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Field emission from single-walled carbon nanotubes modified by annealing and CuCl doping

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In this article, we present a comparative study of field emission (FE) properties of the films of pristine, annealed and CuCl-filled single-walled carbon nanotubes (SWCNTs). The current-voltage dependencies and emission site distributions were measured in the diode configuration with a flat phosphor-coated anode. A significant increase of the threshold field was observed after annealing and doping of the films. It was explained by the selective oxidation of the small-diameter nanotubes confirmed by the Raman spectroscopy. The FE properties of annealed and filled SWCNTs were found to coincide with each other. At the same time, their Raman spectra differ significantly indicating the strong p-type doping induced by encapsulated CuCl. The obtained result reveals that the CuCl filling leads to significant changes in macroscopically averaged electronic properties but do not change the local work function at the apexes of emitting nanotubes, which is important for the further development of SWCNTs-based FE cathodes. *Published by AIP Publishing.*
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A variety of methods for doping of the single-walled carbon nanotubes (SWCNTs) were recently developed.[1] A large group of the doping methods is based on the possibility of filling the interior space of nanotubes with foreign substances.[1,2] It provides a precise control of the doping (i.e., the Fermi level position) that determines the optoelectronic properties of materials and devices based on SWCNTs. For example, recently, it was demonstrated that the conductivity of the thin films of SWCNTs can be increased by an order of magnitude via filling the nanotubes, composing the films, with iodine crystals.[3] This opens a promising possibility for the production of transparent conductive electrodes suitable for application in photonic and optoelectronic devices.

Carbon nanotubes are also known as a highly attractive material for producing the efficient field electron emission (FE) cathodes.[4] The FE properties are sensitive to geometry and electronic properties (in particular, to the work function ϕ) of materials. Thus, the FE measurements may be used for an estimation of the SWCNT work function changes in case of their doping via filling with acceptor or donor heteroatoms. The field emission of electrons usually occurs from the apexes of nanotubes due to the electric field focussing. This effect is described by the field enhancement factor β that is roughly proportional to the ratio of the height h to diameter d of the nanotube electrically connected to a flat conductive surface[5]

$$\beta \sim h/d. \tag{1}$$

The theory of FE from metals gives a well-known Fowler-Nordheim (FN) equation for the emission current I on electric field E

$$I = C_1(\beta E)^2 \exp\left\{-\frac{C_2\varphi^{3/2}}{\beta E}\right\}, \tag{2}$$

where C_1 and C_2 are roughly constants. In particular, these equations give a general relation between threshold field, which is one of the main characteristics of an FE cathode, and parameters β, h, d, and ϕ[6]

$$E_{\text{thr}} \sim \frac{\varphi^{3/2}}{\beta} \sim \frac{\varphi^{3/2}}{h}d. \tag{3}$$

Experimentally, the value of β may be obtained from the electron microscopy observations, while the work function at nanotube apex may be then determined from the FE experiments using an FN formula.[7] In accordance with the previous reports, the values of ϕ obtained for SWCNTs from the FE experiments are close to the work function of graphite (~5 eV) and can be considerably changed by the adsorption of gas molecules on the nanotubes surface[8,9] or by the incorporation of heteroatoms into the structure of nanotube.[10–13] Thus, the FE measurements may be used as a characterization tool for the analysis of nanotubes geometry, surface parameters and electronic properties.

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In this paper, we studied FE from the films of aerosol-grown SWCNTs. The films were modified via annealing and filling of nanotubes with CuCl crystals by a gas phase process. The films contained a mixture of nanotubes having different geometry and electronic properties. By a comparative study of pristine and modified SWCNT films, the effect of nanotubes geometry and doping on FE properties was estimated.

The SWCNT films were produced by an aerosol method described in detail elsewhere.[14] The nanotubes were collected on the nitrocellulose filter during synthesis. The collection time was of 2.5 min. The thickness of the resulting film was about 100 nm, and the optical transmittance was of 90% (at 550 nm). The dry-transfer technique was used to transfer the film from nitrocellulose filter to the 1 cm × 1 cm Si substrates. The filling of SWCNTs was done by the exposure of the film in CuCl gas at 220 °C for 26 h, added to air.[15] Another series of the reference samples was produced at the same conditions, but without CuCl gas, i.e., the films were annealed at 220 °C for 26 h in a normal air atmosphere.

The structure and composition of SWCNTs filled with CuCl molecules were characterized by a high-resolution transmission electron microscopy (HRTEM) and a scanning electron microscopy (SEM). The HRTEM measurements were carried out on a Titan 60–300 TEM/STEM microscope (FEI, The Netherlands) at an acceleration voltage of 80 kV equipped with monochromator and Cs spherical aberration corrector. The SEM measurements were performed on the Jeol JSM-7001F microscope. The film electrical resistance was measured by a Jandel RM3000 Test Unit. The Raman investigations were performed using the Horiba LabRAM HR Evolution spectrometer at the wavelength of 633 nm.

The FE properties of SWCNT films were measured in a vacuum diode configuration with a flat phosphor-coated screen served as an anode at the pressure of 1×10^{-5} Torr.[16] Prior to the FE measurements, the edges of the films were covered with a dielectric varnish in order to avoid additional field enhancement. The FE current-voltage characteristics were obtained by applying DC voltage between the cathode (SWCNT film) and anode with a Keithley 248 power supply and by measuring current with a Keithley 6487 picoammeter. The electric field E was defined as a ratio of the applied voltage V to the cathode-to-anode distance. The FE pattern produced by the emitted electrons on the phosphor-coated screen anode was captured by a CCD photo camera.

A typical SEM image of as-grown SWCNT film is presented in Figure 1. The film consisted of entangled nanotubes aggregated in bundles with diameters of few nanometres and lengths of several micrometres.[17] There were no noticeable differences in SEM images of the pristine and filled SWCNTs. At the same time, optical experiments, performed previously, showed that the doping level saturates with time and after ~20 h the changes in optical characteristics are negligible.[15] The formation of 1D CuCl crystals inside SWCNTs was directly confirmed by HRTEM (Figure 2).

The Raman spectra of SWCNT films are presented in Figure 3. The G mode of the film after CuCl treatment demonstrates a modified shape and a strong shift toward higher frequencies (up to 20 cm^{-1}). The radial breathing modes (RBM) were also shifted and considerably suppressed. The

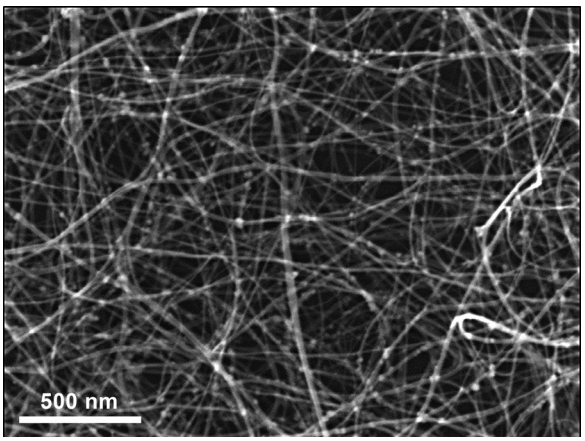

FIG. 1. SEM image of thin film of SWCNT film grown by aerosol technique.

changes in the Raman spectra indicate that the nanotubes were efficiently doped due to an encapsulation of CuCl crystal in their inner space.[15] As a result of doping, the resistance of the films decreased by almost one order of magnitude from 1050 Ω/sq to 120 Ω/sq.[18]

For the reference samples annealed at 220 °C without CuCl gas, the Raman G mode demonstrated practically no changes (Figure 3(a)), while the RBMs were noticeably shifted and almost completely suppressed above 175 cm^{-1} (Figure 3(b)). In the general case, the breathing mode frequency is inversely proportional to the diameter of SWCNT.[19,20] The disappearance of the high-frequency RBM implies that the small-diameter nanotubes were removed from the film due to a selective oxidation during the annealing process.[21]

The FE characteristics of the pristine SWCNT were typical for such kind of films. In particular, the threshold field value was of 1 V/μm (at the current density of 10 $\mu A/cm^2$), which is the value commonly reported for the carbon nanotube cathodes.[22–24] The FE patterns for the pristine films observed on the phosphor anode consisted of bright spots with density in the range of 50–100 per 1 cm^2 (Figure 4(a)), whereas for the

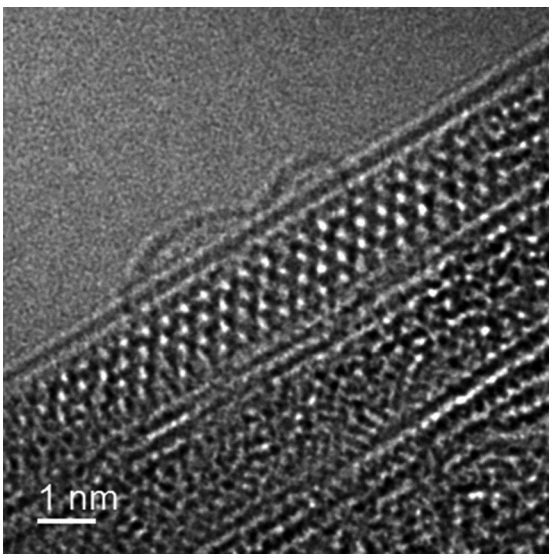

FIG. 2. HRTEM image of SWCNT filled with CuCl crystal.

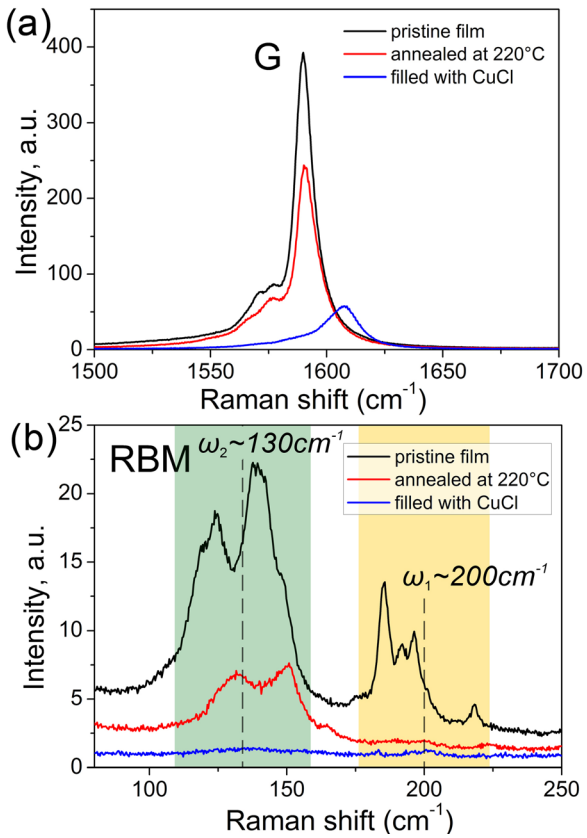

FIG. 3. The Raman spectra of pristine SWCNT film, the film annealed at 220 °C for 26 h and the film exposed to CuCl gas at 220 °C for 26 h. The excitation wavelength is 633 nm.

annealed and doped films the sites density was in the range of 100–200 per 1 cm^2 (Figures 4(b) and 4(c)).

In order to compare I–V characteristics of different samples, the normalized current i was calculated by the ratio of the total current, obtained from the whole film, to the number of emission spots. The electric field E was estimated

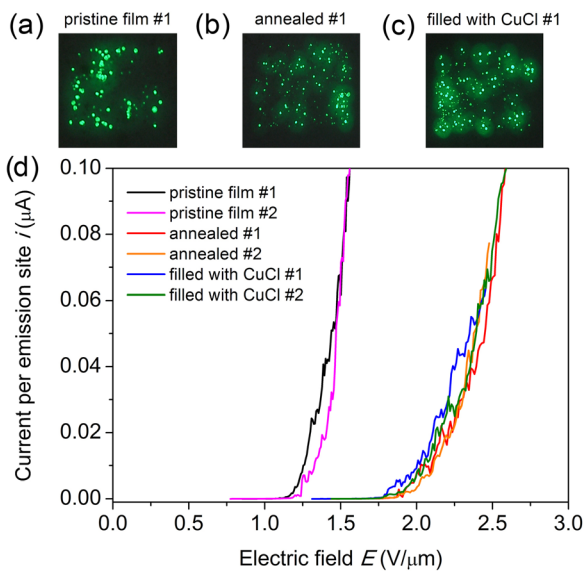

FIG. 4. (a)–(c) Field emission patterns at the current of 10 μA and cathode-to-anode distance of 500 μm for pristine, annealed and doped SWCNT films. Each pattern size is 1 cm × 1 cm. (d) The dependence of the normalized current versus electric field for the three types of SWCNT films. For each type of the film, two experimental curves obtained for the two different samples are presented.

by the ratio of the applied voltage to the cathode-to-anode distance. Figure 4(d) presents the dependence of i versus E for the three types of SWCNTs films. A large shift of $i(E)$ curves was revealed for the pristine and modified SWCNT films. The threshold field (at 0.01 μA) increased from $E_1 = 1.3$ V/μm to $E_2 = 2$ V/μm. However, there were no considerable differences in $i(E)$ between the doped and annealed films.

The shift of the $i(E)$ curves can be explained using the data obtained by the Raman spectroscopy. The RBM frequencies ω are inversely proportional to the diameters of nanotubes contained in the film. At the same time, from Equation (1), it follows that the enhancement factor is inversely proportional to the diameter of a nanotube. Therefore, the FE current is mostly provided by the nanotubes with the smallest diameters. For the pristine film, the smallest diameters are characterized by the RBM frequencies around $\omega_1 = 200\,cm^{-1}$ (see Figure 3(b)). For the annealed films, these RBMs disappear and the characteristic frequencies are around $\omega_2 = 130\,cm^{-1}$. It is easily seen that the ratio of average diameters d_2/d_1 that is given by the ratio $\omega_1/\omega_2 = 200/130$ is equal to the ratio of threshold fields $E_2/E_1 = 2/1.3$. According to Equation (3), this means that the increase of the threshold field is due to the change of d and no significant variance in work function ϕ. Therefore, the changes in the FE properties produced by the modification of SWCNT films may be explained by the removal of nanotubes with the smallest diameters in course of their selective oxidation.

The strong modification of Raman G mode for the filled SWCNTs implies a high doping level.[15] It was expected that the nanotube work function will be changed due to the doping. However, the $i(E)$ curves of the doped and annealed films were practically the same, meaning that the effect of the work function variation is very small. This can be explained by the fact that the FE properties are determined by the combination of field enhancement factor and work function. A significant change in the FE properties is only possible if the work function is changed locally at the apex of the emitting nanotubes with the smallest diameters and the biggest lengths. However, the HRTEM analysis revealed that not all nanotubes are filled with the CuCl crystals. Moreover, the nanotubes with the smaller diameters were doped less efficiently. Therefore, the geometrical effect dominates in the FE experiments over the effect of the work function modification. At the same time, in optical experiments, the Raman signal is measured from the whole surface of the nanotube films. It is also possible that a charge that transfers between the unfilled and filled nanotubes in the bundles will change the overall level of doping.[15] This may provide a more remarkable effect of doping on the optical properties of the SWCNTs.

In conclusion, the FE properties of SWCNT films doped with CuCl by gas-phase process were studied. An increase of the threshold field (at 0.01 μA per nanotube) from 1.3 V/μm for the pristine films to 2 V/μm for the annealed and doped films was observed. It was explained by the removal of the nanotubes with the smallest diameters due to their selective oxidation that was revealed by the modification of the Raman breathing modes. The annealed and doped films demonstrated almost the same FE current-voltage characteristics, meaning that the work function at the apexes of the emitting

nanotubes did not change significantly. The obtained result reveals that since only a small fraction of the nanotubes emit electrons the doping of these particular nanotubes near the apex region is unlikely. The work function modification may be more noticeable in case of prolonged gas filling process in vacuum environment, and this is a subject of our future experiments in this field. Nonetheless, the independence of FE from SWCNTs on the doping, detected in the current work, contradicts to intuitively expected behaviour and, thus, is important for the further development of SWCNT-based FE cathodes for applications in vacuum electronics.

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[1]M. V. Kharlamova, Prog. Mater. Sci. **77**, 125 (2016).
[2]Y. Fujita, S. Bandow, and S. Iijima, Chem. Phys. Lett. **413**, 410 (2005).
[3]A. A. Tonkikh, V. I. Tsebro, E. A. Obraztsova, K. Suenaga, H. Kataura, A. G. Nasibulin, E. I. Kauppinen, and E. D. Obraztsova, Carbon **94**, 768 (2015).
[4]S. C. Lim, K. Lee, I. H. Lee, and Y. H. Lee, Nano **2**, 69 (2007).
[5]V. I. Kleshch, A. N. Obraztsov, and E. D. Obraztsova, Fullerenes, Nanotubes, Carbon Nanostruct. **16**, 384 (2008).
[6]A. N. Obraztsov and V. I. Kleshch, J. Nanoelectron. Optoelectron. **4**, 207 (2009).
[7]Z. Xu, X. D. Bai, E. G. Wang, and Z. L. Wang, Appl. Phys. Lett. **87**, 163106 (2005).
[8]K. A. Dean and B. R. Chalamala, Appl. Phys. Lett. **75**, 3017 (1999).
[9]E. A. Vasilyeva, V. I. Kleshch, and A. N. Obrazsov, J. Nanoelectron. Optoelectron. **7**, 41 (2012).
[10]F. Jin, Y. Liu, C. M. Day, and S. A. Little, J. Vac. Sci. Technol., B **25**, 1785 (2007).
[11]J. Zhao, J. Han, and J. P. Lu, Phys. Rev. B **65**, 193401 (2002).
[12]H. Ahn, K. R. Lee, D. Y. Kim, and S. Han, Appl. Phys. Lett. **88**, 093122 (2006).
[13]V. I. Kleshch, E. D. Obraztsova, N. R. Arutyunyan, V. V. Grebenyukov, A. S. Pozharov, and A. N. Obraztsov, Phys. Status Solidi B **245**, 1990 (2008).
[14]A. Moisalaa, A. G. Nasibulin, and D. P. Brown, Chem. Eng. Sci. **61**, 4393 (2006).
[15]P. V. Fedotov, A. A. Tonkikh, E. A. Obraztsova, A. G. Nasibulin, E. I. Kauppinen, A. L. Chuvilin, and E. D. Obraztsova, Phys. Status Solidi B **251**, 2466 (2014).
[16]V. I. Kleshch, S. Rackauskas, A. G. Nasibulin, E. I. Kauppinen, E. D. Obraztsova, and A. N. Obraztsov, J. Nanoelectron. Optoelectron. **7**, 35 (2012).
[17]A. Kaskela, A. G. Nasibulin, M. Y. Zavodchikova, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D. P. Brown, A. Zakhidov, and E. I. Kauppinen, Nano Lett. **10**, 4349 (2010).
[18]E. D. Obraztsova, A. A. Tonkikh, V. I. Tsebro, E. A. Obraztsova, P. V. Fedotov, T. V. Eremin, V. A. Eremina, A. S. Orekhov, and A. L. Chuvilin, in *Book of Abstracts of XXXth International Winterschool on Electronic Properties of Novel Materials*, Kirchberg, Austria, 13–20 February (2016), p. 140.
[19]A. M. Rao, E. Richter, S. Bandow, B. Chase, P. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smalley, G. Dresselhaus, and M. S. Dresselhaus, Science **275**, 187 (1997).
[20]M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, Phys. Rep. **409**, 47 (2005).
[21]S. N. Bokova, V. I. Konov, E. D. Obraztsova, A. V. Osadchii, A. S. Pozharov, and S. V. Terekhov, Quantum Electron. **33**, 645 (2003).
[22]V. I. Kleshch, T. Susi, A. G. Nasibulin, E. D. Obraztsova, A. N. Obraztsov, and E. I. Kauppinen, Phys. Status Solidi B **247**, 3051 (2010).
[23]I. V. Obronov, V. I. Kleshch, E. A. Smolnikova, D. A. Bandurin, and A. N. Obraztsov, J. Nanoelectron. Optoelectron. **8**, 71 (2013).
[24]D. A. Bandurin, V. I. Kleshch, E. A. Smolnikova, I. V. Obronov, A. G. Nasibulin, E. I. Kauppinen, and A. N. Obraztsov, J. Nanoelectron. Optoelectron. **8**, 114 (2013).