Evidence of electronic cooling from resonance states of nanocrystalline graphite field emitters

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(Received 31 July 2007; accepted 3 January 2008)

We have measured the temperature of a nanocrystalline graphite/carbon nanotube field emitter film as a function of emission current in the range from 1 to 200 μA. Theoretical considerations predict that cooling takes place from these emitters if the electron emission is governed by resonant tunneling. Resonant tunneling manifests itself by a saturation behavior in the *I-V* curve. Maximum cooling should take place near the saturation region. A thermally insulating test system was configured capable of measuring temperature changes in the millikelvin range. For the test sample, at an emission current of about 10 μA, which is the current where saturation is observed, a reduction in the temperature of about 0.01 °C is obtained. The reduction in temperature is attributed to cooling. © *2008 American Vacuum Society.* [DOI: 10.1116/1.2837870]

I. INTRODUCTION

By removing hot electrons from a field emitter and replenishing them by cold electrons which are in thermal equilibrium with the emitter film, in principle, electronic cooling can be achieved. However, in most cases, the field emitting electrons exhibit a relatively broad energy range which results in heating of the emitter film rather than cooling (Nottingham effect). To overcome this problem, it was suggested to use a resonant tunneling emitter in which sub-bands are created.[1] If the electric field aligns the lowest sub-band energy level with an energy level of the hottest electrons in the emitter (a few k_BT above the Fermi level), resonant tunneling of these electrons to vacuum may lead to a very efficient heat removal without substantial back flow of heat to the emitter and thus result in emitter cooling. It was proposed that such an emitter consists of a metal or heavily doped semiconducting film onto which a thin layer (several nm) of a wide band gap semiconductor is deposited. It was also suggested that localized surface states arising from unintentional contaminants on the emitter surface can result in resonant tunneling behavior. Cooling from these emitters was proposed in Ref. 2. In Ref. 1, cooling power densities of at least 30 W/cm^2 are predicted assuming that electrons emit uniformly from the emitter film. This maximum cooling is obtained at current densities of about 1000 A/cm^2 which, with current emitter technology, cannot be achieved. However, since emission takes place at localized sites with areas ranging from 10^{-8} to 10^{-12} cm^2 per site, local current densities of this magnitude are easily achievable. Since, in general, only several emission sites per emitter exist, the expected cooling is very small.

The *I-V* curve of a resonant tunneling emitter manifests itself in a saturation region or even in a region where the current decreases with increasing extraction electrode bias. We have observed that several carbon-based emitters such as nanocrystalline graphite, carbon nanotubes, and even amorphous carbon extracted from diesel engine exhaust exhibit that behavior.[3] It is shown that the saturation region is a necessary condition to observe cooling but not sufficient since other factors can contribute to the shape of these *I-V* curves. These can be thermionic enhanced emission[4] and varying film resistance effects. The latter have been reported for BN in Ref. 5 and for carbon nanotubes (CNTs) in Ref. 6 and 7.

One of the emitter materials tested in our group that showed consistent saturation behavior is that of nanocrystalline graphite (NCG) fabricated by the group of A. T. Rakhimov at Moscow State University. The experimental results reported here are from the Rakhimov emitters and it is assumed that unintentional contaminants are responsible for the resonant behavior.

II. SAMPLE PREPARATION

The emitting film was fabricated on a 5×5 mm^2 silicon chip that was coated with a thin layer (100 nm) of Ta. The nanocrystalline graphite film of about 100 nm was deposited by dc glow discharge at 900 °C in a methane-containing gas mixture. Raman spectroscopy and x-ray diffractometry confirmed graphite crystals with no amorphous carbon present. Throughout the film surface, some carbon nanotubes are present. Figure 1 shows a scanning electron micrograph of

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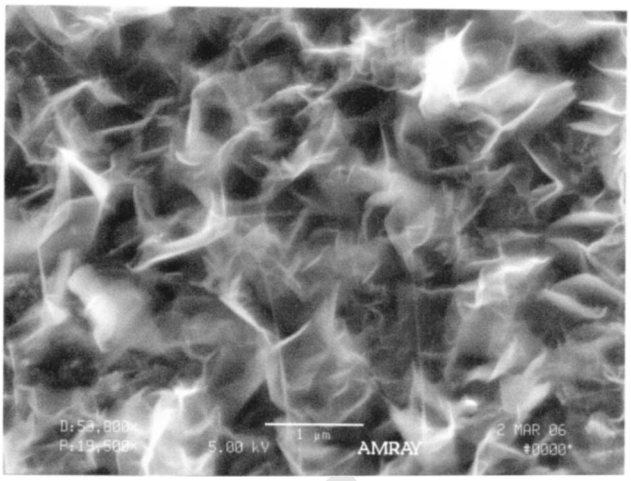

FIG. 1. SEM of the top surface of the nanocrystalline graphite/carbon nanotube film. About four CNTs can be observed in the image.

the film surface. It is not known if the observed emission comes from the nanotubes (there are about four in the image), from the NCG surface, or from both. References for sample preparation and emission behavior of these films are given in Ref. 8.

III. EXPERIMENTAL PROTOCOL

Since the expected cooling effect is very small, the sample was mounted on a thermally insulating acrylic cantilever and the temperature of the silicon chip containing the emitting film was measured by a thermistor (Quality Thermistor, Inc., Boise, Idaho, QTLCB-14C3, 10 kΩ) that was glued to the bottom of the chip using a small amount of silver paint. Since the temperature in the vacuum chamber can change during an experimental run (such as opening or closing a door to the laboratory), a reference cantilever was used which contained a second sample. A thermistor was also glued to the bottom of the second sample. Figure 2 shows a photograph of the top view of the cantilever configuration containing the two 5×5 mm^2 chips. The NCG films are the black regions in the centers of the chips with diameters of about 2 mm. Not shown here are three acrylic posts upon which the sample ring (95 mm outer diameter)

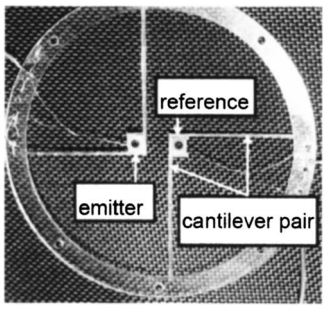

FIG. 2. Photograph of the acrylic test fixture containing two cantilever structures upon which the 5×5 mm^2 test samples are positioned. The two thermistors underneath the chips cannot be seen. The two pair of wires leading to the outer supporting ring originate from the thermistors. The outer diameter of the ring is 95 mm.

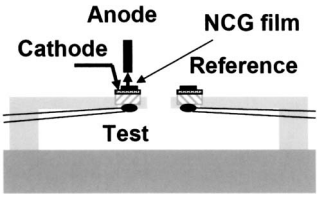

FIG. 3. Cross section of the thermally insulating acrylic cantilever assembly. The cantilevers are about 4 mm above the metal platform that is part of the vacuum system.

was placed to provide thermal isolation of the ring that supports the two cantilevers to the metal platform in the vacuum system. A sketch of the cross section of the test assembly is shown in Fig. 3.

To perform a cooling experiment, a tungsten test probe that is positioned on an *XYZ* manipulator is placed on the tantalum film just outside the NCG film. The anode, consisting of a 0.5 mm diameter, flat polished, copper rod is placed about 100 μm above the sample surface. This is accomplished by first placing the anode onto the Ta film so that electrical contact is made and then slowly raising it to the desired distance using the *Z* axis positioning scale. The probe is then moved into the field containing the emitter film. This procedure avoids damaging the rather soft NCG film.

An emission test is performed next to ensure that the film under test exhibits the saturation region in its *I-V* curve. The *I-V* curve for the sample under consideration is shown in Fig. 4. The solid diamonds are the data obtained prior to temperature measurements and the open symbols are the data obtained during the temperature experiment. At low voltages, a steep rise in the current is obtained which is indicative of enhanced emission by resonant tunneling. This is followed by a transition region and, at the highest voltages, a steep increase in current is observed. For this sample, it is expected that maximum cooling occurs at an emission current of about 10 μA.

The temperature measurement protocol for this experiment was the following: The anode voltage was raised until a current of 1 μA was reached. The current was then held

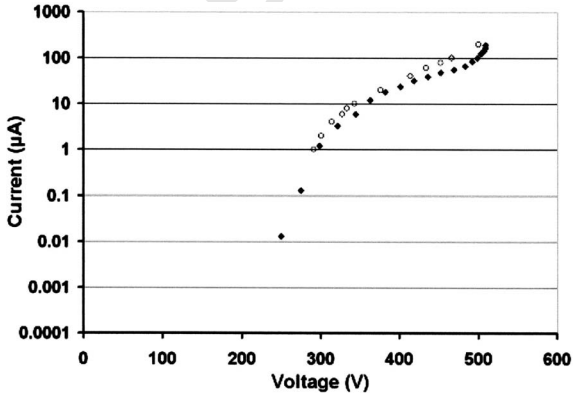

FIG. 4. *I-V* characteristics of the NCG sample prior to the temperature run (solid symbols) and during the temperature run where the voltages were recorded at emission currents of 1, 2, 4, 6, 8, 10, 20, 40, 60, 80, 100, and 200 μA.

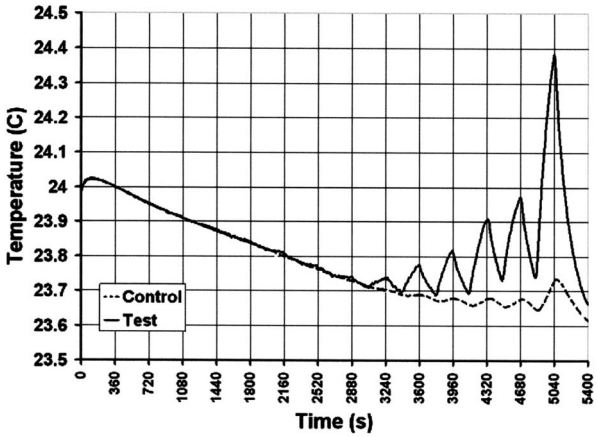

FIG. 5. Temperature vs time plot for the two chips. For the scale used, the temperature rise can only be seen for emission currents of 20 μA and higher. The reference chip also shows an increase in temperature and is caused by thermal leakage through the acrylic support posts and the cantilever arms.

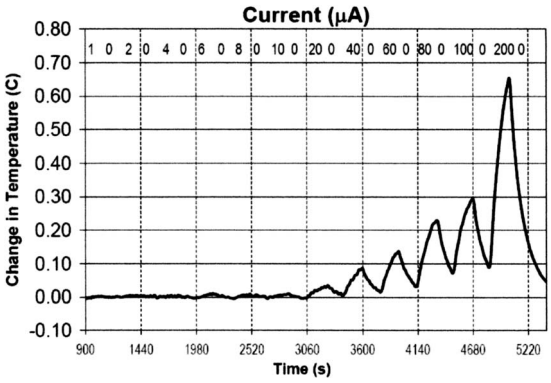

FIG. 6. Temperature vs time plot for the test chip after subtraction of the reference temperature. The numbers on top of the abscissa indicate the currents in μA and "0" marks the time intervals when the current was turned off.

constant for 3 min and the chip temperature, as well as the control sample temperatures, was recorded. The currents through the two thermistors were set at 200 μA each using two Keithly constant current sources and the thermistor voltages were recorded. The temperature of a thermistor is given by

$$T = [\ln(R)/A]/-B, \quad (1)$$

where R is the resistance of the thermistor (V/I) and A and B are constants which are obtained by calibrating the thermistors in ice water (0 °C), at room temperature, and in boiling water (100 °C). Since the two thermistors are not exactly matched, the Microsoft Excel add-on solver was used to calculate A and B so that identical temperatures are obtained when no emission current was present. Prior to extracting emission current, a test run for about 900 s was performed to obtain enough data for thermistor calibration. After the 3 min run at the emission current of 1 μA, the anode voltage was turned off so that the sample could cool off or heat up in case of heating or cooling during the 3 min under operation. The emission current was then increased to 2 μA, again 3 min on and 3 min off. This sequence was then continued with 4, 6, 8, 10, 20, 40, 60, 80, 100, and 200 μA. After subtracting the temperature of the reference thermistor, the data were examined to see if cooling is observed.

IV. RESULTS AND DISCUSSION

Figure 5 shows the temperature versus time plot for the sample under test and for the control chip. At the beginning of the test, with no emission current drawn from the test sample, the temperature increased. This is caused by self-heating of the thermistors at the operating currents of 200 μA. At about 100 s, the temperature in the vacuum system started to decrease. During positioning of the test probes the microscope light was turned on which caused the temperature to rise. After the light was turned off, the two silicon chips start to cool. The emission current of 1 μA is turned on at 900 s into the experiment. The associated temperature rise is not discernable from the scale chosen for the plot. The clearly discernable increase in the temperature at 3240 s corresponds to an emission current of 20 μA. The other peaks in the plot correspond to 40, 60, 80, 100, and 200 μA. The dashed line in the graph corresponds to the temperature of the control chip indicating that there is some heat conduction from the test chip to the control chip via the thermally insulating post and the cantilever arms. Figure 6 shows the data after the temperature of the control chip was subtracted. The bottom of the abscissa is marked in seconds and the top indicates the emission current in microampere during the 3 min time interval when the emitter is turned on. Based on the data for 20 μA and above, which clearly indicate heating, one would expect a similar monotone increase in temperature for 6, 8, and 10 μA if only heating of the sample would occur. Since this is not the case, it is concluded that around 8–10 μA, some cooling of the sample takes place. The magnitude of the heating peaks at the end of the 3 min intervals, including the variances in the signals, as a function of emission current is shown in Fig. 7. A dip in the temperature is observed at an emission current of about 10 μA.

To confirm that the reduction in temperature can be reproduced, the experiment was repeated one week later using the same emitter, but a different area on the surface. During this time, the sample was left in the vacuum chamber but the ion pump was turned off. This procedure avoids potential desorption of the resonant states. Figure 8 shows the results and, again, a dip of about 0.01 °C at 10 μA is observed. To estimate the contribution due to Joule's heating of the contact resistance of the emitter probe to the Ta film, the lateral resistance of the Ta film and the vertical resistance of the NCG film, the anode was lowered until it touched the NCG film. A resistance of about 200 Ω was measured. By varying the current through this configuration, a temperature-time plot, similar to the one in Fig. 5 was obtained. The data are shown in Figs. 7 and 8 as "control (surface test)." It can be seen that the temperature rise, due to this 200 Ω resistor is far less than the temperature rise of the test chip. This might indicate that an additional resistance component is present if

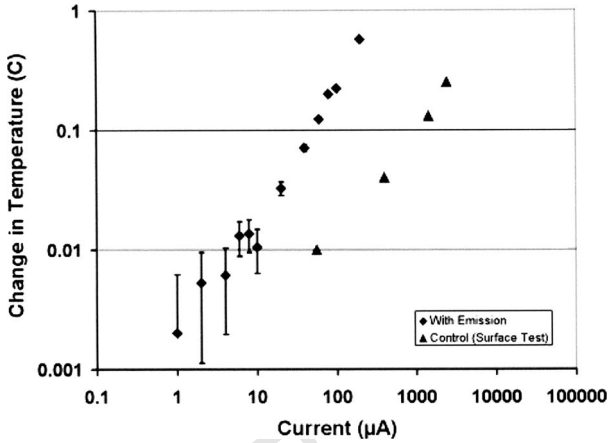

FIG. 7. Change in temperature of the test chip vs emission current. The error bars indicate the variance of the temperature at the end of each 3 min test cycle. There is an indication that the temperature decreases by about 0.01 °C near an emission current of 10 μA. The solid triangle data were obtained by heating the test chip through a series resistance of about 200 Ω that was created by lowering the anode until it touched the emitter surface.

one assumes that the temperature rise of the test chip is caused by a resistive effect. The magnitude of that resistance can be estimated the following way: The power needed to reach a temperature change of 0.01 °C for the 200 Ω resistor is 0.588 μW. Assuming that I^2R heating is responsible for the increase in temperature of the test chip, to reach a temperature change of 0.01 °C, the power is also 0.588 μW. This then yields, for a current of 10 μA, an effective resistance of about 6 kΩ. This is not an unreasonable value considering that by lowering the anode onto the NCG film, local damage could have taken place and portions of the anode could have touched the underlying Ta film. Since emission takes place at very small areas, the resistance near the electron exit point can be quite high. Simulations performed in Refs. 6 and 7 predict resistance values in the megaOhm range for CNTs grown on *n* or *p*-type silicon. In addition to Joule's heating, the observed emitter heating could also be caused by the Nottingham effect. No estimate was performed about the expected magnitude of that effect.

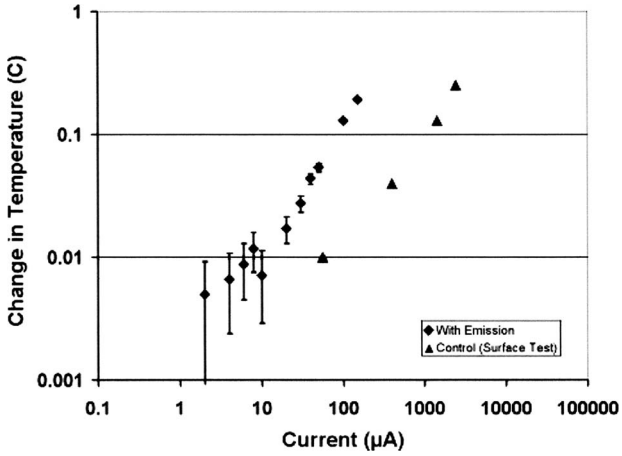

FIG. 8. Change in temperature of the test chip vs emission current. This experiment was performed about a week later using the same emitter film but at a different location as compared to the data in Fig. 7. Again, a small reduction in temperature around an emission current of 10 μA is observed.

V. CONCLUSIONS AND SUGGESTIONS FOR IMPROVEMENT

Based on some theoretical predictions, an experiment was performed to measure possible cooling of nanocrystalline graphite/carbon nanotube emitter films that is caused by resonant tunneling effects from contaminants present at the surface of the emitter film. The temperature was measured on the back of the silicon chip onto which the emitter film was deposited using a small thermistor beat (metal oxide) that was encapsulated in a plastic cover. To increase the sensitivity of the measurement, a reference thermistor was used to monitor possible temperature changes in the vacuum chamber during the experiment. The test chip and the reference chip were positioned on thermally insulating cantilever arms to minimize heat sinking of the test chip to the metal platform in the chamber. Some experimental indication exists that indeed a small degree of cooling, about 0.01 °C, takes place at an emission current that is indicative of resonant tunneling as judged by the shape of the *I-V* curve. The experiment was repeated at a different location on the same sample and, again, a small cooling signal was obtained. If cooling is caused by unintentional contamination at the emitter surface giving rise to the resonance effect, these contaminants can be removed by leaving the sample in the vacuum chamber over an extended period of time (several weeks for the given sample under continuous pumping of the system) or by electron-induced desorption. The fact that desorption takes place is manifested in an *I-V* curve that is shifted to higher extraction voltages for the same emission current and a less pronounced saturation region. Less or no cooling should be obtained. To improve upon this initial experiment, the above mentioned desorption experiment has to be performed. It is also suggested that one or several CNTs be deposited directly onto the thermistor beat after removing the plastic encapsulating layer. Prior to CNT deposition, a thin insulating layer followed by a conductive layer and the catalytic film have to be deposited onto the metal oxide thermistor. Another possibility is to miniaturize the testing approach using MEMS technology for the fabrication of the temperature sensors and the thermally insulating cantilevers.

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