Field emission from crystalline copper sulphide nanowire arrays

Jun Chen, S. Z. Deng, N. S. Xu, Suhua Wang, Xiaogang Wen, Shihe Yang, Chunlei Yang, Jiannong Wang, and Weikun Ge

Citation: Applied Physics Letters **80**, 3620 (2002); doi: 10.1063/1.1478149
View online: http://dx.doi.org/10.1063/1.1478149
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/80/19?ver=pdfcov
Published by the AIP Publishing

Field emission from crystalline copper sulphide nanowire arrays

Jun Chen, S. Z. Deng, and N. S. Xu[a)]
Guangdong Province Key Laboratory of Display Material and Technology, and State Key Laboratory of Optoelectronic Materials and Technologies, Zhongshan University, Guangzhou 510275, People's Republic of China

Suhua Wang, Xiaogang Wen, and Shihe Yang[a)]
Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

Chunlei Yang, Jiannong Wang, and Weikun Ge
Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

(Received 21 November 2001; accepted for publication 25 March 2002)

Straight crystalline copper sulphide (Cu_2S) nanowire arrays have been grown by using a simple gas–solid reaction at room temperature. These were demonstrated to exhibit semiconductor properties. Field emission was observed at a field of ~ 6 MV/m, and its current-field characteristics deviate from Fowler–Nordheim theory, i.e., showing a nonlinear Fowler–Nordheim plot. The uniform emission from the whole arrays was observed using transparent anode technique, and their variation with applied field was recorded. The emission from individual nanowires was also studied using a field emission microscope, and was found to consist of a number of spatially resolved diffuse spots. Finally, stable emission current at different levels and over time was recorded. These findings indicate that semiconductor nanowires as cold cathode have a potential future, worthy of further comprehensive investigation. The technical importance of using semiconductor nanowires as cold cathode emitter is given. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1478149]

There has been increased interest in the study of field emission from carbon nanotubes (CNTs),[1–4] in particular for applications in field emission flat panel display.[5] Some early reports suggested that the emission depends on the electronic property of the CNTs. We know that CNTs may have metallic or semiconducting properties, depending on their structure. However, one is still not able to control these properties. Some have tried to modify the CNTs' electronic property with success.[6,7] Here, we report a type of nanowire array that exhibits semiconductor property, and its field emission properties. As a semiconductor, it will have the advantage of a lower surface potential barrier than that of metals, which is important to field electron emission.

Our Cu_2S nanowire samples can be prepared under ambient conditions by using a very simple procedure, which can be easily scaled up. The details of the growth technique have been described elsewhere,[8,9] only a brief description relevant to the present work is given below. Before use, copper foils (99.98%, Aldrich) with a thickness of 0.25 mm were carefully cleaned for ~ 5 min in an ultrasonic bath of absolute ethanol. The gas–solid reaction was carried out in a homemade reactor. The reactor is essentially a glass cylinder with two inlets on one end of the cylinder and one outlet on the other end. One of the inlets was used to control the flow of the O_2/H_2S gas mixture, and the other was connected to an inert gas (Ar or N_2). The outlet was used to control the reactor pressure. The glass cylinder has a volume of 255 ml, where gas–solid reactions and Cu_2S nanowire growth took place. The copper foils ($0.5\ \text{cm} \times 0.5\ \text{cm}$) were placed in the reactor. A gas flow was directed to the reactor which consists of a mixture of oxygen (99.8%) and hydrogen sulfide (99.8%, Aldrich) at a given molar ratio. The total pressure in the reactor was kept at $\sim 1.05-1.08$ atm, and the reactor was kept at room temperature. The reaction time was set at 10 h based on our previous experience on the synthesis of copper sulfide nanowires. During reaction, the reactor was kept in the dark. When exposed to the mixture of H_2S and O_2, the copper surface became dark red immediately, and then shining cyan and gray in a short time span. After 10 h reaction, the copper surface became black and fluffy, indicating the formation of dense Cu_2S nanowire arrays.

The arrays consist of straight Cu_2S nanowires (Fig. 1) having a diameter of $\sim 50-70$ nm. These nanowires are crystalline, and some of them have a thin layer of oxide coating (fcc Cu_2O) at the surface [Fig. 1(b)]. Bulk Cu_2S is known to be a semiconductor,[10] and, indeed, our photoluminescence spectrum of the Cu_2S nanowires at low temperature shows that it has a band gap of about 1.26 eV, which is slightly larger than the corresponding bulk value.

The electrical conductivity of the Cu_2S nanowires was measured using a HP-4115A semiconductor parameter analyzer. Copper substrate serves as the lower electrode and Au pattern with a diameter of about 0.3 mm is successfully fabricated on the other end of the nanowire arrays by inserting polyimide between nanowires as backbones. Figure 2 shows the $I-V$ curve of the Cu_2S nanowires at various temperatures. It clearly shows that metal-semiconductor Schottky junction was formed at the contact points between the nanowires and the metals. At high voltage, the Schottky

[a)]Authors to whom correspondence should be addressed; electronic mail: stsxns@zsu.edu.cn (N. S. Xu); chsyang@ust.hk (Shihe Yang).

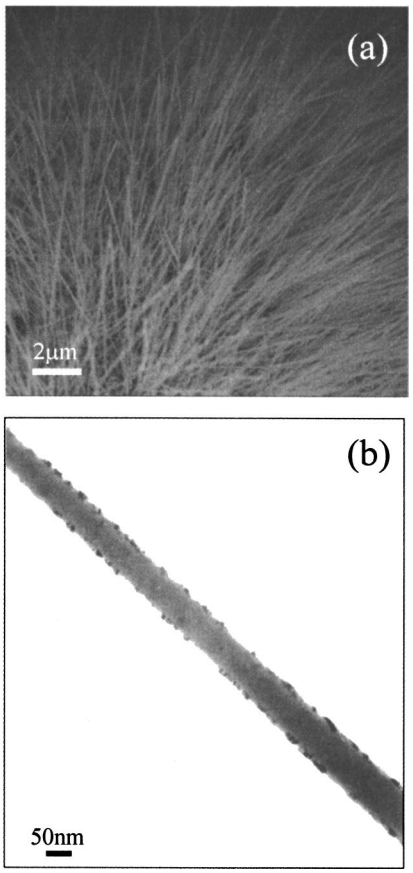

FIG. 1. (a) Transmission electron micrograph of Cu_2S nanowire arrays. (b) High resolution transmission electron micrograph of a bulk section of a Cu_2S nanowire.

junction will break through and the voltage will start to fall on the nanowires. From the slope of the $I-V$ curve at high voltage, we can see that the conductivity of the nanowires increases dramatically with the increase of temperature. This is due to the thermal ionization of the donor or acceptor to give out free carriers to conduction or valence band of the nanowires to form the current. Our experiment has shown that the Cu_2S nanowires are highly conductive at high temperature. The resistivity of the nanowires is estimated to be less than 10 Ω cm at room temperature by taking into consideration the size and density of the wires.

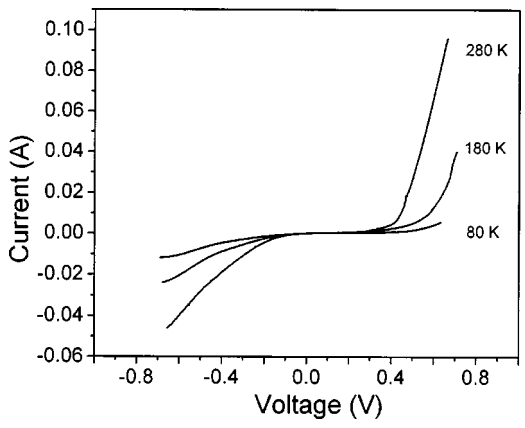

FIG. 2. The direct-current $I-V$ characteristic showing that the nanowires have the semiconductor property.

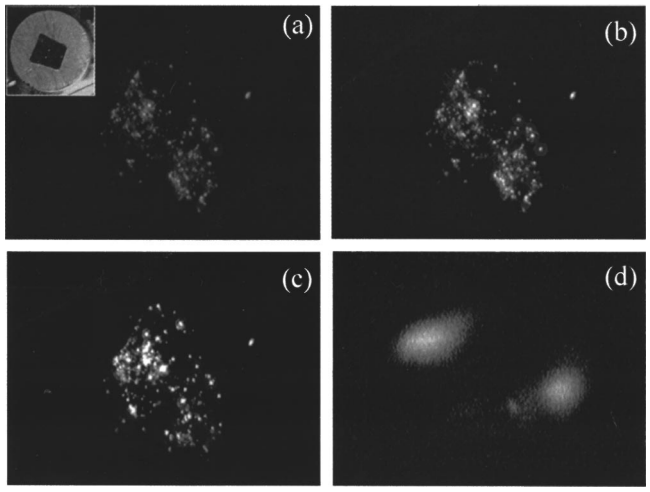

FIG. 3. Emission uniformity of nanowire arrays and their variation with field: (a) 10 MV/m (inset shows the sample), (b) 11 MV/m, (c) 12 MV/m, and (d) the field emission microscopic image.

The measurement of field emission characteristics was carried out in a vacuum chamber having vacuum better than 1×10^{-7} Pa. A sample film was first adhered to the surface of an oxygen free high conductivity copper electrode using silver paint [inset of Fig. 3(a)]. The uniformity of emission from the film was examined using the transparent anode technique,[11] in which a 0.25 mm vacuum gap was used. The spatial distribution of emission sites and its variation with field (10, 11, and 12 MV/m) were recorded [Figs. 3(a), 3(b), and 3(c)]. They consist of points of light generated by the impacting electrons onto the tin oxide film of the transparent anode; many are tiny dots with a few large light spots. With increasing field, the emission became stronger resulting in an increasing number of bright spots. Also, emission came from most areas of the film but more emission sites appeared on the area near the edge of the film.

The information about emitting surface was obtained using a field emission microscope. An anode probe hole of 0.5 mm in diameter is placed in front of the emitting surface with a vacuum gap of 250 μm. Electrons passing the hole are projected to form an emission image on the phosphor screen. The typical images consist of a number of bright diffused

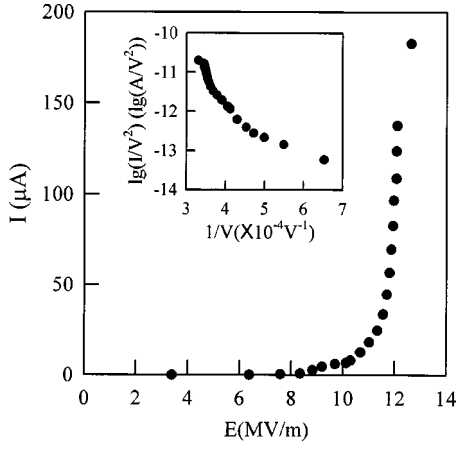

FIG. 4. Field emission current applied field plot and its corresponding FN plot (inset).

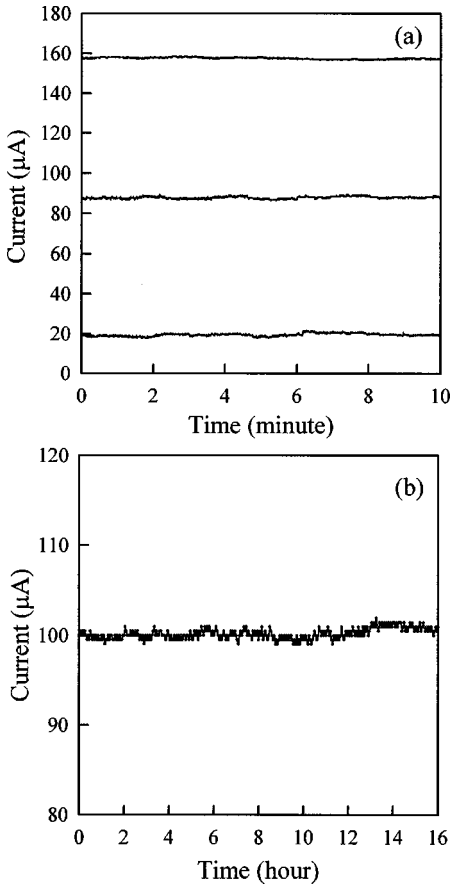

FIG. 5. Showing the current stability at different levels (a) and over time (b).

spots. These spots are relatively stable, and may be due to emission from the tip apex of individual nanowires.

Figure 4 shows a typical plot of emission current versus field ($I-E$) of our films. The typical threshold field for obtaining a current density of 1 μA/mm^2 is 11 MV/m. A current density of ~ 0.6 mA/cm^2 may be obtained regularly from our films. The corresponding Fowler–Nordheim (FN) plot (inset of Fig. 4) was constructed. It is interesting to find that the FN plot exhibits nonlinearity, which could be explained by the diverse field enhancement factor of nanowires. From the transmission electron micrograph picture shown in Fig. 1(a), we observe that the nanowires have different radii and lengths. Therefore, the field enhancements for different nanowires are varied, which would result in different turn-on fields for the individual nanowires. This conforms to the result of emission site observation [Figs. 3(a), 3(b), and 3(c)], i.e., more emission sites are produced at high field.

The emission stability of Cu_2S nanowires was recorded by measuring the current fluctuation with time at a fixed voltage (dc mode). Figure 5(a) shows the short-term stability. In addition, Fig. 5(b) shows the fluctuation during 16 h of continuous operation at the current of about 100 μA (density of about 0.4 mA/cm^2). The current fluctuation was as low as $\pm 2\%$.

In conclusion, semiconductor Cu_2S nanowire arrays have been grown based on a versatile technique at room temperature. Stable and uniform field emission was observed from Cu_2S nanowire arrays. Nonlinearity in Fowler–Nordheim plot was observed. These findings indicate that semiconductor nanowires as cold cathode have a potential future, worthy a further comprehensive investigation.

J.C., S.Z.D., and N.S.X. gratefully acknowledge the financial support from the National Natural Science Foundation of China, Education Ministry of China, the Higher Education Bureau and the Science and Technology Department of Guangdong Province. S.H.Y. gratefully acknowledges the financial support from research Grant No. HKUST6190/99P administered by the UGC of Hong Kong.

[1] A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tomanek, P. Nordlander, D. T. Colbert, and R. E. Smalley, Science **269**, 1550 (1995).
[2] W. A. De Heer, A. Chatelain, and D. Ugarte, Science **270**, 1179 (1995).
[3] Y. Chen, D. T. Shaw, and L. P. Guo, Appl. Phys. Lett. **76**, 2469 (2000).
[4] S. H. Jeong, H. Y. Hwang, K. H. Lee, and Y. S. Jeong, Appl. Phys. Lett. **78**, 2052 (2001).
[5] N. S. Lee, D. S. Chung, I. T. Han, J. H. Kang, Y. S. Choi, H. Y. Kim, S. H. Park, Y. W. Jin, W. K. Yi, M. J. Yun, J. E. Jung, C. J. Lee, J. H. You, S. H. Jo, C. G. Lee, and J. M. Kim, Diamond Relat. Mater. **10**, 265 (2001).
[6] X. C. Ma, E. G. Wang, W. Z. Zhou, D. A. Jefferson, J. Chen, S. Z. Deng, N. S. Xu, and J. Yuan, Appl. Phys. Lett. **75**, 3105 (1999).
[7] J. M. Bonard, R. Kurt, and C. Klinke, Chem. Phys. Lett. **343**, 21 (2001).
[8] S. H. Wang and S. H. Yang, Adv. Mater. Opt. Electron. **10**, 39 (2000).
[9] S. H. Wang and S. H. Yang, Chem. Phys. Lett. **332**, 567 (2000).
[10] *Numerical Data and Functional Relationships in Science and Technology—Physics of Non-Tetrahedrally Bonded Elements and Binary Compounds, I*, edited by O. Madelung (Springer, Berlin, 1983), Vol. 17(e), pp. 137–153.
[11] J. Chen, A. X. Wei, S. Z. Deng, Y. Lu, X. G. Zheng, D. H. Chen, D. Mo, S. Q. Peng, and N. S. Xu, J. Vac. Sci. Technol. B **16**, 697 (1998).