Graphite Thin Film Deposition using Laser Induced Plasma

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Abstract

The Excimer KrF laser (of wave length 248 nm, pulse energy of 13-50 mJ and pulse width of 20 ns) has been used to ablate graphite solid target. Thin films of graphite material have been grown on silicon (Si) substrate at different temperatures (25°C & 300°C). The techniques x-ray diffraction (XRD) and scanning electron microscopy has been used to study the structure and surface morphology of the deposited thin films. The whole experiment has been performed in the stainless steel chamber under pressure 10^{-4} torr and each thin film has been deposited for 10,000 laser shots. The graphite thin film deposited at higher substrate temperature has smooth structure and the film is uniform.

Keywords: Pulsed Laser Deposition, Surface morphology, XRD, SEM, Carbon plasma

1. Introduction

Thin films of various materials have significant technological importance in many disciplines as electronic packaging, magnetic recording media, optical devices and chemical and mechanical protection of engineering components. Mechanical properties play a crucial role in the functioning and long-term performance of thin films. Among the mechanical properties of interest, hardness, elastic modulus and fracture toughness are measured using indentation methods [1-3]. The properties (smoothness, transparent insulating, high hardness, low friction coefficient and high mass density) make the carbon thin films useful in a large variety of applications where surface properties are of primary concern. The film properties depend strongly on the method and conditions of formation.
Two key parameters for the film properties are the sp2 to sp3 ratio and the hydrogen content. Different deposition methods have been used to form amorphous carbon films, such as vacuum arc deposition [4-7], laser evaporation [8-10], direct ion beam deposition [11, 12], evaporation with concurrent ion bombardment [13], and various sputtering methods [14, 15].

Amorphous carbon films with diamond-like properties are good materials for a wide range of technological applications. In particular, these films are currently used in the production of hard coatings because of their extreme hardness, chemical inertness and excellent tribological, corrosion and adhesive properties [16].

Understanding the structure-processing relationships important to the deposition of a-C by PLD is further exacerbated by incomplete descriptions of the chemistry and structure of these films. Growth of thin film on substrate is strongly depends on following parameters as laser sources, deposition parameters, target, substrate materials and the ambient conditions. PLD technique has many advantages over numerous standard deposition techniques such as CVD, PVD and MBE etc. specially the stoichiometry of the target is generally maintained with deposition under broad range of ambient environment. The only disadvantage is that the thickness of the deposited film is not uniform [17].

The surface parameters such as absorption and reflection coefficient, normal electrochemical potential, microstructure and morphology, surface binding energy, surface energy play a vital role in determining the use of the deposited thin films or nanostructures the best field where these may be applied. Next generation sensors, detectors, and applications show that nano-structured thick films would be one of the paramount electron and x-rays emitter that could be used in many industrial and medical applications [18, 19].

This paper reports the deposition of graphite thin film on Si substrate by pulsed laser deposition at temperatures 25°C and 300°C. The scanning electron microscope (SEM) used for surface morphology to measure the size of particles (clusters) and XRD technique for structure analysis of deposited thin films at different temperature. The structural parameters as d-spacing, size of deposited particles and dislocation density has been estimated.

2. Experimental Setup

The UV Excimer laser of wavelength 248 nm, pulse width of 20 ns and Pulse energy 13-50 mJ focused tightly with the help of UV lens of focal length ~ 40cm. The laser pulse has been focused at an angle 45° to irradiate 4N pure graphite solid target. To avoid crater step motor has been used to rotate graphite target continuously during laser ablation. The silicon substrate (of dimension 2x2 cm²) has placed at distance of 15 mm normal to the target surface. The in 8-port stainless steel chamber with vacuum system has been used to deposit thin film and the films were deposited under pressure of ~ 10⁻⁴ Torr, maintained by rotary and turbo molecular pump. Graphite thin films have been grown at two different substrate temperature 25°C (room temperature) and 300°C which has been achieved by hydrogen lamp. Each film has been grown on the substrate for 10,000 laser shots. The structural and surface analysis of deposited thin films has done by XRD and SEM respectively. The schematic diagram for experimental setup has shown in Figure 1.
3.1 XRD Analysis

The Figures 2 (a & b) illustrate the XRD pattern of Carbon thin films deposited by pulse laser deposition (PLD) on Si substrates at temperatures 25°C and 300°C respectively. The XRD graphs show that the two thin films deposited at substrate temperature 25°C and 300°C have amorphous structure however the film deposited at high substrate temperature shows some crystallinity. The higher substrate temperature of substrate is in favor to the diffusion of atoms absorbed on the substrate surface and accelerates. The high substrate temperature favor the migration of incident atoms or molecules to the energy favorable positions, resulting in the enhancement of the smoothness of film, which results the increase of peak strength and decrease of full-width and the half-maximum (FWHM) value. Table 1 shows the structural parameters as particle size, d-spacing and the value of FWHM corresponding to angle 2θ. It is found that the strength of peak increases and FWHM value decreases with increase in substrate temperature as the intensity of peak corresponding to angle 2θ = 6.2° increases while the value of FWHM decreases form 0.72 to 0.59.

The structural parameters are calculated using the standard Debye-Scherrer formula [20].

\[ D = \frac{\left( \lambda \times 0.94 \right)}{\beta \cos \theta} \]  

where \( \lambda \) is the wavelength of X-ray, D is the particle size and \( 2\theta \) is the angle between the incident and the scattered X-rays.

The FWHM value of XRD patterns shows with the increase in substrate temperature the dislocation density decreases and many dislocations are annihilated or moved into lower energy configuration. The above results show that the uniformity of the deposited films increases with higher substrate temperature.
### Table 1: XRD data for C thin film at room

<table>
<thead>
<tr>
<th>No.</th>
<th>Position [2θ°]</th>
<th>I₀(Counts)</th>
<th>I_r – (I / I_max) × d-spacing [Å]</th>
<th>FWHM [2θ°]</th>
<th>Particle Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2</td>
<td>468</td>
<td>100</td>
<td>14.2</td>
<td>0.59</td>
</tr>
<tr>
<td>2</td>
<td>69.6</td>
<td>36</td>
<td>18.63</td>
<td>1.3</td>
<td>0.72</td>
</tr>
<tr>
<td>3</td>
<td>6.1</td>
<td>458</td>
<td>100</td>
<td>14.2</td>
<td>0.72</td>
</tr>
</tbody>
</table>

#### 3.2 Surface Morphology

Figure 3 shows the SEM micrographs of graphite thin films deposited on silicon substrate at temperatures a = 25°C and b = 300°C. The graphite particles of varying size and shapes can be seen on the thin films which depend upon generation rate, the velocity, size, chemistry, phase, microstructure and the substrate temperature [21]. The size of most of the particulates lie in the nanometer range and shapes range from spherical to irregular regime, indicative of both liquid and solid ejected material in nanometer regime. The micrometer sizes of the particles illustrate the exfoliation over hydrodynamic sputtering [17]. The particles density is higher for the film deposited at temperature 25°C which shows the film deposited at higher substrate temperature more smooth.

![Figure 3: SEM micrograph image of a C thin films on Si substrate (a)250C and (b)300C](image)

Laser fluence plays important role for the size of particles, laser fluence less than critical value, the variation in particle size and particles density is not significant. Moreover, the placement of substrate with in the plume length there is no marked difference in particle size and the density.
4. Conclusion

Surface morphology and XRD analysis has been investigated for amorphous carbon thin films grown on silicon substrate at temperatures 25°C and 300°C by pulsed laser deposition. The XRD and surface morphological graphs show that the substrate temperature plays important role to the structure and smoothness of deposited film. The deposited graphite thin films at different temperatures are structurally amorphous but film deposited at higher substrate temperature smoother than low substrate temperature.

References