Doped carbon nanostructure for cold-field emission guns: Structural and EELS studies

Rongrong Wang, Aurélien Masseboeuf, David Neumeyer, Marc Monthioux, Alejandro Lopez-Bezanilla, Raul Arenal

R. Wang, A. Masseboeuf, D. Neumeyer, M. Monthioux, A. Lopez-Bezanilla and R. Arenal

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Along with the development of the transmission electron microscope (TEM), cold field emission gun (C-FEG) becomes more and more popular. As a result of working at ambient temperature (300K), the C-FEG can offer narrower electron beam energy spread than that of Schottky gun [1]. Such a low working temperature also permits a smaller emission area. From Fowler-Nordheim (F-N) equation (1), the three tailorable parameters play a pivotal role to achieve better performances. They are the emission area A, the work function W and the field enhancement factor γ:

$$I = \frac{aA\gamma^2V^2}{Wd^2t^2(y)}\exp\left(\frac{-bdf(y)W^{3/2}}{\gamma V}\right) \quad (1)$$

The field enhancement factor can be raised by reducing the apex radius of emitter. In C-FEG, the apex radius of W (310) emitter is only 10% of ZrO coated W(100), which is used in Schottky gun. Consequently, the spatial coherence of electron beam is extremely enhanced [2]. In recent studies, the carbon nanotubes (CNTs) are considered as a better emitter [3]. Due to their quasi one-dimension structure, the oriental σ bonds offer a high mechanical performance along the axis direction [4]. This makes them capable of resisting the strong electrostatic force under the cold field emission condition. Their high melting point allows them to be degassed by the classical flash procedure. The chemical inert surface can keep their surface clean. In addition, their high carrier mobility enables to bear a higher current density [5]. More recently, the carbon cone nanotips (CcNTip) are considered even better than the CNTs [6]. Their root at micrometer level is more convenient for their manipulation and installation and more stable against external vibrations. As their apex radius is around 5 nm, the great spatial coherence of electron beam has been proved, and a higher resolution electron holography can be expected [7].

Besides the enhancement factor and the emission area, the work function is a key factor to achieve high electron beam brightness as well. Doping is an effective method to lower the work function of nanomaterials [8]. In the wake of doping with foreign atoms, the local electric field is tailored, which is also reflected in the band structure modification. Concerning carbon nanomaterials, boron and nitrogen are frequently used to modulate their band structure [9-11]. However, the influence of these dopants strongly depends on their position and atomic configuration, i.e. the graphitic nitrogen doping can create the donor state near the Fermi level by reason of the contribution of the excess electrons to the conjugated bond system [12]. On the contrary, pyridinic and pyrrolic nitrogen create the acceptor state near the Fermi level [9]. In the substitutional nitrogen doping case, the up-shifted Fermi level will bring about a lowered work function. Therefore, a higher emission current density can be expected. In this work, the electronic properties of these kinds of carbon nanostructures, used as high performance cold cathodes in TEM, were adjusted by BN co-doping. This co-doping was investigated by different characterization techniques.

In order to avoid introducing additional defects into the CcNTip's lattice and forming bamboo-like structure, the post-growth doping method was considered as the most suitable candidate. On the account of the relative low CcNTip production and the highly similar structure with the CNTs, this research was started from the doping of the CNTs. The CNTs were doped in a tubular furnace from 1300°C to 1500°C under the various atmospheres. The high resolution TEM imaging (HRTEM) investigated the structural influence from the thermal treatment (Fig. 1). Due to the good thermal resistance of CNTs, there is no significant structural modification observed. Spatially-resolved electron energy loss spectroscopy (SR-EELS), developed in a scanning TEM (STEM), confirmed the generation of BN nanodomain inside

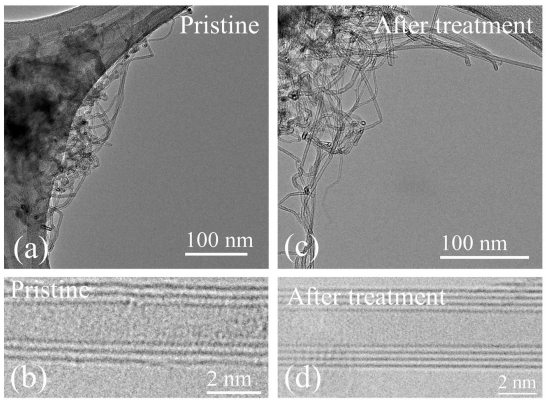

Figure1. Structural comparison between pristine (a), (b) and doped CNTs (c), (d) at different magnification.

the CNTs (Fig. 2) [13]. Furthermore, the homogeneous BN layer inside the CNTs shows the generation of BN@CNT hybrid nanotubes. Those TEM based studies were developed by employing two different aberrations corrected TEMs (FEI-Titan), working at low acceleration voltage (80 kV) in order to prevent the nanotubes from the damage caused by the electronic irradiation. Moreover, the formations of C-B bonding and C-N bonding are macroscopically confirmed by X-ray photoelectron spectroscopy (Fig. 3). The electronic

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R. Wang is with the CEMES, Univ. Toulouse, CNRS UPR 8011, Toulouse, 31400 France and the LMA-INA, Univ. Zaragoza, Zaragoza, 50018 Spain (rongrong.wang@cemes.fr).

A. Masseboeuf, D. Neumeyer, M. Monthioux are with the CEMES, Univ. Toulouse, CNRS UPR 8011, Toulouse, 31400 France.

A. Lopez-Bezanilla is with the Materials Science Div., Argonne National Lab., Illinois, IL 60439 USA.

R. Arenal is with the Fundacion ARAID, Zaragoza, 500018 Spain and the LMA-INA, Univ. Zaragoza, Zaragoza, 50018 Spain (arnal@unizar.es).

property of such a kind of doped device and the influence of

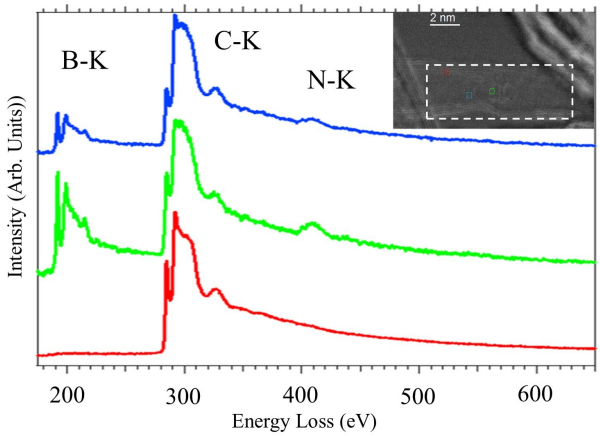

Figure2. Selection of EEL spectra extracted from the spectra image; blue, red and green spectra correspond to the pixels outlined in blue, red and green in insert image.

the introduced hetero-elements is clarified by the DFT calculations. All these results will be discussed in depth in this contribution.

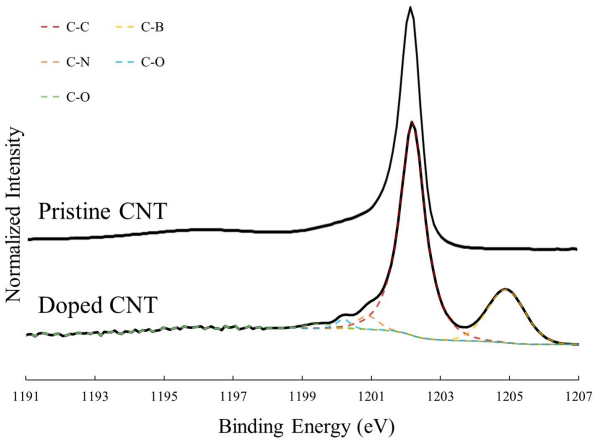

Figure3. XPS spectra of carbon C1s binding energy for pristine CNT and Doped CNT

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