccs/min) was introduced along with the argon gas. The final operating pressure was 5×10^{-2} torr. The reflected power was reduced to zero by adjusting the four stub tuners and position of the sliding short. These adjustments also resulted in plasma uniformity over the substrate surface used for depositing the coatings. The final plasma column length in the quartz tube after contraction due to methane addition was around 15 cms. The substrates inserted in the plasma were given the bias of ~ -150 V. The deposition for a period of 1 hour resulted in coatings of around 1 μm thickness. Optically transparent with golden yellow color, electrically insulating and hard DLC films were prepared by plasma assisted chemical reaction involving hydrocarbon species e.g. CH_4. The nature and properties of the deposited films depend on the process parameters i.e. power, gas pressure, gas flow rate and bias voltage. The thickness, hardness and electrical resistivity of the films were measured. The corrosion resistance was seen by putting the coated components in tap water for few weeks. DLC films grown on optically flat Si substrates were used in order to determine its optical constants. Fourier transform infra-red (FTIR) spectra were recorded on a Bomem DA3 spectrometer. Ellipsometric measurements were carried out with a phase modulated spectroscopic ellipsometer (model UVSEL $^{\rm TM}$460, ISA JOBIN-YVON, SPEX) in the range of 300–1000 nm [14].

3. Results and discussion

During plasma CVD process where solid films are deposited at the surface of the substrate, as the films are deposited they are bombarded with ions while they grow and they undergo a process much like heavy quenching. This is most probably responsible for the metastable and mostly amorphous structure of plasma CVD layers. On the other hand ion bombardment also means resputtering of the part of layers while it is being deposited. As this resputtering prefers weak atomic bonds, the stronger ones survive thus imparting high density and microhardness to the resulting layers.

The microwave plasma creates conditions where both sp^2 and sp^3 bonding is favorable. With the proper bias conditions on the substrate, these species are attracted onto the substrates with high energy resulting in the amorphous diamond like carbon coating.

The typical FTIR reflectance spectrum taken on s.s. substrate [15] is shown in figure 1. The deconvoluted peaks are also shown in the figure. The assigned peak position for various C-H stretching modes are shown in table 1.

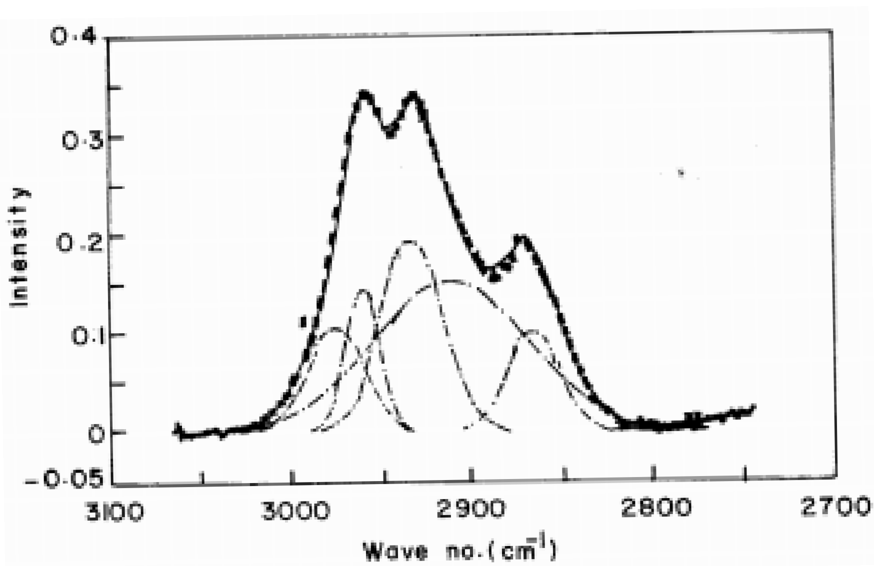

Figure 1. FTIR reflectance spectra (DLC on s.s.).

Table 1. C–H stretch absorption bands.

Sample	Configuration frequency (cm^{-1})	Predicted frequency (cm^{-1})	Observed	% Area
s.s.	sp^3 CH_3 (sys.)	2870	2866.4	10
	sp^3 CH	2915	2912.1	45.6
	sp^3 CH_2(asym.)	2925	2933	23.4
	sp^3 CH_3(asym.)	2960	2961	9.4

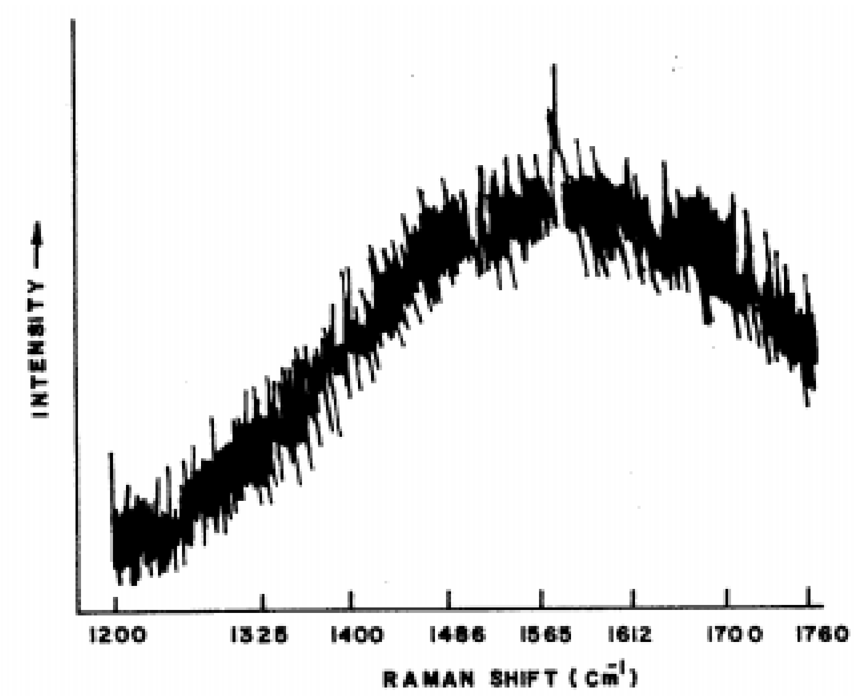

Figure 2. Raman spectra of DLC on s.s.

The ratio of the area of the curve representing particular type of bonding to that of total area under the curve represents the fraction of bond types for carbon which is involved with hydrogen. The ratios of the areas of the C–H absorption envelopes are shown in table 1. It is seen that about $> 95\%$ of the incorporated hydrogen is tied up in the sp^3 bonded carbon. The analysis of the spectrum shows that we have achieved depositing $\sim 95\%$ sp^3 bonded carbon in the films. Thus our analysis confirms the observations of Cauderc and Catherin [12]. The Raman spectra taken on DLC film on s.s substrate [15] is shown in figure 2 and shows amorphous nature of the DLC film. The Raman spectra of the DLC film is quite typical of DLC produced by other methods. The films are found to be excellent insulators with resistivity > 100 MΩ. The thickness of the films as measured by profilometer was ~ 1 μm for 1 hour deposition time and Vickers hardness of DLC coating on s.s. substrate was $\sim$ 2500 Kg/mm^2. Corrosion resistance by putting the coated parts in water for 15 days was found to be excellent.

The ellipsometric measurement data was analyzed to obtain the optical constants. From these studies the optical gap and band tailing were found to be 1.24 eV and 0.12 eV respectively. The variation of the refractive index (n) and extinction coefficient (k) with wavelength is shown in figure 3. The value of the refractive index (n) was found to be maximum at 600 nm while the extinction coefficient (k) was found to be minimum at 900 nm indicating that films are transparent above 900 nm.

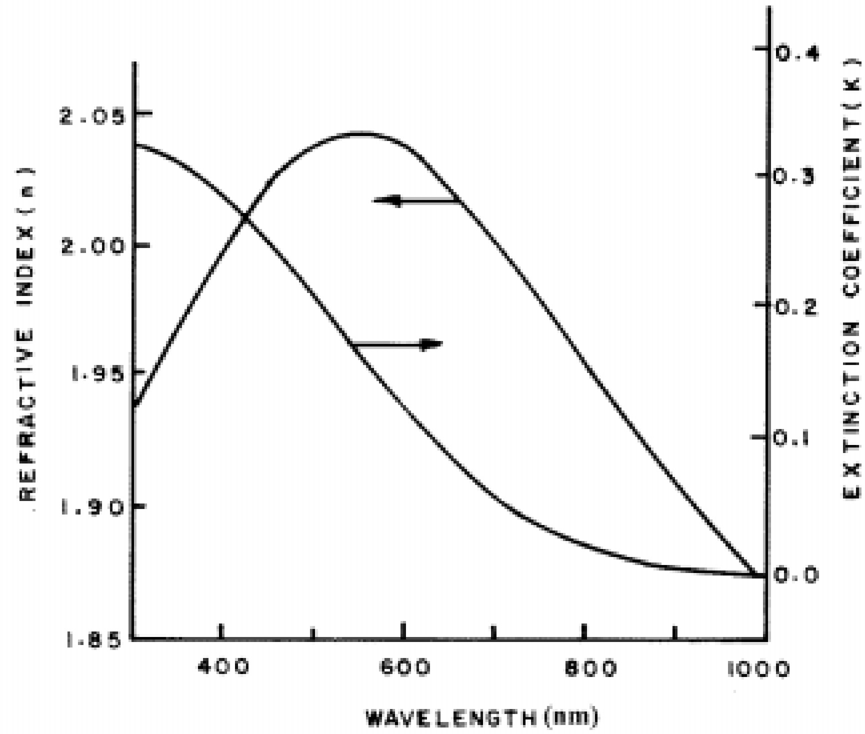

Figure 3. Variation of the refractive index (n) and extinction coefficient (k) with wavelength (DLC on Si).

4. Conclusions

The coatings/thin films deposited during this study using Ar–CH_4 mixtures, which is decomposed in 2.45 GHz microwave plasma are hard diamond like carbon. This is evident from the FTIR and Raman analysis.

The majority of the carbon bonding in the films produced is sp^3. This is seen by Raman analysis and electrical resistivity. The hydrogenated amorphous carbon films contain C–H bonds, more than 95% of which are in sp^3 bonded form as confirmed by FTIR. Ellipsometric measurement of the optical constants indicate that the films are transparent above 900 nm.

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