Proceedings of the 15th
IEEE International Conference on Nanotechnology
July 27-30, 2015, Rome, Italy

Field emission from tungsten oxide nanowires W_5O_{14} film

G. Ulisse, C. Ciceroni, A. D. Carlo, F. Brunetti
Department of electronic engineering, University of Rome Tor Vergata, Rome, 00133, Italy

J. Jelenc, A. Varlec, M. Remskar
Solid State Physics Department, Jozef Stefan Institute, Ljubljana, 1000, Slovenia

***Abstract*—Large area film of W_5O_{14} nanowires was realized with synthesized by iodine transport method. The field emission characteristics of The W_5O_{14} nanowires were then investigated. The measured samples showed up to 50 µA of emitting current at very low electric field of about 3 V/µm. Furthermore very good stability was achieved, the sample was allowed to emit for more than 70 hours without showing significant decays of the emitting current and without high current oscillations. This characteristics make these nanowires very promising for the realization of field emitting cathodes.**

Keywords*— *Field emission, cold cathode, tungsten oxide nanowire

I. Introduction

Field emission cathodes can be used in different applications such as field emission display, portable x-ray generators, microwave sources and amplifiers [1]-[4]. Field emitters represent an important alternative to thermionic cathode in the field of vacuum electron devices thanks to the possibility to work at room temperature and to their smaller size. For this reason many field emission studies have been performed on 1D nanostructures, such as carbon nanotubes, metallic or semiconductive nanowires [5]-[7].

In particular carbon nanotubes (CNTs), have been extensively studied in the last twenty years for their excellent field emission properties due to their very high aspect ratio, the low-voltage emission, the robustness. In the last decade some investigations on the field emission characteristics of tungsten oxide nanowires, including WO_2, WO_3, $W_{18}O_{49}$ [8]-[10], have been performed. In particular $W_{18}O_{49}$ exhibits very good field-emission characteristics. Field emission measurements on a single W_5O_{14} nanowire have been performed demonstrating that these nanowires have all the properties required to become a good field emitter [11].

In this work we studied the field emission characteristics of W_5O_{14} nanowires film in order to verify the possibility of use them in a real device with large emitting area. The main parameter to define the quality of field emitters is the field enhancement factor. In order to extrapolate this value from the I-V characteristics it is necessary to know the work function of the emitters [12]. The work function of the W_5O_{14} nanowires has been then measured by Kelvin microscopy in non contact atomic force microscopy (UHV-AFM Omicron). As further investigation a long stability field emission measurements of over 70 hours have been done to demonstrate the robustness of such nanoemitters.

II. Experimental

W_5O_{14} nanowires have been synthesized by iodine transport method [13] using nickel as a growth promoter and WO_3 as source of tungsten and oxygen. The starting material consisted of: 352,7 mg WO_3 powder (Sigma Aldrich, 99,99 %), 37,5 mg of nickel (mechanically cut metal foil) and 567 mg of iodine (1-3 mm beads, Sigma Aldrich, 99,7 %) was evacuated in quartz ampoule, sealed and put into a furnace. The furnace has the possibility to have two zones with different controllable temperatures. The temperature was increased for 24 hours from room temperature to the working conditions. Material was transported from the hot zone (860 ˚C) to the cold zone at (736 ˚C) of the furnace under 6.2 ˚C/cm temperature gradient. Transport reaction run for 500 hours and then cooled down under 35°/h cooling rate. Transported material of deep blue color consisted of long, rigid nanowires that tend to clump into bundles. The nanowires bundles creates a deep blue filme with lateral dimensions in the order of few centimeter.

XRD was performed on the nanowires at room temperature with a D4 Endeavor diffractometer (Bruker AXS) using quartz monochromator Cu Kα 1 radiation source (λ=0.1541 nm) and Sol-X dispersive detector. An angular range 2θ was chosen from 0° to 45° with a step size 0.02˚ and collection time of 3 s. The samples were rotated during measurements at 6 rpm.

The SEM images performed on the W_5O_{14} film are reported in Fig. 1. As shown the nanowires are randomly oriented with an average length of several tens of micrometer while their diameter is around 100 nm. The nanowires diameter was also confirmed from atomic force microscopy characterization. The nanowires film was then fixed with silver paste on a metallic substrate in order to be measured in a field emission characterization system.

978-1-4673-8156-7/15/$31.00 © 2015 IEEE

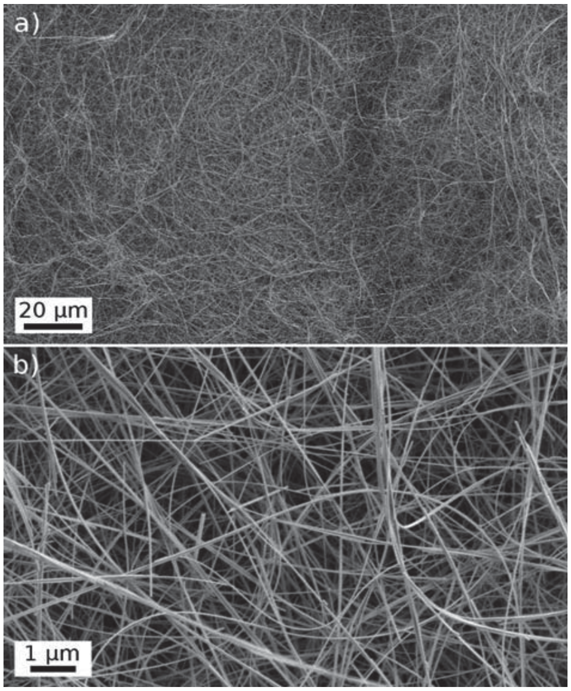

Fig. 1 SEM images of W_5O_{14} nanowires

In order to calculate the field enhancement factor the work function (WF) of the nanowires has been measured by Kelvin probe microscopy in non contact atomic force microscopy (AFM). By this way a value around 4.5 eV were obtained considering graphite as reference (4.6 eV). In average, the W_5O_{14} nanowire WF is slightly lower than the typical value of carbon nanotubes or molybdenum. The lower work function is advantage in the field emission phenomena since it helps in extraction of electrons from the emitters.

III. Results and discussion

The crystalline structure of nanowires was examined by X-ray diffraction analisys (XRD). The XRD spectrum of the tungsten nanowire are reported in **Fig. 2**. For this measurement, as-grown nanowires film was fixed onto a sample holder with a modeling clay. In this way nanowires were not damaged. Since sample has preferential orientation, the relative intensity of 001 is considerably smaller from the one in the database.

The modeling clay contributes two $CaCO_3$ peaks, denoted by asterisk. There are no indications of presence of any other crystalline phase, not even any other tungsten (sub)oxide structure. XRD of W_5O_{14} nanowires confirms purity of the sample.

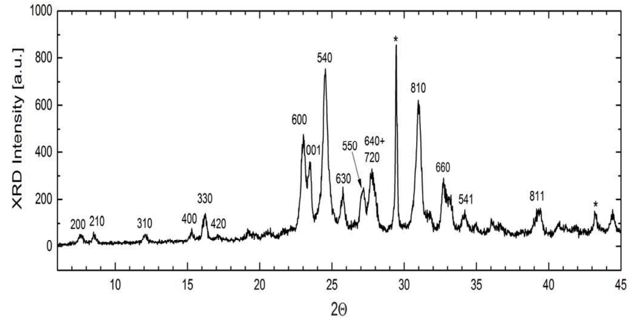

Fig. 2 XRD of W5O14 nanowires confirms purity of the sample. Peaks denoted by asterisk are from the modeling clay, used for fixing the sample onto a holder.

The nanowires film was then fixed with silver paste on a metallic substrate with an area of 8 mm X 8 mm. The realized samples are then mounted in a holder where the anode-cathode system has a sphere to plan geometry, with a changeable anode-cathode distance. The anode is a metallic sphere with a diameter of 1 mm. For this characterization we maintained fixed the anode-cathode distance of 500 µm (see D_{ka} in Fig. 3). The sample holder is in a vacuum chamber, the pumping system is composed by a cascade of rotative pump and a turbo-molecular pumping system. The vacuum level typical reached for the characterization phase is in the range of $1\text{-}2 \cdot 10^{-7}$ mbar.

A high programmable voltage source is used to apply on the anode up to 5 kV. The emitted current is measured with a picoammeter Keithley 6485 that has a measurement range from 2 nA to 20 mA. A 220 kΩ resistance is used in order to protect the picoammeter from high voltage discharge. The electrical scheme of the characterization setup and a sketch of the cathode anode configuration are reported in Fig. 3.

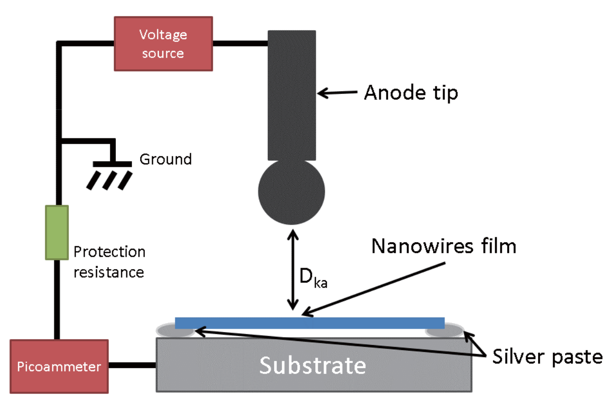

Fig. 3 electrical scheme of the characterization setup

The I-V characteristics are reported in **Fig. 4**, a maximum emitting current of 50 µA at an anode voltage of 1600 V that correspond to an applied electric field of 3.2 V/μm, the electric field was calculated dividing the applied voltage for the anode cathode distance. In the inset of **Fig. 4** the Fowler-Nordheim plot is reported where the logarithm of current voltage ratio is plotted as function of the inverse of the square voltage. The FN plot shows the typical linear behavior. From the Fowler-Nordheim plot it is possible to extrapolate the field enhancement factor using the following equation:

$$\beta = \frac{-B_{FN} \cdot \varphi^{1.5} \cdot d}{s}$$

where 'd' is the cathode anode distance, 's' is the slope of the Fowler-Nordheim plot, 'B_{FN}' is the Fowler-Nordheim constant (6.8308 $eV^{-3/2} \cdot V \cdot nm^{-1}$) and 'φ' is the emitter work function.

By fitting the plot it is possible to calculate a field enhancement factor of 4186 that is much higher than the typical values obtained with carbon nanotubes (1000-2000) [15]. For the calculation of the field enhancement factor the work function of 4.5 eV measured by Kelvin probe microscopy has been used.

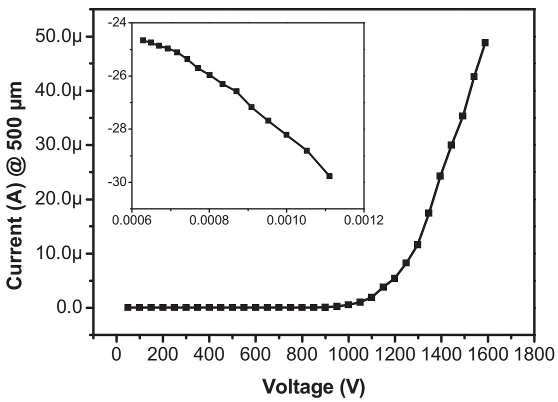

Fig. 4 I-V curve and Fowler-Nordheim plot in the inset

A long time stability measurement was performed to verify the durability of such cathode: the field emission was measured for 70 hours fixing the anode voltage of 1000 V (**Fig. 5**). The measurements was carried out at low emitting current around 1 μA. The emitting current was quite stable with an average current emission of 1.13 μA with a standard deviation lower than 0.291 μA. The most important information is that the sample didn't show any degradation during all the measurement time.

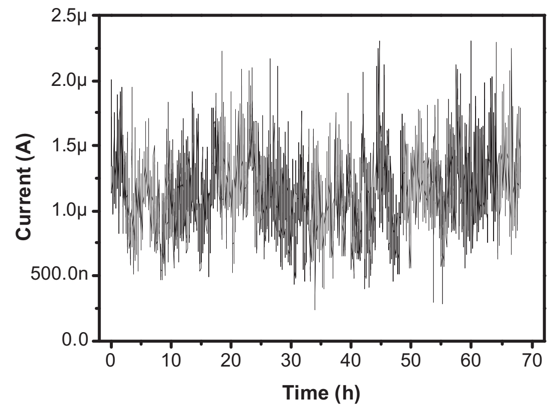

Fig. 5 time stability measurements

IV. Conclusions

The field emission characteristics of W_5O_{14} nanowires film was reported. Due to their relatively low electric resistance and specific surface structure [13], these single crystal nanowires enabled a good emitting current up to 50 μA at very low electric field of about 3 V/μm. The long term stability test showed that the nanowires can continuously emit electrons for more than 70 hours showing characteristics comparable with carbon nanotubes [16]. Very uniform large area cathodes can be realized from these rigid nanowires of homogeneous diameter. These characteristics could be further improved such as patterning and aligning the nanowires and decreasing the dimension of the nanowires diameter. The electrical characteristics of these nanowires are very promising for the realization of long life field emitting cathodes.

Acknowledgment

We thank Slovenian Research Agency for financing.

References

[1] J. Chen, Y.Y. Dai, J. Luo, Z.L. Li, S.Z. Deng, J.C. She, and N.S. Xu, Appl. Phys. Lett. 90, 253105 (2007).

[2] C. Kottler, R. Longtin, S. Giudice, R. Jose-James, P. Niedermann, A. Neels, R. Kaufmann, J.R. Sanchez-Valencia, H.R. Elsener, O. Gröning, C. Leinenbach, P. Gröning, and A. Dommann, Microelectron. Eng. 122, 13 (2014).

[3] F. André, P. Ponard, Y. Rozier, C. Bourat, L. Gangloff, and S. Xavier, IEEE Int. Vac. Electron. Conf. IVEC 2010, , pp. 83–84, (2010)

[4] G. Ulisse, F. Brunetti, F. Ricci, A.M. Fiorello, A.D. Carlo, IEEE Electron Device Letters, 33 (9), 1318-1320, (2012)

[5] Y.J. Huang, H.Y. Chang, H.C. Chang, Y.T. Shih, W.J. Su, C.H. Ciou, Y.L. Chen, S.I. Honda, Y.S. Huang, and K.Y. Lee, Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 182, 14 (2014).

[6] L. Vila, P. Vincent, L.D. De Pra, G. Pirio, E. Minoux, L. Gangloff, S. Demoustier-Champagne, N. Sarazin, E. Ferain, R. Legras, L. Piraux, and P. Legagneux, Nano Lett. 4, 521 (2004).

[7] G Ulisse, F Brunetti, A Vomiero, MM Natile, G Sberveglieri, A Di Carlo, Applied physics letters 99 (24), 243108 (2011)

[8] T. Guo, Z. Xu, F. Liu, and J. Chen, (IVNC), 2013 26th, 2, (2013).

[9] J. Zhou, Y. Ding, S.Z. Deng, L. Gong, N.S. Xu, and Z.L. Wang, Adv. Mater. 17, 2107 (2005).

[10] W.Q. Chen, R.Z. Zhan, S.Z. Deng, N.S. Xu, and J. Chen, J. Appl. Phys. 116, 133506 (2014).

[11] M. Zumer, V. Nemanicˇ, and B. Zajec, The Journal of Physical chemistry letters C, 5250 (2008).

[12] J.M. Bonard, J.P. Salvetat, T. S., Walt A. de Heer, L. Forró, and A. Châtelain, Appl. Phys. Lett. 73, 918, (1998)

[13] M. Remškar, J. Kovac, M. Viršek, M. Mrak, A. Jesih, A. Seabaugh, Adv. Funct. Mater. 17, 1974 (2007).

[14] V. Semet, V.T. Bihn, P. Vincent, D. Guillot, K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, P. Legagneux, and D. Pribat, Appl. Phys. Lett. 81, 343 (2002).

[15] S. Neupane, M. Lastres, M. Chiarella, W. Li, Q. Su, and G. Du, Carbon N. Y. 50, 2641 (2012).

[16] L. Williams, Electron Devices, vol. 57, no. 11, pp. 3163–3168, 2010.