Applied Surface Science 426 (2017) 456–465

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Electrical current at micro-/macro-scale of undoped and nitrogen-doped MWPECVD diamond films

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ARTICLE INFO

Article history:
Received 31 May 2017
Received in revised form 13 July 2017
Accepted 16 July 2017
Available online 22 July 2017

Keywords:
Diamond films
Grains
Grain boundaries
Nitrogen doping
Scanning capacitance microscopy
Electrical current at micro-/macro-scale

ABSTRACT

Chemical, structural, morphological and micro-/macro-electrical properties of undoped and nitrogen-(N-)doped diamond films are determined by X-ray photoelectron spectroscopy, Raman and photoluminescence spectroscopies, field emission scanning electron microscopy, atomic force microscopy, scanning capacitance microscopy (SCM) and two points technique for I–V characteristics, respectively. The characterization results are very useful to examine and understand the relationship among these properties.

The effect of the nitrogen incorporation in diamond films is investigated through the evolution of the chemical, structural, morphological and topographical features and of the electrical behavior. The distribution of the electrical current is first assessed at millimeter scale on the surface of diamond films and then at micrometer scale on small regions in order to establish the sites where the carriers preferentially move. Specifically, the SCM images indicate a non-uniform distribution of carriers on the morphological structures mainly located along the grain boundaries.

A good agreement is found by comparing the electrical currents at the micro- and macro-scale. This work aims to highlight phenomena such as photo- and thermionic emission from N-doped diamond useful for microelectronic engineering.

1. Introduction

Diamond is a wide band gap material and possesses unique and superior properties, such as high thermal conductivity, high electron and hole mobility, high resistance to radiation, high chemical stability and so on. The importance of defects and impurity atoms in diamond is of crucial importance thanks to the variety of applications that can take advantage from their presence in the crystal lattice. Indeed, the impurities together with the vacancy have been proven to give rise to optical colour centres [1,2]. Nitrogen is one of the most known and common among the impurities found in diamond, it is considered as *n*-type dopant with deep donor states at ~1.7 eV below the conduction band minimum. At low concentration the substitutional incorporation of nitrogen occupies some diamond lattice sites [3] and changes the chemical, physical and electrical properties of the diamond film.

Many studies were carried out to dope micro- (MCD), nano- (NCD) and ultrananocrystalline (UNCD) diamond films by adding N_2 to CH_4—H_2 [4] and CH_4-Ar [5,6] gas mixtures, respectively. Small additions of ammonia (1%) [7] and nitrogen (140–1430 ppm) [4] in the gas phase decreased the conductivity of the diamond films. Mort et al. [7] found a decrease of several orders of magnitude of the electrical conductivity for nitrogen concentrations of about 3×10^{18} atoms/cm^3 in the films. Precisely, the conductivity of *n-doped* films (10^{-13} ohm^{-1} cm^{-1} at 293 K) was reduced by a factor of 10^3 at room temperature with respect to undoped ones (10^{-10} ohm^{-1} cm^{-1}). Later, Bénédic et al. [4] observed a decrease of surface conductance (10^{-14} ohm^{-1}), in *n-doped* MCD films deposited on *n-doped* silicon substrates, of six orders of magnitude less than that in undoped ones (10^{-8} ohm^{-1}) at 293 K. For both gas mixtures the authors [4,7] explained the higher conductivity of undoped films due to transport through in-gap defect states (acceptors). Contrarily, the conductivity decrease in *n-doped* films was attributed to the compensation of the defect acceptor states by deep nitrogen donor states.

Large additions of N_2 (1–20%) to CH_4-Ar microwave plasma produced UNCD with nitrogen content in the films that initially increased, but then saturated at about 2×10^{20} atoms/cm^3 (i.e. 0.2%) total nitrogen content, as assessed by secondary ion mass spectrometry (SIMS), for 5% N_2 in the gas phase. The electrical

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http://dx.doi.org/10.1016/j.apsusc.2017.07.132
0169-4332/

conductivity increased from 0.016 Ω^{-1} cm^{-1} (for 1% N_2) up to 143 Ω^{-1} cm^{-1} (for 20% N_2) [5]. Additionally, flat surface of UNCD films with appropriate amount of nitrogen incorporated in grain boundaries (GBs) showed low threshold electric fields [8].

Sankaran et al. [9,10] found an increase of the conductivity up to 186 Ω^{-1} cm^{-1} and of field emission properties in diamond obtained adding N_2 to CH_4 and CH_4—H_2 microwave plasmas, respectively.

The enhancement of the conductivity and of the electron emission was explained by the electron transport via GBs where the nitrogen is incorporated. Generally, the presence of GBs (containing the sp^2 carbon) and their increasing density in micro-, nano- and ultrananno-crystalline diamond films, were considered of crucial importance in determining not only the electrical/electronic properties, but also in enhancing the field-, photo- and thermo-emission in undoped and doped films [11,12]. In fact, the pioneering work of Karabutov et al. [13] showed that the scanning tunneling microscopy is a tool to map simultaneously the field emission intensity and the topography of the films, demonstrating the GBs as preferred emission sites. Recently Chatterjee et al. [14] and Sankaran et al. [15], employing the tunneling atomic force microscopy, observed directly the electron emission from GBs of CVD diamond films.

An alternative technique able to study the local dielectric and electrical properties of *near-surface layers* is the scanning capacitance microscopy (SCM). SCM is a technique implemented in conventional atomic force microscopy (AFM) and allows to get information on the change in electrostatic capacitance between the surface and the probe tip [16–20]. Usually, SCM was used to obtain a map of carrier distribution in *p-n* junction surface [21].

In this work the SCM technique was employed to map the AFM topography along with dark and photo-current (under UV irradiation) of undoped and N-doped diamond surfaces. A set of diamond films was produced by adding variable percentages of N_2 (P_{N2}) from 0 to 6% to CH_4—H_2 gas mixtures. The nitrogen incorporation in the films was detected by means of X-ray photoelectron (XPS), Raman and photoluminescence (PL) spectroscopies, and its effect was examined by field emission scanning electron microscopy (FE-SEM), AFM, SCM techniques and I–V characteristics. Specifically, the current imaging in SCM mode was used to directly monitor the dark and the enhanced photo-current at micrometer scale and at the same time to get information on the sites strongly involved in the electrical conduction. At millimeter scale, the dark and the UV photo currents were determined by the I–V characteristics through the two points technique.

2. Materials and methods

2.1. Undoped and nitrogen-doped diamond films

The diamond films (listed in Table 1) were deposited on 2.6 cm × 2.6 cm polished *p*-doped (B) silicon (100) substrates by microwave plasma enhanced chemical vapor deposition (MWPECVD) technique, in a home-made cylindrical stainless steel ASTeX-type reactor. Details of the deposition process are described elsewhere [22–24]. Before the deposition process, the silicon substrates were ultrasonically cleaned in isopropyl alcohol for 10 min and then ultrasonically seeded for 1 h in an ethanol suspension of 40–60 μm diamond powder to promote the diamond nucleation on it.

The diamond films were grown starting from a typical CH_4—H_2 gas mixture and adding various N_2 flows (from 0 to 15 sccm), in place of the corresponding decrease of H_2 flow (from 247.5 down to 232.5 sccm) in order to keep constant at 250 sccm the total flow rate. During the deposition for each composition of gas mixture, the pressure (p), the microwave power (P), the heater temperature (T_{PID}), the deposition temperature (T_D), the total (Φ_T) and CH_4 flow rate (Φ_{CH4}) were maintained fixed at 50 mbar, 1000 W, 700 °C, 850 °C, 250 and 2.5 sccm, respectively.

Table 1
Discharge conditions for the deposition of diamond films grown on treated silicon substrate at fixed pressure of 50 mbar, power of 1000 W, deposition temperature of 850 °C, total and CH_4 flow rate of 250 and 2.5 sccm, and variable N_2 percentage (P_{N2}), H_2 and N_2 flow rate. Averaged film thickness (t_{film}) as determined by pyrometric interferometry and laser reflectance interferometry.

Samples	CH_4-H_2-N_2 (sccm)	P_{N2} (%)	t_{film} (nm)
DIAM109	2.5–247.5-**0.0**	0.0	2157 ± 29
NDIAM6	2.5–247.0-**0.5**	0.2	1981 ± 119
NDIAM4	2.5–246.2-**1.3**	0.5	2021 ± 16
NDIAM9	2.5–246.2-**1.3**	0.5	2045 ± 2
NDIAM3	2.5–245.0-**2.5**	1.0	1806 ± 50
NDIAM7	2.5–238.7-**8.8**	3.5	1202 ± 79
NDIAM5	2.5–235.0-**12.5**	5.0	654 ± 76
NDIAM8	2.5–232.5-**15.0**	6.0	495 ± 116

During the growth process, T_D and the deposition rate (r_D) were continually monitored in situ and in real-time by means of the pyrometric interferometry (PI) [24] technique using a dual-wavelength (λ_1 = 2.1 μm and λ_2 = 2.4 μm) infrared pyrometer (Williamson Pro 9240). A laser reflectance interferometry (LRI, λ=632.8 nm) [24] was also used to determine r_D.

The composition of gas mixture, the N_2 percentage in the gas phase ($P_{N2} = (\Phi_{N2}/\Phi_T)$ x100)) and the film thickness (t_{film}) for each sample are reported in Table 1. Moreover, the *n-doped* diamond films at P_{N2} = 0.5% were produced not only on *p-doped* Si, but also on *n-doped* Si substrates and called NDIAM4 and NDIAM9 samples, respectively, see Table 1. At values >500 nm of film thickness, the electrical properties of diamond surfaces are not affected by the bulk current of *p*-Si substrate and depends only on the amount of nitrogen incorporation which modifies the chemical, structural and morphological features.

2.2. XPS spectroscopy

X-ray photoelectron spectroscopy analysis was carried out on the diamond films, using a Theta Probe Spectrometer (Thermo Fisher ScientificTM) equipped with a monochromatized AlK_α source and a beam spot diameter of 300 μm. XPS spectra were registered in constant analyzer energy (CAE) mode. Survey spectra were acquired at a pass energy (E_p) of 150 eV and step size of 1.0 eV, while high-resolution (HR) spectra (C1s, O1s, N1s) were recorded at E_p of 100 eV and step size of 0.1 eV. No artifacts and damages due to excessive X-ray irradiation occurred. HR spectra were processed by a commercial software (Avantage v. 5.937, © 1999–2014 Thermo Fisher Scientific) applying a Shirley background and fitting signals with proper mixed Gaussian/Lorentzian functions. Binding energy (BE) was corrected for charge compensation by fixing the aliphatic C1s component at BE value of 284.8 eV.

2.3. Raman and photoluminescence (PL) spectroscopies

Raman and PL spectra were measured at room temperature by means of a Raman confocal micro-spectrometry apparatus (Labram from Jobin-Yvon Horiba) in the backscattering configuration using an Ar-ion laser beam at 488 nm for determining the chemical and structural features of the undoped and N-doped diamond films.

The Raman signals were obtained by a 100 x objective, focusing the beam on a spot of about 1 μm diameter and sent to spectrometer with a 1800 grooves/mm grating. For each sample, the Raman spectra were performed on different regions.

The PL emissions were collected by a 10 x objective focusing the beam on a spot of about 10 μm diameter on the sample surface