Carbon nanotubes synthesized by biased thermal chemical vapor deposition as an electron source in an x-ray tube

Y. B. Zhang,[a] S. P. Lau, and L. Huang
School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

M. Tanemura
Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

(Received 16 November 2004; accepted 8 February 2005; published online 18 March 2005)

Carbon nanotubes (CNTs) with supreme field emission properties were synthesized by depositing Co-containing amorphous carbon (*a*-C:Co) composite films using filtered cathodic vacuum arc technique with a 15 at % Co-containing graphite target and subsequently growing CNTs using biased thermal chemical vapor deposition at 580 °C with the *a*-C:Co composite film as a catalyst layer. The as-grown CNTs with a thin diameter of about 10 nm have a low threshold field of 1.6 V/μm and a stable current density of 2.1 mA/cm^2 at 3 V/μm. Thus an x-ray source was built in a diode configuration using the CNTs as its cold electron source showing good potential in x-ray radiography. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1891299]

An x-ray system using a thermionic electron emission cathode normally requires a water-cooling system due to heat converted from input power, thus making it difficult to construct a compact one.[1] It has been reported recently that x-ray tubes in a triode configuration use carbon nanotubes (CNTs) (Refs. 2 and 3) or graphite nanocraters[4] as their cold electron sources. With the trend of device miniaturization, a point x-ray source and a miniature x-ray tube have been obtained in a diode configuration using a graphite-nanofiber cold cathode[1] and a carbon-nanofiber field-electron emitter, respectively.[5] A diode type is superior to a triode type in x-ray generation efficiency and in construction of a compact and low-cost system since a gate electrode is not required in the diode configuration. Thus high-resolution x-ray radiography images of biological samples have been achieved.

In this study, a compact and highly efficient x-ray source was built by combining the compactness of a diode configuration with the low threshold field and high emission current density of CNTs. The CNTs electron source was prepared as follows. By using filtered cathodic vacuum arc (FCVA) technique with a 15 at % Co-containing graphite target,[6] Co-containing amorphous carbon (*a*-C:Co) composite films were initially deposited at room temperature on an arc tungsten wire or a highly doped ⟨100⟩ p^{++}-type silicon wafer. Then dense CNTs were grown on the as-deposited *a*-C:Co composite films by biased thermal chemical vapor deposition (CVD) using Co in the composite films as a catalyst. A vertical tube furnace with a base pressure of 10^{-3} Torr was ramped to 580 °C in 10 min with the flow of 30 sccm nitrogen and 40 sccm hydrogen. Then acetylene gas with a mass flow of 5 sccm was introduced into the furnace and a negative dc bias of 400 V was applied to the *a*-C:Co composite films on the tungsten wire or silicon substrate. The total pressure was maintained at 100 Torr for 5 min with a furnace temperature of 580 °C. Finally the furnace was cooled down to room temperature with the flow of nitrogen only. Another as-deposited *a*-C:Co composite film on silicon substrate was annealed with the same process except in nitrogen only.

Figure 1(a) shows an atomic force microscopy (AFM) image of the *a*-C:Co composite film on silicon substrate after annealing in nitrogen only. Co nanocrystalline grains were clearly found on the surface. The size of Co grains is estimated to be around 10 nm. The surface Co content of the *a*-C:Co composite film after annealing was found to be 53% by x-ray photoelectron spectroscopy measurement. Figure 1(b) shows a scanning electron microscopy (SEM) micrograph of CNTs grown on the *a*-C:Co composite films on silicon substrate. After biased thermal CVD, a black-colored CNTs layer was formed on the surface of the *a*-C:Co composite film. Continuous dense distribution and random tangles of tubes were observed. Co particles can be found on the tip of tubes. The diameter of tubes is around 10 nm. The results show that after annealing the Co nanocrystalline grain in the *a*-C:Co composite film dominates the CNTs growth and its size is similar to the diameter of grown CNTs.

Figure 1(c) shows emission current density versus applied electric field (J–E curve) of the as-grown CNTs film. The J–E curve was obtained with the first three rounds of ramping. The data in the ramping rounds show similar characteristics. It can be found that with the ramping of the electric field in field emission measurement, a low threshold field of 1.6 V/μm was obtained for the CNTs film. The threshold field is defined here as the electric field at which the current density of 0.1 μA/cm^2 is obtained. As the electric field increased to a certain value, the emission current tended to saturate due to the current-limited resistor and the series-resistance of the film.[7] The maximum emission current density of several mA/cm^2 can be achieved. At 6 V/μm, an average emission current density of 7 mA/cm^2 was obtained. The inset of Fig. 1(c) shows the corresponding Fowler–Nordheim (FN) plot of the J–E curve of the as-grown CNTs film. The FN plot of $\ln(J/E^2)$ versus $1/E$ is linear, indicating that emission is governed by electronic tunneling from CNTs with metallic conduction characteristics.[8] At high fields, the saturated emission current deviated from the FN law. From the deviation a saturation field of 3 V/μm and the corresponding current density of 2.1 mA/cm^2 were obtained. By taking an approximate work function of 5 eV for CNTs,[9] a field enhancement factor of 2700 is derived.

[a]Author to whom correspondence should be addressed: electronic mail: eybzhang@ntu.edu.sg

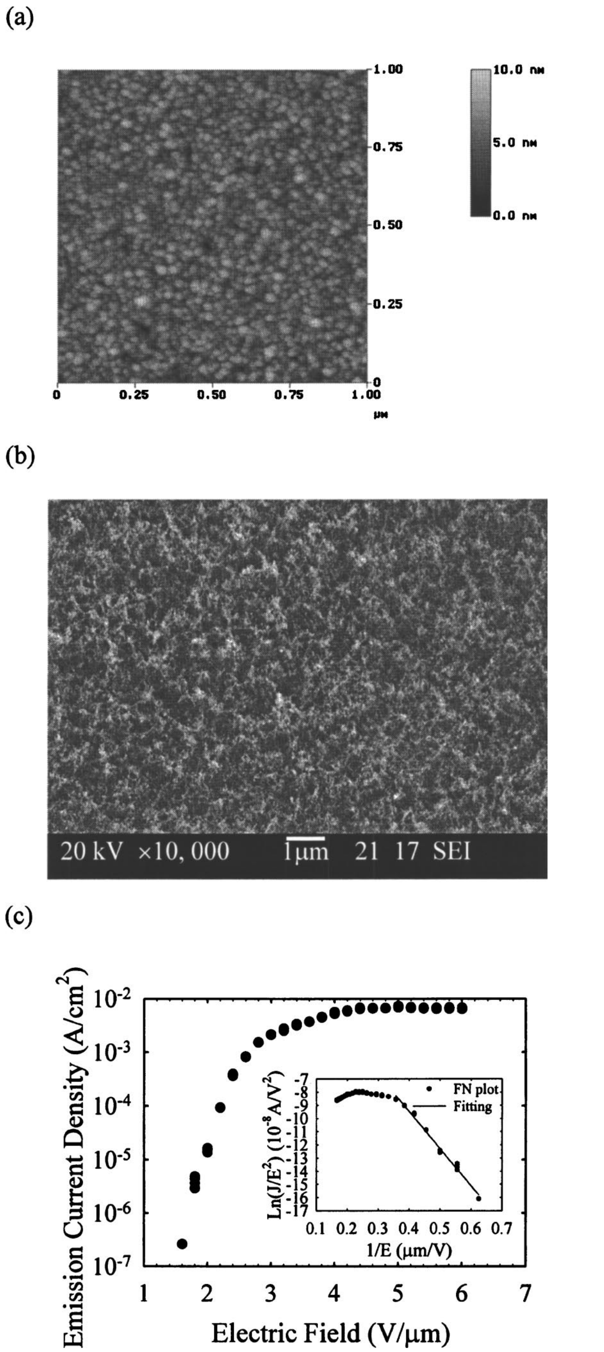

FIG. 1. (a) An atomic force microscopy (AFM) image of the *a*-C:Co composite film on silicon substrate after annealing in nitrogen only. (b) A scanning electron microscopy (SEM) micrograph of CNTs grown on the *a*-C:Co composite film. (c) Electron field emission J–E curve of the as-grown CNTs. Inset shows the Fowler–Nordheim (FN) plot of the J–E curve of the as-grown CNTs and its fitting.

Due to the random distribution of CNTs, it is impossible to obtain such a high geometric enhancement factor. This indicates a possible decrease of work function on the surface of CNTs due to a small radius of curvature of CNTs and an electrostatic effect.[10] Lifetime measurement shows a stable emitting current density of 2 mA/cm^2 at 3 V/μm for 15 h with marginal fluctuation possibly from accidental arching in a test chamber of 2×10^{-6} Torr. Then the current density decreases slightly due to some CNTs degradation and failure.

Figure 2(a) shows a schematic of a diode-type field emission x-ray tube, which is composed of a CNTs cathode, a Cu metal target, and a stainless steel sheath. Figure 2(b) magnifies its field emission electron source—CNTs on the tip of an arc tungsten wire with a diameter of 0.125 mm. In this cathode design emission electrons are focused to reduce x-ray emitting area. The distance between the cathode and the Cu target is around 1 mm. The x-ray tube was evacuated by a mechanical pump and a turbomolecular one to a base pressure of 10^{-6} Torr. A high voltage pulsed power supply previously used for plasma immersion ion implantation was applied to provide pulsed voltage to the x-ray tube.

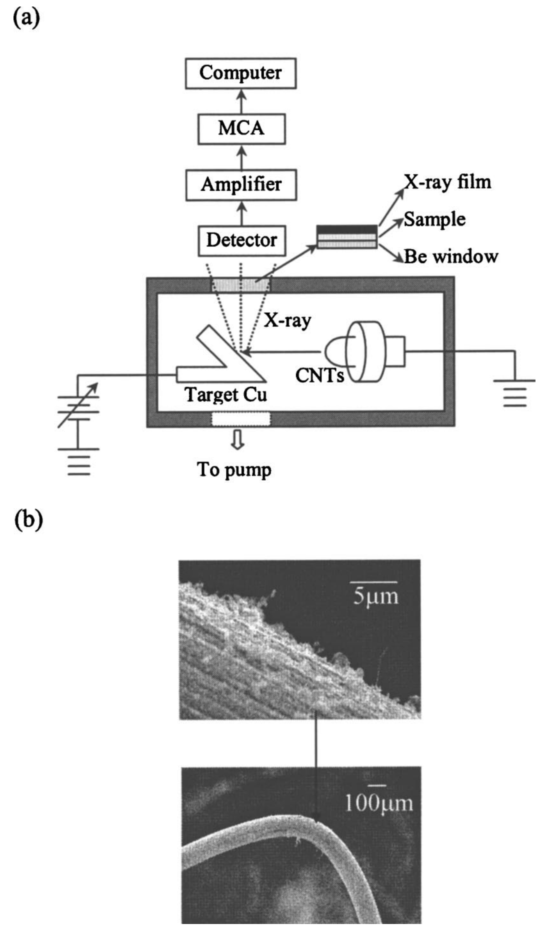

FIG. 2. (a) A schematic of a diode-type field emission x-ray tube. (b) SEM micrographs of a CNTs cathode. Bottom: an arc tungsten wire with a diameter of 0.125 mm; Top: CNTs on the tip of the tungsten wire.

The spectrum of x-ray generated by bombarding the Cu target with high-density and high-energy electrons from the CNTs cathode was measured by a Si-PIN photodiode detector (XR-100T-CZT) and a multichannel analyzer (MCA-8000). In the measurement a pulsed voltage from 5 to 15 kV was applied with a fixed pulse width of 25 μs and a frequency of 600 Hz. The x-ray energy was calibrated using a standard x-ray radiation cadmium source (469 channel value corresponds to 23.1 keV and 1860 channel value to 88 keV). Figure 3(a) shows the x-ray spectrum from the Cu target obtained within 120 s at an applied bias of 14 kV. It presents strong characteristic Cu $K\alpha$ (8.04 keV) and $K\beta$ (8.91 keV) lines and a broad bremsstrahlung background. High frequency and high-intensity pulsed x-ray is desirable for both medical and industrial applications. Pulsed x-ray with different width and repetition rate can be easily produced using the device described here by changing the width and frequency of pulsed voltage. Figure 3(b) shows pulsed electron emission from CNTs detected by oscilloscopy with a pulsed bias

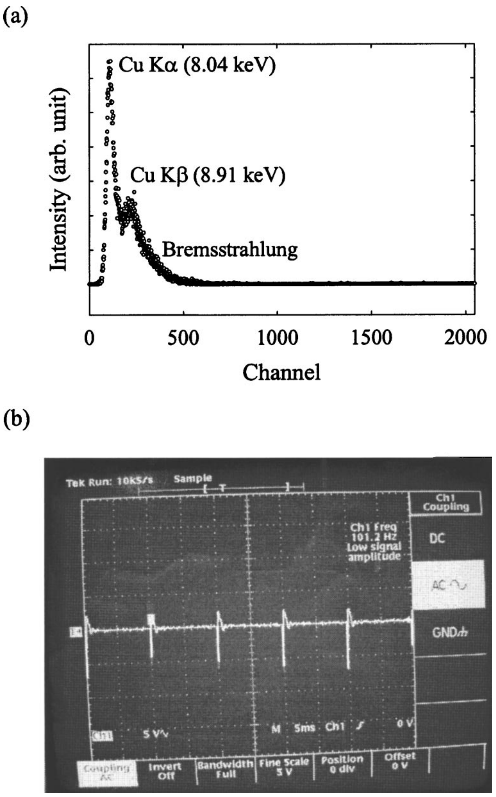

FIG. 3. (a) The x-ray spectrum from the CNTs/Cu x-ray tube obtained within 120 s at an applied bias of 14 kV. The characteristic x rays, such as $K\alpha$ and $K\beta$, are clearly evident in addition to the broad bremsstrahlung background. (b) Pulsed electron emission from CNTs detected by oscilloscopy with a pulsed bias of 5 kV, a pulse duration of 25 μs, and a frequency of 100 Hz.

of 5 kV, a pulse duration of 25 μs, and a frequency of 100 Hz.

One of the important x-ray applications is x-ray radiography. Figure 4 demonstrates the high-resolution x-ray transmission images of (a) fresh tree leaf, (b) frog leg, and (c) ikan bill samples. Figures 4(a)–4(c) are taken within 7 min at an applied bias of 12 kV, within 15 min at 15 kV, and within 9 min at 12 kV, respectively, with a pulse width of 25 μs and a frequency of 600 Hz. The corresponding real x-ray imaging time is 6.3, 13.5, and 8.1 s, respectively. Hence an x-ray image intensifier can be used to produce a reliable one-shot image in a short time. Compared to the exposure time of 1 h for the preliminary x-ray tube, the working efficiency of the x-ray tube improves remarkably.[2] It results from the good field emission properties of CNTs and the diode design. Subject to pulsed bias with various frequency and voltage for 2 weeks, the CNTs emitter still continues to work well in the x-ray tube. It was found from SEM that most CNTs on the tip of the arc tungsten wire are durable, which indicates good adherence of the interface between the CNTs and the tip of the tungsten wire.

In summary, dense CNTs with a diameter of around 10 nm were grown using biased thermal CVD on *a*-C:Co composite films deposited by FCVA. The as-grown CNTs presented a low threshold field of 1.6 V/μm and a high emission current density of 2.1 mA/cm^2 at an external applied field of 3 V/μm. Accordingly a compact x-ray tube was constructed in a diode configuration using the CNTs as its cold electron source, showing good potential in high-resolution x-ray radiography.

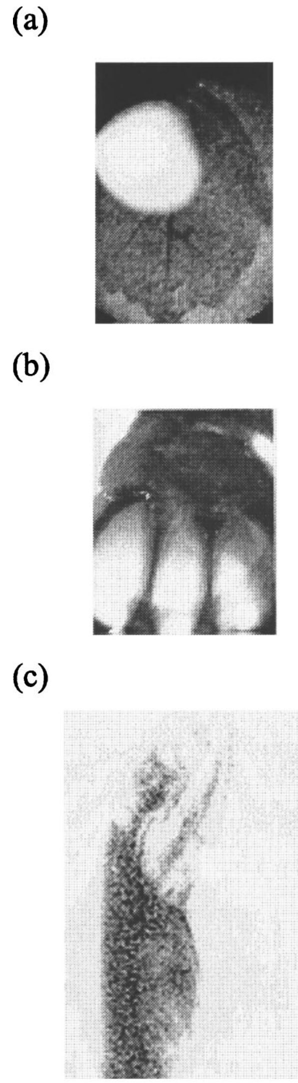

FIG. 4. High-resolution x-ray transmission images of (a) fresh tree leaf, (b) frog leg, and (c) ikan bill samples.

This work was supported by the Agency of Science, Technology and Research of Singapore.

[1]T. Matsumoto and H. Mimura, Appl. Phys. Lett. **82**, 1637 (2003).
[2]H. Sugie, M. Tanemura, V. Filip, K. Iwata, K. Takahashi, and F. Okuyama, Appl. Phys. Lett. **78**, 2578 (2001).
[3]G. Z. Yue, Q. Qiu, B. Gao, Y. Cheng, J. Zhang, H. Shimoda, S. Chang, J. P. Lu, and O. Zhou, Appl. Phys. Lett. **81**, 355 (2002).
[4]T. Matsumoto and H. Mimura, Appl. Phys. Lett. **84**, 1804 (2004).
[5]A. Haga, S. Senda, Y. Sakai, Y. Mizuta, S. Kita, and F. Okuyama, Appl. Phys. Lett. **84**, 2208 (2004).
[6]S. Xu, B. K. Tay, H. S. Tan, L. Zhong, Y. Q. Tu, S. R. P. Silva, and W. I. Milne, J. Appl. Phys. **79**, 7234 (1996).
[7]J. B. Cui, K. B. K. Teo, J. T. H. Tsai, J. Robertson, and W. I. Milne, Appl. Phys. Lett. **77**, 1831 (2000).
[8]W. A. de Heer, A. Chatelain, and D. Ugarte, Science **270**, 1179 (1995).
[9]J.-M. Bonard, J.-P. Salvetat, T. Stockli, L. Forro, and A. Chatelain, Appl. Phys. A: Mater. Sci. Process. **69**, 245 (1999).
[10]Y. J. Li, Z. Sun, S. P. Lau, G. Y. Chen, and B. K. Tay, Appl. Phys. Lett. **79**, 1670 (2001).