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FIELD EMISSION STUDIES OF NITROGEN DOPED DIAMOND LIKE CARBON FILMS DEPOSITED BY ELECTROLYSIS OF ORGANIC LIQUID

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Abstract

The aim of the work was to deposit amorphous Nitrogen doped diamond like carbon (a:N-DLC) films by electrodeposition process and to study the field emission properties of the films with different nitrogen content. a:N-DLC films were deposited on Si (400) substrates by electrolysis of methanol-urea solution under high voltage, at atmospheric pressure and at temperature below 350 K. The compositional analysis of the films was done by X-ray photoelectron spectroscopy (XPS). Bonding informations of the films were also obtained from Fourier transform infrared spectroscopy (FTIR) measurements. The results showed that the incorporated nitrogen was chemically bonded to carbon with C-N and C=N bonds. Nitrogen content in the films was varied from 3.5 to 6.0 at.% with the increase of urea concentration in the solution. Hardness values of the films were in the range of 11-15 Gpa. It was found that turn-on field and effective emission barrier were greatly reduced by N doping in DLC. The lowest turn-on field was obtained as 6.97 V/μm.

Keywords:

Electrodeposition;
Diamond like carbon;
N doping;
XPS;
Field emission.

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1. Introduction

Cold cathodes or electron field-emitters are potentially useful for field emission displays (FEDs). Diamond films possessing negative electron affinity (NEA) have a great potential for applications as electron emitters in vacuum microelectronics such as FEDs [1,2]. According to previous reports, threshold fields for the electron emission were usually 3-40 V/μm for the chemical vapour deposited (CVD) diamond films [3-6], which are considerably lower than those of metals or Si surfaces (1000 V/μm). Besides diamond, diamond like carbon (DLC) films are also attractive materials for the field-emitter applications. Diamond like carbon is a semiconducting

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form of amorphous carbon with a significant fraction of sp^3 bonding. DLC has the properties like diamond such as high hardness, high thermal conductivity, physical and chemical inertness. As electron affinity depends fundamentally on bulk bonding, not on crystallinity, amorphous DLC also has a low electron affinity [7]. In order to get stable electron emission it is needed to make the bulk or surface of the DLC films conductive. DLC can be doped n-type by the addition of nitrogen or phosphorous, and this increases their electron emission at low turn-on fields by raising their Fermi level and lowering the work function of the material. There are several reports on N doping to DLC films deposited by a variety of techniques, such as plasma enhanced chemical vapour deposition [8,9], filtered cathodic vacuum arc [10,11] etc., to enhance the emission current density at lower turn-on fields than undoped DLC. But all theses are vacuum deposition processes and involve complex equipment. From the viewpoint of practical applications the electrodeposition technique has many advantages over chemical vapour deposition (CVD) technique, such as simplicity of the apparatus, low deposition temperature, easy scalability, low cost, use of complex shaped substrates and availability for large area deposition. These are necessary conditions for producing large area flat panel display at reasonable cost.

In recent years several attempts have been made to synthesize diamond like carbon films by electrodeposition from various organic liquids under high voltages [12-16]. We have deposited crystalline carbon nitride films on Si (400) substrates by electrolysis of methanol-urea solution [17, 18]. Kiyota et al. [19] and Roy et al. [20] studied electron field emission from DLC films deposited by electrolysis of methanol and acetic acid + deionized water solution respectively. In our previous report [21] we have shown that field emission properties of DLC films were improved by nitrogen doping. Yan et al. [22] and Li et al. [23] studied electron field emission from electrodeposited nitrogen incorporated DLC films. However there are no much reports on optimum field emission from nitrogen doped DLC films by electrodeposition. Hence, research is still needed. In this work, N-doped DLC films were deposited on Si substrates by electrolysis of methanol-urea solution, structural analysis of the films was done and dependence of electron field emission properties on nitrogen content in the films was studied.

2. Research Method

The electrolysis deposition system was similar to that was used in our previous work [21]. The Si (400) substrate with a resistivity of 20 Ω-cm was mounted on the negative electrode. The counter electrode was a graphite plate. Substrate size was 1.5x1.0 cm^2. The distance between the electrodes was nearly 7 mm. Before deposition, the substrates were treated by 20% HF solution, then cleaned by distilled water and finally by ultrasonic cleaner. A D.C. power supply, which can be varied from 0 to 3 kV was used to apply high voltage to the cathode.

To deposit amorphous DLC (a:DLC) film methanol-camphor solution was used as the electrolyte. Camphor was used with the methanol to get more methyl groups in the solution which was favourable for deposition of a:DLC by electrolysis. In camphor ($C_{10}H_{16}O$) there are three carbon atoms attached to three methyl groups while the remaining seven carbon atoms are associated with a ring structure. The solution was prepared by mixing 5.0 gm. of camphor (99%) per liter of analytically pure methanol (99.5%). As the dielectric constant (ε) of methanol is higher (32.70) [24] and the growth rate of deposited films increased with the increase of ε values, methanol was used as the source solution instead of using any other liquid containing ethyl groups.

For nitrogen doping in a:DLC films, methanol-urea solution was used for the electrodeposition process. Different solutions were prepared by mixing 0.25gm and 0.5 gm. of urea ($CO(NH_2)_2$) (99.5%) per litre of analytically pure methanol. During experiment electrolysis voltage was kept constant at 1 kV while the current was varying from 200 mA to 180 mA. This decrease in substrate current density with time may be due to increased resistance of the deposited film on the conducting substrate. The temperature of the solution during all the experiments was nearly 350 K and deposition time was 30 minutes.

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The deposited films were characterized by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), hardness measurement and electron field emission studies.

3. Results and Analysis

The deposition mechanism may be discussed as follows:

Under high voltage, the molecules of CH_3OH and $C_{10}H_{16}O$ were polarized. The alkyl groups ($-CH_3$) from methanol and camphor with a part of positive charge moved towards the cathode and finally amorphous DLC film was deposited on the substrate. When urea was used with methanol in the electrolysis process, under high voltage the molecules of CH_3OH and $CO(NH_2)_2$ were polarized, two groups became partly discharged and moved in the electric field. The alkyl group ($-CH_3$) from methanol and ($-NH_2$) radical from urea both with a part of positive charge moved towards the cathode and a:N-DLC film was deposited on the substrate.

The composition of the films was investigated by X-ray photoelectron spectroscopy (XPS) (Kratos Analytical, A Shimadzu Group Company). A typical XPS spectrum of the a:N-DLC film is shown in fig. 1. The measurements indicated that the films contained carbon, nitrogen and oxygen elements. Probably, oxygen element comes from the surface adsorption of the films. The nitrogen content in the films was calculated from the integrated intensities of the N_{1s} and C_{1s} lines corrected by their sensitivity factors. Nitrogen content in terms of atomic percentage was varied from 3.5 % to 6.0 %, as concentration of urea in the electrolyte solution increased from 0.25 to 0.5 gm / litre. Fig. 2.(a) and (b) show the core-level line spectra of C_{1s} and N_{1s}. Deconvolution of the C_{1s} peak by Gaussian curve fitting suggests that three types of bonding exist around carbon atoms. The peak positions of the deconvoluted peaks are at 285.0, 286.6 and 288.8 eV. In the C_{1s} spectrum the peak at 285.0 eV can be assigned with C-C bonds in the film and to some C contamination at the surface of the film, which is often observed in XPS [25]. The peaks at 286.6 eV and 288.8 eV can be attributed to sp^2 trigonal and sp^3 tetrahedral CN bonding respectively [26]. The N_{1s} peak located at 398.9 is assigned to nitrogen bonded with sp^3 carbon [25, 26]. It was observed that as the N content increased, the C_{1s} peak became broader (not shown here). This broadening was due to the incorporation of nitrogen into the carbon network [15, 25].

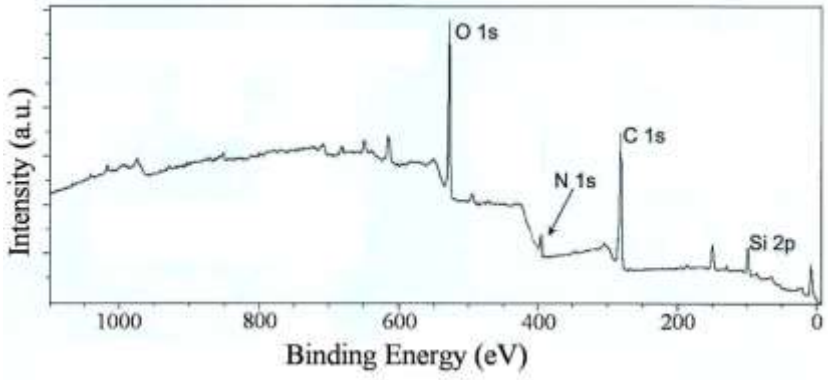

Figure 1. A typical XPS spectrum of a:N-DLC film

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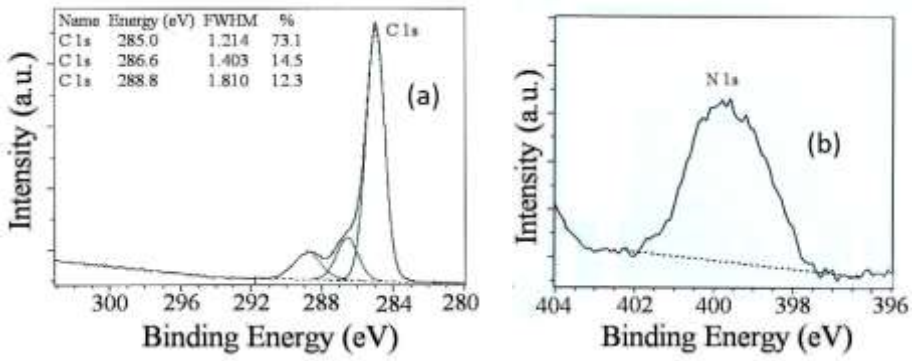

Figure 2. The core-level line spectra of (a) C_{1s} (deconvoluted peaks) and (b) N_{1s}

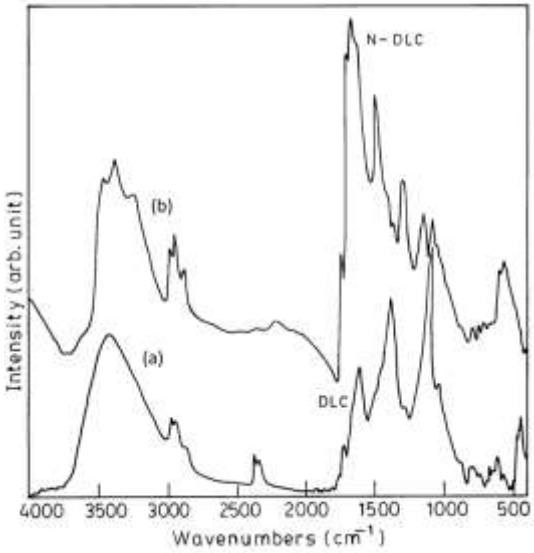

Figure 3. FTIR spectra of (a) undoped DLC and (b) nitrogen doped DlC films

IR spectroscopic studies were carried out to analyze the structure and bonding state of the deposited sample. The spectra were recorded in a FTIR spectrometer (Nicolet Magna - 750) in the wavelength range 400 to 4000 cm^{-1} by subtracting the absorption due to the Si substrate. Fig. 3(a) shows the FTIR spectrum of a typical undoped DLC film deposited by electrolysis on Si substrate. The 2958 cm^{-1} peak is assigned to an asymmetric mode of a saturated sp^3 $-CH_3$ group and the band at 2932 cm^{-1} corresponds to asymmetric mode of sp^3 $-CH_2$ stretching vibration. The 2850 cm^{-1} peak is assigned to a symmetric mode of sp^3 bonded $-CH_2$ group. The peaks in the range of 1375-1600 cm^{-1} are assigned to vibrations due to sp^2 carbon bonding. The broad band around 3400 cm^{-1} can be attributed to $-OH$ stretching vibrations. In the IR spectrum of a:N-DLC (Fig. 3. (b)) apart from the different C-H vibrational bands of DLC films, few new bands appeared due to nitrogen incorporation. Absorption at 3200-3500 cm^{-1} suggests the existence of NH_X (x=1, 2) bonds. The strong absorption at 1624 cm^{-1} can be attributed to the presence of C=N bonds [27]. The absorption bands around 1100-1300 cm^{-1} can be assigned with C-N stretching vibration. There is no evidence for the existence of C≡N stretching vibration (sp hybridization). The peaks at 1598 and 1353 cm^{-1} can be assigned as G and D peaks of amorphous carbon, which are normally IR forbidden but appear here due to symmetry breaking by N incorporation. Thus FTIR results confirmed the incorporation of N into the DLC matrix.

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The hardness of the films was measured by a microhardness tester V-Tester 4911(MXT-α1) with a Knoop indenter by applying 0.3, 0.5 and 1.0 kgf loads to the sample. Knoop hardness values of the films were in the range of 11-15 GPa.

Electron field emission properties of the films were studied. Field emission measurements were carried out by using a parallel plate configuration with the sample mounted on the cathode and a stainless steel anode having an area of 0.076 cm^2. The anode was attached to a micropositioner for varying the cathode-anode spacing (d_{CA}) with an accuracy of ±10 μm. Measurements were performed in a high vacuum of 10^{-7} mbar. All measurements were taken at d_{CA} of 100 μm. Fig. 4 shows the emission current density (J) plotted against applied field (E) for undoped DLC and a: N-DLC films. It was observed that turn-on field was 24.3 V/μm for undoped DLC. For a: N-DLC these were 10.5 V/μm and 6.97 V/μm for nitrogen content 3.5 at.% and 6.0 at.% respectively. The turn-on field (E_c) was defined as the electric field needed to get a current density of 20 μA/cm^2 and the field was computed as E_c=applied voltage/cathode-anode spacing. Exponential increase in current density was observed, exhibiting strong effect of N addition on J-E behavior. Turn-on field was greatly reduced by nitrogen incorporation. Also it was decreased with increased nitrogen content. Current densities were greatly increased with the increase of nitrogen content. With the applied field of 10 V/μm, a considerable current density of $2.9x10^{-4}$ A/cm^2 was obtained for 6.0 at.% nitrogen content. An explanation of the mechanism by which nitrogen caused increase in field emission properties of DLC can be provided. N acts as a weak donor in DLC, moves the Fermi level up, provides electrons close to the conduction band and lowers the work function of the material. Incorporation of N also introduces structural defects. These defects lead to tailing of the valance band maxima and conduction band minima and creating sub-bands within the mid-gap states (band gap), thus contribute electrons for emission at low electric fields. Also due to nitrogen incorporation more sp^2 sites are generated in DLC films [9]. These sp^2 sites form conducting channels in insulating DLC matrix and can cause large local field enhancement [23]. Hence, field enhancement required for electron emission at very low fields was achieved due to donor activity of nitrogen and conductive sp^2 sites, thus field emission properties were improved.

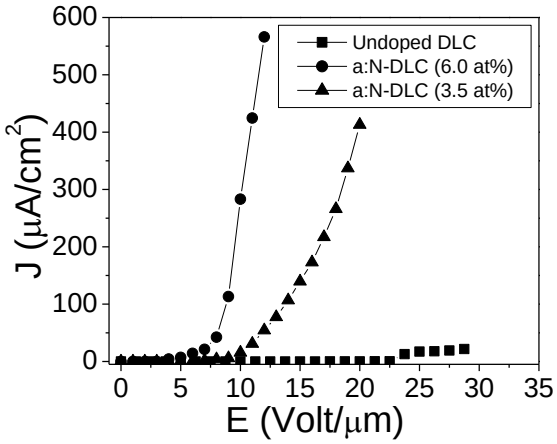

Figure 4. Emission current density (J) against applied field (E) plots for undoped DLC and a: N-DLC films

Field emission characteristics were studied using standard Fowler-Nordheim (FN) theory [28]. A simplified FN equation for the local current density J (Amp/cm^2) at some point on the emitting surface may be written as [29]:

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$$J = S\frac{1.54\times10^{2}F^{2}}{\phi}\exp\left[\frac{-6.83\times10^{3}\phi^{3/2}}{F}\right]$$

where F is the local field, ϕ is the local work function called the emission barrier in eV. F is not simply V/d, which is the macroscopic field obtained with an applied voltage of V between two electrodes separated by distance d. But, in most cases F = βE, where E = V/d, β is the geometrical enhancement factor at the surface of the emitter, S is the fraction of area emitting electrons, E is in Volt/μm.

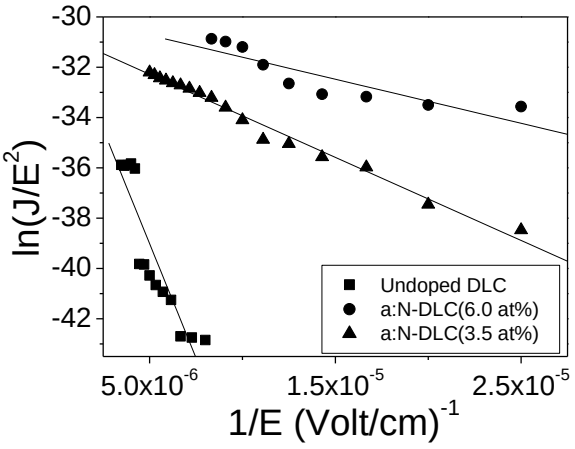

Figure 5. FN plots for undoped DLC and a:N-DLC films

The FN curves for undoped DLC and a:N-DLC films with different nitrogen content are shown in Fig.
5. The linearity of these FN plots in the high field region points towards the field emission mechanism. Assuming plane flat emitter with β=1, emission barriers (ϕ) were calculated from the slopes of FN plots. The values were 0.042 eV for undoped DLC, 0.013 eV and 0.009 eV for a:N-DLC with nitrogen content 3.5 at.% and 6.0 at.% respectively. It can be inferred that effective barrier height was reduced due to N doping in DLC films. Also emission barriers were reduced by increasing N content in the films causing reduction of turn-on fields and increment of emission current densities. But, true barriers must be larger than these values obtained from FN plots. Such low work functions obtained might be due to underestimation of the field enhancement factor β. However, an optimum nitrogen concentration within our experimental range to achieve the lowest turn-on field and to obtain maximum current density was 6.0 at.%.

4. Conclusion

Nitrogen doped diamond like carbon films have been deposited successfully on Si (400) substrates by the electrolysis of urea-methanol solution. XPS and FTIR spectra confirmed the incorporation of nitrogen into the DLC matrix. N doping enhanced the field emission properties of DLC. Turn-on field was reduced from 24.3 V/μm for undoped DLC to 6.97 V/μm for a: N-DLC with 6.0 at.% of nitrogen content. A considerable emission current density of 2.9 x10^{-4} A/cm^2 was obtained from a: N-DLC films with applied electric field of 10 V/μm, which is suitable for application of the material in field emission displays. Enhancement in field emission properties was attributed to the alteration of the electronic structure by the incorporation of substitutional defect states and the donor activity of nitrogen.

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