Solid State Communications 151 (2011) 1105–1108

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

"Heat trap": Light-induced localized heating and thermionic electron emission from carbon nanotube arrays

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ARTICLE INFO

Article history:
Received 6 May 2011
Accepted 13 May 2011
by P. Hawrylak
Available online 24 May 2011

Keywords:
A. Nanostructures
A. Fullerenes
D. Electron emission
D. Heat conduction

ABSTRACT

Light-induced heating of a typical bulk conductor to thermionic electron emission temperatures usually requires high-power lasers. This is because of the efficient dissipation of heat generated at the illuminated spot to the surroundings, since electrical conductors are normally also good thermal conductors. We show that the situation can be drastically different in a carbon nanotube forest and a spot on the surface of the forest can be heated to above 2000 K using a low-power beam of visible light, leading to localized thermionic electron emission. This unique phenomenon may be explained by a rapid drop in thermal conductivity with increase in temperature, leading to a positive feedback that thermally isolates an island on the forest. Applications include thermoelectrics, photocathodes, optical switches, solar cells and even solar displays.

1. Introduction

One way to heat a material locally is by illuminating it with a beam of light. Although this can be achieved easily for a spot on an insulating surface, it requires significantly higher optical power for a similar spot on a metallic surface, due to efficient dissipation of heat to the surroundings. We found in light induced electron emission experiments that a continuous-wave visible laser beam with a diameter as small as ∼100 μm results in a heated, incandescent spot with approximately the same size on the surface of a macroscopic-size nanotube forest. We obtained an emission current of 100 nA for an optical power as low as 4 mW from a small handheld laser. The emission current showed a strong non-linear increase with laser power and reached 25 μA at 350 mW.

Forests of vertically aligned carbon nanotubes are excellent absorbers of light over a wide spectral range, similar to a perfect black body [1,2]. Laser-induced heating of nanotube films [3] and thermionic electron emission from nanotube forests [4] have been reported. On the other hand, the high or moderate thermal conductivity of nanotubes [5–10] has motivated applications in thermal management [11]. In the above experiments, therefore, high-power pulsed lasers or a beam wide enough to heat the entire nanotube sample were needed, as one expects that any heat generated locally in one section of a nanotube would efficiently dissipate by conduction through the rest of it and not lead to a major increase in temperature, such as observed in optical absorption and thermal transport experiments on suspended nanotube bundles [12]. Here, we show that the situation is different if the light intensity is beyond a certain threshold, even for low total optical power.

2. Methodology

Fig. 1 shows a schematic of the device and experimental configuration. A laser beam illuminates a small spot on the sidewall surface of a nanotube forest, which has lateral dimensions of ∼5 mm and a height of ∼1 mm (see details in Supplementary Information). The photon energies of 2.33–2.54 eV used (wavelengths of 488–532 nm) are well below the workfunction of carbon nanotubes (4–5 eV [13,14]) for pure photo-emission (photoelectric effect) to happen; no current is expected if the collection voltage at the anode is not high enough for field-emission. Indeed, that was the case if the laser beam was not highly focused. Remarkably, however, as we focused the beam to smaller spots (increasing the intensity at fixed power), we observed a drastic change in behaviour: a bright, localized incandescent glow appeared suddenly on the forest sidewall at the location of the laser spot (Fig. 1(b)) and an emission current appeared. For example, at 100 mW of laser power focused to a 0.2 mm^2 area (corresponding to an intensity of 0.5 W mm^{-2}), we measured an emission current of ∼100 pA.

3. Results and discussion

Fig. 2 shows the emission current as a function of laser power when the laser is focused beyond the threshold intensity. The observed non-linear increase is consistent with thermionic emission. Fig. 3 shows the measured current as a function of device

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doi:10.1016/j.ssc.2011.05.024

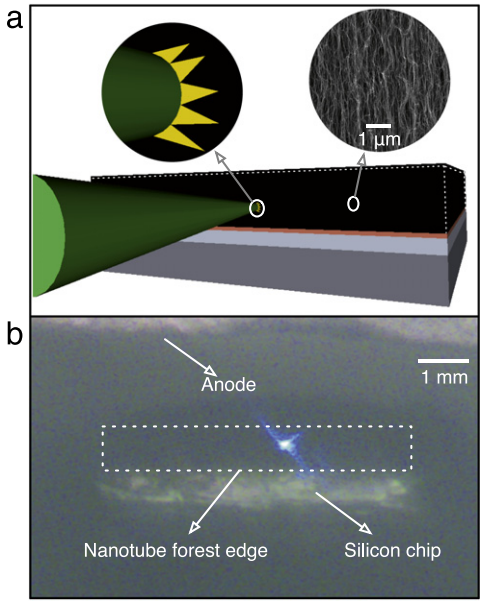

Fig. 1. (a) Schematic of the device showing the laser spot on the sidewall of the carbon nanotube forest. An incandescent spot is observed as the intensity of the laser is increased. The top left inset demonstrates that the incandescent spot is localized to the position of the laser beam and does not spread as the laser intensity is increased. The top right inset shows a scanning electron macrograph of the sidewall of an actual carbon nanotube forest and the nanotubes' overall alignment. (b) A photo of the device with the incandescent spot. The laser light has been filtered out and the glow has been attenuated in order to image the spot using a CCD camera. The white dotted box is used to draw attention to the sidewall of the forest. The silicon chip, on which the nanotubes are grown, and the edge of the copper anode, which collects the emitted electrons, are also shown.

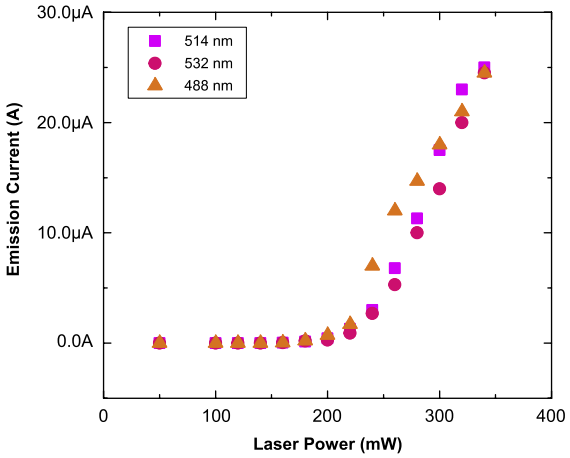

Fig. 2. The measured emission current versus the laser power for several wavelengths (488 nm, 514 nm, and 532 nm) shows a non-linear increase. The behavior is very similar in all cases, consistent with broad spectral absorption [1,2]. The laser spot was ∼250 μm in radius. A collection voltage of 50 V was applied, which is below that needed for field-emission (the dark current is below the measurement noise). The error bars are much smaller than the graph markers and therefore not seen.

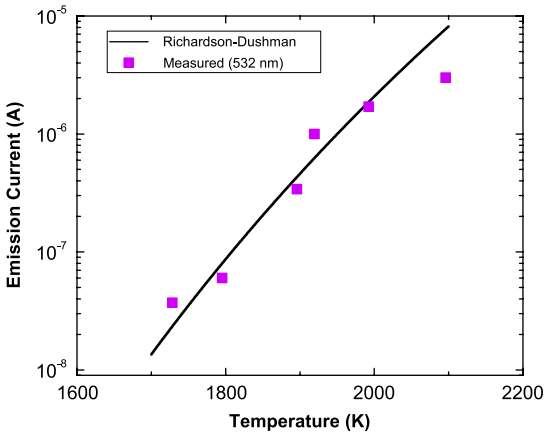

Fig. 3. The measured emission current as a function of emission spot temperature (at 532 nm) shows a trend similar to that predicted by the Richardson–Dushman equation. The laser spot had a radius of ∼250 μm. The squares show the current as a function of the measured temperature, which was determined by fitting the black body spectrum to the spectrum of the incandescent spot (see Supplementary Information for more detail). The solid line shows the prediction of the Richardson–Dushman equation, where an emission spot radius of ∼230 μm was chosen to obtain this fit.

temperature (obtained by fitting the optical spectrum of the glow spot to that of black body radiation—Supplementary Information), as well as the calculated current using the Richardson–Dushman equation for thermionic emission, following the trend of the experimental data. Another possible mechanism would be optical field-emission (field-emission as a result of the modulation of the vacuum barrier by the electric field of the laser) [15]; however, even at the maximum intensity used here, the electric field of the laser beam was only $\sim 0.1\,\mathrm{V}\,\mu\mathrm{m}^{-1}$, significantly below the required field of $\sim 1\ \mathrm{V}\ \mu\mathrm{m}^{-1}$ for field-emission from carbon nanotubes. Effects such as two-photon photo-emission or a combination of photo- and thermionic emission [16] may also play a role, although the dominant mechanism seems to be thermionic.

When slowly moving the sample out of the focal point, we first noticed a gradual decrease in the emission current, indicating that widening the beam and reducing the intensity leads to a lower temperature at the emission spot. At a threshold intensity, however, the current dropped suddenly and the visible glow disappeared (video in Supplementary Information).

The extreme localization of heat observed here (incandescent spot size approximately the same as laser spot size) is highly unusual and, given the relatively high thermal conductivity of nanotubes, very counterintuitive. We explain the phenomenon as follows. We believe the key lies in the fact that thermal conductivity drops as a function of temperature at high temperatures (indeed, a $\frac{1}{\alpha T+\beta T^2}$ behaviour for thermal conductivity has been reported for temperatures up to 800 K in individual single-walled carbon nanotubes [17–19] (beyond this temperature nanotubes could not survive in air) and attributed to umklapp and second-order three-phonon scattering [17,20,21]). As the laser intensity increases, the rate of heat generation in the nanotube forest increases. Below the threshold intensity, this heat dissipates to the surrounding areas easily and the temperature slowly rises by a small amount, as in Ref. [12]. Above the threshold, however, the rate of heat generation is significantly higher than that of dissipation, such that the temperature at the laser spot rises quickly, reducing thermal conductivity in that region, which then leads to an even more effective heating of that spot. The resulting positive feedback mechanism leads to a significant increase in the temperature and corresponding drop of thermal conductivity in that region, thermally isolating it from the surrounding area. We used the power conservation law (laser power equals the sum of power losses due to electron emission, black body radiation and heat dissipation to the surrounding areas) to investigate the temperature dependence of thermal conductivity. A $\frac{1}{\alpha T+\beta T^2}$ behaviour provided a good fit to the experimental data (see Supplementary Information for the calculation details). We note that defects could also reduce thermal conductivity [22]; however, defects cannot explain the abrupt turn-on we observe at the threshold intensity. Moreover, one expects defects to partially heal at the elevated temperatures attained here. However, we have not observed weakening

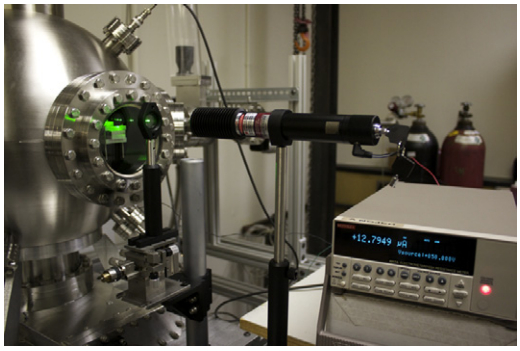

Fig. 4. A 50 mW, battery-operated handheld laser was capable of heating the sample enough for thermionic emission. The laser was focused onto the sidewall of the forest using a lens with a 15 cm focal length. The sample is inside of the high-vacuum chamber seen on the left and placed close to the sapphire viewport. An emission current of ∼13 μA is recorded by the electrometer through an insulated BNC feedthrough by applying a collection voltage of 50 V. This experiment demonstrates that laser-activated thermionic cathodes do not have to rely exclusively on sophisticated high-power pulsed lasers anymore—a laser pointer and potentially even integrated lasers may also work.

of the phenomenon after repeating the experiment many times, which suggests defects may not play a major role here.

The observed efficient, localized heating at optical powers down to 4 mW is remarkable since it opens up the possibility of photon-to-electron conversion devices using readily available light sources such as laser pointers, lamps and even the sun. In Fig. 4 we show a photograph of the experiment where an inexpensive handheld laser was used at a power of 50 mW to generate ∼13 μA of emission current. This corresponds to a quantum efficiency (if we were to define one for thermionic emission) of 0.06%; however, this value can be increased if the laser is focused to a smaller spot to increase the intensity further.

We also repeated the experiment by focusing the laser on the top surface of the nanotube, again obtaining a similar effect, in agreement with the fact that in Ref. [1] a low reflectance was observed for a wide range of illumination angles. The experiments were repeated numerous times over several months, while other experiments (such as ultra-violet photo-emission) were also performed on the same device in between. The device showed remarkable robustness and the results were consistently reproducible (although damage did happen when extreme intensities were used—see Supplementary Information). Three other nanotube forests, prepared with a different growth system/recipe, were also tested and they all exhibited the same effect in a reproducible manner at various locations on each forest. It is thus evident that the observed phenomenon is not a coincidence and has its origin in the fundamental structure and properties of the nanotube forest. It is also important to establish whether this effect is unique to nanotube forests or can happen in bulk conductors, too. A good candidate material that can be heated to such high temperatures is tungsten, which we also tested (we used a tungsten filament obtained from a light bulb). In order to observe a current of 100 nA, an intensity of three orders of magnitude higher than that for nanotube forests was needed, although reflectance from tungsten is only 50%. In addition, the size of the glowing region was ∼100 times larger than the size of the laser spot, indicating high heat dissipation to the surrounding areas. The response of the tungsten wire was also very slow as the gradual heating was easily observed with the naked eye to take a few seconds, and a rise time of ∼2 s was seen in the thermionic emission current. In the case of the nanotube forest, the response was instantaneous as seen by the naked eye and, when we chopped the laser beam with a frequency of up to 100 Hz, the emission current showed an alternating behaviour with the same frequency. All these observations point to the unique behaviour of the nanotube forest. Of course, similarly sparse nanostructured arrays of other materials (such as various nanowires) might exhibit a similar behaviour, although most materials would melt or evaporate before reaching thermionic emission temperatures and carbon nanotube forests are rather unique in this respect.

Finally, a note is in order on the effect of polarization of the incident light: the thermionic current was substantially higher (one to three orders of magnitude higher in experiments on various samples and different locations on each sample) for polarization parallel to the axis of the nanotubes, consistent with our previous optical absorption simulations where we observed significantly stronger optical absorption for parallel polarization [23].

4. Conclusion

Previously, electrically driven thermal light emission [24] and thermionic emission [25] have been demonstrated in nanotubes. Trapping of optically induced thermal energy in individual single-walled nanotube bundles has also been observed (not observed in multi-walled samples) [26]. A localized heating and glow of nanotube arrays under an ultra-violet laser focused to a submicron spot has been reported in Ref. [27]. The glow spectrum in that case exhibited photoluminescence behaviour rather than black body radiation. Here, we reported light-induced heating, incandescence and thermionic emission confined to an island on the surface of a macroscopic-size multi-walled nanotube forest. Given that the observed phenomenon happens for various visible wavelengths and at very low powers, has an abrupt turn-on transition at the threshold, and the fact that nanotube forests are easy and inexpensive to make and can potentially be operated in modest vacuum conditions with high stability and lifetime, the effect has important implications for optical absorbers and detectors, optical switching and modulation devices, thermopower wave guides [28], vacuum-based solar energy harvesters [29], solar electron sources for a multitude of applications such as display technologies, laser-assisted nanostructure growth [30], and thermoelectric devices [31]. It will be interesting to see whether similar effects also occur in other nanostructured systems such as various nanowires or graphene.

Acknowledgments

We thank G.A. Sawatzky and D.P.H. Hasselman for fruitful discussions. We also thank L. Chrostowski and N.A.F. Jaeger for making their optical spectrum analyzer and camera available to us, as well as S. Motavas for the use of her camera, A. Kashefian Naeini for help with electron microscopy and M. Michan for assistance with the vacuum chamber. Funding for this work was provided by the Natural Sciences and Engineering Research Council, the Canada Foundation for Innovation, the British Columbia Knowledge Development Fund, the BCFRST Foundation/British Columbia Innovation Council and the University of British Columbia.

Appendix. Supplementary data

Supplementary material related to this article can be found online at doi:10.1016/j.ssc.2011.05.024.

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