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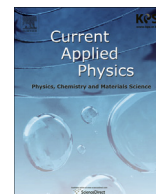
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Electrical and electronic properties of nitrogen doped amorphous carbon (a-CN_x) thin films



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ABSTRACT

Nitrogen-doped amorphous carbon thin films (a-CN_x) were prepared on silicon substrate by pulsed laser deposition process using methane (CH₄) and nitrogen (N₂) as source gas. The electrical properties of a-CN_x films changes with nitrogen concentration in the film structure. The intensity ratio of the D and G peak (I_D/I_G) increases with higher nitrogen concentration, which means that sp^2 -clusters were formed in these films and is responsible for the enhancement of conductivity of the a-CN_x films. We observed that the amorphous carbon (a-C) films becoming more graphitic in nature yielding higher conductivity/lower resistivity with increase of nitrogen concentration. Electron field emission result shows that the emission current density enhances with nitrogen doping that indicates the useful in electron field emission devices application.

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1. Introduction

Amorphous carbon (a-C) thin film has attracted attention as a cheap and environmentally benign material with outstanding properties such as chemical inertness, high hardness, high electrical resistivity and tunable band gap by adjusting sp^2 and sp^3 carbon bonding ratio for semiconductor technology [1]. Amorphous carbon (a-C) films shows a semiconducting nature that are of great technological importance because as many of their properties can be tailored by varying the amount of diver's industrial application [2]. It also promotes the application in the field of semiconductor technology, such as in fabrication of photovoltaic solar cells [3], different electrical/electrochemical performances [4], electrochemical storage of energy in capacitors and electrodes [5], field emission devices [6] and micro humidity sensors. Nitrogen additions to amorphous carbon (a-C) is motivated by the synthesis of the possible super-hard compound C₃N₄ [7] and the electronically nitrogen doping. It has been known that the radius of nitrogen atom is very close to that of carbon atom, so nitrogen is very preferable species for doping agent with carbon. Nitrogen can be doped with carbon nanotube to increase the electronic quantum transport properties [8] energy and catalytic applications [9,10],

nano-devices [11] and electro-analytical performance [12]. Nitrogen being a gaseous phase has the advantage of better control of dopant concentration in a-C films, and the incorporation of nitrogen can strongly decrease the defect density, which gives prospects on its use as a semiconductor material [13] for different energy related applications.

In this paper, we have studied the electrical properties of nitrogen doped a-C thin films (a-CN_x) at different deposition condition. The main novelty of this study is to improvement the electrical properties on nitrogen doing in a-C thin films and their possible application as semiconductors and optoelectronic devices.

2. Material and methods

The a-CN_x films were deposited on single-crystal silicon (100) substrates at different nitrogen concentration (at %) by xenon chloride (XeCl) excimer pulsed laser deposition (PLD) process. The PLD system consisted of a Ti-sapphire laser ($\lambda = 800$ nm) with a repetition rate of 1 KHz and a full width at half maximum (FWHM) of 50 fs. The laser beam was focused at an angle of incidence of 45° to the target normal. The substrate-to-target distance remained at 4 cm. All depositions were carried out at room temperature. Prior to each deposition chamber was pumped down to approximately 9.8×10^{-6} mbar. A laser fluence of 0.64 J/cm² was used to ablate a graphite target (purity 99.999%). The films were prepared as a

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function of nitrogen pressure i.e nitrogen doping in the a-C films is achieved by introducing the nitrogen gas into the arc region of the graphite cathode. The N_2 doping concentration can be controlled by changing the nitrogen gas flow rate (nitrogen partial pressure). During deposition, the nitrogen was released into the chamber with a mass flow controller used to control the background nitrogen pressure. Films were prepared at various nitrogen pressures ranging from 1×10^{-3} to 0.7 mbar. The deposition time for these films was approximately 15 min in which the thickness ranged from 150 to 200 nm for samples with low nitrogen content (from 0–4 at% N). Moreover at higher nitrogen contents (14 at% N) film thicknesses were approximately 95–115 nm [14]. The compositional and quantificational analyses were performed using X-ray photoemission spectroscopy (XPS) and described in details elsewhere [14]. A Jobin Yvon T64000 Raman spectrometer equipped with an Ar ion laser (448 nm) was used to examine the microstructure of the films. The laser power on the sample was 5 mW, and the spectra were recorded over a 20 s period having LASER beam spot size ~ 1 m. The electrical resistivity was measured by I – V characteristics of 4140B pA Meter/DC voltage source at room temperature (as well as temperature variation resistance) using a two-point probe resistance measurement method. Electron field emission characteristics were performed using a Keithley power supply (Keithley: model 237). The cathode voltage was applied by an analog programmable 1.0 kV power supply under computer control, and the measured emission current was logged at each voltage. The measurements were carried out under a low 10^{-6} torr ambient pressure. The movement of the anode tip (1 mm diameter) was

measured digitally, and the gap between emitter and collector was confirmed by optical microscope. During the measurements the anode and cathode distance in the field emission system was fixed at 200 μm , which is the thickness of the microglass spacer used to isolate the cathode from the anode.

3. Results and discussion

Raman spectra of a- CN_x at different N at % concentration with laser excitation wavelength $\lambda = 448$ nm Fig. 1, after de-convolution into G-peak and D-peak of each spectrum using Gaussian lines and their results are tabulated in Table 1. The G-peak and D-peak positions are shifted towards higher Raman frequencies level with increase of nitrogen concentration. The full width at half maximum (FWHM) of the G peak and D-peak decreases and increases respectively indicating the formation of more and more graphitic a- CN_x thin films. We have obtained the intensity ratio of D-band and G-band from the area (height) of the respective convoluted peak and it shows that the I_D/I_G ratio increases as a function of nitrogen concentration (see Table 1). This increase of I_D/I_G ratio further confirms the formation of more disorder-like a-C thin films. An I_D/I_G ratio of 0.51 (0.43) was calculated for the film deposited without incorporated N_2 . With increase of nitrogen to 14 at% we have observed the intensity ratio reaches the value of 2.01 (0.96). The G peak became narrower when they have more incorporated the nitrogen content. The results indicate the increase of disorder in the thin films structure. Increase of I_D/I_G ratio also relates to an increase in the number and size of sp^2 sites clusters in the a- CN_x film matrix. In our previous report [14] we have observed that the hardness is decreases with increase of N-content in the film structure which is good agreement with the increase of sp^2 -sites clusters in the a- CN_x film matrix because the hardness is decrease with increase of sp^2 -sites clusters. We also observed in our previous report [15] in x-ray absorption near edge structure (XANES) spectroscopy that the both sp^2 -N and sp^2 -C are increases with increase of N-content in the a- CN_x film structure, further confirms the formation of low hardness a- CN_x thin film.

The electrical resistivity of amorphous carbon can be strongly reduced by several orders of magnitude through incorporation of nitrogen in the films. Doping was better identified in a-C films where nitrogen was found to be a good n-type dopant causing a shift of the Fermi level with increasing nitrogen concentration [16]. The variations of nitrogen content in the thin film structure influence the electrical properties. The electrical properties of a- CN_x films significantly improves with increase of N content (at %). The current transport in a CN_x film-semiconductor junction is mainly due to majority carriers as opposed to minority carriers in the semiconductor-semiconductor junction. The current (I) – voltage (V) characteristics of the Au/a- CN_x /Au structure deposited at different nitrogen concentration (0–14 at%) are plotted in different ways and are shown in Fig. 2(a) linear; Fig. 2(b) log – log and Fig. 2(c) semi-log scale. When no nitrogen is used as the sputtering gas, a very poor conducting carbon film can be formed. As nitrogen

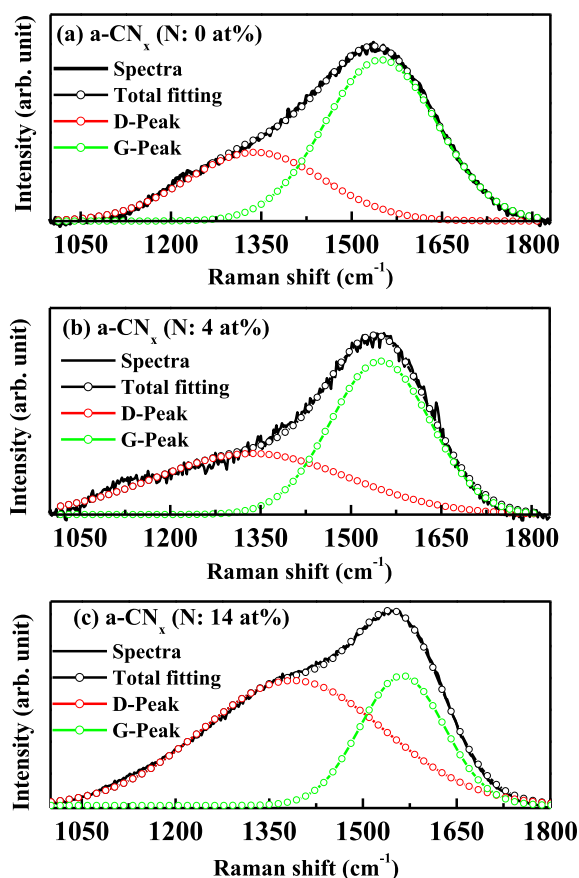


Fig. 1. De-convoluted into D-Peak and G-peak of Raman Spectra of a- CN_x films deposited at different nitrogen concentration (a) 0 at%, (b) 4 at %, (c) 14 at % [$\lambda_{\text{exc}} = 448$ nm].

Table 1

Raman band Parameters obtained after de-convolution of Raman spectra (laser excitation wavelength, $\lambda_{\text{ex}} = 448$ nm), turn on electric field (E_{TOE}) and resistivity of a- CN_x thin films.

Sample description (N at %)	Peak position		Width		(I_D/I_G) ratio		E_{TOE} (V/ μm)
	D-Peak (cm^{-1})	G-Peak (cm^{-1})	ω_D (cm^{-1})	ω_G (cm^{-1})	From area	From height	
0	1340	1549	225.4	187.0	0.51	0.43	26.3
4	1336	1549	320.0	165.7	0.77	0.40	18.5
14	1388	1563	291.5	135.1	2.01	0.96	17.5

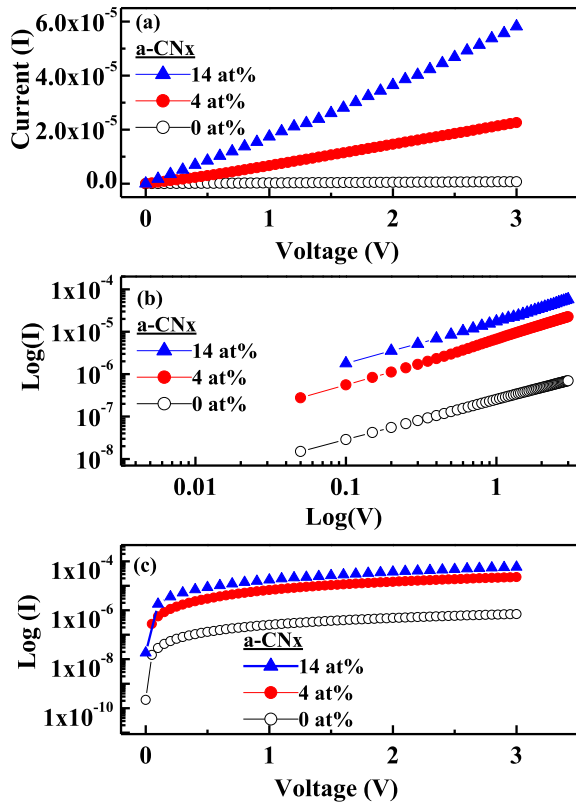


Fig. 2. Current (I) – Voltage (V) characteristics of the Au/a-CN_x/Au structure deposited at different nitrogen concentration (0–14 at%) are plotted (a) linear; (b) log – log and (c) semi-log scale.

(N at%) concentration increases, the current (the slope increases) also increase and it reaches the maximum at higher N-concentration. The conductivity of a-CN_x thin films increase with the formation of sp² rings cluster which resulted in the increase of localized hopping states. During nitrogen doping, the N–H, C–N, and C≡N bonds increased with increase in N₂ concentration. The increase in electrical conductivity could be attributed to C–N and C≡N bond creation in the a-C films [17]. Fig. 3 shows the temperature (T) dependence resistance (R) of these a-CN_x thin films. The R – T curves clearly indicated that the resistances gradually decrease with increase of temperature as well as nitrogen doping concentrations. Raman spectroscopy measurements revealed two peak D

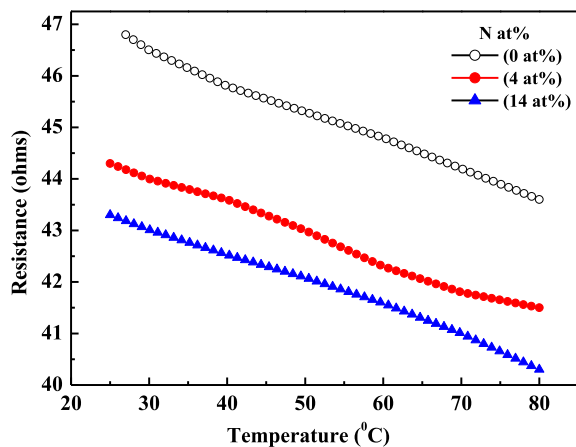


Fig. 3. Temperature dependence resistance of a-CN_x thin films.

and G bands, and the D band was more intense than the G band. The intensity ratio of the D and G peak augments with higher nitrogen concentration, which means that a sp² cluster [18] was formed in this films and is responsible for the enhancement of conductivity of the a-CN_x films. We conclude that at higher nitrogen concentration, a-C films show the increasing of graphitic characteristics yielding higher conductivity i.e lower resistivity as we found in our present study. Since, electrical conductivity as well as emission current density is improves with increase of N-content in the film structure as both sp²-N and sp²-C are increases with N-content.

Fig. 4(a) shows the results of the field emission measurements, the current density (J) versus applied electric field (E_A). Fig. 3(b) shows the Fowler-Nordheim (F–N) plot for the field emission of nitrogen treated and non-treated a-C thin films. It is observed that the field emission augments for a-CN_x compare to a-C thin films. The inset of Fig. 3(a) is the magnified lower part of J versus E_A of a-C and a-CN_x to see the difference of J among them. The turn-on electric field (E_{TOE}) of a-C is 26.3 V/μm that we obtain from the F–N plot, as plotted in Fig. 3(b). Interestingly, this E_{TOE} reduces to 17.5 V/μm on nitrogen doping although the turn-on field is very high with respect to reported a-C related thin films. The turn on electric field is the minimum amount of electric field applied (V/μm) on the sample that gives the emission current density is 10 μA/cm² [19]. Further, we have also obtained the field emission current density in the mA/cm² range for both undoped and nitrogen doped a-C thin films that shows that the nitrogen doped a-C is 10³ times higher current density than undoped a-C thin films. It is noted that

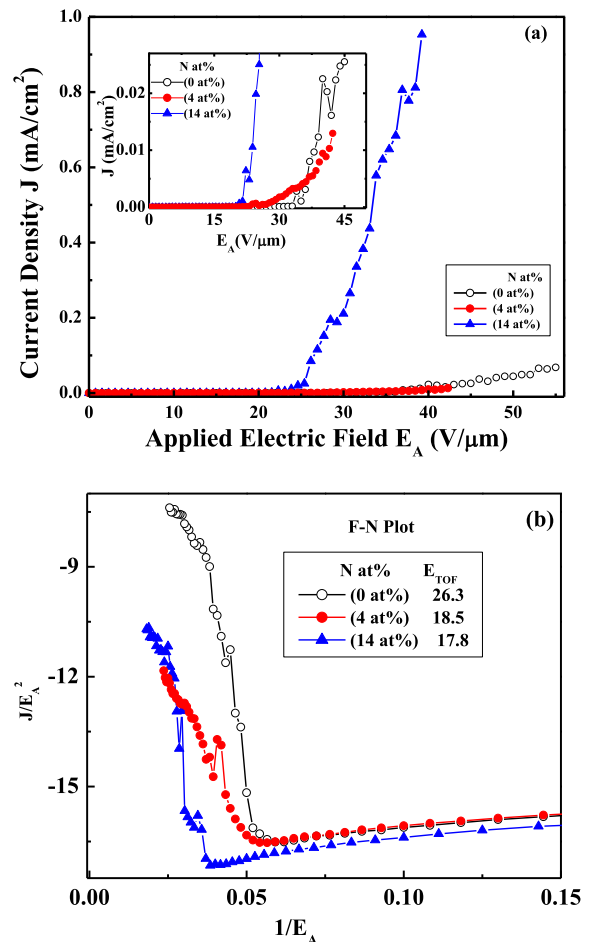


Fig. 4. Electron field emission characteristics of a-CN_x thin films deposited at different nitrogen concentration (a) 0 at%, (b) 4 at% and (c) 14 at%.

all these measurements were confirmed by repeating them at several points through the samples' surfaces. This improvement in field emission on nitrogen treatment is attributed to the change in chemical properties that occur during the process of nitrogen doping. The result of Raman spectra as discussed above implies that field emission current density increases with increase of I_D/I_G ratio. In principle, the field emission enriches with an increase in sp^2 -content in the film structure due to an increase in graphitization in a-C. The increase of I_D/I_G ratio implies the increase of sp^2 -content (order) and hence increases of emission of field electron from the a-CN_x thin film surface.

4. Conclusion

Metal free nitrogen-doped amorphous carbon thin films (a-CN_x) were prepared on silicon substrate by pulsed laser deposition process. The electrical resistivity changes with nitrogen concentration as well as change of temperature. The (I_D/I_G) ratio increases with nitrogen concentration, which means that sp^2 -clusters were formed in these films and are responsible for the enhancement of conductivity of the a-CN_x films. The electron field emission results show that the emission current density improves with nitrogen doping. These thin films could be used as energy based devices like optoelectronics and in fabrication of photovoltaic solar cells.

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