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Author

Tong, William

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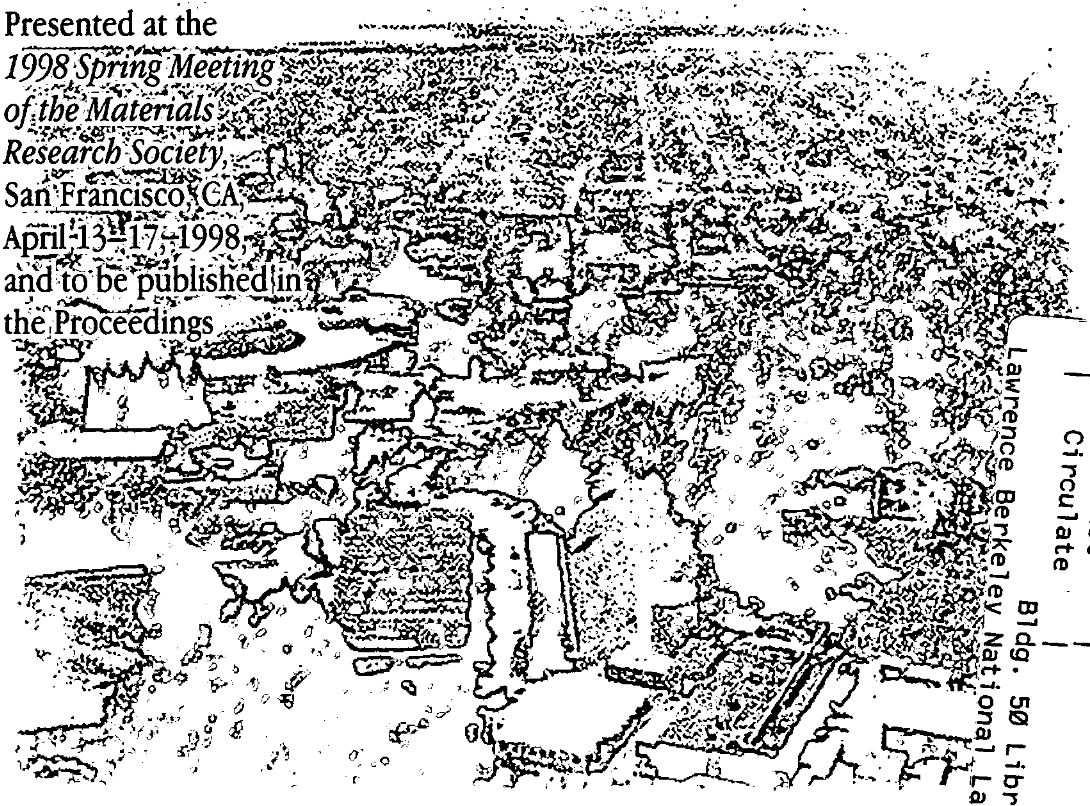

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William Tong[1], Lawrence S. Pan[2], Thomas E. Felter[1],
Simone Anders[3], Aline Cossy-Facre[3], and Thomas Stammler[3]

[1]Lawrence Livermore National Laboratory, Livermore, California 94550

[2]Candescent Technologies Corporation, San Jose, California 94550

[3]Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720

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WILLIAM TONG[1], LAWRENCE S. PAN[2], THOMAS E. FELTER[1],
SIMONE ANDERS[3], ALINE COSSY-FACRE[3], and THOMAS STAMMLER[3]

[1]Lawrence Livermore National Laboratory
[2]Candescent Technologies Corporation
[3]Lawrence Berkeley National Laboratory

THE EFFECT OF ASPECT RATIO AND SP^2/SP^3 CONTENT ON THE FIELD EMISSION PROPERTIES OF CARBON FILMS GROWN BY N$_2$-SPIKED PECVD

WILLIAM M. TONG§, LAWRENCE S. PAN‡, THOMAS E. FELTER§
Sandia National Laboratories, Livermore, CA 94550, USA

SIMONE ANDERS, ALINE COSSY-FAVRE, THOMAS STAMMLER
Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94710, USA

§Present address: Lawrence Livermore National Laboratory, Livermore, CA 94550, USA
‡Present address: Candescent Technologies Corporation, San Jose, CA 94550, USA

ABSTRACT

We have deposited carbon films from mixtures of methane and N$_2$ using Plasma Enhanced Chemical Vapor Deposition. By changing the percentage of N$_2$ in the feed gas, we were able to produce films that have various aspect ratios and sp^2/sp^3 contents. The film with the highest field emission contains spears of aspect ratio of 10:1. We also found that in our sp^3-rich films, higher sp^2 content enhanced field emission. This is ascribed to improved charge transport to the field emission sites.

INTRODUCTION

The electrons of a solid are normally confined within the material by a potential energy barrier at the surface. For a metal, this barrier is called the work function. When an external voltage is applied to the surface, the barrier is both narrowed by the electric field and reduced in height by the Schottky effect. Tunneling of electrons from the interior of the material through this barrier into the vacuum can be achieved under sufficiently high electric fields. For a typical flat metal substrate, fields greater than 2000 V/μm are required for substantial currents to be extracted. In recent years, however, there have been reports of field emission being measured from diamond and related carbon films at fields that are orders of magnitude lower. For example, Geis *et al.* [1] reported drawing current from a nitrogen-doped diamond at fields of < 0.2 V/μm. Okano *et al.* also reported that nitrogen incorporation lowered the threshold field to < 0.5 V/μm [2].

No definitive mechanism has been presented to explain the emission at these unexpectedly low fields. A number of models have been put forth, not all of which are mutually exclusive. Among these are back-contact injection [1], the antenna model [3], dielectric breakdown and discharges [4,5], and valence band emission [6,7]. In the present work, we show that geometrical field enhancement and charge transport are also important factors.

EXPERIMENTAL PROCEDURE

Our films were growth by plasma enhanced chemical vapor deposition on unpolished Si substrates. To facilitate growth, a nucleation layer of 5 μm was deposited from a plasma of 10% methane and 90% hydrogen (33 torr total pressure). A bias of –400 V was applied to the substrate (Bias enhanced nucleation [8]). Scanning electron micrographs of the resulting films show the formations of balls of about 100 nm in diameters. We believe that the –400 V bias accelerates the ionized species in the plasma toward the surface and promotes bonding and deposition.

The active layer was grown under the same condition as the nucleation layer, except the total pressure of the plasma was 50 torr and a bias of +400 V was applied to the samples instead of –400 V. A positive bias repels the ionized species, allowing mostly neutral radicals and electrons to arrive at the substrates. The electron bombardment of the sample also served to heat the sample and create reactive dangling bonds. However, the exact effect of the positive bias to the growth mechanism is not clear at this point. The temperature of the film during this stage of the growth is estimated to be about 800°C. We observed that reducing growth temperature by more than ~100°C resulted in no deposition.

Okano [2] reported diamond films grown with urea precursors have significantly improved emission properties attributed to the incorporation of nitrogen in the film. The simple reason behind this is that nitrogen is a donor in carbon and would thus raise the Fermi level of the film and lower the escape barrier for electrons. We were motivated by these results to incorporate nitrogen to our films by using a plasma of the following pre-ionized proportions: 10% CH_4, X% N_2, (90-X)% H_2, where X=0, 20, 50, 70, and 90%. However, no nitrogen was observed in these films by any of our analytical methods (Auger, energy-dispersed x-ray). Nevertheless, some of them were found to have enhanced field emission, and its origin is the object of this investigation.

The emission properties of our films were measured with our "lamp" system, which consisted of an indium-tin oxide coated anode placed 122 μm from the sample being tested. The area of the anode is 0.4 cm^2. This allows the spatial distribution of the emission sites to be videotaped while the field emission current vs. field curve was being recorded.

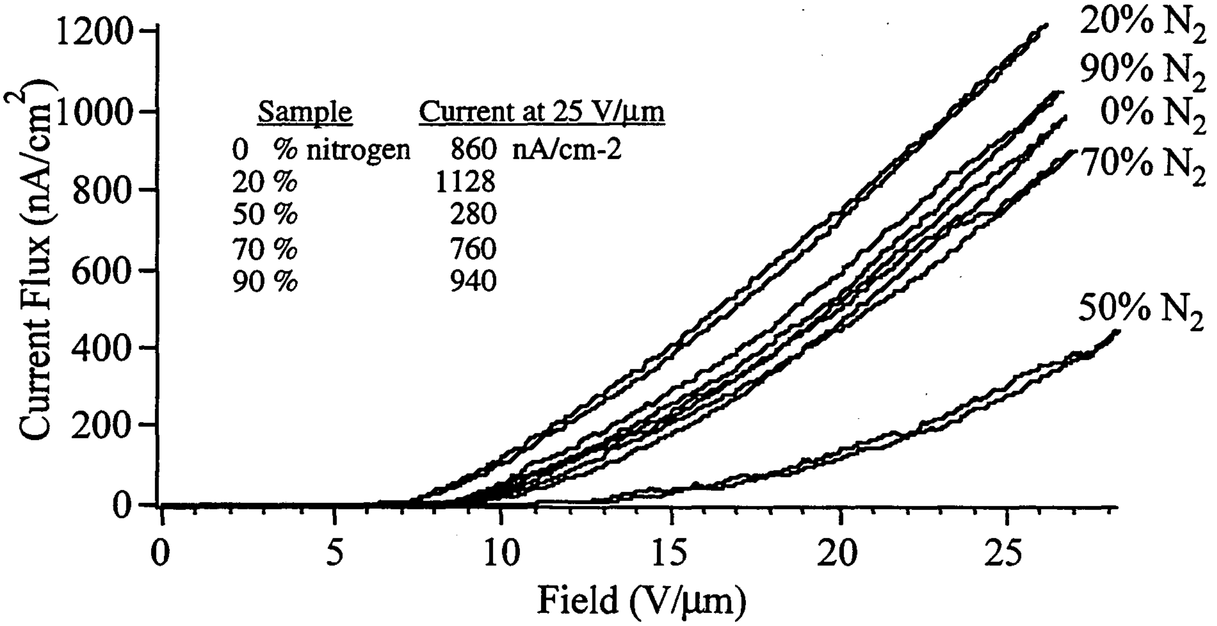
The scanning electron microscopy in this investigation was carried out with a JEOL 6400FV field-emission source microscope. It has a quoted resolution of 1.5 nm, which is an order of magnitude smaller than any feature we saw in our films. Typical electron kinetic energy was 4 keV, but lower kinetic energies were also used in some samples to reduce the graphitization/damage to the sample during the imaging process.

Near-Edge Extended X-ray Absorption Fine Structures (NEXAFS) measurements were made at the Advanced Light Source at Lawrence Berkeley National Laboratory. The spectra were taken in the total yield mode, by recording the secondary electron emission from the sample with a channeltron or with a picoammeter.

RESULTS

Field Emission

The Current vs. Field curve of these films as measured by the "lamp" setup is plotted in Fig. 1.



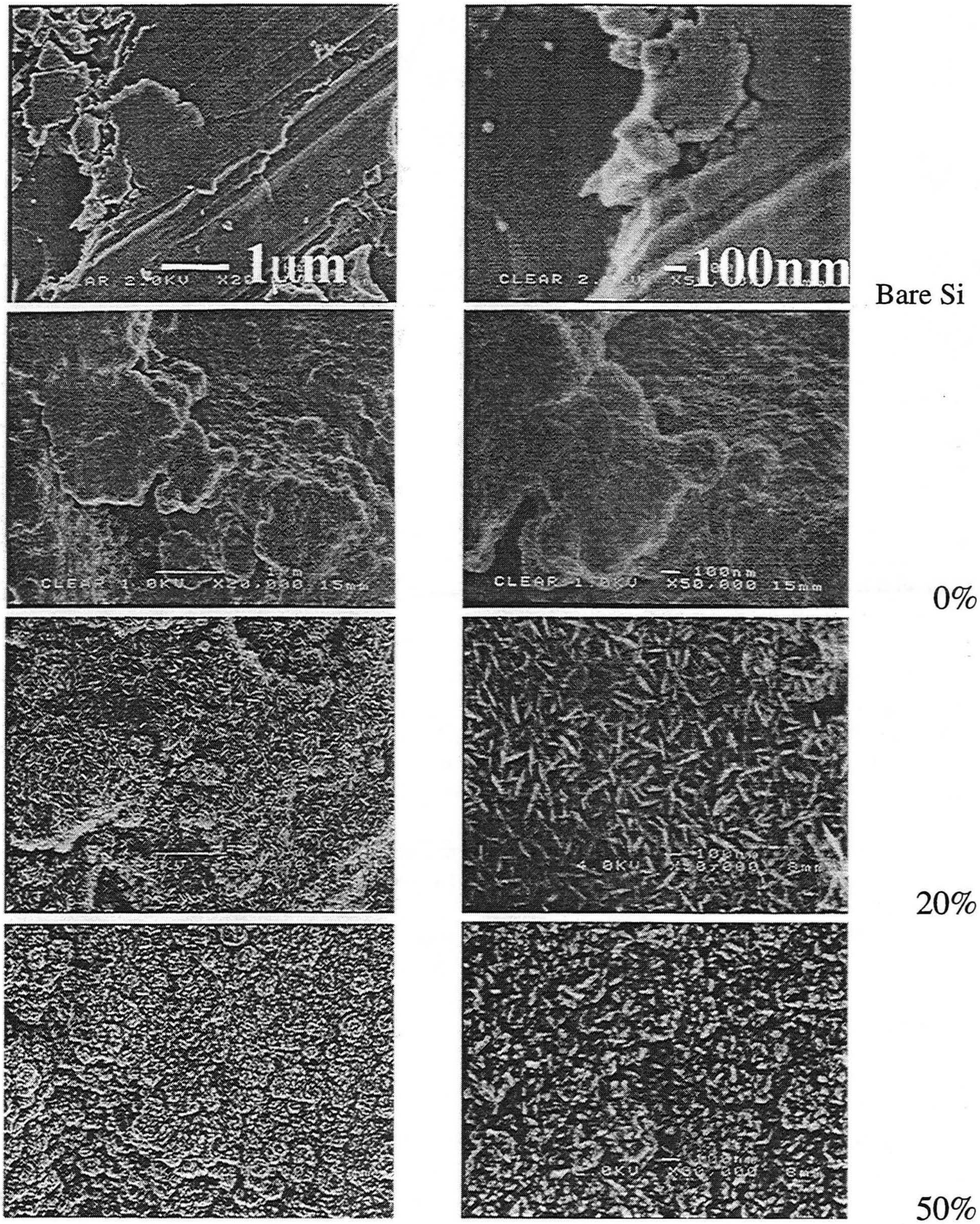
Sample	Current at 25 V/μm
0 % nitrogen	860 nA/cm-2
20 %	1128
50 %	280
70 %	760
90 %	940

Fig.1: I-E curves for the four samples, corrected for voltage drop caused by ballast resistors. Inset table: Current density at 25 V/μm as a function of percent N_n in plasma during growth.

The field drop caused by the ballast resistors (2.1 MΩ) has been subtracted out. Overall, we found that spiking the plasma with 20% N_2 led to a large enhancement in field emission, but the field emission became lower when the N_2 concentration in the plasma was increased further.

Structure

SEM images, shown in Fig.2, revealed that the surface films grown without N_2 contain smooth nodular structures covering the underlying rough structure of the unpolished Si substrate.



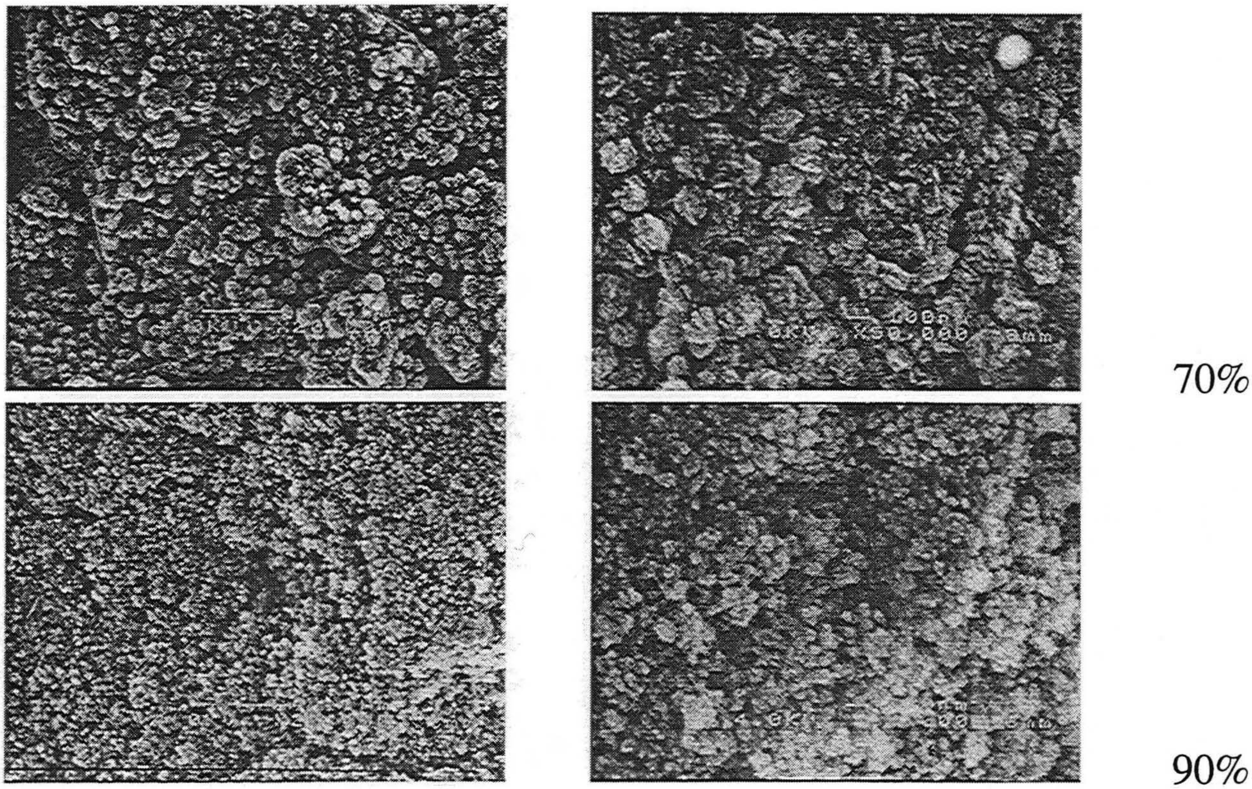


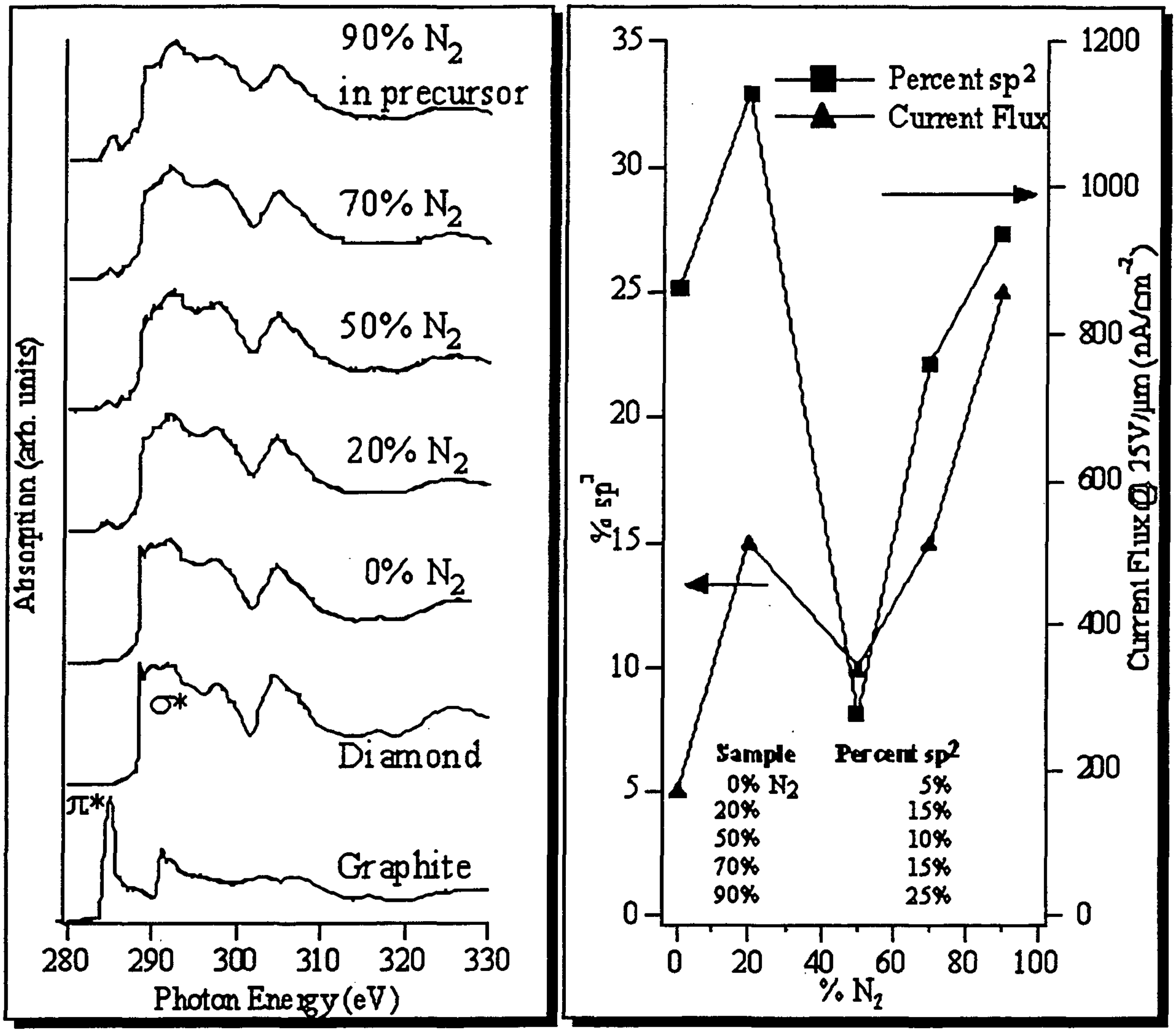
Fig.2: SEM images of the bare substrate and 0, 20, 50, 70, & 90% N_2 films at 20,000x (left) and 50,000x magnifications.

On the other hand, all films grown with nitrogen are much rougher than the substrate. The 20% film, in particular, consisted of a bed of spears that were on the average 100 nm in length and 10 nm in width. The field enhancement factor β of an object with an aspect ratio of 10 is about 50× [9]. Increasing the nitrogen concentration in the plasma to 50% altered the structure of the film greatly, producing small raisin-like structures of about 200 nm. The aspect ratios of these raisins are about unity which corresponds to a β of only 3×. This explains why the emission current is small, only a quarter of that of the 20% film. Surprisingly, this film also emitted less than the 0% film, despite its higher aspect ratio and presumed higher nitrogen content. This suggests that factors other than aspect ratio are at work. Further increase in N_2 concentration to 70 and 90% in the plasma leads to smaller raisins of 100 and 50 nm, respectively, but the aspect ratios remain close to unity.

The formation of nanostructures in our films may be similar to the mechanism of producing Bucky balls and Bucky tubes. The standard technique for the production of carbon Bucky balls and Bucky tubes involves forming a DC arc in the presence of 10–1000 torr of He or Ar [10]. The choice of noble gas and its pressure depends on the product desired and varies from one production chamber to another. The consensus view is that the noble gas acts as a third body which absorbs the excess kinetic energy of the carbon species in the plasma arc and to prevent them from dispersing too rapidly [11]. In our case, nitrogen fulfills that role.

Near Edge X-ray Absorption Fine Structure (NEXAFS)

NEXAFS is an element-specific local probe of empty electronic states of solids and is sensitive to both electronic structure and chemical bonding. Briefly, an incident x-ray photon excites a core level electron to an empty state or the vacuum level. The cross section of the absorption depends on the density of empty states and the dipole selection rule. NEXAFS is especially suitable for identifying the presence of π bonds, as the 1s to π* transition is dipole-allowed and especially intense. Therefore even a small amount of π bonding in a system will show up in a NEXAFS spectra. The π* orbitals are more tightly bound than the σ* orbitals which are composed of sp^3, sp^2, or sp orbitals.



Sample	Percent sp^2
0% N_2	5%
20%	15%
50%	10%
70%	15%
90%	25%

Fig.3: a) NEXAFS spectra of the carbon films grown with N_2. The diamond and graphite spectra are plotted for comparison. b) Joint plot of percent sp^2 and emission current flux for each film as a function of percent N_2 in the plasma during growth. The last three films show that the higher the sp^2 content for a film, the better it emits. The superior field emission for the 20% $N_{2\,\mathrm{film}}$ is due to the field enhancement of the its spears (see. Fig.2).

The NEXAFS spectra of four films grown with nitrogen closely resemble that of pure diamond. The sp^2/sp^3 content of a film can be approximated by the ratio between the height of π* peak at 285 eV and of the σ* edge at 291 eV. The results, tabulated in Fig. 3b, indicate that most of the carbon atoms in the films are sp^3 hybridized. The double plot in Fig. 3b shows the correlation between the sp^2 content of a film and its field emission. Among the three films at 50%, 70% and 90%, surface aspect ratios are similar and emission correlates with the amount of sp^2. The 50% N_2 film has the weakest emission and the 90% N_2 film has the strongest. The 90% N_2 film still has inferior field emission than the 20% N_2 film, despite having a higher percentage of sp^2, because the strong geometrical enhancement by the spears in the latter film dominates (3× vs. 50×, respectively).

The fact that a higher sp^2 content, which is associated with graphite, would increase field emission is a little surprising, since the underlying reason for growing diamond films is to exploit the diamond's "negative electron affinity." However, NEXAFS has shown that there is an abundance of sp^3 hybridized (diamond) carbon atoms in our films. The rate-limiting step for field emission from diamond-rich carbon films such as ours is the transportation of charge. A higher graphite content would improve the conductivity and therefore enhance field emission.

SUMMARY

We have successfully deposited carbon films that emitted a current flux of 1128 nA/cm^2 at 25 V/μm. The presence of nitrogen in the plasma during growth causes high-aspect ratio spears of 100 nm in length and 10 nm in diameter to form. The field enhancement factor β for objects of such an aspect ratio is about 50×. We also found that amongst our samples the carbon film with an aspect ratio of unity, the film with the highest sp^2/sp^3 has the best field emission.

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ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY
ONE CYCLOTRON ROAD | BERKELEY, CALIFORNIA 94720

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