STRUCTURAL AND OPTICAL PROPERTIES OF DIAMOND LIKE CARBON FILMS USING DIRECT CURRENT PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

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To my beloved family and friends

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ABSTRACT

The amorphous diamond like carbon (a - DLC) thin films were deposited in 3 hours on glass substrates at the vacuum pressure, 8.0 x 10^{-2} Torr ; deposition pressure, 4.0 x 10^{-1} Torr and deposition temperatures, 300 – 500 ºC by using direct current plasma enhanced chemical vapour deposition (DC - PECVD) system with the precursor gas, 1 % of methane, 39 % of hydrogen and 60 % of argon. The (a - DLC) films which have completely been deposited were post annealed for 3 hours in the tube furnace at 500 – 700 ºC with nitrogen ambient to obtain the nitrogen doped amorphous diamond like carbon (a:N - DLC) films. The characterizations were studied by using X-Ray Diffractometer, Energy and Dispersive Analysis of X-Ray, Fourier Transform Infrared Spectrometer, UV / VIS / NIR Spectrophotometer and Photoluminescence Spectrometer. The annealed films are verified as amorphous structure as discovered by X-Ray Diffractometer. It was revealed that carbon, nitrogen, oxygen and silicon are emitting the x-ray energy spectra at 0.28 keV, 0.39 keV, 0.5 keV and 1.74 keV, respectively. The infrared absorptions have shown at 880 cm^{-1} as C-H bending bonds, 1100 and 1220 cm^{-1} as C-N stretching bonds, 1300 cm^{-1} as C-C stretching bonds, 1600 cm^{-1} as C=N stretching bonds and 2200 cm^{-1} as C≡N stretching bonds for the films annealed from 500 ºC to 700 ºC. Stretching bond has been observed when annealed at 500 ºC and C≡N stretching bond has formed when annealed at 700 ºC. Moreover the transmittance of (a:N - DLC) films was increasing from 24.9 % to 70.7 % when annealing temperature increased from 500 ºC to 700 ºC; transition changed from allowed indirect transition, r = 2 to forbidden direct transition, r = 3/2; the optical band gap decreases from 1.60 - 0.85 eV at 500 - 650 ºC, but increases to 1.62 eV at 700ºC. With the fixed excitation wavelength at 245 nm within the measurement range of 200 – 800 nm, the emission wavelengths were obtained at 290 nm and 393 nm which correspond to n - π^* transition and violet emission transition, $4P^{0}_{1/2} \rightarrow \rightarrow 4P_{1/2}$, respectively.

ABSTRAK

Filem tipis berlian amorf seperti filem karbon (a - DLC) yang dimendap selama 3 jam atas substrat kaca pada tekanan vakum, 8.0 x 10^{-2} Torr; tekanan pemendapan, 4.0 x 10^{-1} Torr dan suhu pemendapan, 300 - 500 ^{0}C menggunakan sistem pemendapan plasma wap kimia arus terus (DC - PECVD) dengan gas pelopor, 1% metana, 39% hidrogen dan 60% argon. Filem (a - DLC) yang dimendap dengan lengkap disepuh lindap selama 3 jam di dalam relau tiub pada 500-700 ^{0}C dengan sekitaran nitrogen untuk memperolehi filem berlian amorf seperti filem karbon (a: N - DLC). Pencirian telah dikaji menggunakan difraktometer sinaran-x, analisis serakan dan tenaga sinaran-x, spectrometer transformasi Fourier inframerah, spektrofotometer UV / VIS / NIR dan spektrometer kefotopendarcahayaan. Filem yang disepuh telah disahkan sebagai struktur amorf seperti ditemui oleh difraktometer sinaran-x. Karbon, nitrogen, oksigen dan silicon didapati memancarkan tenaga spectra sinaran-x masing-masing pada 0.28 keV, 0.39 keV, 0.5 keV dan 1.74 keV. Serapan inframerah menunjukkan pada 880 cm^{-1} sebagai ikatan lenturan C-H, 1100 dan 1220 cm^{-1} sebagai ikatan regangan C-N, 1300 cm^{-1} sebagai ikatan regangan C-C, 1600 cm^{-1} sebagai ikatan regangan C=N dan 2,200 cm^{-1} sebagai ikatan regangan C≡N untuk filem disepuh lindap dari 500 ^{0}C kepada 700 ^{0}C. Ikatan regangan telah diperhatikan apabila disepuh lindap pada 500 ^{0}C dan ikatan regangan C≡N terbentuk apabila disepuh lindap pada 700 ^{0}C. Selanjutnya, pemindahan cahaya dari filem (a: N - DLC) telah meningkat dari 24.9% kepada 70.7% apabila suhu sepuh lindap meningkat dari 500 ^{0}C kepada 700 ^{0}C; peralihan berubah dari peralihan tidak langsung yang dibenar, r = 2 kepada peralihan langsung yang dilarang, r = 3/2; sela jalur optik menurun dari 1.60 - 0.85 eV pada 500 - 650 ^{0}C, tetapi meningkat kepada 1.62 eV pada 700^{0}C. Dengan penetapan panjang gelombang pengujaan pada 245 nm dalam julat pengukuran dari 200 - 800 nm, panjang gelombang sinaran pemancaran yang dipeolehi adalah 290 nm dan 393 nm yang masing-masing sepadan dengan peralihan n - π^* dan peralihan pemancaran ungu, $4P^{0}_{1/2} \rightarrow \rightarrow 4P_{1/2}$.

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LIST OF SYMBOLS

A	-	Absorption
Ar	-	Argon
a-C	-	Amorphous carbon
C	-	Carbon
C_{60}	-	Buckminster fullerene
CH_4	-	Methane
C_2H_2	-	Acetylene
CVD	-	Chemical vapour deposition
c	-	Velocity of light
DLC	-	Diamond like carbon
DC-PECVD	-	Direct current plasma enhanced chemical vapour deposition
d	-	Thickness of films
E_F	-	Fermi level
E_g	-	Energy band gap
E_{opt}	-	Optical band gap
E_i	-	Energy initial state
E_f	-	Energy final state
ECR	-	Electron cyclotron resonance
ECWR	-	Electron cyclotron wave resonance
EDAX	-	Energy and dispersive analysis of x-ray
FCVA	-	Filtered cathodic ablation deposition
FTIR	-	Fourier Transform Infrared
H	-	Hydrogen
H_2	-	Hydrogen gas
h	-	Plank constant
hv	-	Photon energy
ICP	-	Inductively couple plasma

k	-	Wave number
m_h^*	-	hole effective mass
m_e^*	-	electron effective mass
MFC	-	Mass flow controller
MSIB	-	Mass selected ion beam
MW-PECVD	-	Microwave plasma enhanced chemical vapour deposition
N	-	Nitrogen
N_2	-	Nirogen gas
n	-	Reflective index
O	-	Oxygen
PL	-	Photoluminescence
PBS	-	Plasma beam source
PLD	-	Pulsed laser ablation deposition
PVD	-	Physical vapour deposition
R	-	Reflection
RF-PECVD	-	Radio frequency plasma enhanced chemical vapour deposition
r	-	Electronic transition
Si	-	Silicon
T	-	Transmittance
T_a	-	Annealing temperature
T_d	-	Deposition temperature
ta-C	-	Tetrahedral amorphous carbon
ta-C:H	-	Tetrahedral hydrogenated amorphous carbon
UV-VIS	-	UV visible
XRD	-	X-Ray Diffraction
α	-	Absorption coefficient
λ	-	Wavelength

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

The earliest research of DLC films was done by Heinz Schmellenmeier. Andre *et al.*, 2008 who has reported that fabricated a black carbon film by discharging the acetylene (C_2H_2) gas with arc-evaporation vacuum system in 1953 (Byon *et al.*, 2003; Kim *et al.*, 2003). He has found that a shiny black layer was deposited on the cathode, which has great adhesion but delaminated after hours or days. The black layer shown extraordinary hard due to cannot be scratched by sharp diamond tip (Bilek *et al.*, 1996).

The research and interest in DLC films increased rapidly with its typical properties such as high optical transparency in visible and infrared region, high electrical resistivity, high hardness, chemical inertness and etc. Instead, diamond is known as having the most tremendous properties such as the highest hardness, highest atomic density, highest Young's modulus, highest room temperature thermal conductivity. But diamond films are less to be considered because of its growth temperature is high and costly.

Physical vapour deposition (PVD) methods have been widely used in the incorporation of nitrogen to carbon films. From the previous studies, magnetron sputtering method has successfully fabricated carbon films with nitrogen doped (a-C:N) which containing 6-8% of nitrogen composition. Besides that, chemical vapour deposition (CVD) methods were also been used to produce the nitrogen doped amorphous carbon thin films (Sanchez-Lopez *et al.*, 2008).

In general, CVD methods result with low deposition rates due to the formation of volatile species likely of the type hydrogen cyanide (HCN) and cyanogen (C_2N_2) where the ratio of nitrogen incorporation is just about 1:17 with carbon. Furthermore, large nitrogen content in the plasma will cause the nitrogen incorporation ratio decreases to 1:44 over carbon. Therefore, amorphous C:H:N films have been investigated regarding to their biocompatibility, optical and electrical properties.

Regarding to the properties of DLC films noted above, DLC gives a wide range of mechanical, tribological, optical, electrical and biomedical applications (Khun *et al*., 2010).

1.2 Problem of Statement

There are two main categories of DLC thin films deposition which are chemical vapour deposition (CVD) and physical vapour deposition (PVD). Plasma CVD is one of the methods from CVD and preferable for DLC deposition due to the preparation and deposition method is convenient and economic. The main advantage of using plasma CVD is can utilize the plasma to enhance the chemical reaction rates of the precursors with lower substrate temperature. In previously, some researchers have deposited the DLC films by using the radio frequency plasma enhanced chemical vapour deposition (RF-PECVD) system followed by post-annealing of the films. Steven *et al*., 2001 has reported that the nitrogen doped of DLC films by using RF-PECVD system deposited on n-type Si <100> substrate with the post annealing at the temperature from 400 to 1000 ^{o}C. Moreover, Kuo *et al*., 2001 has also discovered the DLC films doped with nitrogen on quartz glass by using RF-PECVD system and undergone thermal annealing with the temperature from 100 to 450 ^{o}C. Choi *et al*., 2008 has found that DLC films doped with nitrogen could be deposited on p-type Si <100> by using RF-PECVD system with the annealing temperature from 300 to 900 ^{o}C in steps of 200 ^{o}C. Additionally, Khan *et al*., 1999 has conducted their research by annealing the DLC films in nitrogen ambient at temperature 150 to 400 ^{o}C with the n-type Si <100> and p-type Si <100> substrate. In our research, we use the low cost customized DC-PECVD system and thermal annealing process for fabricating the DLC films with nitrogen incorporation. This DC-PECV system was designed with low temperature and low pressure deposition environment. The tube furnace being used was also modified to create a vacuum ambient upon thermal annealing for avoiding any contamination on the films. Hence, the effect of deposition and annealing parameter on the structural and optical properties will be studied in detail.

1.3 Research Objectives

i. To deposit the DLC films using DC-PECVD system.
ii. To study the effect of deposition temperature and annealing temperature on the structural and optical properties of DLC films.

1.4 Scope of Research

This research has constructed by three main scopes which are the DLC films deposition, DLC films annealing treatment and the films characterizations. DC-PECVD system was used to synthesize the DLC films on glass substrate by varying the substrate temperature from 300 to 500 °C with every step increment of 50 °C in 3 hours deposition time. The other deposition parameters such as vacuum pressure, deposition pressure, direct voltage and precursor gas flow rate were also being well controlled and fixed at 8 x 10^{-2} Torr, 4 x 10^{-1} Torr, 800 V and 0.2 L/M, respectively. For the annealing process, the DLC films that have been deposited will be annealed in nitrogen ambient with the temperature from 500 to 700 °C at vacuum pressure, -0.09 MPa and annealing pressure, -0.07 MPa for 3 hours annealing treatment. The structural properties of the films were studied by using X-Ray Diffractometer (XRD), Energy and Dispersive Analysis of X-Ray (EDAX) and Attenuated Total Reflection Fourier Transform Infrared Spectrometer (ATR-FTIR). Moreover, the optical properties of films were characterized by using the UV-VIS spectrophotometer (UV-VIS) and Photoluminescence spectrometer (PL).

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