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Spectroellipsometric characterization of nanocrystalline diamond layers

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ABSTRACT

The complex refractive index and the layer thickness of nanocrystalline diamond films was determined by ex situ variable angle spectroscopic ellipsometry in the wavelength range of 191–1690 nm. During the layer depositions argon, methane and hydrogen gases were used as source gases. The combined effect of argon addition and substrate bias was investigated in the microwave plasma assisted chemical vapor deposition of diamond. Multilayer optical models were constructed for the evaluation of the measured ellipsometric spectra. The effective medium approximation and the Lorentz dispersion relation were employed for the modeling of the optical properties of the diamond films.

1. Introduction

Nanocrystalline diamond (NCD) has many attracting material properties such as chemical inertness, high wear resistance, excellent thermal conductivity, biocompatibility, high hardness, offering opportunity for many applications. Recently, there has been considerable scientific interest in the synthesis and characterization of nanocrystalline diamond (NCD) films [1–19]. Lee et al. investigated the substrate temperature dependence of the deposition rates for nanocrystalline thin films prepared by microwave plasma enhanced chemical vapor deposition (MWPECVD) method [4]. Csorbai et al. described a multi-step nucleation/deposition process and prepared a pinhole-free protective nanocrystalline diamond coating using the MWPECVD method onto the surface of a micromachined capacitive pressure sensor chip [7]. The role of inert gas in microwave-enhanced plasmas during the deposition of nanocrystalline diamond films was investigated and described in ref. [16]. Williams summarizes the recent progress in deposition methods and application areas of nanocrystalline diamond films [17]. Barbosa et al. studied systematically the role of renucleation rate in ultrananocrystalline diamond growth [19].

The aim of the present study is to perform optical characterization on MWPECVD diamond layers prepared with different argon content and bias voltage. Spectroscopic ellipsometry (SE) was employed in our study, SE has been used earlier for the noncontact and non-destructive characterization of the complex refractive index, layer thickness, microstructure and other properties of a wide range of materials [1–6,10,11,13,18,20,21].

2. Experimental

The diamond films were deposited on single crystalline silicon substrates using MWPECVD. For sample pre-treatment we have applied the bias enhanced nucleation technique with a bias voltage of −200 V. In the bias enhanced nucleation stage we have applied a mixture of $CH_4 + H_2$ at a total flow rate of 100 sccm, the substrate temperature was elevated to 750 °C, whilst the chamber pressure was kept at 25 mbar, and the microwave power was regulated to 750 W. For the growth stage mixtures of CH_4, H_2, and Ar have been used as source gases. During the growth the pressure was 40 mbar, the substrate temperature was kept at 700 °C, the microwave power was adjusted to 1200 W. The methane concentration was always kept at 1%, while the concentration of argon was varied from 10% to 90% by adjusting the flow rate of both hydrogen and argon to maintain a constant total flow rate of 300 sccm. We applied zero or negative bias during the growth: 0 V, −50 V, −100 V, −150 V. The further details of the equipment can be found in ref. [14]. The parameters of sample preparation are shown in Table 1.

The optical properties and the thicknesses of thin film structures can be derived from (Ψ,Δ) values measured by SE, where Ψ and Δ describe the relative amplitude and relative phase change upon reflection on the sample of interest. Ψ and Δ were measured by a Woollam M-2000DI rotating compensator ellipsometer [22] in the 191–1690 nm wavelength range at angles of incidence of 55°, 58°, 61°, 64°, 67° and 70°. As the sample complexity increases, the need for multiple angle of incidence increases. In other words, additional

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Table 1
The parameters of sample preparation: argon content in the gas mixture during the MWPECVD process, the bias voltage and the deposition time.

Sample	Argon content (%)	Bias voltage (V)	Deposition time
ncd110z	10	0	1 h
ncd111	10	−50	1 h
ncd112	10	−100	1 h
ncd113	10	−150	1 h
ncd120	30	0	1 h 7 min
ncd121	30	−50	1 h
ncd130	50	0	1 h 35 min
ncd131	50	−50	1 h 30 min
ncd140	70	0	2 h
ncd141	70	−50	2 h 30 min
ncd150	90	0	3 h
ncd151	90	−50	2 h 30 min

information can be gained by measuring and analyzing multiple angle data simultaneously. As the angle of incidence changes, so does the path length of light through each of the sublayers. These changes improve considerably the ability to precisely and accurately determine thicknesses of a multilayer structure [23]. The calculated (generated) spectra were fitted to the measured ones using linear regression. The measure of the fit quality is the mean squared error (MSE) which is compared for different samples and optical models. The MSE quantifies the difference between the measured spectra and the spectra generated on basis of various optical models [24]. The evaluation of the spectra was done using the computer code WVASE32 created by J.A. Woollam Co., Inc. [22]. The evaluation consists of two steps: global parameter search and iteration. In the step of global parameter search one has to define the allowed range of the parameters (layer thickness, volume fraction, parameters of a dispersion relation) and the number of guesses (steps) for the search. The global parameter search can be as long as several hours using a personal computer, it is important that

Table 2
The layer thicknesses and concentration of diamond, glassy carbon, and void in the sublayers were extracted from evaluation of SE data using model-1 for all the six angles of incidence. The diamond (Cauchy) represents the reference dielectric data obtained by evaluation of experimental data published in ref. [27] using the Cauchy relationship. Glassy-c represents the reference dielectric function data published in ref. [28].

Sample argon conc., bias voltage	Sublayer-1 adjacent to substrate	Sublayer-2	Sublayer-3 (surface roughness) (nm)	MSE
ncd110z	40.4 ± 0.2 nm	279.5 ± 0.3 nm	14.76 ± 0.07	30.26
	diamond (Cauchy) 69.7 ± 0.5%	diamond (Cauchy) 99.0 ± 0.1%		
10% Ar	glassy-c 29.9 ± 0.3%	glassy-c 0.97 ±0.03%		
0 V	void 0.4 ± 0.2%	void 0.0 ± 0.1%		
ncd111	40.7 ± 0.2 nm	302.9 ± 0.3 nm	12.21 ± 0.07	31.51
	diamond (Cauchy) 56.7 ± 0.5%	diamond (Cauchy) 98.4 ± 0.1%		
10% Ar	glassy-c 34.2 ± 0.3%	glassy-c 0.39 ±0.03%		
−50 V	void 9.1 ± 0.2%	void 1.2 ± 0.1%		
ncd112	50.7 ± 0.1 nm	595.6 ± 0.4 nm	20.42 ± 0.05	23.44
	diamond (Cauchy) 54.0 ± 0.4%	diamond (Cauchy) 94.7 ± 0.1%		
10% Ar	glassy-c 44.6 ± 0.2%	glassy-c 1.32 ±0.01%		
−100 V	void 1.4 ± 0.2%	void 3.95 ± 0.09%		
ncd113	74.1 ± 0.3 nm	1081.5 ± 0.5 nm	8.92 ± 0.04	18.91
	diamond (Cauchy) 37.1 ± 0.8%	diamond (Cauchy)		
10% Ar	glassy-c 62.8 ± 0.5%	90.18 ± 0.08%		
−150 V	void 0.1 ± 0.3%	glassy-c 4.08 ±0.02%		
		void 5.74 ± 0.06%		
ncd120	39.4 ± 0.2 nm	241.4 ± 0.3 nm	11.03 ± 0.07	30.52
	diamond (Cauchy) 72.5 ± 0.5%	diamond (Cauchy) 99.5 ± 0.1%		
30% Ar	glassy-c 27.5 ±0.3%	glassy-c 0.51 ± 0.03%		
0 V	void 0.0 ± 0.2%	void 0.0 ± 0.1%		
ncd121	38.2 ± 0.3 nm	220.2 ± 0.4 nm	10.38 ± 0.08	36.99
	diamond (Cauchy) 77.6 ±0.6%	diamond (Cauchy) 98.8 ± 0.2%		
30% Ar	glassy-c 22.4 ±0.3%	glassy-c 0.41 ± 0.04%		
−50 V	void 0.0 ± 0.3%	void 0.8 ± 0.2%		
ncd130	39.6 ± 0.3 nm	204.9 ± 0.4 nm	11.00 ± 0.07	33.74
	diamond (Cauchy) 79.6 ± 0.6%	diamond (Cauchy) 98.9 ± 0.1%		
50% Ar	glassy-c 20.4 ±0.3%	glassy-c 0.51 ±0.04%		
0 V	void 0.0 ± 0.3%	void 0.6 ± 0.1%		
ncd131	39.0 ± 0.3 nm	219.5 ± 0.3 nm	9.77 ± 0.08	36.11
	diamond (Cauchy) 75.3 ± 0.6%	diamond (Cauchy) 98.6 ± 0.2%		
50% Ar	glassy-c 24.7 ±0.3%	glassy-c 0.44 ±0.04%		
−50 V	void 0.0 ± 0.3%	void 1.0 ± 0.2%		
ncd140	38.1 ± 0.2 nm	125.4 ± 0.2 nm	12.24 ± 0.06	29.78
	diamond (Cauchy) 75.1 ±0.5%	diamond (Cauchy) 99.1 ± 0.2%		
70% Ar	glassy-c 24.4 ±0.3%	glassy-c 0.0 ± 0.05%		
0 V	void 1.5 ± 0.2%	void 0.9 ± 0.1%		
ncd141	40.00 ± 0.03 nm	209.0 ± 0.4 nm	14.21 ± 0.09	37.4
	diamond (Cauchy) 71.4 ± 0.7%	diamond (Cauchy) 96.1 ± 0.3%		
70% Ar	glassy-c 28.6 ±0.4%	glassy-c 0.97 ± 0.05%		
−50 V	void 0.0 ± 0.3%	void 2.9 ± 0.2%		
ncd150	37.7 ± 0.4 nm	106.4 ± 0.3 nm	14.2 ± 0.08	29.75
	diamond (Cauchy) 75.5 ± 0.8%	diamond (Cauchy) 95.0 ± 0.2%		
90% Ar	glassy-c 24.5 ± 0.4%	glassy-c 1.18 ±0.06%		
0 V	void 0.0 ±0.4%	void 3.8 ±0.1%		
ncd151	37.0 ± 0.2 nm	111.5 ± 0.2 nm	13.92 ± 0.06	29.54
	diamond (Cauchy) 71.4 ± 0.6%	diamond (Cauchy) 96.9 ± 0.2%		
95% Ar	glassy-c 28.6 ± 0.3%	glassy-c 0.0 ±0.05%		
−50 V	void 0.0 ±0.3%	void 3.1 ±0.1%		