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The field emission properties of ''porous diamond-like'' carbon structures have been characterized. A hot filament chemical vapor deposition system fed with ethyl alcohol vapor diluted in helium was used to deposit the samples. Morphological analysis by field emission scanning electron microscopy revealed that they had a highly porous structure, which was attributed to the modification of the kinetics of the carbon deposition process due to the presence of helium as a buffer gas. Micro-Raman spectroscopy showed two peaks in the graphene and microcrystalline graphite frequencies and a new peak at 1620 cm^{-1}. Low threshold fields (E_t) and hysteresis in the current versus voltage characteristic have been observed, and a model to explain the hysteresis is proposed. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1517724]

Considerable attention has been given in recent years to the electronic properties of different forms of nanostructured materials, since these properties are different from those in the bulk state. For example, nanostructured carbon has the exceptional property of easy emission of free electrons from its surface to the vacuum when low external electric fields are applied, even at room temperature.[1–7] This process, named cold field emission, has potential applications in vacuum microelectronics,[8] microwave amplifiers, and luminescent flat panel displays,[7] among others.

Field emission from different samples of diamond-like carbon[3] and carbon nanotubes (CNTs)[1,2,4–7] have been studied. From these reports, the best field emission characteristics have been achieved using CNT samples, and this is often attributed to their high aspect ratio geometry and small tip radii which enhance the local electrical field at the tips for the electron emission process.[2,7] Therefore, it is also of interest to investigate the field-emission properties of other forms of high roughness nanostructured carbon, such as the variety of ''porous diamond-like'' materials that may be produced using new preparation techniques.

In this letter we investigate the electron emission from porous diamond-like structures synthesized by chemical vapor deposition (CVD) in a hot-filament reactor fed with ethyl alcohol vapor and helium. The use of inert helium instead of reactive hydrogen was to modify the kinetics of the carbon crystallization process at the atomic level, and to contribute to the increase of the final surface roughness of the samples. We show that the samples prepared by this process have very high porosity and electron emission of 10 $\mu A\,cm^{-2}$ with a threshold field (E_t) of 1.3 V μm^{-1}. A clear hysteresis in the Fowler–Nordheim (FN) current–voltage characteristic is observed. Analysis of the structures made by micro-Raman spectroscopy and field emission scanning electron Microscopy (FESEM) are discussed.

The samples were prepared by a hot-filament CVD reactor originally optimized for diamond synthesis.[9] However, instead of the conventional H_2 gas chemistry, the system was fed with a vapor mixture of ethyl alcohol (C_2H_5OH) diluted only in helium. Total gas flow rate (regulated by precision mass flow meters) and pressure were maintained at about 110 sccm and 20 mbar, respectively. Substrates were polished Si wafers of low electrical resistivity, with temperature monitored by a thermocouple, embedded in the substrate holder. Temperature was kept constant at 1128 K by the control of the power applied to the filament (about 200 W). A total processing time (nucleation and growth) of 7 h was used. The samples were characterized by micro-Raman spectroscopy (at ambient temperature) employing a Jobin–Yvon T64000 Raman spectrometer, with the argon line at $\lambda = 514.5$ nm used for excitation at a laser power of about 6 mW. Morphological analyses were made by FESEM using a JEOL JSM6330F. The characterization of field emission properties was performed by the measurement of current versus voltage ($I-V$) curves for different anode–cathode (sample) spacing in parallel plate configuration.[6] Spacers of known thickness (d) and anodes and cathodes of the same area have been used. The threshold field (E_t) for a given threshold current (I_t) was determined by the slope of the V_t versus d curves fitted to straight lines. To plot the $I-V$ curves in the FN form the emission current was measured either with increasing or decreasing bias voltage, indicated in the plot as ''rise'' or ''fall,'' respectively.

Figure 1 shows the typical micro-Raman spectrum of the samples. Three scattering peaks may be seen: two prominent peaks centered at 1350 cm^{-1} and 1580 cm^{-1}, together with a small broad peak centered at 1620 cm^{-1}. The peak at 1350 cm^{-1} corresponds to disorders on the graphene layers, and the peak at 1580 cm^{-1} corresponds to graphene crystal-

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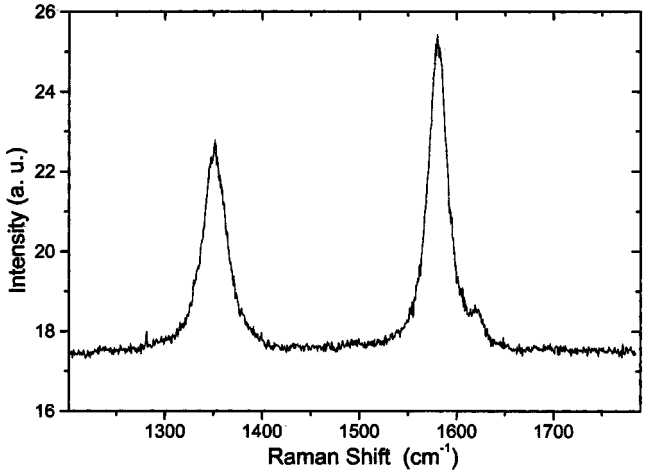

FIG. 1. Typical room-temperature micro-Raman spectrum of the porous diamond-like samples.

line layer. Both peaks are observed in the Raman spectra of several types of CNT,[10,11] microcrystalline graphite,[12] and fullerenes.[13] The small broad peak at 1620 cm^{-1} was not identified and was not observed in other carbon materials. It may, therefore, represent a signature of the present porous diamond-like samples.

The typical morphology of the sample shows the coalescence of round-shaped features of diameter in the range of 1 to 2 μm, forming three-dimensional mesostructures of entangled wires, deposited on the Si surface, with no apparent preferential orientation. Figure 2 shows a FESEM image of a typical entangled wire surface. There is clear evidence of a highly porous structure, since the pores and flaws which appear dark are much larger than the thickness of the pore walls ($\sim$10 nm). A rough estimate indicates that the porosity is higher than 80%. The elevated inert gas concentration increases the gas-phase diffusion barriers and also decreases the adatom mobilities at the growing surface.[14] Starting from the first nucleation step these mechanisms inhibit the lateral deposition rate of carbon atoms on the substrate to the end of the growth process, and may be the main factors responsible for production of the highly porous morphologies observed in these samples.

The typical threshold voltage V_t versus distance d mea-

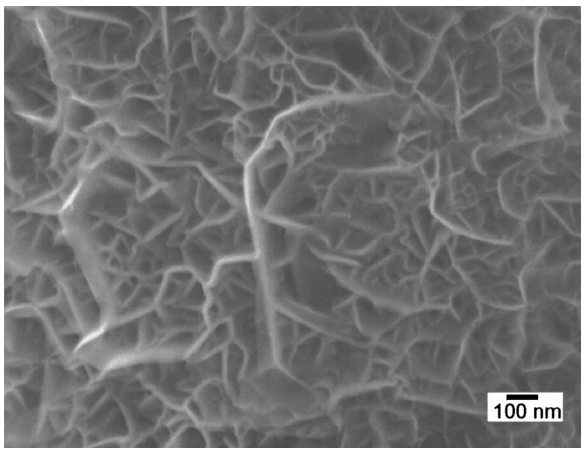

FIG. 2. Typical FESEM image of the samples grown with ethyl alcohol and He in the chamber feed.

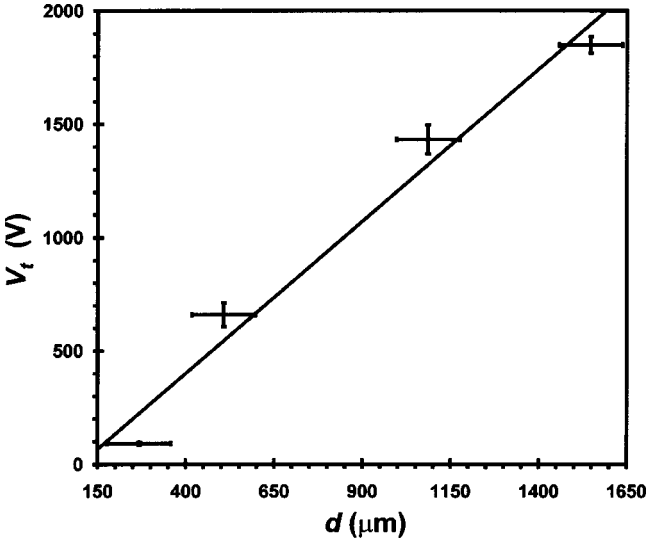

FIG. 3. Typical threshold voltage V_t versus distance d measurements necessary to produce a current density of about 10 μA cm^{-2}.

surements, carried out for a fixed threshold current, is shown in Fig. 3. The error bars are associated with the emission fluctuation due to flickering and spacing uncertainty. A linear fit to this data provides a threshold field (E_t) of 1.3 V μm^{-1}. The threshold current used ($I_t = 8.4$ μA) averaged over the cathode area (84 mm^2) corresponds to a current density of 10 μA cm^{-2}, which is a value normally used for comparing emission data in the literature.[7]

The typical electron emission results using a fixed distance ($d = 1.08$ μm) are shown in Fig. 4 by plotting the (I–V) data in FN diagram for increasing or decreasing bias voltage, as indicated. For high voltages the data points may be fitted to a single statistical slope, that is, a usual FN plot, either for increasing or decreasing bias. However, for medium voltages there is a remarkable hysteresis; that is, the slope for the sweep rising bias is much higher than the slope for the sweep decreasing bias. Although the data points of

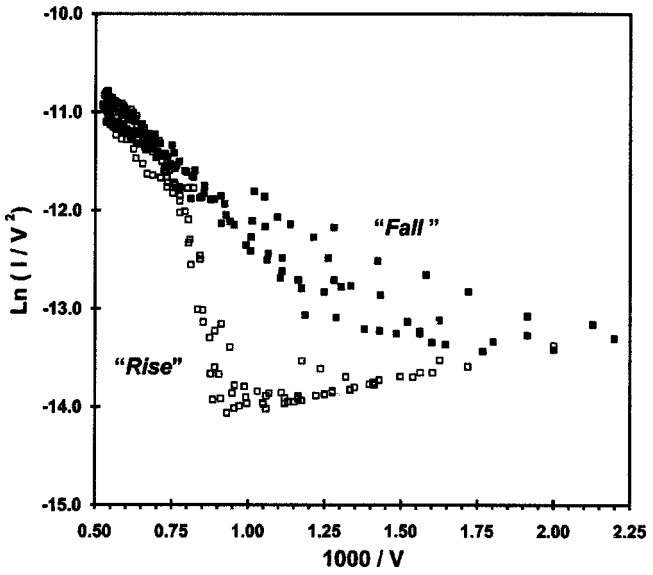

FIG. 4. Typical current–voltage data plotted in FN diagram for increasing (open squares) or decreasing bias voltage (black squares), as indicated. A parallel plate configuration was used with anode and cathode having the same area of about 84 mm^{-2}, separated by a distance d of 1.08 μm.

the sweep decreasing bias may be statistically fitted to a single slope for high, medium, and low voltages, the current fluctuation is comparatively high in the mid and low voltages range. This kind of hysteresis has been observed in vertically aligned CNTs[15] also.

As a nanoscopic phenomenon, the properties of the field emission depend strongly on: (i) the atomic and radical species that terminate the emitting surface (carbon atoms, metallic impurities, adsorbed radicals, adsorbed gases), and (ii) on the local field at these terminating species (which depends on the nanoscopic geometry of the emitting tips). During the rising bias sweep, besides the polarization of the terminating species, long molecules like the CNTs themselves, other carbon chains, or carbon-whiskers, that are lying on the surface, are electrostatically induced to be ''piled-up'' to align their main longitudinal axis with the externally applied electric field vector. This process creates tips with extremely high localized electrical fields, which further enhances the current emission. In sequence, when the falling sweep bias starts, the aligned tips have an inherent inertia to remain piled-up, since there is no change in the direction of the externally applied electric field, but only its intensity decreases. Therefore, the current emission during the falling sweep bias remains high compared to that during the rising sweep bias current, which explains the hysteresis.

We demonstrated that it was possible to obtain porous diamond-like structures of carbon with good field emission characteristics by the direct CVD of ethyl alcohol vapor, using He as a noble gas buffer. Although the complex surface structure of this material is not yet know, micro-Raman analysis indicated scattering peaks corresponding to graphene layers, microcrystalline graphite, and a new peak at $1620\ \mathrm{cm}^{-1}$, which we suggest as a signature of this new material. Characterization of the field emission properties, reveals that this new material has low threshold fields and hysteresis in the FN current–voltage curves. We suggest that the hysteresis is related to the electrostatic alignment of the terminating species with the externally applied electric field vector which creates tips with extremely high localized electrical fields. The result that porous diamond-like structures are good electron emitters may be of great importance for future electronic devices.

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