

Effect of substrate bias voltage on the properties of diamond-like carbon thin films deposited by microwave surface wave plasma CVD

Sudip Adhikari ^{a,*}, Dilip Chandra Ghimire ^b, Hare Ram Aryal ^b, Golap Kalita ^b, Masayoshi Umeno ^a

^a Department of Electronics and Information Engineering, Chubu University, 1200 Matsumoto-cho, Kasugai 487-8501, Japan

^b Department of Electrical and Electronic Engineering, Chubu University, 1200 Matsumoto-cho, Kasugai 487-8501, Japan

Available online 23 October 2007

Abstract

Diamond-like carbon (DLC) thin films were deposited on silicon and ITO substrates with applying different negative bias voltage by microwave surface wave plasma chemical vapor deposition (MW SWP-CVD) system. The influence of negative bias voltage on optical and structural properties of the DLC film were investigated using X-ray photoelectron spectroscopy, UV/VIS/NIR spectroscopy, Fourier transform infrared spectroscopy and Raman spectroscopy. Optical band gap of the films decreased from 2.4 to 1.7 with increasing negative bias voltage (0 to –200 V). The absorption peaks of sp^3 C–H and sp^2 C–H bonding structure were observed in FT-IR spectra, showing that the sp^2/sp^3 ration increases with increasing negative bias voltage. The analysis of Raman spectra corresponds that the films were DLC in nature.

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Keywords: DLC film; Bias voltage; Microwave surface-wave plasma CVD; Optical properties

1. Introduction

Carbon is a remarkable material existing in different stable forms such as diamond, graphite and nanotubes. In recent years, there is a growing interest in diamond-like carbon (DLC) films; consists of a three-dimensional network structure constructed by a medium-range order (MRO) of trihedral (sp^2) and tetrahedral (sp^3) hybridized carbons because of their well-know outstanding properties such as high hardness, chemical inertness, high electrical resistivity, high thermal conductivity, optical transparency from ultraviolet to infrared and tunable optical band gap by manipulating sp^3 and sp^2 bonding ratio [1–4]. However, there are some problems such as the presence of both σ and π states and high density of defects due to sp^2/sp^3 bonding structure and difficulties in controlling the conduction type, carrier concentration and band gap [5,6]. Synthesis of DLC films by other deposition method with applying negative bias voltage during deposition has been reported, and the result revealed that the properties of the films depend with negative bias voltage [7], however properties of DLC films deposited by microwave

(MW) surface wave plasma (SWP) chemical vapor deposition (CVD) with negative bias voltage during films deposition has rarely been reported. The details of the MW SWP-CVD system is described elsewhere [8–10].

In this paper we report the effects of bias voltage on optical and structural properties of DLC thin films deposited by MWSWP-CVD at room temperature.

2. Experimental setup

In this study, MWSWP-CVD system was used for deposition of DLC thin film on silicon and indium-tin-oxide (ITO) substrates at low temperature. Before films deposition, all substrates were cleaned in ultra-sonic organic solvents and finally etched in $H_2O:HF$ (10:1) solution to remove the oxide layer on the surface. The CVD chamber was evacuated to a base pressure at approximately 4×10^{-4} Pa using a turbo pumps. For films deposition, Argon (Ar: 200 sccm), Acetylene (C_2H_2 : 20 sccm) and nitrogen (N: 5 sccm) were used as carrier, source and dopant gases respectively and negative bias voltage was supply (0 to 200 V) on the substrates. The launched microwave power was typically 800 W and a constant gas composition pressure is maintained at 100 Pa during deposition. The duration of films deposition was 30 min.

* Corresponding author. Tel.: +81 0568 51 9244; fax: +81 0568 51 1478
E-mail address: sudipchubu@yahoo.com (S. Adhikari).

To study the optical and structural properties of the DLC films, X-ray photoelectron spectroscopy (XPS), ultraviolet–visible (UV–VIS) spectroscopy, Raman spectroscopy, and Fourier transmission infrared (FT-IR) spectroscopy were employed.

3. Results and discussion

The deposition rate of the DLC films synthesized by applying negative bias voltage on the substrate is increased approximately three times as compared with the DLC film synthesized without applying negative bias voltage. It is assumed that the increase in the deposition rate was caused by increasing the number of irradiating ions. But there was no significant differences on the deposition rates of the films with different negative bias voltage (–50 to –200 V) apply on the substrate. The results were qualitatively similar with other researches [11].

Compositional chemical analysis of the DLC films was performed by X-ray photoelectron spectroscopy (XPS) measurement (SSX-100) utilizing Al K α ($h\nu=1486.6$ eV) radiation. It is a useful technique to characterize the chemical bonding structure and acquire useful information on the chemical environment around C, N and O [12,13]. Fig. 1 shows the core level XPS spectra of C 1s and N 1s of the DLC films deposited with different negative bias voltages. The core level C 1s spectra were shifted toward lower binding energy (from 287.0 to 286.5 eV)

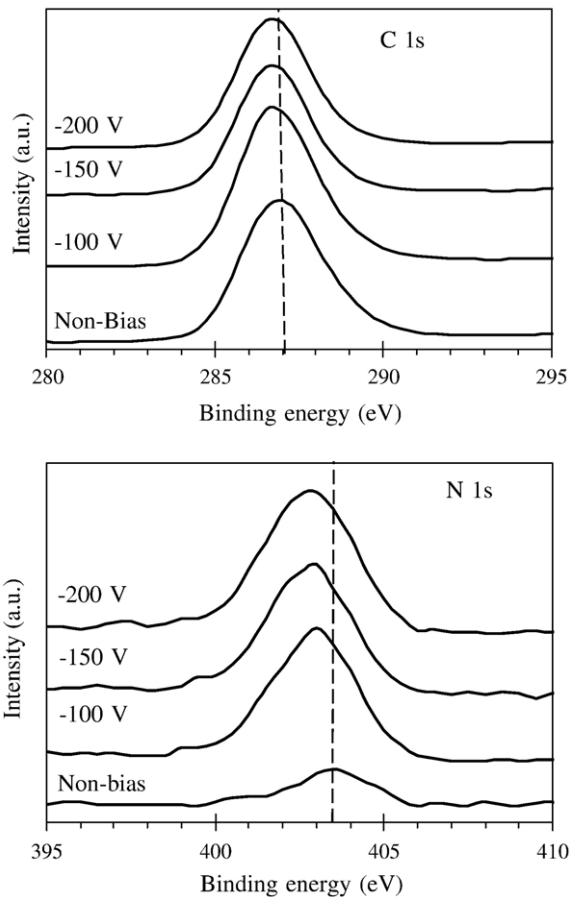


Fig. 1. Core level XPS spectra of C 1s and N 1s of the DLC thin films deposited with different negative bias voltages.

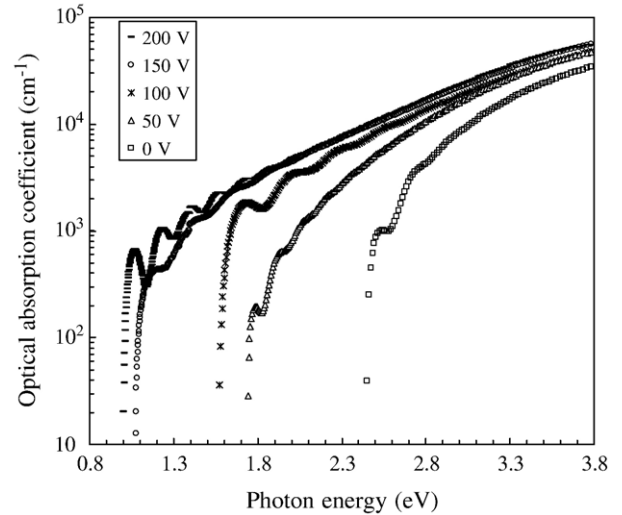


Fig. 2. Optical absorption coefficient (α) versus photon energy (eV) of the DLC films with different negative bias voltage.

with increasing negative bias voltage. The results reveal that the binding structure of the films leads towards graphite (284.25 eV) nature with increasing applied negative bias voltage on substrates. Similarly the core level N 1s spectra also shifted towards lower binding energy (403.5–402.5 eV) with respect to applied negative bias voltages. The N peak was found in all spectra indicates N has incorporated into the films [14]. The atomic concentration (at.%) of N was found to increase with increasing negative bias voltage. In addition, oxygen peak (very low at.%; not seen here) is also observed in all the spectra due to surface chemisorbed oxygen species [15]. This peak shift can be explained as the bonding state of the a-C films changes from sp^3 tetrahedral bonding to sp^2 trihedral bonding with the increasing bias voltage. This phenomenon has been supported by other results such as optical band, FT-IR and Raman measurements as described below.

The optical properties of the DLC films were characterized by spectral transmittance and reflectance using JASCO V-570 UV/VIS/NIR spectrometer in the range of 200–2000 nm. Absorption coefficient (α) was calculated by the spectral reflectance and transmittance and films thickness data. Fig. 2 shows the α as a function of photon energy ($h\nu$) of DLC films with different negative bias voltage (0 to –200 V). It can be seen that the α of the films are broad and increase with increasing negative bias voltage. It is believed that the α of the films indicates changes in the bonding structure. The optical band gap (E_g) was obtained by Tauc plot [16,17]. The Tauc E_g was obtained from the extrapolation of the linear part of the curve at $\alpha=0$ by using the Tauc equation,

$$(\alpha h\nu)^{\frac{1}{2}} = B(E_g - h\nu) \quad (1)$$

where B is the density of the localized state constant.

Fig. 3 shows the E_g as a function of negative bias voltage. The E_g decreased from 2.4 to 1.7 eV with increasing negative bias voltage (0 to –200 V). It is probably due to the sp^3 bonding structure of the DLC films has decreased (increased sp^2 bonding

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