Silicon incorporated Diamond like Carbon films for field emission display

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Abstract: *Silicon incorporated diamond like carbon (Si-DLC) films were deposited via DC plasma-enhanced chemical vapor deposition, at substrate temperature 300°C. The precursor gas used was acetylene and Si incorporation was achieved by sending tetraethyl orthosilicate dissolved in methanol into the plasma chamber during deposition. Si concentration in the films was varied from 0 % to 19.31 % as measured from energy dispersive X-ray analysis (EDX). The binding energies of C 1s, Si 2s and Si 2p were determined from X-ray photoelectron spectroscopic studies. Surface morphology of the Si-DLC films studied by an atomic force microscope. We have observed low-macroscopic field electron emission from Si-DLC thin films deposited on glass substrates. The emission properties have been studied for a fixed anode-sample separation of 80 μm for different Si concentrations in the films. The turn-on field was also found to vary from 16.19 to 3.61 V/μm. Approximate calculated effective work function lies in the range 0.065 eV to 0.016 eV. It was found that the turn-on field and effective emission barrier were reduced by Si doping than undoped DLC.*

Keywords: Si-DLC; EDX; XPS; Field - emission; Low –threshold

Introduction

Field emission displays (FED) and vacuum microelectronic devices have recently attracted attention for low power panel applications because of their thin profile, high production efficiency, fast response, high brightness, wide operating temperature range, possible expansion of size and last but not the least, excellent picture quality at a lower cost [1]. During the last decade, the advent of low-macroscopic field (LMF) emission from carbon based films, such as diamond, diamond like carbon (DLC), carbon nanotubes and nanofibers etc., made them the candidate materials for FEDs. DLC has been extensively studied all over the world during the last two decades, as it possesses properties close to those of diamond, which make them a powerful candidate for the next generation of high performance electronic devices and other vacuum micro-electronic devices. DLC films have several inherent problems, such as their high internal stress and low thermal stability. The high intrinsic stress generated in the film causes some serious problems in various applications of this material, like degradation of electrical and optical properties and leads to peeling-off of the films from the substrate and poor adhesion. Silicon incorporated DLC films reduced residual internal stress without sacrificing the hardness, leads to good adhesion to metal alloys, steels and glasses, improved high temperature stability, reduced hydrogen loss, graphitization and resistance to oxidation [2-4]. Due to these noble properties of Si-DLC, it has been studied in the last few years and has potential applications in many areas. Most important is that, Si-DLC films are wide-band gap semiconductor material. This variability renders Si-DLC potentially attractive for electronic applications, such as in solar cells, photoluminescence cells, optoelectronic devices, and high-temperature engineering materials [5]. In this paper we report synthesis of silicon incorporated DLC films by plasma enhanced chemical vapor deposition (PECVD) method and studied the field emission properties for different silicon concentration in the films for fixed anode-sample spacing. The turn-on field, field enhancement factor and approximate effective work function are calculated.

Experimental details

The PECVD chamber was designed with appropriate stainless steel (SS) vacuum couplings through which different feed-throughs like vacuum port, pressure gauge, gas mixture inlets, thermocouple etc. could be introduced. The plasma was produced between two parallel plate SS electrodes. The lower disc was grounded upon which the substrate was placed. A substrate heating arrangement was made with appropriate substrate heater placed on the grounded electrode. The upper disc was used as the cathode electrode. When the chamber pressure attained 10^{-5} mbar, then C_2H_2 gas was introduced and diamond like carbon films were deposited at a pressure of 0.4 mbar. Glass and alumina were used as substrates. Deposition was made at 1.0 kV DC supply and the corresponding current density was 12.5 mA cm^{-2} for 30 min. For silicon incorporation tetraethyl orthosilicate (TEOS) dissolved in methanol solution was used. Ar gas was passed through the solution for bubble formation and then introduced into the chamber with appropriate needle valve arrangement. Si concentration was varied in the deposited films by varying the concentration of TEOS in the methanol solution.

Results and discussion

3.1 Compositional Analysis: Composition of the films (Si, C) were determined by energy dispersive X-ray analysis (EDX, Oxford, model-7582). Fig.1 shows a typical EDX spectrum of the Si-DLC film deposited on alumina substrate. It was seen that, the percentage of silicon in the films were nearly same with that of nominal concentration of TEOS in the methanol solution. Table 1 shows the composition of the films for different TEOS concentration. In Fig.1, other peaks of aluminium and oxygen appeared due to substrate.

3.2 XPS analysis: The carbon and silicon bonding configuration and composition of the DLC films were determined by X-ray photoelectron spectroscopy (XPS). The analysis was performed on the samples using a Specs (Germany) system with a hemispherical energy analyser. A non-monochromatic Mg Kα X-ray (1253.6 eV) was used as the excitation source operated at 10 kV and with an anode current 17 mA. The residual pressure of the system was ~10^{-9} mbar. The XPS survey scan of the silicon-doped DLC films shows clearly the contributions from C 1s (~285 eV), Si 2p (~100 eV), Si 2s (~151 eV) and O 1s (~531 eV) [6]. Typical spectra of DLC film and silicon incorporated DLC film shown in Fig. 2. Since XPS is a very surface sensitive technique, the detection of oxygen suggests various sources of surface contamination.

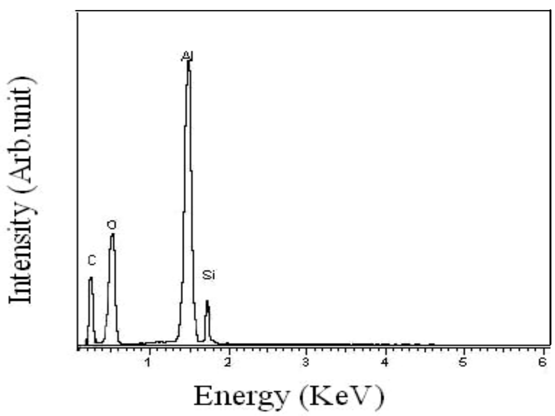

Figure 1. EDX spectrum of a Si-DLC film for 15% TEOS solution

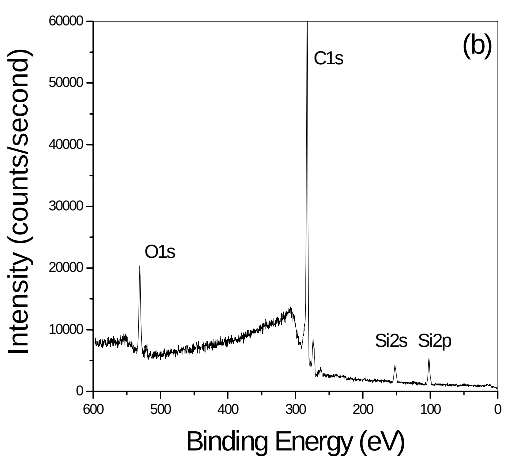

Figure 2. The XPS spectra of the DLC films (a) without silicon and (b) 14.28 % silicon incorporated DLC films deposited on alumina substrate.

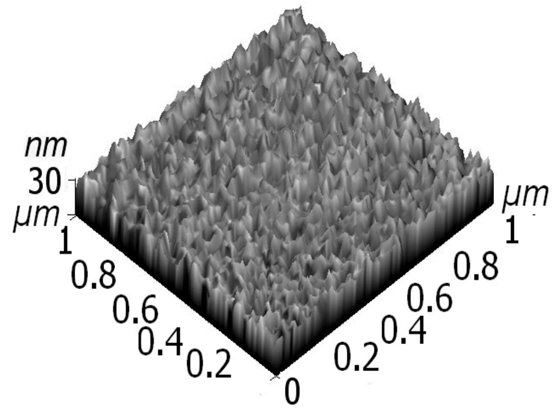

Figure 3. AFM 3D pictures of 19.31 % silicon incorporated DLC film

3.3 Morphology studies: AFM imaging provides more detailed information involving the surface morphology of the Si-DLC films. Fig. 1 shows typical AFM pictures of the 14.28% silicon incorporated DLC films, respectively. It was seen that Si-DLC films are uniform and compact, which indicates that the incorporated silicon particles are well dispersed in the amorphous DLC matrix. The measured surface roughness shows the surfaces of the Si-DLC films are rougher than that of the undoped DLC film. The RMS roughness of the silicon incorporated DLC film is approximately 3.7 nm within the surface area of 1 µm × 1 µm.

Field-Emission measurement: The electron field emission properties of the films deposited on Si substrates have been studied by our high vacuum (~10^{-7} Torr) field emission setup [7]. The measurements were performed at a base pressure of ~7 x 10^{-7} mbar. The negative terminal of the high voltage dc power supply (range 0 to 5 kV) was connected with the films by silver paint, at least 6 mm away from the position of the anode tip. The tip-sample distance was continuously adjustable to a few hundred µm by spherometric arrangement with screw-pitch of 10 µm. The anode-sample spacing was set at a particular value by rotating the micrometer screw which served as an anode electrode. The position of just touching the anode with the sample was determined by an optical microscope and then various spacings were obtained by rotating the micrometer screw as its screw-pitch is known. The current was measured by a Keithley Electrometer (model 6514). The whole surface of the film was visible through the chamber view port, which enabled us to recognize the electron emission and discharge. It was confirmed that there was no discharge and the current observed due to cold field emission of electron from Si-DLC films. Fig. 4(a) shows the emission current (I) vs. macroscopic field (E) curves of for undoped and Si-DLC films for different Si concentration taking anode-sample separation (d) of 80 μm. The macroscopic field is calculated from the external voltage applied (V), divided by the anode-sample spacing (d). Theoretically, the emission current I is related to the macroscopic electric field E by

$$I = Aat_F^{-2}\,\phi^{-1}(\beta E)^2 \exp\{\frac{-bv_F\phi^{3/2}}{\beta E}\} \qquad (1)$$

where, ϕ is the local work-function, β is the field enhancement factor, A is the effective emission area, a is the first Fowler-Nordheim Constant (1.541434 x 10^{-6} A eV V^{-2}), b is the second F-N Constant (6.830890 x 10^9 $eV^{-3/2}$ V m^{-1}), and v_F and t_F are the values of the special field emission elliptic functions v and t, evaluated for a barrier height ϕ.

An experimental F-N plot is modeled by the tangent, which can be written in the form [8]:

$$\ln\{\frac{I}{E^2}\} = \ln\{rAa\phi^{-1}\beta^2\} - \frac{(sb\phi^{3/2}\beta^{-1})}{E} \qquad (2)$$

where r and s are appropriate values of the intercept and slope correction factors, respectively. Typically, s is of the order of unity, but r may be of order 100 or greater. Both r and s are relatively slowly varying functions of 1/E, so a F-N plot (plotted as a function of 1/E) is expected to be a good straight line. The F-N plots of our sample are shown in Fig. 4(b). It has been observed that all the I-E curves in the present work are satisfactorily fitted with the F-N equation (Eqn. 2). This suggests that the electrons are emitted by field emission process. The turn-on field (E_c), which we define as the macroscopic field needed to get an emission current I = 0.034 μA, were lying in the range 3.61 to 16.19 V/μm.

It has been observed that the turn-on field was greatly reduced for the Si-incorporated DLC films than that of the film grown without silicon. The lowest turn-on field achieved was 3.61 Volt/μm for the sample with 19.31 % Si, while for the intrinsic material it was 16.19 Volt/μm. The turn on field and corresponding Si % in the films are given in table 1. Assuming plane flat emitter with β=1, emission barriers (ϕ) were calculated from the slopes of FN plots. The value of ϕ was reduced

Table I. Comparison of turn on field for different % of Si in the films from EDX measurements.

Sample name	Nominal % of Si in solution	Si % from EDX	Turn on field (V/μm)
DLC-20	20	19.31	3.61
DLC-22	15	14.28	5.30
DLC-24	10	9.63	6.51
DLC-25	5	4.79	8.29
DLC-28	0	0	16.19

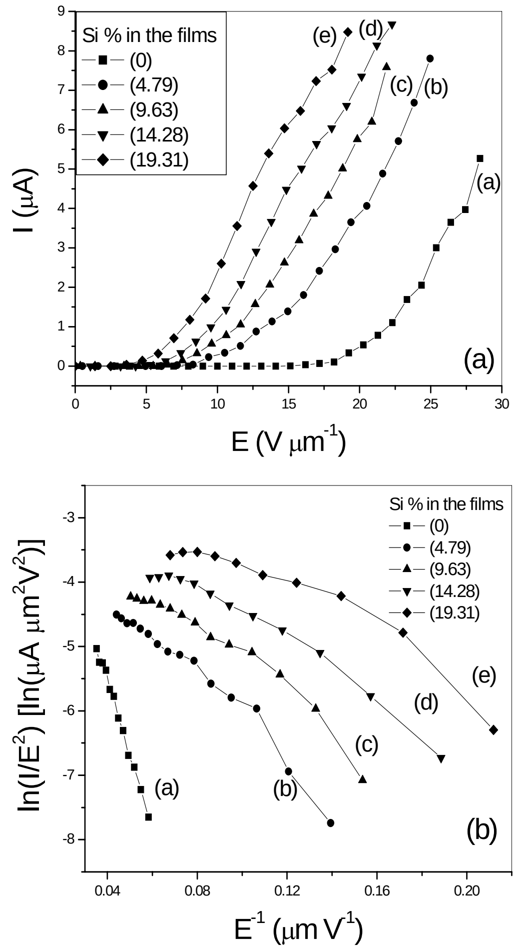

Figure 4(a). Emission current (I) vs. macroscopic field (E) curves of Si-DLC films for different silicon concentration and **Figure 4(b).** F-N plot of Si-DLC thin films for different Si concentration.

from 0.065 eV to 0.016 eV for an optimum Si incorporation. But, true barrier must be larger than these values. Such low work function obtained may be due to an underestimation of the field enhancement factor β. Such low barriers are not compatible with field electron emission and are significantly lower than 2.5–3.5 eV electron affinity found in amorphous carbon material [9]. The emission mechanism may involve a strong field enhancement at the front surface. Previously Amaratunga and Silva [10] proposed a hot electron space charge induced band bending model to account for the emission from amorphous carbon films. To understand the F–N emission process in our Si incorporated DLC films, it is necessary to explain the origin of the large enhancement factor required to lower the barrier for easy electron emission. Ilie et al. [11] proposed that the presence of sp^2 clusters within the insulating sp^3 matrix could give rise to field enhancement in amorphous carbon (a:C) films containing large defect densities (>10^{-19} cm^{-3}). It was proposed that the presence of such dielectric inhomogeneity is responsible for field enhancement in these films. Groning et al. [12] explained the emission mechanism from DLC films in a way that, like a freestanding conductive tip in the vacuum, sp^2 bonded carbon clusters are assumed to form a conductive channel in an insulating matrix, which leads to local field enhancement and hence to an enhanced electron emission. The effect of introducing any foreign element into the DLC matrix, like silicon may be to allow an easier formation of sp^2 channels. In the case of our deposited Si-DLC films, Si particles along with the sp^2 regions within the insulating sp^3 matrix are assumed to form conductive channels extended through the whole thickness of the film to the vacuum. The electron traversing through the channels experiences a high electric field. The effective barrier height was reduced with the addition of silicon impurity in the amorphous DLC matrix.

Conclusion

Silicon incorporated DLC in thin film form have been successfully synthesized on glass and alumina substrates via PECVD. The percentage of Si in the films has been varied from 0% to 19.31% as measured from energy dispersive X-ray analysis (EDX). The XPS survey scan of the silicon-doped DLC films shows clearly the contributions from C 1s (~285 eV), Si 2p (~100 eV), Si 2s (~151 eV) and O 1s (~531 eV). Si-DLC film has showed good electron field emission properties with a low turn-on field. The turn-on field lying in the range 3.61 to 16.19 V/μm for the films with different Si concentration and for an anode-sample separation of 80 μm. Approximate calculated effective work function lies in the range 0.065 eV to 0.016 eV. 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 silicon. This study shows that Si-DLC films might become good candidates for low-threshold field emitter, among other applications.

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