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Observation of MWCNTs with low-energy electron point source microscope*

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The low-energy electron point source (LEEPS) microscope, which creates enlarged projection images with low-energy field emission electron beams, can be used to observe the projection image of nano-scale samples and to characterize the coherence of the field emission beam. In this paper we report the design and test operation performance of a home-made LEEPS microscope. Multi-walled carbon nanotubes (MWCNTs) synthesized by the CVD method were observed by LEEPS microscope using a conventional tungsten tip, and projection images with the magnification of up to 10^4 was obtained. The resolution of the acquired images is ∼10 nm. A higher resolution and a larger magnification can be expected when the AC magnetic field inside the equipment is shielded and the vibration of the instrument reduced.

Keywords: LEEPS microscope, field emission, carbon nanotube
PACC: 6116D, 6146, 7970

1. Introduction

The low-energy electron point source (LEEPS) microscope, first introduced by Morton and Ramberg in 1939,[1] projects a low-energy electron beam on a transmission object to create an enlarged shadow image on a screen placed far behind the sample object.[2] With the modern position control technique in scanning tunnelling microscopy (STM), the LEEPS microscope allows the direct observation of opaque objects in real space with nanometric or atomic resolution.[3−5] Figure 1 shows a schematic interpretation of the low energy electron projection concept based on simplest geometric optics. When the sample is placed a distance d from the source, the magnification M of a LEEPS image formed on the screen at distance D away from the source is calculated as $M = D/d$. Thus, images projected by sample placed tens of nanometres away from the electron source on a screen about 10 cm away can give a magnification of $\sim 10^6$.[6] Theoretically, the resolution of the LEEPS microscope is limited by the angle θ of the electron beam emitted from the source,[7] i.e. the coherence of the beam. Thus, if field emission tips sharp and stable enough are used, nanometric or atomic resolution can be achieved. Compared with other microscopes that reach atomic resolution such as the transmission electron microscope (TEM) and the atomic force microscope (AFM), the LEEPS microscope causes less perturbation and damage to samples that cannot endure high-energy electron beams.[8]

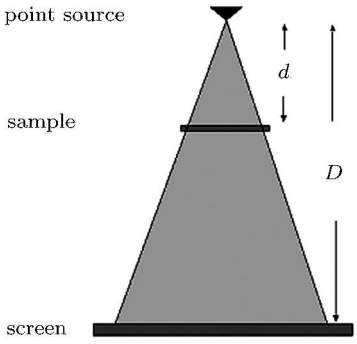


Fig.1. Schematic diagram of LEEPS microscope, the tip-to-sample distance and the tip-to-screen distance are d and D, respectively.

With the addition of another movable tip in the instrument, the LEEPS microscope provides an easy way to manipulate the sample while observing it in real space.[9] Nowadays, the nanometre-scale materials, among which the carbon nanotube is one of the most important, are under intense investigation for their promising applications in the future.[10−13] Accordingly, the characterization of these materials is

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also undergoing rapid development.

As described in this paper, we have developed a LEEPS microscope and used it to observe multi-walled carbon nanotubes (MWCNTs). The largest magnification in the test runs of the instrument reaches up to 10^4. Theoretical and practical limitations of the resolution of the equipment are also investigated in the test experiments.

2. Experimental

Our LEEPS microscope system is designed to obtain enlarged images of nano-scale objects at a magnification of up to 10^6. Figure 2 shows the structure of the system. It is a field emission/field ion microscope (FEM/FIM) combined with a movable sample stage placed between the field emission tip and the fluorescent screen. The sample stage is controlled by a 3-dimensional manipulator and a cross-shaped piezo, so that the sample can be adjusted in three orthogonal directions with a minimum step of 0.1 mm and a maximum length of 5 mm.

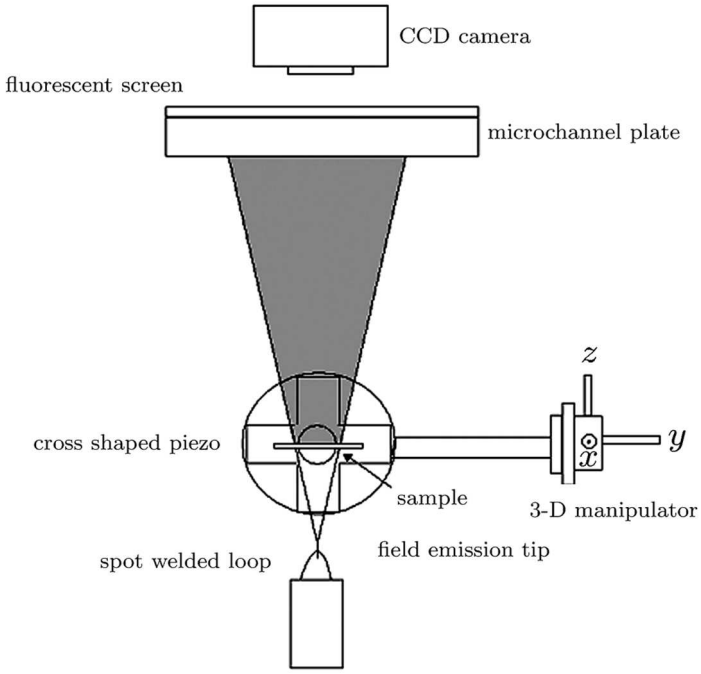


Fig.2. Schematic setup of the LEEPS microscope system.

A commercial holey carbon grid as used in TEM is fixed on a bronze sample holder to hold the nanoscale samples. An electrochemically etched polycrystalline tungsten tip is used as the field emitter tip. The tungsten tip is spot welded onto a loop for heat treatment. A fluorescent screen incorporating a microchannel plate for image intensification is placed immediately behind the sample stage at a distance to the tip holder of 17.1 cm. A CCD camera is employed to record and digitize the LEEPS image patterns observed on the screen. In order to test the field emission ability and the apex state of the tip, the sample holder can be moved away to enable direct observation of the field emission patterns of the tip on the screen to show whether the tip is sharp and stable enough to serve as the projection source. The chamber can be filled through a needle valve with high-purity helium gas to observe the FIM pattern of the tip and to clean the tip surface by field evaporation. The entire system is enclosed in an ultrahigh vacuum chamber with a base pressure of 2×10^{-8}Pa. The carbon nanotubes used in our observations are fabricated by the chemical vapour deposition (CVD) method. Ferrocene was pyrolyzed at 1000°C in an argon atmosphere for 30 minutes. Highly paralleled MWCNTs are thus synthesized on silicon substrates. Details of the experiment can be found elsewhere.[14] The nanotubes were sonicated in ethanol; then a droplet of the solution was applied on a commercial holey carbon grid for the LEEPS image observation. As shown in the TEM image of Fig.3, the CNTs thereby prepared are several microns in length and 50 to 80 nm in diameter.

Tungsten tips electrically etched in KOH and $NH_3 \cdot H_2O$ solution were used as the electron source of the microscope. To acquire a clear and stable image of the observed object, it is a necessary condition that the tip is pre-treated carefully so that it is in a clean and stable condition. The method of flash heating the tip repeatedly is commonly used in the tip treatment process.[15,16] However, we consider field evaporation as an alternative way to clean the tip rapidly and effectively.

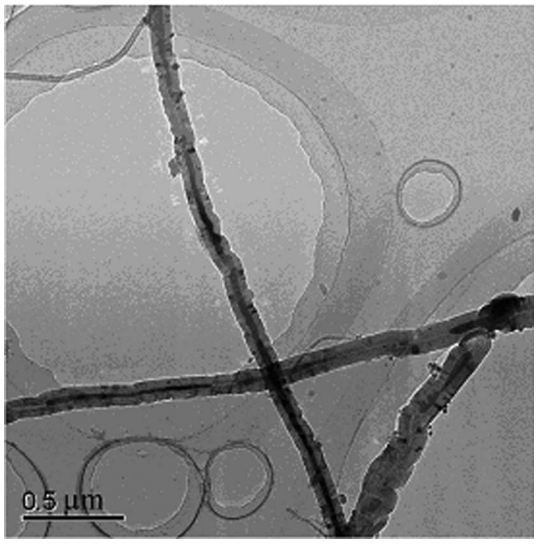


Fig.3. TEM image of the carbon nanotubes and the carbon film of the TEM grid.

In the field evaporation process, a positive voltage of 7 kV or higher is applied to the tip under a pressure of 10^{-7} Pa. With the sputter-ion pump turned off, the pressure of the chamber quickly rises to higher than 1×10^{-5} Pa and discharges from the tip are often observed. After the tip has discharged either once or twice, the sputter-ion pump is turned on and the positive voltage on the tip is maintained until the chamber pressure is lower than 5×10^{-8} Pa. The field emission pattern of the treated tip shows that it is cleaned by the field evaporation without being blunted.

3. Results and discussion

The transmissivity of the triode configuration in the LEEPS microscope is defined as $I_{\text{screen}}/I_{\text{total}}$, where I_{screen} and I_{total} represent the current acquired by the screen and the total field emission current from the tip, respectively. As shown in the inset of Fig.4, the transmissivity is in the range of 3% to 5% when the voltage V_{G} applied to the grid is higher than 1 kV. That is, most electrons emitted from the tip are absorbed by the grid and only a fraction of them arrive at the screen. As the current that contributes to sample imaging is only of the order of several nanoamperes, a microchannel plate is always necessary for enhancing the projection images. The LEEPS microscope has proved to show a relatively high resolution under low voltages.

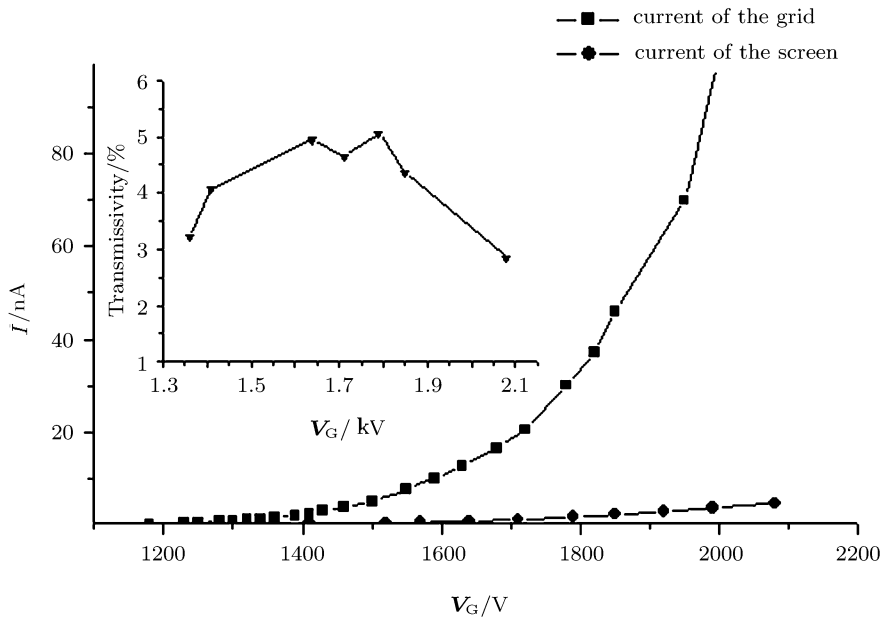


Fig.4. Field emission currents I respectively received by the sample grid and the screen. The inset shows the calculated transmissivity as a function of the grid voltage V_{G}.

Figure 5 shows the images of holey-carbon film and carbon nanotubes produced. The magnification of the image rises as the tip approaches the sample grid. Simultaneously, the negative voltage applied to the tip is lowered to prevent the field emission current from increasing dramatically. A rough approach of the tip to the sample from 5 mm down to several tens of microns is enabled by the z-direction manipulator, and further fine-tuning is made by the z-piezoelectric crystal. The manipulators in the x and y directions and the y-piezo are used to search and select the areas to be observed on the grid.

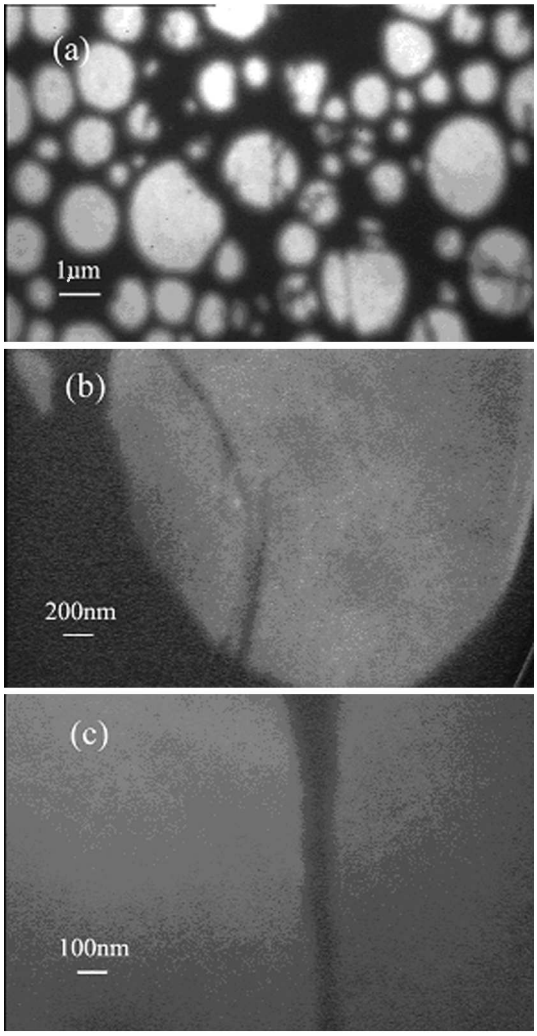


Fig.5. Sequential images of the holey carbon film and MWCNTs. (a) $M = 1.75\times10^3$, $d = 101$ μm; (b) $M = 5.1\times10^3$, d=35 μm; (c) M = 1.4×10^4, d= 13 μm, the field emission voltage is 230V. The magnification of CCD is about 10.

Stocker *et al* reported two calibration methods of determining the tip-to-sample distance, the object size and thus the magnification of the LEEPS images.[2] The first is to scale down from objects of known size, e.g. the width of the carbon grids or the holes of the carbon film. The second is to move the sample in a direction parallel to the sample surface and measure the corresponding macroscopic movement of the image. The distance that the sample moves is given by the calibration of the piezo. In our experiment, the magnification and the scale bar of the images are calculated from the diameter of the holes of the amorphous carbon film (2 μm on average) and the diameter of MWCNTs (65 nm on average). By measuring the diameter of the image of the holes and the MWCNTs, the magnification can be simply calculated as $M = R_{\rm image}/r_{\rm object}$. The maximum magnification we attain so far is about 1.45×10^4 and the sample-tip distance is 12.7 μm. The main obstacle to a further approach of the sample to the tip is external vibrations.

In Fig.5(b), the shadow images of two CNTs, which are approximately 50 nm in diameter and 20 nm away from each other, are barely distinguishable. We therefore estimate the resolution of the LEEPS image at several tens of nanometres on average. This resolution is not comparable to that of a TEM under the same magnification, chiefly because of the vibration of the instrument. The tip and sample vibration blurs the LEEPS image on the screen and reduces the resolution remarkably. The AC magnetic field generated by the electronic components inside the instrument is also an important factor that practically influences the resolution of the microscope. Theoretically, the resolution limit of the LEEPS microscope is due to emission source size and diffraction.[17] The resolution limit due to geometrical size of the tip, Δg, and that due to diffraction, Δd, can be respectively calculated as

$$\Delta g = \frac{w}{M} \approx 2r \tag{1}$$

$$\Delta d \approx \frac{1}{2}(\lambda d)^{\frac{1}{2}}, \tag{2}$$

where w is the virtual resolution limit at the screen due to the electron source size with a radius of r, M is the magnification factor and λ is the wavelength of the electron beam. Thus, the resolution is determined by the emission source size and the tip-to-sample distance. The smaller the projection source is, the higher the resolution that can be achieved. Nanometric resolution is possible only when the tip-to-sample distance, d, is small and the magnification is high.

4. Conclusion

We have developed a LEEPS microscope and attained projection images of MWCNTs with a maximum magnification of up to 10^4. When an image with a magnification of 1.4×10^4 is observed, the tip-to-sample distance is 13 μm and the applied voltage is 230 V. The field emission voltage is even lower when the sample approaches closer to the tip or the tip is sharper. Thus the LEEPS microscope causes little perturbation and damage to the sample because the energy of the electron beam employed to form the image is low. We are now endeavoring to reduce the influences of environmental vibration and internal magnetic field for the purpose of achieving larger magnification and higher resolution.

Acknowledgments

The MWCNTs used in the observation were fabricated by Mr Chai Yang and Dr Zhang Qifeng.

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