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Determining the work function of a carbon-cone cold-field emitter by *in situ* electron holography

Ludvig de Knoop*, Florent Houdellier[1], Christophe Gatel[2], Aurélien Masseboeuf[3], Marc Monthioux[4], Martin Hÿtch[5]

CEMES-CNRS, Université de Toulouse, 29 rue Jeanne Marvig, 31055 Toulouse, France

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ABSTRACT

Cold-field emission properties of carbon cone nanotips (CCnTs) have been studied *in situ* in the transmission electron microscope (TEM). The current as a function of voltage, $i(V)$, was measured and analyzed using the Fowler–Nordheim (F–N) equation. Off-axis electron holography was employed to map the electric field around the tip at the nanometer scale, and combined with finite element modeling, a quantitative value of the electric field has been obtained. For a tip-anode separation distance of 680 nm (measured with TEM) and a field emission onset voltage of 80 V, the local electric field was 2.55 V/nm. With this knowledge together with recorded $i(V)$ curves, a work function of 4.8 ± 0.3 eV for the CCnT was extracted using the F–N equation.

1. Introduction

Carbon nanotubes (CNT) (Iijima, 1991) are possible candidates for emitters in the next generation of cold-field emission guns (CFEG) (de Jonge, 2009; de Jonge et al., 2002; de Jonge and van Druten, 2003). When compared with standard tungsten cold-field emitters, they have higher spatial coherence and brightness, improved emission stability and lower onset voltage and energy spread (de Jonge, 2009; Saito and Uemura, 2000). These properties could be valuable for applications like for example dark-field electron holography (Hÿtch et al., 2008), high-resolution electron energy loss spectroscopy (Yuge et al., 2012) or in monochromated scanning transmission electron microscopy (Krivanek et al., 2013). Despite these advantages, CNTs have never been put into practice for a number of reasons; of which the small diameter of CNTs make them difficult to handle (de Jonge et al., 2003; Ribaya et al., 2008) and due to its high aspect ratio regarding the shape, it is prone to vibrate (Saito et al., 2005).

A carbon cone nanotip (CCnT, see Fig. 1) (Jacobsen and Monthioux, 1997) has recently been developed to overcome these issues. Their wide base of several μm allows the tips to be mounted in a routine way within a focused ion beam (FIB) and the conical shape limits vibrations. The benefits of the CCnT with respect to a W-tip have been demonstrated in a working 200 kV CFEG transmission electron microscope (TEM, Hitachi HF2000) by Houdellier et al. (2012).

For electrons to escape a material, they need to overcome an energy-barrier called the work function ϕ (Hazra et al., 2011). In thermionic emission, an electron close to the Fermi level, that gains additional energy through thermal processes, equal to or greater than the work function, can leave the material. In electron field emission, the electrons instead pass through the barrier using the quantum mechanical tunneling effect. In the presence of a strong electric field, the barrier is reshaped and diminished until the electrons can tunnel through. A good knowledge of the work function is therefore necessary to understand the energy-addition needed for the electrons to be emitted.

For this, we have used an *in situ* TEM sample holder to apply a bias between a CCnT and an Au anode until the electrons started to tunnel through the energy barrier. The current can be recorded and analyzed using a Fowler–Nordheim (F–N) equation (Eq. (1)). We have also used electron holography to understand the electric field more locally around the tip. And, in order to quantitatively determine the electric field, we have compared these results with finite element method (FEM) modeling. Similar approaches have been used before (Cumings et al., 2002; He et al., 2013). Finally, by combining the F–N equation, electron holography and

* Corresponding author. Tel.: +33 5 67 52 43 66; fax: +33 5 62 25 79 99.
E-mail addresses: deknoop@cemes.fr (L. de Knoop), florent@cemes.fr (F. Houdellier), gatel@cemes.fr (C. Gatel), aurelien.masseboeuf@cemes.fr (A. Masseboeuf), marc.monthioux@cemes.fr (M. Monthioux), martin.hytch@cemes.fr (M. Hÿtch).
[1] Tel.: +33 5 62 25 78 80; fax: +33 5 62 25 79 99.
[2] Tel.: +33 5 67 52 43 49; fax: +33 5 62 25 79 99.
[3] Tel.: +33 5 62 25 78 85; fax: +33 5 62 25 79 99.
[4] Tel.: +33 5 62 25 78 86; fax: +33 5 62 25 79 99.
[5] Tel.: +33 5 62 25 78 83; fax: +33 5 62 25 79 99.

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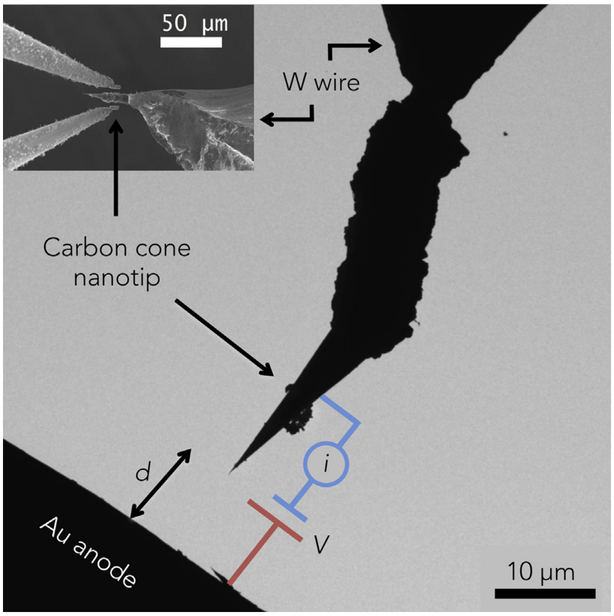

Fig. 1. TEM micrograph showing the Au-anode plate and the CCnT mounted on a W-tip. The Au anode was biased and the CCnT was connected to ground. The tip-anode separation distance, before the final approach has been made, is indicated by *d*. The inset shows a SEM image of the micro-tweezers that were used inside the FIB-SEM to mount the CCnT on a W-wire.

FEM, we have found an estimate of the work function of the CCnT.

2. Theory

By recording the tunneling current *i* during an experiment, the approximated F–N equation (Brodie and Spindt, 1992) can be used to obtain parameters for the field emission process (Eq. (1)). The original F–N equation (Fowler and Nordheim, 1928; Murphy and Good, 1956) was used for field emission between two flat metal surfaces at 0 K but has been proved valid for other situations as well (Good and Mueller, 1956).

The field emission current *i* is given by

$$i = A\frac{1.5\times10^{-6}}{\phi}E_{\mathrm{loc}}^{2}\quad \exp\left(\frac{10.4}{\sqrt{\phi}}\right)\quad \exp\left(-\frac{6.44\times10^{9}\phi^{3/2}d}{\gamma V}\right) \tag{1}$$

where A is the virtual source area, E_{loc} is the local electric field around the tip, d is the tip-anode separation distance, γ is the field enhancement factor, V is the potential applied to the anode and ϕ is the unreduced work function. The so-called F–N plot is described by $\ln(i/V^2)$ as a function of $1/V$ and its slope equals $-6.44\times10^{9}\phi^{3/2}d/\gamma$ in the equation above (Gröning et al., 2000). Since the tip-anode separation distance d is easily observed in the TEM, only the field enhancement factor γ needs to be found, to be able to obtain the work function ϕ. The field enhancement factor γ describes how much the local electric field E_{loc} around the tip is enhanced when compared with a global electric field E_0 from a system consisting of two infinite and parallel plates, i.e. $E_{\mathrm{loc}} = \gamma E_0 = -\gamma V/d$. We know the applied voltage V and d, so by finding E_{loc} we would attain γ and thus ϕ.

Off-axis electron holography is a powerful technique for retrieving the phase of the electron beam at the nanoscale. It has the advantage that the phase measured in the electron hologram is linearly related to the electrostatic potential experienced by the electron and can be used to quantify electrostatic fields. The phase shift of electrons traversing an electrostatic potential is obtained by integrating the potential along the electron beam path and is described by

$$\varphi(x,y) = \int_{\mathrm{beampath}} C_{\mathrm{E}}V(x,y,z)\,dz \tag{2}$$

where $C_{\mathrm{E}} = \pi E/\lambda$ and E being the relativistic energy of electrons, which depends on the acceleration voltage of the TEM, and λ is the electron wavelength. Here, in order to reduce the knock-on damage of the carbon atoms by the incoming electrons (Banhart, 1999), we used 100 kV acceleration voltage, which results in $C_{\mathrm{E}} = 9.2\times10^{-3}$ rad V^{-1} nm^{-1}. Since the potential various continuously along the electron path, and particularly near to the tip where the field is stronger, it is not possible to directly compute the gradient of the phase shift map to obtain the electrostatic field components. The phase is a projection of the potential. We have therefore developed a three-dimensional model using FEM to quantitatively determine the local electric field E_{loc} around the tip by comparison with the experimental values.

We have assumed the beam path of the electrons to be straight, while in fact their paths have a small curvature due to the presence of an electric field around the apex of the CCnT. Considering that the electric field is extremely localized around the tip together with that the energy of the incoming electrons is in the order of 100 keV, we consider this deviation to have a negligibly small effect.

3. Experimental details

The CCnTs were made by chemical vapor deposition of carbon on a thin carbon wire produced by a catalytic process (Allouche et al., 2003; Jacobsen and Monthioux, 1997). The cones were extracted using a Kleindiek microtweezer inside a Zeiss Gemini scanning electron microscopy (SEM)-FIB workstation (see inset in Fig. 1 and Houdellier et al. (2012)). Gas-injection needles with tungsten-precursor were used to weld the CCnT on a mechanically cut W-wire which was later mounted inside a Nanofactory Instruments *in situ* TEM-scanning tunneling microscopy (STM) sample holder (Svensson et al., 2003), that has a nanomanipulator and biasing functionality. An anode was made by mechanically flatten out a Au-wire of an original diameter of 330 μm, which resulted in an area of the anode facing the CCnT of around 250 μm × 30 μm. A separation distance of 680 nm between the CCnT and anode was used, verified with the TEM (image Cs-corrected Schottky FEG FEI Tecnai F20), operated at 100 kV and with a vacuum around the specimen of 2.4×10^{-5} Pa. The TEM was operated in aberration corrected Lorentz mode, with the objective lens turned off and with the first transfer lens of the Cs-corrector used as Lorentz lens.

A Möllenstedt biprism (Möllenstedt and Düker, 1955) biased to 74.5 V was used to superimpose the incoming wave front that passed through the strong electric field close to the tip, with a reference wave that travelled further away from the tip (Fig. 2). The anode bias was increased in 1 V steps and holograms were recorded every 10 V or less, with an exposure time of 5 s. Reference holograms were obtained at 0 V. Using DigitalMicrograph (Gatan Inc.) and a modified version of HoloDark 1.2.1 (HREM Research), the holograms were Fourier transformed, and by choosing a mask (size chosen for a resulting spatial resolution of 6 nm) around the side-band towards the tip, an inverted Fourier transformation created the phase map in Fig. 3a. Internal reference areas of the phase map in Fig. 3a and the unwrapped phase map in Fig. 3b were used in order to see the relative phase shift of the electrons. In these areas the phase and the phase gradient were set to zero.

Profiles (Fig. 4) of the experimental and simulated phase shift (Figs. 3b and 7b, respectively) were made in DigitalMicrograph averaging over 16 nm.

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