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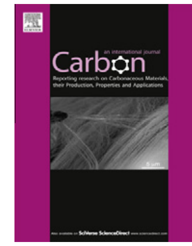

New carbon cone nanotip for use in a highly coherent cold field emission electron microscope

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ABSTRACT

A new cathode for cold-field emission gun using a pyrolytic carbon-cone supported onto a carbon nanotube as the electron emitting tip has been developed. This tip was mounted in a TEM using a FIB based method, and the brightness measured under real operating conditions is five times better than obtained with a standard tungsten tip. Its use overcomes the many technical difficulties which have dogged the use of carbon nanotube-based tips as proposed replacements for tungsten tips. The resulting properties of the final CFEG exhibit a very good energy spread of 0.32 eV, a reduced brightness of 1.6×10^9 A m^{-2} sr^{-1} V^{-1} and a very good long-term stability with a current damping less than 16% per hour.

1. Introduction

The recent spectacular improvements in instrumentation for transmission electron microscopy, notably aberration correction [1–3], have highlighted the relative lack in progress of an essential part of the microscope column, i.e. the electron gun itself. The highest brightness electron guns are based on cold-field emission from tungsten tips, a technology strongly improved from the electron optics and vacuum point of view but still using the same cathode materials [4]. Until now, most of the latest generation electron microscopes are equipped with so-called Schottky field emission guns based on thermally field-assisted emission which are generally brightness-limited by coulomb interactions [5,6]. The development of a cold field-emission electron source with higher brightness and coherence would benefit electron microscopy techniques across the board from high-resolution imaging [7] and atomic-resolution electron-energy-loss spectroscopy (EELS) [8], to electron holography [9,10].

Indeed, electron sources for electron microscopy can be divided into two main families known as thermionic and field emission [5]. A thermionic gun uses a current-induced thermal excitation to allow electrons to pass over the energy barrier between the metal tip (usually a LaB_6 single crystal) and the vacuum. The high emission currents are due to the fact that electrons are emitted from a large area of the tip. This makes these guns suitable for a wide range of conventional electron microscopy techniques. However, spatial and temporal coherence is poor due to the large virtual source size and the wide energy spread of the emitted electrons. This prevents their use as a source for electron holography or high-resolution electron energy loss spectroscopy. Field-emission guns (FEG) overcome these limitations by significantly decreasing the emission area (to about 50 nm diameter) and increasing the spatial coherence of the beam. Electrons are extracted by a strong electric field which enables them to tunnel through the energy barrier. However despite very good coherence (both spatial and temporal), the current decreases continuously during emission due to the adsorption of atoms (from the residual species in the vacuum or from degassing of the anode) onto the emitter surface. The surface can be cleaned by applying a burst of heat to the tip (called “flashing”), which can perturb experiments. Hence, FEGs are foremost restricted to scanning TEM instruments dedicated to electron spectroscopy and commonly named CFEG (for cold field emission gun). Schottky emitters are a hybrid combination of both above-described families more like

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a field-assisted thermionic emission than a genuine field emission [6]. A reasonable compromise is thus obtained between spatial coherence and beam current leading to a brightness which is higher than thermionic emitters but lower than cold-field emission. This compromise solution avoids the main disadvantages of a cold-field emitter and most electron microscopes which need a high brightness electron beam are equipped with such a gun. However, CFEGs remain superior for advanced spectroscopy as well as for specific TEM modes such as electron holography. Hence, pushed by the strong customer's demand to overcome the difficulties inherent to CFEGs, new vacuum and gun technologies are currently proposed by various TEM companies (namely Nion, Jeol and Hitachi) which allow flashing the tip not more than once a day or enable operators to clean the tip during the experiments without having to change the operating conditions, i.e. the flashing may be made under high voltage environment. However, in all nowadays new CFEG technologies on the market, the cathode material, made of tungsten, remains unchanged. The most promising candidates for replacing the tungsten tips used in cold-field emission are carbon nanotubes (CNTs) [11], which were demonstrated some years ago to be able of brightness one order of magnitude higher than tungsten tip as measured in an optical bench [12]. However, since then, such sources have not been successfully integrated in a high-voltage transmission electron microscope because of technical difficulties. Only low-accelerating voltage Scanning Electron Microscopes (SEM) with modified Schottky guns were investigated [13,14]. The nanotube needs to be correctly mounted onto the filament which includes the laborious task of selecting a CNT which is suitably straight, aligning the selected CNT in the right direction for emission, and fixing the CNT so as to insure a good electrical contact. Reproducibility is poor due to the difficulty of the mounting operation [15] and the variation in field-emission characteristics and conductivity of the CNTs [16]. Growing a single, well-aligned CNT at the right place is tricky as well. A review of various procedures for such delicate mounting can be found elsewhere [17]. Furthermore, nanotubes are long and thin making them prone to vibrate [18], a feature which is able to provoke their breakage during emission [19] and a loss of spatial coherence for the electron beam extracted. The nanotube low diameter also limits the electron current that can be driven through the whole length of the tube, due to Joule heating [20]. Because of all these points, the efficiency of CNTs for cold-field emission in a high-voltage TEM has actually not been demonstrated so far.

Here we present the development of a new cathode for cold-field emission gun using a carbon nanotube-supported pyrolytic carbon cone [21–24], as a superior alternative to both standard tungsten tips and carbon nanotube tips. The relatively easy procedure to mount the carbon tip as the emitting tip is described, and the superior performances of the tip, as investigated both in a test-bench and in a TEM, are described a well.

2. Experimental

The carbon cones used in the study are prepared by a so-called "time-of-flight chemical vapor deposition" process which consists in depositing pyrolytic carbon onto previously grown carbon nanotubes used as substrates [21]. The overall morphology of the carbon objects used in the study is actually more complex than a mere carbon cone, as it can be precisely described as a carbon-nanotube-supported pyrolytic carbon deposit which includes a short microfiber segment with rough surface and two opposed cones with smooth surface which terminate the short fiber segment ends (Fig. 1). However, the objects will be referred as "carbon cones" throughout the paper for practical use. Synthesis conditions and formation mechanisms were extensively described earlier as well as the various cone-bearing carbon morphologies which are able to be prepared by this process [22–24], including those used here. Briefly, the formation of the cone morphology is assumed to require the transient formation of specific hydrocarbon-rich droplets in the gas phase, whose average size with respect to that of the nanotube diameter should be such that they make possible the conditions for partial wetting [24].

A tungsten tip is first prepared using a standard procedure, namely the micro-welding of a [310]-oriented tungsten wire on a regular V-shape TEM tungsten filament. The tip of the tungsten wire is then electrochemically etched in a KOH solution. The resulting tungsten support can be illustrated by what is shown on right-hand in the inset of Fig. 2D.

Afterwards, the various steps for mounting a carbon cone onto the home-made [310]-oriented tungsten tip are carried-out in a dual Focused Ion Beam/FEG Scanning Electron Microscope (FIB/SEM) fitted with a nano-manipulator, as summarised in Fig. 2.

A suitable carbon cone (Fig. 2A) is selected under SEM according to the proper alignment of the cone axis with respect to the microfiber portion axis. It is then lifted from the surface using micro-tweezers after cutting it from its base using a Ga ion beam (see Fig. 2C). The apex of the tungsten tip formerly prepared is also truncated by means of the Ga ion beam (Fig. 2B). The cut face of the carbon microfiber segment bearing the cone is then welded by W ion beam induced-deposition (from a W precursor, namely $W(CO)_6$) to the truncated tungsten tip apex (Fig. 2D). An original CFEG shape is thus obtained displaying an apex radius below 5 nm. A particular attention is paid to protect the carbon cone from parasitic deposition or ion irradiation of the cone by tilting the stage by 20°. This enables a protection of the cone from the ion beam by the tweezers during the whole procedure (as can be seen on Fig. 2C). Indeed, TEM investigations of the carbon tip after mounting provided images similar to that in Fig. 3A taken on an as-grown cone, showing that the carbon cone structure was unaffected by any of the in-FIB irradiation steps. The whole mounting procedure is robust, reproducible, and takes only 2 h (including 30 min for preparing the supporting tungsten tip). It is worth noting that the same positioning, aligning, and fixing steps are required when attempting to use a pristine single carbon nanotube as emitting tip, but they are much facilitated by the specific multi-part morphology used here. Indeed, thanks to the short microfiber body, the object can easily be grabbed and welded, and thanks to the cone-microfiber self-alignment, the carbon cone can also be suitably positioned in spite of the nanometer size of the cone tip that will be the emitting part.

To fully characterize the emission properties of the new tip, two emission test benches were used. One is a home-made ultra-high vacuum (UHV) point projection microscope,