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Ferroelectric behaviours of ultra-nano-crystalline diamond thin films

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ABSTRACT

The ferroelectric behaviour of ultra-nano-crystalline diamond (UNCD) thin films with low content nitrogen (<1 at.%) is investigated by measuring the electrical, mechanical, Raman and X-ray photoemission spectroscopy. The electrical measurements I–V curve shows that the films doped with low content nitrogen possessed n-type conduction with ferro-electric behaviour at room temperature. The degree of ferroelectric behaviour changes with small change of nitrogen content incorporated in the film structure. The mechanical and microstructural properties are consistent with electrical measurements and these UNCD could be used in non-volatile memory devices.

1. Introduction

The ultra-nano-crystalline diamond (UNCD) has excellent mechanical and optical properties, high surface area and tunable surface structure [1], high surface acoustic wave velocity, high electron mobility, high thermal conductivity, and good chemical and thermal stability; there is considerable interest in the use of diamond as a semiconductor for the fabrication of high performance electronic devices applied in high temperature and heavy radiation environments [2]. The UNCD film is a special form of diamond film that has attracted increasing attention from researchers because of its exclusive granular structure [3]. The UNCD film has ultra-small diamond grains (5–10 nm) and smooth surface characteristics. The grains of UNCD films have sp^3 character and the grain boundaries have a mixture of sp^2, sp^3, hydrocarbon, and amorphous carbon (a-C), in which the sp^2 character is predominant [4]. Because of outstanding electrical behaviour of UNCD films compared to other forms of diamond films (microcrystalline or nanocrystalline), UNCD films show large potential for electrical and electronic applications such as cold cathode field emitters and other vacuum microelectronic devices [5]. It has been reported that the electrical conductivity of an ultra-nano-crystalline (UNCD) thin film, prepared by chemical vapour deposition (CVD), is enhanced with an increase in the nitrogen content in the film structure [6]. The origin of this enhancement in conductivity mainly depends on the increase in the number of sp^2 bonds in the grain boundaries (GBs). The nitrogen atoms preferentially incorporated into the (GBs) between UNCD grains and boundaries between UNCD grains and an a-C:H matrix. This causes a shift in the Fermi energy level toward the conduction band [7]. However, the influence of other factors such as the formation of other phase and the kind of bonding still requires clarification. The undoped UNCD/a-C:H films have a structure wherein a large number of UNCD grains with diameters of approximately 5 nm are embedded in an a-C:H matrix [8] and the films also have electrically insulating properties.

In this present work we studied the UNCD films, about their modification of electrical properties by changing the microstructural and mechanical properties with incorporation of small content nitrogen (<1 at.%) within the UNCD structure.

2. Experimental

The UNCD films were grown on n-type mirror polished silicon (100) substrates in IPLAS microwave plasma enhanced chemical vapour deposition system. The substrates were first ultrasonically cleaned by acetone to remove any surface contamination and then dipped in HF for 1 min to remove native oxides, followed by ultra-sonication in diamond powder (30 nm) slurry of methanol. The substrates were again ultrasonically cleaned and dried by blowing nitrogen gas. The UNCD films were grown at different composition gas plasma atmospheres at 1200 W (2.45 GHz) in a 120 Torr chamber pressure. The total gas flow rate is 100 sccm, which contains 1 sccm CH_4, 5–20 sccm N_2 with the rest of Ar gas and have no H_2. No external heater was used and the substrate temperature was estimated to be around ~475 °C during the growth of the UNCD films, which was presumably heated due to the bombardment of the plasma species. The thickness of the UNCD films was about 250 nm, which was estimated from a cross-sectional field emission scanning electron microscopic image as described in details in our previous reports [9,10]. The microstructural and bonding properties are measured using Raman and X-ray photoelectron spectroscopy (XPS);

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whereas electrical measurements are measured at room temperature using Keithley 4200 semiconductor characterization system. Raman measurements were carried out using four different LASER excitation wavelengths *viz*. 488, 515, 647 and 785 nm with the LASER beam spot size ~1 μm and the incident power was ~1 mW. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using KRATOS AXIS X-ray photoelectron spectrometer UNISA (Florida Science Campus), South Africa. In order to measure the electrical properties, Ag-metal top electrodes with a thickness of 200 nm and a diameter of 100 μm were deposited at room temperature by electron beam evaporation with an in-situ metal shadow mask. The *I–V* characteristics of Ag/GO/Ag structures were measured at room temperature with voltage sweeping mode. During the measurement, a bias voltage was applied between the top and bottom electrodes with the latter being grounded.

3. Results and discussion

Raman spectra of UNCD films obtained at four different LASER excitation wavelengths *viz*. 488, 515, 647 and 785 nm are shown in Fig. 1(a–d). Due to the resonant Raman scattering the intensity of the bands related to sp^2 C clusters is a few orders of magnitude higher than that of the sp^3C matrix and the diamond grains; the clusters have different topologies and therefore different band gaps and characteristic vibrational frequencies. Usually, in carbon related materials an increase in sp^2C clusters size is associated with a decrease in band gap, so the Raman spectra measured with particular excitation energy will be dominated by the resonantly enhanced peaks of sp^2C clusters of a specific size [11]. By changing the excitation wavelength vibrations of a different set of sp^2C clusters are selectively enhanced [11]. Moreover, Raman spectra of UNCD contain characteristic peaks of both the diamond crystallites and the grain boundaries. These peaks include a narrow diamond peak at ~1333 cm^{-1}, the broad D and G bands at ~1330–1380 and ~1550–1600 cm^{-1}, respectively (sp^2 clusters), and broad peaks at 1050–1200 and 1420–1470 cm^{-1} (clusters of conjugated sp^2 C chains). Their exact peak positions depend on the laser excitation energy [12]. The clusters of conjugated sp^2C chains terminating the σ bonds of the surface atoms in diamond crystallites [13] are the fingerprint bands of UNCD. The resonantly excited bands overlap and as a consequence, the resulting broad peaks provide only generalized information on the bonding configuration of carbon atoms in grain boundaries. So, by suppressing the resonant Raman scattering the characteristic peaks of specific structural units could be detectable. This was achieved by using lower excitation energies [13] and using the near-infrared excitation the characteristic vibrations of structural units of grain boundaries are detected. The Raman peaks are very diffuse and no sharp diamond-peak (at ~1332 cm^{-1}) was observable, which can be ascribed to the smallness of the grain size in these films [14]. But this peak is shifted to 1345 cm^{-1} and is due to disorder of diamond peak and the peak 1553 cm^{-1} is assigned as graphite peak [12]. Raman peaks around ~1150 cm^{-1} and 1480/1450 cm^{-1} are assigned as vibrations from trans-polyacetylene groups presenting at the grain boundaries [12]. A wide peak is also observed at the centre ~2050 cm^{-1} and probably due to nitrogen inclusion in the film structures.

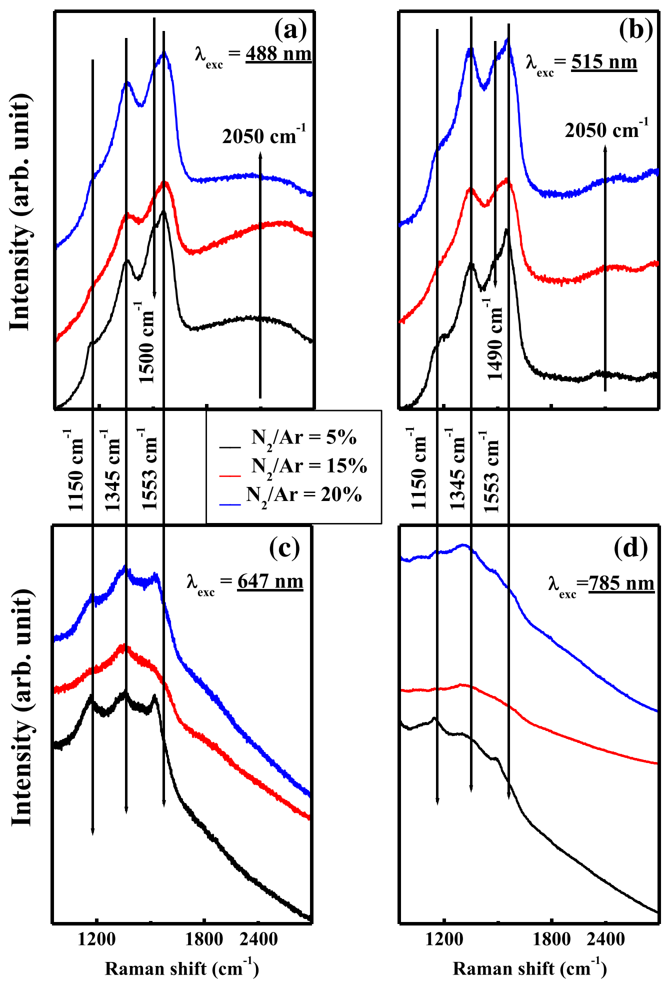

Fig. 1. Raman spectroscopy of UNCD thin films having % of N_2/Ar = 5–20% having LASER excitation wavelength (λ_{exc}): (a) 488 nm, (b) 515 nm, (c) 647 nm and (d) 785 nm.

Young's modulus of each UNCD film is measured with displacement and shown in Fig. 2 (a–c). It can be seen that Young's modulus is adversely affected by an increase in % of N_2/Ar during growth which is unlikely. In the case of the high N_2/Ar ratio regime, the best Young's modulus is just above 350 GaP at 20% N_2/Ar and decreases to below 200 GaP at 5% N_2/Ar. It is assumed that the sp^2 content decreases with the increase of % N_2/Ar; as a result Young's modulus increases, which is also unlikely. We are not sure about the incorporation of nitrogen content in the film structure, so we have estimated the nitrogen content present in the film structure using XPS measurements. It is found that the nitrogen content decreases with the increase of % N_2/Ar from 0.88 to 0.44 as tabulated in Table 1 and this is the reason why Young's modulus decreases with the increase of % N_2/Ar during deposition process. Hence, due to the decrease of nitrogen at.% in the film structure the sp^2 content decreases and hence Young's moduli increase. This may occur because these UNCD films are grown at low temperature (~450 °C) and such observation implies that N_2 is added in the plasma at such a low N-species that react with the C species. We have studied the C1s and O 1s XPS of UNCD films. Fig. 3(a) shows the C1s XPS of all UNCD films that shows that the peaks are shifted from higher energy level indicating the formation of sp^3 rich UNCD films and are consistent with Young's modulus of the films discussed above. Fig. 3(b) shows that the O1s XPS of all UNCD films also shows that the peaks are shifted at higher energy level with the increase of % N_2/Ar during deposition of UNCD films. XPS quantitative analysis shows that UNCD films have <5 at.% O and <1 at.% N in the film structure as tabulated in Table 1.

The *I–V* (current–voltage) characteristics of the Cu/UNCD/Ag are studied by dc voltage sweep measurements to evaluate the electrical effects of the obtained devices. Fig. 4(a) plots show a typical linear *I–V* curve within the range of 0–3.5 V with a sweeping step of 0.01 V of a Cu/UNCD/Ag cell. This curve clearly shows that the UNCD are semiconductor with saturation current of 3.0–0.5 × 10^{-10} A. This result shows that the conductivity decreases with the increase of % of N_2/Ar gas incorporation (with increase of nitrogen content) during UNCD preparation. Such behaviours also observed in our previous report on electron field emission study [9] and are similar with the observation of Chen et al. [15], in which the electrical properties of nitrogen doped UNCD films increased with the amount of nitrogen incorporated in the plasma. It is noted that the UNCD prepared by Chen et al. [15] is at high temperature (~800 °C), but our UNCD films are prepared without