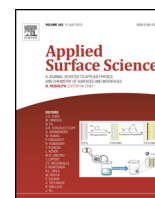




Contents lists available at [ScienceDirect](#)

Applied Surface Science

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



Thermal stability of hydrogenated diamond films in nitrogen ambience studied by reflection electron energy spectroscopy and X-ray photoelectron spectroscopy

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ARTICLE INFO

Article history:

Received 26 August 2015
Received in revised form 8 October 2015
Accepted 10 October 2015
Available online xxx

Keywords:

Hydrogenated diamond films
Thermal stability
REELS
Rapid annealing

ABSTRACT

(1 1 0)-oriented diamond films were grown by microwave plasma chemical vapor deposition technique, followed by an optimized hydrogen-plasma treatment process. Thermal stability of hydrogenated diamond films were studied by annealing in nitrogen atmosphere at temperature varied from 400 to 950 °C. Reflection electron energy spectroscopy associated with X-ray photoelectron spectroscopy indicates that approximate at 50% hydrogen was present at the surface of hydrogenated diamond films, which is close to the theoretical value. Pinning effect in surface Fermi level in hydrogenated diamond films could not be eliminated by annealing in nitrogen until the temperature was exceeded 950 °C. The films underwent hydrogen desorption and subsequent graphitization mainly on the very surface region without significant bulk modification. Besides, hydrogenated diamond films annealed in N₂ at 950 °C showed similar hydrophilicity and resistance to that of the oxidized one, indicating rupture of C-H bond on the surface of hydrogenated diamond films.

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1. Introduction

Diamond films-based devices have attracted considerable attention in the past few decades for their potential electronic and optoelectronic applications with unique and excellent properties, such as high-temperature high-power diodes, high-frequency field-effect transistors (FETs), high energy particles detectors, etc. [1–7]. Most diamond field-effect transistors (FETs) are based on (0 0 1) homo-epitaxial diamond films with a hydrogen-terminated diamond film acting as a conductive channel without any doping impurities [8–11]. However, the size of a single-crystal chemical vapor deposition (CVD) diamond films is estimated to be several millimeters, which limits its application in wireless communications systems. Many researches show that highly (1 1 0) oriented diamond films grown on large-area foreign substrates would be perfect candidates to homo-epitaxial diamond films, as well as hydrogen-terminated (1 1 0) diamond film-based FETs exhibit excellent properties [1,7,12,13].

It is reported that none broken-up of C–H bond appears on both (1 0 0) and (1 1 1) surface of hydrogenated diamond films until annealing temperature exceeds 700 °C in an ultra-high vacuum (UHV) condition [14,15]. Besides, the surface conductivity of hydrogenated diamond films with (1 0 0) aligned grains is irretrievably lost if a sample is annealed above 200 °C in air due to desorption of hydrocarbon. However, there was little study on thermal stability of hydrogenated diamond films with (1 1 0) preferential orientation, which are widely used as conductive channels in diamond FETs. Generally speaking, the hydrogen content in hydrogenated samples is always quantified by elastic recoil detection analysis (ERDA), nuclear reaction analysis (NRA), Time of flight secondary ion mass spectrometry (TOF-SIMS) and nuclear magnetic resonance (NMR), etc. [16]. ERDA, NRA and TOF-SIMS technique, however cannot be used routinely to determine hydrogen content for the requirement of ion accelerators which are expensive and not readily available in many laboratories. NMR, on the other hand requires the mass of material (on the order of 100 mg), which is not easily available when dealing with thin films. While reflection electron energy loss spectroscopy (REELS) associated with X-ray photoelectron spectroscopy (XPS) is an emerging technique to semi-quantitatively identify almost whole elements including light elements (H or He) within just several nanometers depth, which meets our need to

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study the very surface of films. Furthermore, less literature were available on the quantification of H content in hydrogenated diamond films, except for diamond-like carbon or polymeric thin films by reflection electron energy loss spectroscopy.

In this study, hydrogenated polycrystalline diamond films with (110) orientation were grown by microwave plasma chemical vapor deposition (MPCVD) method. The thermal stability of hydrogenated films was studied in nitrogen ambience in temperature range from 400 to 1000 °C. The content of H, C and O of diamond films with different treatment were quantified by REELS associated with XPS. Besides, annealing temperature dependence of wettability and resistance of samples were investigated.

2. Experimental

Diamond films with (110) preferential orientation were deposited on (100) silicon substrates by a MPCVD system with a hydrogen–methane mixture precursor. As-prepared diamond films were oxidized by H₂SO₄/HNO₃ acid solution at 300 °C for 60 min. An optimized hydrogen-plasma treatment process was employed to obtain hydrogen-terminated diamond films in the same chamber. During hydrogen etching process, the working pressure was kept at 65 Torr with a hydrogen flow of 500 sccm. Besides, the substrate temperature maintained at 880 °C for 1 h. In order to evaluate the thermal stability of hydrogenated diamond films, post-annealing treatment was taken in nitrogen atmosphere at a temperature range from 400 to 950 °C for 15 min in a rapid thermal processing system. Au electrodes with spacing of 2 mm for *I*–*V* measurement were fabricated on the films by E-beam evaporation technique.

The X-ray diffraction (XRD) operated on D/MAX 2500 diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) and Raman spectrometer (JY, HR800UV) excited by 514.5 nm wavelength laser were used to determine crystalline phase, microstructure and vibration modes of films. XPS associated with REELS were carried out with an X-ray photoelectron spectrometer (XPS, Thermo Fisher Scientific, ESCALAB 250Xi model). A monochromated Al K α X-ray source was used with pass energy of 150 eV. XPS measurements were taken in normal emission with a spot size of 500 μm at a base pressure of 10^{–9} mbar. Energy level of XPS was calibrated with Au single crystal. Incident electrons with kinetic energy of 1 keV and scattering angle of 165° were used in REELS in a standard mode. The spectra were further analyzed using Advantage processing software. Both spectra were background corrected using the “Smart” base line function available in the software, and peak fitting was done using a Gaussian (70%)–Lorentzian (30%) convolution function. Atomic ratios were calculated from the integrated intensities of core levels after photoionization cross-section corrections. *I*–*V* characteristics were measured using a Keithley 4200 semiconductor characterization system at room temperature. The surface wettability was studied with an Easy Drop goniometer (Eastern-Dataphy, OCA 15EC) at room temperature. Pictures of the droplets were taken immediately after dispensing 1 μl of distilled water on the sample and were subsequently analyzed using drop-shape analysis software. The measurements were taken at 5 different spots on the film to obtain the average static water contact angle (WCA).

3. Results and discussion

Typical XRD pattern for as-prepared diamond films is shown in Fig. 1 with a scanning range 40–100° (2θ). The pattern shows two major diffraction peaks at 43.92° and 75.30°, originating from (111) and (220) lattice plane, which corresponds to the diamond phase with cubic structure (JCPDS 06-0675). Besides, a broad shoulder peak located at ~69.50° can also be observed, assigned to the

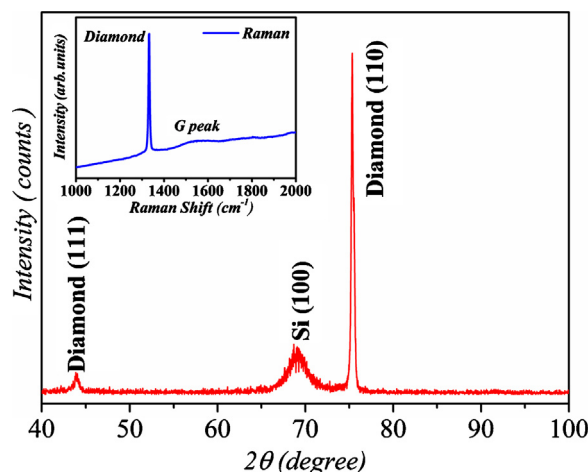


Fig. 1. Typical XRD pattern for as-prepared diamond films. The inset displays visible Raman spectroscopy for diamond films.

Si substrate. The preferred orientation of diamond films can be predicted by the Lotgering factor *f*, which was defined as [17,18]:

$$f = \frac{(I_{hkl} / \sum I_{hkl})_L - (I_{hkl} / \sum I_{hkl})_P}{1 - (I_{hkl} / \sum I_{hkl})_P} \quad (1)$$

where *L* indicates as-prepared film and *P* represents powder sample (or the theoretical value).

Table 1 lists the integrated intensities for as-prepared film and powder sample. After calculating by the formula, we can obtain $f_{(111)} = -1.39$, $f_{(220)} = 0.93$, indicating (110)-textured diamond films. The inset of Fig. 1 displays Raman spectrum of as-prepared diamond films. The Raman feature is dominated by an intense peak located at ~1332 cm^{–1}, assigned to diamond Raman scattering; besides, G peak related to bond stretching of sp² can also be observed. From the experimental and theoretical analysis, it is proposed that as-synthesized diamond films are of good quality with (110) texture.

The physical basis for the detection of H atoms at the surface of materials containing light elements is the expected difference in the recoil energy ΔE_r in the interaction of a fast electron with a static nucleus, either hydrogen or another type of atom, which can be estimated by the expression [16]

$$\Delta E_r = 4 \frac{m_e}{M_H} E_0 \sin^2 \frac{\theta}{2} \left(1 - \frac{1}{A} \right) \quad (2)$$

where m_e , M_H , and *A* represent the electron mass, the atomic weight of the H atom and other nucleus considered, respectively. In this study, besides H atom, C nuclei is taken into consideration. θ is the scattering angle and E_0 is the primary energy of the incoming electron. During our measurements, a typical scattering angle of $\theta = 165^\circ$ and a primary energy of 1000 eV are used. That is to say, the difference in recoil energies between H and C is 1.96 eV, so that we might easily distinguish the loss energy gap between H and C presenting in the sample with the standard energy resolution of REELS measurements.

Fig. 2 shows the REELS spectra, taken with a primary electron beam of 1000 eV, for diamond films under different treatment. In order to minimize the electron damage at the surface of diamond

Table 1
Integrated intensities of XRD for as-prepared diamond films.

Samples	(111)	(220)	(311)	(400)	(331)
Powder	100	25.0	16.0	8.0	16.0
Film	226	3573	~	~	~

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