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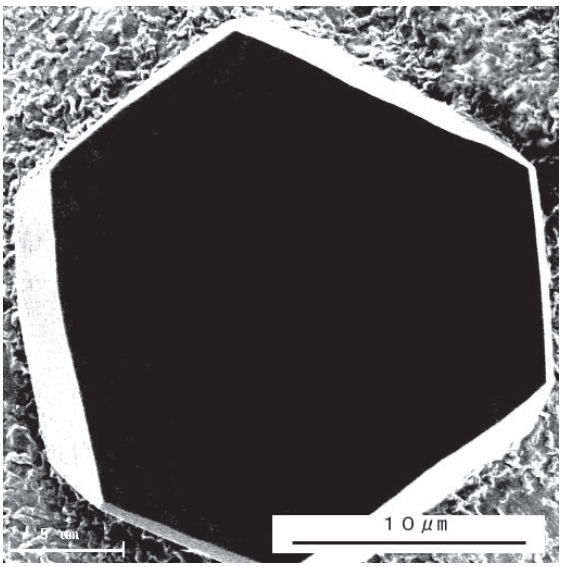
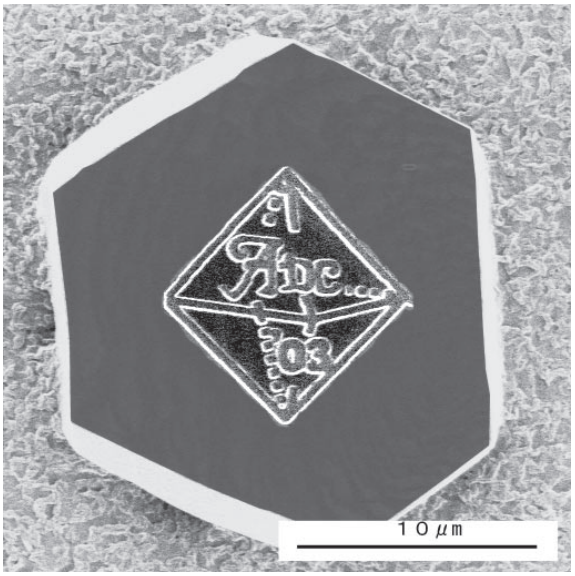
Proceedings of the Seventh Applied Diamond Conference/Third Frontier Carbon Technology Joint Conference (ADC/FCT 2003)





August 2003

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Proceedings of the Seventh Applied Diamond Conference/Third Frontier Carbon Technology Joint Conference (ADC/FCT 2003)

M. Murakawa, K. Miyoshi, Y. Koga, L. Schäfer, and Y. Tzeng, editors

Proceedings of a conference held at Epochal Tsukuba International Conference Center
cosponsored by the Nippon Institute of Technology,
National Institute of Advanced Industrial Science and Technology,
Japan New Diamond Forum,
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August 2003

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CVD diamond process:
All diamond (111) flats as large as 20 µm were grown in air with the oxyacetylene torch (combustion synthesis).

High-speed, nano machining process of logos carved on CVD diamond:
The nano machining of the ADC conference logo was conducted using the focused ion beam with a beam diameter of approximately 20 nm at an accelerating voltage of 40 keV for a machining time of 2 minutes. All the nanomachining of the NIT, JNC, NASA, and AIST logos shown herein were conducted using the focused ion beam with a beam diameter of approximately 30 nm at an accelerating voltage of 40 keV for a machining time of 2 minutes with each logo.

Nanomachining process of ADC logo carved on CVD diamond:
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Note that all CVD and nanomachining processes were performed at the Nippon Institute of Technology.

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FOREWORD

The Applied Diamond Conference was established in 1991. During its first stage, emphasis was put on promoting practical applications and discussing the sciences and technologies associated with diamond and related superhard materials. In its second stage, advances in novel carbon materials and nanostructures such as fullerenes and nanotubes were explored. Momentum grew when the diamond and frontier carbon technology community convinced the Japanese government (then the Ministry of International Trade and Ministry) to sponsor the diamond and frontier carbon technology project (known as the Industrial Science and Technology Frontier Program). As a result, the International Conference on Frontier Carbon Technology (FCT) was established and the two conferences were held jointly at the Fifth Applied Diamond Conference (ADC/FCT '99) in Tsukuba, Japan, in 1999. The Industrial Science and Technology Frontier Program is being continued in a more focused way, this year emphasizing nanotubes and their commercialization.

These are the Proceedings of the Seventh Applied Diamond Conference/Third Frontier Carbon Technology Joint Conference hosted and supported by the Nippon Institute of Technology and the National Institute of Advanced Industrial Science and Technology from August 18 to 21, 2003, in Tsukuba, Japan. The conference received 178 papers from 18 countries: 77 from Japan, 24 from China (including 7 from Hong Kong), 17 from the United States, 14 from Russia, 11 from Germany, 11 from the United Kingdom, 4 from France, 4 from Singapore, 3 from Ukraine, 3 from South Korea, 2 from Brazil, 2 from Taiwan, and 1 each from Armenia, Canada, India, Italy, Sweden, and Switzerland.

We thank all the sponsors, invited speakers, contributors, attendees, committee members, and session chairs who have made this conference a success.

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Proceedings of the Seventh Applied Diamond Conference/
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M. Murakawa, M. Miyoshi, Y. Koga, L. Schäfer, and Y. Tzeng (Editors)

FORMATION OF C-N NANOFIBERS IN HIGH ISOSTATIC PRESSURE APPARATUS AND THEIR FIELD EMISSION PROPERTIES

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ABSTRACT

Carbon-nitrogen (CN) nanofibers have been formed in High Isostatic Pressure (HIP) apparatus in 1:1 nitrogen-argon gas mixture at 75 GPa using graphite electrical heater. Bamboo-like, beads-like, corrugated and spring-like nanofibers with the diameter of about 100-150 nm and the length over 10 μm have been found in a deposit with a low content of amorphous carbon. The nitrogen content up to 8.5 % was found in fibers by EELS analysis. The CN nanofibers were printed on cathode plate and the dode-type flat vacuum lamp with 1 inch diagonal was assembled for the field emission study with the gap between anode and cathode varying in the range of 300 – 900 μm. The turn-on fields were about 1.3 V/μm, the current density was 0.05 mA/cm^2 at 1.35 V/μm. The time reliability and light emission test were carried out for above 100 hours. We suggest that CN nanofibers can be applied to the high brightness flat lamp because of low turn-on field and time reliability.

Keywords: carbon-nitrogen naofibers, high isostatic pressure apparatus, structure, field emission.

INTRODUCTION

The possibility of utilization of carbon nanostructures as electron emitters attracts growing scientific interest (refs. 1to 6). Carbon nanotubes (CNT) and other nanostructures are capable of emitting high currents (up to 1 A/cm^2) at low fields (~ 5 V/ìm). They already used for producing some cold electron emitter devices (refs. 3 to 6). Despite pure carbon nanostructures CN, SiCN nanostructures attract considerable interest as alternative materials for cold emitters (refs. 7-9). R. Kurt et al. (ref. 7) investigated emissive properties of decorated C/N nanotubes. Plasma enhanced hot filament chemical vapor deposition (PE-HF-CVD) combined with micro-contact printing of catalysts was performed in order to deposit patterned films of nitrogenated carbon (C/N) nanotubes. Each tube was not straight but twisted. The length of a single tube was in the range of 10 - 50 ìm, the diameter 50 - 1000 nm. Nitrogen concentration in C/N nanotubes was found to be 4.3 %. On catalytic samples the lowest onset, turn – on and threshold fields required to extract a current density of 10 nA/cm^2, 10 μA/cm^2 and 10 mA/cm^2, respectively, were E_i= 3.8 V/ìm, E_{to}= 4.7 V/ìm and E_{thr}= 7.4 V/ìm. In the case of autocatalytic growth very similar results were obtained, except E_{thr}= 11.5 V/ìm. Regarding their field emission properties, C/N nanotubes compare quite well with films of pure carbon nanotubes. For arrays of C/N nanotubes thinner than 50 nm an onset field below 3 V/ìm was observed.

The influence of C-N bonds concentration on the emission properties of films was investigated in reference 8.

The following conclusions have been drawn out. High concentration of tetrahedral C-N bonds lowers the threshold voltage for electron emission. The lower the percentage of double C=N bonds, the higher the emittance.

The carbon-nitride nanobells were obtained by G.Y. Zhang et al (ref. 9) with nitrogen content of about 2%. The onset voltage was about 1 V/ ìm and the threshold field about 10 V/ìm. They point out that according to *ab initio* calculations, such nanostructures have very high electronic density of states at the open edges.

A method of high isostatic pressure (HIP) growth of carbon nanostructures was designed first by Blank et al (refs. 10,11) and nitrogen concentration up to 13 % have been obtained (ref. 11). Elevated gas pressure promotes desirable chemical reactions due to elevation of chemical potential and diffusion coefficients. This method provides wider range of morphologies of nanostructures and higher nitrogen concentration in C-N nanotubes than CVD techniques.

In this article we investigated structure, nitrogen content and emissive properties of CN nanostructures obtained by HIP apparatus and found that they are competitive with those of pure carbon once for the first time.

EXPERIMENTAL

Nitrogen containing carbon nanostructures were formed in the High Isostatic Pressure (HIP) unit. The block diagram of the unit is shown in Fig. 1. In our experiments we used the HIP apparatus, designed for the maximum pressure value of 350 MPa. Its inner dimensions for mounting heater and screens are the following: diameter 40 mm, height 125 mm. Check valve (6) was used for the better stability of pressure during experiment. High gas pressure was created using the one-stage piston gas compressor (2).

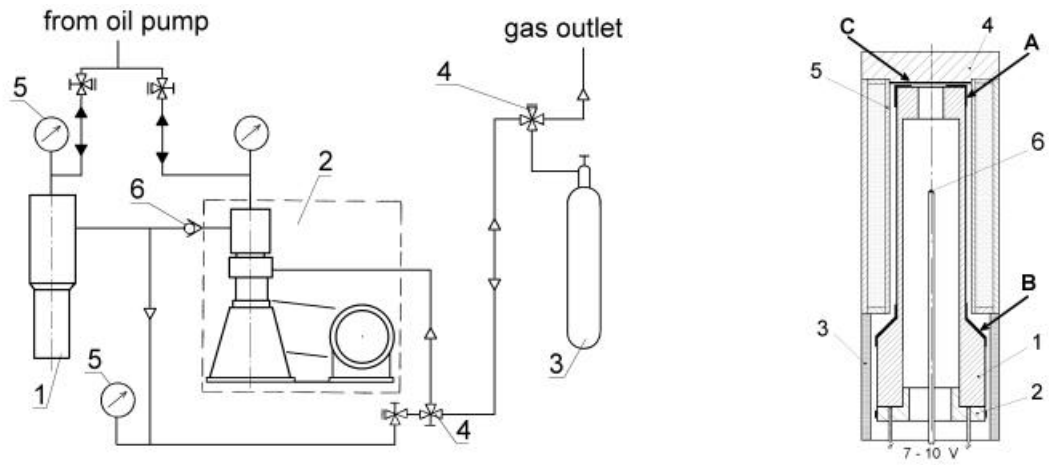

Figure 1. The block diagram of High Isostatic Pressure (HIP) unit (left) and the heating unit (right).
In left : 1 - High Isostatic Pressure (HIP) Apparatus; 2 - High pressure Gas Compressor; 3 - Gas-cylinder (or cylinders); 4 - Shutoff valve; 5 - Manometer; 6 - Check valve.
In right: 1 – carbon resistive heater; 2 – copper contacts 3 – supporting ring (graphite); 4 – upper screen; 5 – side screen (graphite); 6 – thermocouple;A, B, C – carbon nanofibers deposition zones.

We used carbon heater as the carbon source. The shape of the graphite heater and heat shielding are shown in Fig. 1(right). The heat shielding is manufactured from graphite, it contains ring 3, plug 4 and cylinder 5. The heating zone with the thickness equal to 0.7 mm was made in the middle part of the heater 1. Carbon deposit was taken from the top part of the heater (zone A). The thermocouple type A insulated by corundum - straw 7 has been used for measurement of temperature. Details of experimental procedure have been presented in (ref. 10). The argon – nitrogen mixture with equal content of gases was prepared in the mixture unit (3) in Fig.1(left). The gaseous pressure was 75 MPa, duration of synthesis 40 min, temperature of the hot zone above 1400°C. Carbon evaporation was carried out by direct resistive electrical heating and improved by presence of nitrogen. We suppose that nitrogen improves carbon evaporating due to formation of C-N clusters on the heater surface and next transfer them into gas phase. Carbon deposit was investigated by transmission (TEM) and scanning

transmission electron (STEM) microscopy, using JEM-200CX, CM20 Philips TEM, VG 601 UX STEM and Hitachi S-4300.

The CN nanofibers were printed on the active area of cathode plate and then the diode-type flat lamp with 1 inch diagonal emitting area was assembled for the field emission study (Fig.2). The cathode electrode lines were formed with metal Cr on cathode glass plate. The green phosphor was printed on ITO coated anode glass. The field emission measurements were performed with the gap between anode and cathode varying in the range of 300 – 900 μm in vacuum chamber at a pressure of 10^{-6} Torr using F.u.G. Elektronik DC Power Supply. The sample temperature during the measurement was 300K.

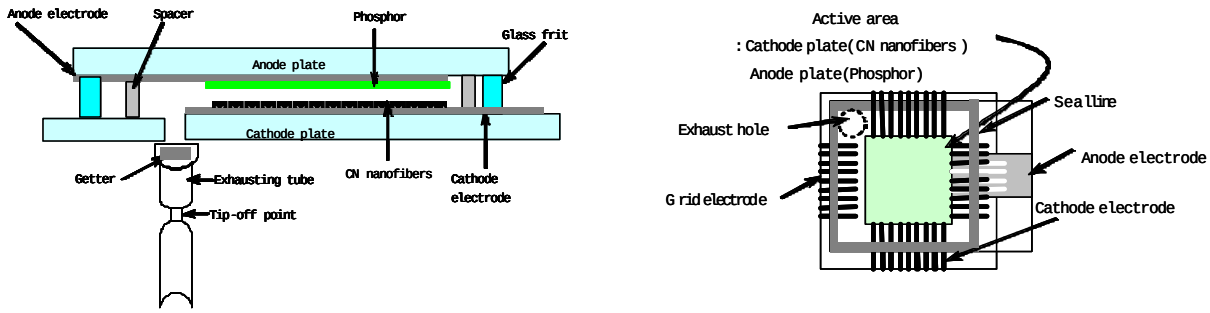

Figure 2. The geometrical structure of vacuum packaged CN nanofibers flat lamp: side view (left) and top view (right) .

The green phosphor was printed and the glass frit was dispensed on anode glass plate. And then, it was put on the cathode glass plate with exhausting tube followed by heating to 420 C to melt a glass frit in N_2 ambient. A sheet type getter (ST122) was inserted to panel through the tube, as shown in Figure 2. The panel was connected to tip-off system followed by pumping to 10^{-6} Torr.

STRUCTURE

Figure 3 shows SEM images of CN nanofibers formed by HIP. Figure 3a shows a cluster and figure 3b has higher magnification. The CN nanofibers were grown in random with the diameter of about 100-150 nm and the length over 10 μm. Increase of the nitrogen pressure caused increase of the carbon deposit and an appearance of variety of different structures. It can be explained by active gas convection, which caused more active mass transport and fluctuations of temperature. We found bamboo-like nanotubes with equidistant diaphragms, wrinkled bead necklace-like (BdL) tubes with thin walls, nanotubes with thin, not completely formed walls, like corrugated nanofibers (Cor-fibers) and spring-like periodical structure. The examples are shown in Figure 4. All these structures are characterised by curved carbon layers as a result of the presence of included nitrogen atoms. EELS investigations showed presence of nitrogen in tubes. The peak at 401ev of EELS-spectra corresponds to trivalent nitrogen atoms replacing graphite ones in a hexagonal lattice (Fig. 5a). The average nitrogen concentration was calculated to be about 3-4%. The value of nitrogen concentration in BdL tubes was found up to 8.5%.

Although the role of nitrogen for structure formation as well as for modification of material properties is not completely clear, we believe that low value of electron emission onset field found for our nanofibers, can be explained by peculiarities of their structures caused by the presence of nitrogen. At conditions of high argon pressure in HIP apparatus mach smaller amount of nanostructure deposit have been formed and that was mainly cylindrical nanotubes, while relatively big amount of nanofibers of various different configurations were formed at the same pressure-temperature conditions at nitrogen atmosphere. The curved intersected inner C-N layers forming a wavy net-like structure have been observed inside nanofibers (ref. 12). Analogous nanostructure was found in bamboo-like fibres, bead necklace-like fibres and net-fibres with a more complex structure consisting of intersecting graphene layers inside the fibre. The reason for an appearance of curved intersected graphene layers inside the fibre is the presence of nitrogen atoms in graphene layers. It is assumed that nitrogen effectively substitute carbon atoms in the graphitic lattice, resulting in bending of fringes (ref. 13).

a) b)

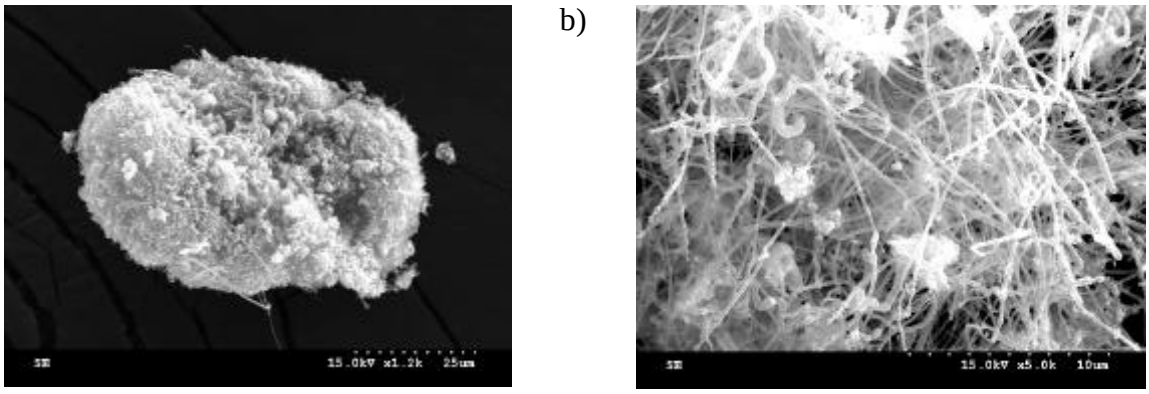

Figure 3. SEM image of carbon-nitrogen (CN) nanofibers formed by HIP; (a) magnification ×1.2k ; (b) magnification ×5k.

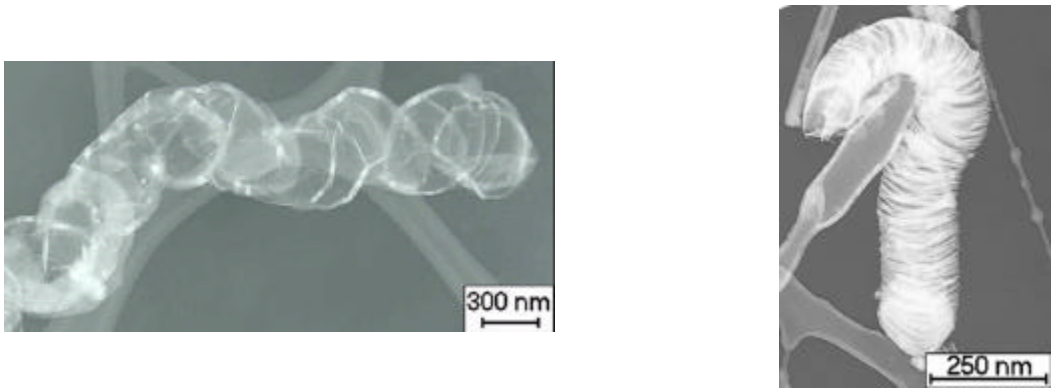

Figure 4. HRTEM image of corrugated (left) and spring-like (right) nanofibers.

a) b)

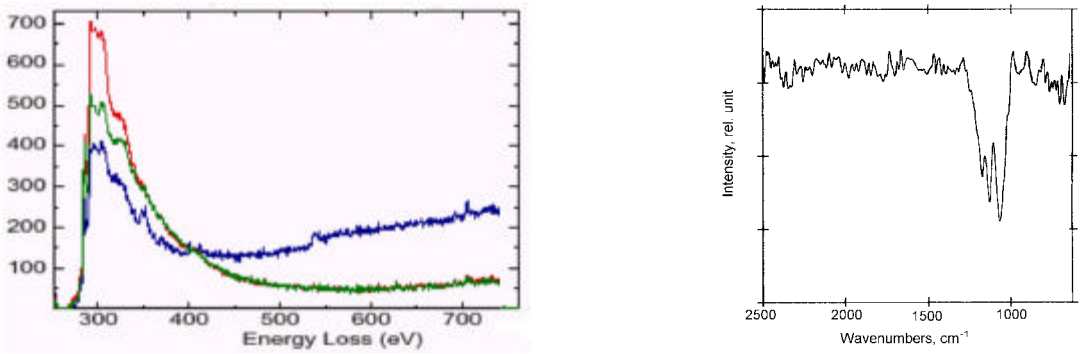

Figure 5. EELS (a) and IR spectra (b) of CN deposit obtained in HIP unit

The corrugated structure was explained in (ref. 14) by formation of pyridine-like bonds between nitrogen and carbon atoms. These bonds are characteristic mostly for edges of graphene layers. The availability of interstitial nitrogen into the graphite layers leads to the distortion and disruption of lattice. Even the small difference between C-C and C-N bond lengths (0.1422 and 0.1429 nm, respectively (ref. 15) causes large inner tensions in the growing layer, giving rise to elastic deformations and the bending of layers. Formation of fullerene-like structures can be considered as another reason for explanation of the structure of the inner layers (ref. 16). The C-N interaction may take place in a form of substitution of carbon atoms by nitrogen ones in (002) graphite planes, but to a greater extent it can create interlayer bonds, cause defects and formation of sp^3-bonds. IR-spectroscopy investigations showed that only single C-N bonds present in the nanostructures synthesized (Fig. 5b). The band at 1100 usually is attributed to C-N single bonds vibration frequencies (ref. 17). It is assumed, that namely single C-N bonds are favourable for field emission properties (ref. 8).

FIELD EMISSION

Figure 6 shows the field emission curves of the CN nanofibers and the corresponding Fowler-Nordheim curves. Turn on field at the spacer gap of 300, 500, 700 and 900 µm was measured 1.56 V/µm, 1.48 V/µm, 1.2 V/µm and 1.44 V/µm, respectively. The emission uniformity in the active area was quite good.

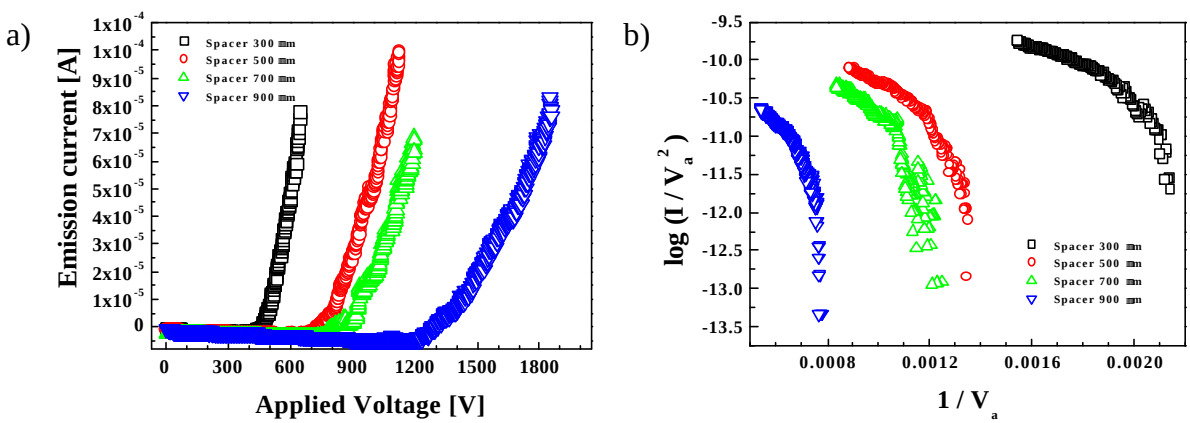

Figure 6. Field emission curves (a) and the corresponding Fowler-Nordheim plot (b) of CN nanofibers.

It is assumed in various studies of the field emission of carbon nanotubes, that electrons are usually emitted from their top tips (ref. 18). But in the case of CN nanofibers, we suppose that besides top tips, electrons can be emitted from nanofiber sides. Substitution of carbon atoms with nitrogen ones in graphene sheet causes its corrugation and appearance of sp^3 carbon sites, favourable for field emission due to the negative electron affinity. Besides that nitrogen atoms may strongly affect on the electron structure of the fibers and supposedly this may also improve emission properties. The Fowler–Nordheim (FN) theory is used to describe field emission behaviour of metallic materials at high applied electric field. According to the theory the plot of log (I/V^2) vs. $1/V$, is expected to be a straight line. However, our FN plots in figure 6 show distinct non-linearity. This deviation from FN theory in field emission probably may be attributed to the geometric structure of the emitters, effect of space charge in the chamber and to a change in the contact resistance between CN nanofiber emitters and the substrate (ref.19).

CONCLUSION

The CN nanofibers were formed by HIP process for the first time. From the field emission measurements CN nanofibers show an excellent characteristics of emitter, better than carbon nanofibers and other known carbon-nitrogen structures. The CN nanofibers flat lamp provides high brightness and uniformity of the light beam. The

CN flat lamp can be applied to automotive, avionics industries, high performance back-lights for liquid crystal displays, view box and so on.

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CHARACTERIZATION OF <111> DIAMOND THIN FILMS BY MICRO-RAMAN SPECTROSCOPY

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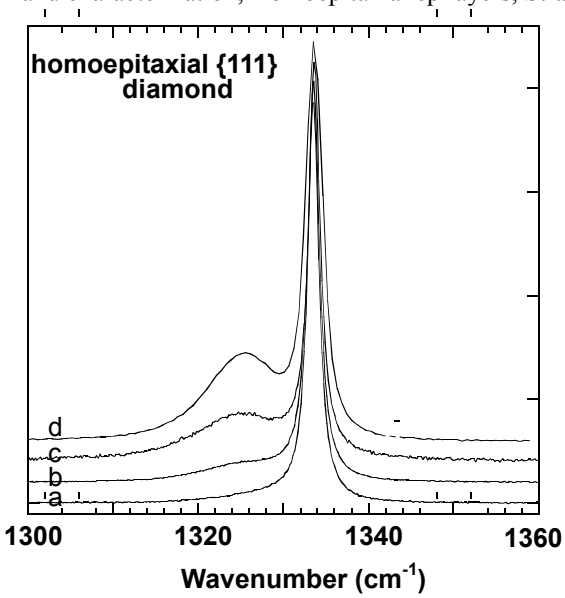
ABSTRACT

Homoepitaxial growth on <111> oriented synthetic type Ib surfaces has been so far the most successful way to an efficient n-type doping of diamond by using phosphorus. However, such epilayers often present stress-relieving macroscopical cracks, which hamper their application as p-n diodes and other electronic devices.

High-resolution confocal micro-Raman spectroscopy results described in this work show that for this particular growth direction the zone-centre phonon peak of the phosphorus-doped epilayers occurs a few cm^{-1} below the peak of the relaxed diamond, indicating a strong tensile strain present in undoped films as well. Surface frequency mappings indicate that this strain is locally relaxed near the cracks that originate from the film/substrate interface. In-depth frequency cross sections show that close to this interface the substrate is under compressive strain and has a perturbed Raman signature under the cracks. Correlated maps of the spectral features associated to specific defects such as disordered carbon phases or nitrogen and silicon incorporation, give some evidences for the origin of the tensile strain in the layers.

This study is performed on n-type phosphorus-doped films grown by CVD in three different laboratories. Comparison of Raman data allows us to discuss the influence on the residual internal strain of various deposition parameters such as the substrate surface quality, the gas pressure, the growth temperature and the purity of the active gases.

Keywords: Diamond growth and characterization, Homoepitaxial epilayers, Strain, Raman spectroscopy



Room temperature Raman spectra obtained under tight confocal conditions. a: undoped epilayer, 1.4 µm thick, b: undoped epilayer, 2.8 µm thick, c: undoped epilayer, 5.6 µm thick, d: phosphorus-doped layer, 8 µm thick.

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13. ABSTRACT ***(Maximum 200 words)***

These are the Proceedings of the Seventh Applied Diamond Conference/Third Frontier Carbon Technology Joint Conference held at Epochal Tsukuba International Conference Center from August 18 to 21, 2003. The diamond CVD process was first reported by Dr. Spitsyn in 1981 and Prof. S. Iijima reported his discovery of carbon nanotubes in 1991. In the past years, both diamond-related materials and novel carbon materials have attracted considerable interest by the scientific, technological, and industrial community. Many practical and commercial products of diamond materials are reported in these proceedings. A broad variety of applications of carbon nanotubes and novel carbons have also been explored and demonstrated. Having more than 175 invited and contributing papers by authors from over 18 countries for presentations at ADC/FCT 2003 clearly demonstrates that these materials, due to the combination of their superior properties, are both scientifically amazing and economically significant.

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