Investigation of Carbon thin films by pulsed laser deposition at different temperatures

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Effect of temperature on the deposition of Carbon thin is reported in paper. KrF Excimer laser (248 nm, 13-50 mJ and 20 ns) is focused at an angle of 45° on pure graphite target. Silicon (111) wafer, as a substrate is placed at distance of 15 mm from the target surface. The carbon thin films have been deposited at temperatures 20°C and 300°C. 10,000 pulses of KrF laser are irradiated to deposit each film under a vacuum ~ 10⁻⁴ Torr. Surface morphology is investigated by analyzing micrographs of Atomic Force Microscope (AFM). X-Ray Diffraction (XRD) and Fourier Infrared Transformation Spectroscopy (FTIR) techniques are employed for the structure analysis and to study nature of bonding of deposited thin films at different temperatures. Results obtained from techniques AFM, XRD and FTIR support each other and explain the effect of substrate temperature on carbon thin films deposited by Pulsed Laser Deposition (PLD) method.

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1. Introduction

The silicon carbide (SiC) films have attractive properties as wide band gap, high electrical breakdown field, high saturated electron velocities, high thermal conductivity, good radiation resistance, optical transparency from ultraviolet to infrared, high hardness and good electrical and chemical stabilities [1]. These characteristics make the SiC thin films significant technological materials for photo-voltaic, thin films transistors and in optoelectronic devices by changing their band gaps and refractive index. The mechanical strength, chemical stability and radiation resistance at high temperature makes them attractive for heat resistance coating in metallurgy [2].

Various methods are used to grow thin films on substrates as chemical vapour deposition (CVD), sputtering and ion beam implantation. Films produced at low temperatures are usually amorphous. Pulsed laser deposition (PLD) is a very promising method to grow carbon thin films on silicon substrate at high temperature and capable of producing thin layer of a variety of semiconductors [3]. There are a number of suitable and attractive characteristics of PLD sources that make this technique better than the others and have good adherence on a variety of substrates, high hardness, chemical inertness, low friction coefficient, electrical resistivity and have ability to yield higher deposition rates [4,5].

Substrate temperature and the properties of the deposited energetic species are the major factors, effects the growth of thin films on substrate which depend on laser wavelength and fluence. These factors control the atom mobility on film surface and determine the physical characteristics of the deposited films as optical indices, microstructure, composition and bonding structure

between atoms in the deposited carbon films. By varying the pulse voltage and implantation time shows the changes in properties under different implantation conditions [6-10]. The carbon coating formed on the substrate has carbide interface, strengthening film adhesion and exhibit better corrosion. Mechanically, the implanted and annealed carbide layer is stronger [11]. Substrate temperature enhances the mobility of surface atoms, causing dissociating of the weak C bonds and the relaxation of the sub planted C atoms, which contributes to the decrease of other contents and the progressive graphitization of the films deposited at higher temperature [12].

The present paper reports on the carbon thin films deposited on Si substrate by PLD at different temperatures. The aim of study to investigates properties of thin films deposited by PLD in vacuum at different temperature. The diagnostics AFM has been used to study the surface morphology and structural analysis and nature of bonding investigated by XRD and FTIR techniques respectively.

2. Experimental setup

The Excimer (KrF) laser with wavelength 248 nm, pulse energy 13-50 mJ and pulse width 20 ns has employed as a source of energy. Laser is focused through UV lens of focal length 40 cm to irradiate the 4N pure graphite target at an angle of 45°. The target is continuously rotated using step motor to avoid local heat, crater or drilling so that uniform ablation of target is achieved. The silicon (111) has used as substrate, which has placed at distance of 15 mm in front of the target surface where the graphite plume has generated. The experiment has been performed at different temperatures

20 °C (room temperature) and 300 °C (which was achieved by using hydrogen lamp). Film has deposited by 10,000 shorts of KrF laser. The whole experiment has performed in 8-port stainless steel chamber under pressure $\sim 10^{-4}$ Torr, attained by rotary and turbo molecular pump. The structural analysis of deposited carbon thin films is

carried out by XRD and FTIR respectively. The surface morphology of deposited thin films has been done by AFM. The schematic diagram of experimental setup is depicted in Fig. 1.



Fig. 1. A schematic of experimental setup.

3. Results and discussion

When the laser pulse interacts with the graphite (target) and has energy more than the threshold energy of target material, it melts and ablates material from the target surface. Carbon cluster and ions are formed during the ablation and ejection of material from graphite involves different mechanisms as direct ablation, chemical reactions (multi-photon ionization, cascade ionization) and dissociation of large clusters, depends upon laser parameters leads to the formation of plasma plume. Expansion of the plume leads to induce charge separation by fast electrons in form of a sheath. The carbon ions produced by direct ablation are in high field region of plume by forefront electrons. The films grow in these high energy ionization conditions are predominantly have tetrahedral configuration, deposit in an amorphous and stressed configuration. And the deposit film has characteristics low thickness, very smooth surface and general stability to moderate temperature. At shorter wavelength (UV Laser) and higher fluence, smaller carbon clusters are enriched due to photo-fragmentation (multiphoton ionization, cascade ionization) of large clusters. The smaller and high energetic species give a compact and amorphous structure at room temperature [13]. The microstructural analysis has discussed under the following headings:

3.1 XRD analysis

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials [13]. Figs. 2 & 3 represent the XRD pattern (diffractograms) of carbon thin films deposited at temperature 20°C & 300°C respectively.

The XRD patterns show the amorphous structure of deposited thin films. However, the peak at angle $2\theta = 70^{\circ}$ illustrated in Fig. 3 (film deposited at temperature 300°C) corresponds to diamond like structure, have good agreement with R.K. Roy et al. High substrate temperature migrate the incident deposited particles to the energy favourable positions. And high substrate temperature is in favour to the diffusion of atoms on the substrate surface and also gave them acceleration. As a result smoothness and C-axis orientation of film has been observed, which has been indicated by the increase of peak strength and decrease of full-width at the half-maximum (FWHM) value. It is also found that the strength of peak increases and FWHM value decreases [14]. As given in Table 1 and 2 with increase in substrate temperature the intensity of peak corresponding to angle $2\theta = 6.2^{\circ}$ increases while the value of FWHM decreases form 0.72 to 0.59.



Fig. 2. XRD Patterns for Carbon thin film On Si at temperature of 20°C.



Fig. 3. XRD Patterns for Carbon thin film on Si at the temperature of 300 °C.

Table 1. XRD data for C thin film at temperature 25°C.

No.	Pos. [2θ°]	Ip (Counts)	I _r =(I / I _{max}) x 100	d-spacing [Ű]
1	6.2156	468	100	14.22003
2	69.6153	36	18.63	1.34945

Table 2. XRD data for C thin film at temperature 300°C.

No.	Pos. [2θ°]	Ip (Counts)	$I_r = (I / I_{max}) \times 100$	d-spacing [Ű]
1	6.198	458	100	14.24858

3.2 FTIR analysis

Materials at a nano-meter scale often exhibit unusual chemical properties that are helpful for preparation and characterization of different nano structured materials and also in the application of these materials for various purposes [15]. Fourier Transform Infrared (FTIR) spectroscopy provides information about bonds and groups of bonds vibrate at characteristic frequency. The transmittance and reflectance of the infrared rays at different frequencies from specimen is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials.

Figs. 4 & 5 represent the FTIR absorption graph of carbon thin film deposited at temperature 25°C and 300°C respectively. The two spectra confirm the presence of elements Si, C and H and provide information about the bonding between above three constituent elements. The band centred around 2900 cm⁻¹ region, assigned to C-H symmetrical and asymmetrical stretching vibrations show the presence of CH_n groups. The absorption features in the region 1300-1500 characterized the overlapping of the symmetric and asymmetric bending of CH₃ group in Si—CH₃ or C—CH₃. The peak at 680cm⁻¹ represents the Si—C stretching mode [2]. The absorption region 1500-1700 cm⁻¹

¹ characterized the hydrocarbon bonds (such as C—C, C==C, C—C and C—O) [16-18]. The absorption spectrum of deposited film at higher substrate temperature has higher C—H absorption band. This shows with increase in substrate temperature, increases the hydrogen contents in deposited film due to increase in sp³–bonded carbon. The higher absorption peak and wide band gap corresponding to the wavenumber 680cm⁻¹ in Fig. 5 shows the good adhesion of C thin film on Si substrate for higher temperature substrate. The FTIR analysis shows that at high substrate temperature the deposited thin film is smoother and has amorphous structure. The carbon film deposit at low temperature has DLC structure [19].



Fig. 4. FTIR spectra of carbon thin film on Si substrate at room temperature 25°C.



Fig. 5. FTIR spectra of carbon thin film on Si substrate at high temperature 300°C.

3.3 AFM analysis

Fig. 6 shows the typical surface morphological AFM images of carbon thin film deposited on silicon substrate using 248 nm KrF laser at substrate temperatures of 20°C and 300°C. The carbon thin film deposited at temperature 20°C is smoother with roughness of 0.5 nm near to diamond like carbon film thin film deposited for high substrate temperature 300° is less smooth with roughness bout 50 nm. The high roughness of the carbon thin film at low temperature (20°C), because the incident ablated carbon material on substrate surface is less mobile and reside inside the interstitial space. In case of high substrate temperature (300°C) the incident carbon particles are more mobile on the substrate surface due to high substrate temperature and do not reside inside interstitial positions. The nucleation is one of the reasons to smooth thin film

surface at high substrate temperature. The energy of incident laser radiation also plays an important role in smoothness of carbon thin film. With higher laser energy, the ablated particles are more energetic and mobile that affects the smoothness of carbon thin film [20].



Fig. 6. Surface morphological AFM images at different temperature (a) 20°C and (b) 300°C.

b

Fig. 7 shows the three dimensional AFM images of carbon thin film on Si substrate. The films deposited at room temperature are composed of uniform nano-clusters. With increasing deposition temperature from 20 °C to 300 °C, the nano-clusters disappear and big flat features can be observed as in Fig. 7. The further increase of deposition temperature leads to further increase of cluster size to micron. This indicates that the increase of deposition temperature results in the continuous increase in the cluster size [12]. It is found that the smoothness and microstructure of deposited thin film is defined by the temperature of the substrate [21].



Fig. 7. 3D AFM images of carbon thin film at temperature (a) 20 °C and (b) 300 °C.

4. Conclusions

Pulsed laser deposition (PLD) of SiC thin film at high substrate temperature thermal annealing and nucleation results the growth of smoother film. It has found that the substrate temperature is the important parameter for deposition of thin film. At low substrate temperature the SiC film is amorphous predicted by XRD analysis. The FTIR results shows at low temperature the impurity (hydrogen, oxygen etc.) contents in the deposited films are less.

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