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Room-temperature deposition of diamond-like carbon field emitter on flexible substrates

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Abstract

Room-temperature fabrication of diamond-like carbon electron field emitters on flexible polyimide substrate is reported. These thin film field emitters are made using an Ar gas cluster ion beam assisted C_{60} vapor deposition method. The bond structure of the as-deposited diamond-like carbon film was studied using Raman spectroscopy. The field emission characteristics of the deposited films were also measured. Electron current densities over 15 mA/cm² have been recorded under an electrical field of about 65 V/µm. These diamond-like carbon field emitters are easy and inexpensive to fabricate. The results are promising for flexible field-emission fabrication without the need of complex patterning and tip shaping as compared to the Spindt-type field emitters. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The development of mobile computation, communication and entertainment platforms has created an enormous demand for flat-panel displays. In such a situation, fieldemission displays (FEDs) are of most interest as a promising flat-panel display technology. The realization of such field-emission vacuum microelectronics requires high and stable electron emission currents. The attractive physical and chemical properties of diamond-like carbon (DLC) compared to the Si Spindt tips [1], along with its high thermal conductivity, chemical inertness, its relatively high optical gap, its high breakdown field strength and its simple, low-cost manufacturing processes make it a promising cold-cathode field emitter. The room-temperature deposition of DLC thin film field emitters on plastic substrates would be of great interest for flexible FED applications that look like print on paper. Flexible carbon nanotube field emitter devices have been realized recently using plasma enhanced chemical vapor deposition at 200 °C [2]. However, there is no report on any DLC thin film flexible field emitters. The use of a DLC thin film field emitter rather than a Spindt tip enables device fabrication without complex patterning and tip shaping.

DLC films have been produced by numerous methods for the field-emission application [3–8], for instance, filtered vacuum arc discharge systems, chemical vapor deposition process, physical vapor deposition process and ion beam assisted methods. However, they each present various problems for practical implementation.

Recently, a new DLC thin film deposition method employing evaporation of C_{60} onto a substrate with

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simultaneous irradiation of an energetic argon gas cluster ions beam (GCIB) was demonstrated [9]. When the Ar gas cluster beam impacts the target, the synergy effect of cluster-solid interaction produces a transient condition of high pressure and high temperature [10], which can enhance the phase transition from sp² to sp³ even when the substrate is at room temperature. As deposited, the DLC films possess superior mechanical properties compared to DLC films produced using other methods. However, the electronic properties of the DLC films fabricated using GCIB-assisted method have not yet been fully determined.

In this paper, studies of electron field-emission properties from DLC films deposited on high conductivity n-type doped Si and flexible plastic substrates by deposition from C_{60} vapor, under simultaneous bombardment by Ar-cluster ions are reported. The as-deposited DLC films exhibit an emission current density that is sufficient for applications in flexible FEDs. Moreover, uniform quality over a large deposition area is easily realized by scanning the cluster ion beam or moving the substrate.

2. Experiment

A schematic view of the gas cluster ion beam experimental setup used for the DLC thin film deposition has been presented elsewhere [11]. Briefly, the neutral Ar-cluster beams were generated by supersonic expansion of highpressure (~ 8000 Torr) Ar gases through a lava nozzle into a vacuum chamber. Ionization of the neutral cluster beam was achieved by electron bombardment from a hot cathode source. The cluster mean size was estimated around 3000 atoms. Subsequently, the cluster ions were accelerated up to 30 keV and scanned to uniformly irradiate the target substrate. In this study, we choose 140-µm-thick commercially available Kapton® polyimide foil (Dupont) as the flexible substrate because it is widely used and is compatible with microelectronic device processing. A 0.2 µm thick PVD titanium nitride (TiN) film was deposited at room temperature $(\sim 70 \text{ °C})$ on the polyimide foil to act as the back metallic contact. The residual pressure was around 10^{-8} Torr; the pressure during film growth was $\sim 10^{-6}$ Torr (mostly nitrogen from the source). Energetic nitrogen ions bombardment at 40 eV provided good adhesion of the TiN film to the polyimide foil. During the DLC thin film deposition, the substrates were kept at room temperature. No degradation or stress-related curvature on the flexible plastic substrate was observed. Atomic Force Microscopy (AFM) was used to characterize the surface morphology of the as-deposited DLC film on the Si substrate. The detailed bonding structure of the DLC deposited on Si and polyimide foil was studied by Raman spectroscopy using a Jobin Yvon HR640 spectrometer equipped with a microscope, a notch filter and a liquid-nitrogen-cooled CCD detector. The 632.8-nm line of a He-Ne laser was used for excitation. A $100 \times$ objective was used both to focus the incident laser (power of approximately 1 mW) at a spot of approximately 2 µm diameter and collect the scattered light.

3. Results and Discussion

In general, the Raman spectra of amorphous carbon consist of two modes (the G and D peaks). The G peak $(1580-1590 \text{ cm}^{-1})$ originates from the in-plane E_{2g} mode of graphite. The D peak at about 1350 cm^{-1} , is the A_{1g} mode of disordered graphite.¹² Fig. 1 shows a typical Raman spectrum of our deposited DLC film on Si using the 30 keV Ar-GCIB-assisted C₆₀ evaporation method, with a C_{60} to Ar-cluster ratio of approximately 22. The effect of C₆₀ to Ar-cluster ratio on the DLC formation is studied in detail elsewhere. As shown in Fig. 1, the spectrum shows a broad peak centered at about 1507 cm^{-1} and a secondorder Si line at 940–980 cm⁻¹. The DLC films deposited on flexible polyimide foil have the same feature around 1507 cm^{-1} region. Following Prawer's procedure [12], the broad peak at 1507 cm⁻¹ can be fitted with a Breit-Wigner-Fano (BWF) line and a linear background using a least-squares method. The BWF line is given by

$$I(\varpi) = \frac{I_0 [1 + 2(\varpi - \varpi_0)/Q\Gamma]^2}{1 + [2(\varpi - \varpi_0)/\Gamma]^2}$$
(1)

where I_0 is the maximum peak intensity, ϖ_0 is the peak position, Γ is the full-width-half-maximum (FWHM) and Q^{-1} is the coupling or skewness coefficient. The data can be fitted using a single BWF line with the peak position at 1507 cm⁻¹ and a coupling coefficient Q of -22. The solid line in Fig. 1 is the resulting fit. According to Prawer, the red-shifting of the peak position and the low Q value indicate that the sp³ concentration of the DLC sample in this study is higher than 80% [13].

The AFM image of the as-deposited DLC film on Si is shown in Fig. 2. The inset shows an amplified view of 1 µm square with a height of 20 Å. Atomic level smooth DLC film was achieved with a root-mean-square roughness $R_{\rm ms} \sim 2.5$ Å. This ultra-smoothness is possibly due to a combination of the lateral sputtering effect in cluster-solid



Fig. 1. Raman spectrum of DLC deposited on Si with a 30 keV Ar gas cluster ion beam assisted C_{60} evaporation at a C_{60} to Ar-cluster ratio of around 22. Circle dots are experimental data; solid line is Breit–Wigner–Fano (BWF) fitting curve, which indicates the sp³ concentration, exceeds 80% in this DLC film.



Fig. 2. AFM image of DLC deposited on Si with a 30 keV Ar gas cluster ion beam assisted C_{60} evaporation at a C_{60} to Ar-cluster ratio of around 22. The root-mean-square roughness $R_{\rm ms} \sim 2.5$ Å. The inset is an amplified landscape of 1 μ m square with a height of 20 Å.

interactions, and the impact-transient surface diffusion mechanism [11,14].

The resistivity of the DLC film is about $9 \times 10^3 \,\Omega$ cm measured by four-probe technique. Field-emission characteristics of the DLC films were studied in a high vacuum chamber with a pressure below 10^{-7} Torr. The voltage was applied between a flat-ended tungsten tip and the film surface, with the tip-surface distance being varied between 10 and 100 µm. An XYZ stepper motor stage was used to control the tip motion in three directions. An optical telescope system with a CCD camera and monitor are used for monitoring tip positioning, and for immediate in situ observation of any electrical field induced modification of the sample surface. A high dc voltage, up to 8 kV, is applied between the sample and the probe to induce field emission. The measurement procedure included recording of the emission current during the automated cycling of an applied electric field. The emission current density was calculated by dividing the measured current by the total surface area of the tip used, which is about 0.25 mm^2 . The turn-on electric field and the emitted current density were measured for several DLC samples deposited under different conditions. Stability measurement of the emission process with time was also performed.

Field-emission characteristics of DLC thin films deposited on conductive silicon substrates were first measured. Electron emission initiated at an average electrical field of about 40 V/µm with a current density of 6.0 mA/cm² at 50 V/µm. There was a slight increase in the turn-on electrical field for DLC films deposited on the polyimide foil. However, the current density was substantially higher for those samples that were deposited under higher C₆₀/argon cluster ratios. Fig. 3 shows the current density vs. electrical field of a 120 nm thick DLC film, which was deposited at room temperature on polyimide foil using a C₆₀/argon ratio of ~22. The turn-on electrical field is about 55 V/µm at a current density of 17 mA at 68 V/µm. The inset graph shows the Fowler–Nordheim fit of the field-emission data



Fig. 3. Emission current density as a function of the applied electric field for the Ar-GCIB-assist deposited DLC field emitters on TiN covered Kapton. The inset is corresponding Fowler–Nordheim plot. The linearity of the curve indicates field-emission characteristics.

indicating that the collected current does indeed has fieldemission characteristics. The plotted current density data was averaged over four quadrant sites with a step distance of 0.28 mm from each other. Because the DLC film surface was extremely smooth, an estimation of the emission of the emission current density fluctuation in the XY direction was less than 5%. A temporal stability measurement on the same sample shows less than 5% current density fluctuations during one-hour testing operation and longer test runs are underway.

4. Conclusion

In summary, diamond-like carbon was successfully deposited on both Si and flexible polyimide substrates using an Ar gas cluster ion beam assisted C_{60} vapor

deposition method. Raman spectroscopy study reveals that the sp³ concentration is more than 80%. A field emission current density of over 15 mA/cm² has been realized under an electric field of about 65 V/ μ m for DLC deposited on flexible polyimide substrate. The results are promising for the fabrication of flexible flat-panel displays.

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