Int. J. Electrochem. Sci., 8 **(2013)** 3472 - 3482

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

One Step Fabrication of Low Noise CuO Nanowire-Bridge Gas Sensor

Sheng-Bo Wang[1], Chih-Hung Hsiao[1], Shang-Chao Hung[2,], Shoou-Jinn Chang[1], Sheng-Joue Young[3],Bo-Chin Wang[1], San-Lein Wu[4], Bohr-Ran Huang[5] and Hsieh-Cheng Han[6]*

[1]Institute of Microelectronics & Department of Electrical Engineering Center for Micro/Nano Science and Technology Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 701, TAIWAN
[2] Department of Information Technology & Communication, Shih Chien University, Neimen, Kaohsiung 845, TAIWAN
[3] Department of Electronic Engineering, National Formosa University, Huwei, Yunlin 632, TAIWAN
[4] Department of Electronic Engineering, Cheng Shiu University, Kaohsiung 833, TAIWAN
[5]Graduate Institute of Electro-Optical Engineering Department of Electronic Engineering, National Taiwan University of Science and Technology Taipei 106, TAIWAN
[6]Research Center for New-generation Photovoltaics, National Central University, Taoyuan 320, TAIWAN
[*]E-mail: schung99@gmail.com

Received: 7 January 2013 / *Accepted:* 4 February 2013 / *Published:* 1 March 2013

We report a new method to fabricate the CuO nanowire-bridge device operating one step thermal treatment and implementing as gas sensor. The X-ray Diffraction (XRD), micro Raman, and high resolution transmission electron microscopy measurements indicated that the CuO nanowires are single crystalline with high crystal quality. Both gas sensor performance and electrical properties of the nanowires-bridges are also investigated. The sensitivity of CuO nanowire-bridge device for sensing oxygen molecule is about 2 times higher than that of the CuO thin film device in room temperature. The enhanced sensitivity of the nanobridges can be attributed to the higher surface band bending due to the larger potential barrier as the accumulation layer between nanowire/nanowire junctions. The mechanism of sensing and electron transport are also discussed. Furthermore, the electrical noise property of the CuO nanowire-bridge device followed Hooge's 1/f-type fluctuations model, which suggests a high reliability of the gas-sensing device. This straightforward method of growing CuO nanowire bridging provides a new type of gas/bio sensing device to enhance sensing capability.

Keywords: CuO nanowire, oxygen sensor, bridge nanowire

1. INTRODUCTION

Recently, metal-oxide semiconductor with one dimensional (1D) nanostructures including nanowires [1], nanobelts [2] and nanotubes [3] have attracted considerable interest for their unique properties. Owing to their high aspect ratios, good crystal quality, thermal and chemical stability, these metal-oxide semiconductor nanostructures are considered as potential building blocks for future nanodevices. Currently, various nanoscale metal-oxide semiconductor devices have been demonstrated such as field-effect transistors (FETs), P-N diode, nanolasers, light emitting diode, solar cell and photodetectors. However, a major application of these 1D nanostructures will be expected in chemical/gas sensor, due to their high surface-to-volume ratios, in which the sensing sensitivity also can be enhanced compared to thin film material. Nowadays, several approaches were used to advance chemical sensors performance that have been reported including high operational temperature (T>100℃)[4], surface modification with noble metal nanoparticles such as Au[5], Pd[6], Pt[7] and plasma surface treatment[8]. In addition, multiple-nanowire device also provides largely improved gas sensing performance, due to the suspended nanowire webs has much higher fluxes of gases surrounding, which could reinforce its efficiency. Note that increasing the sensing surface can enhance a signal level and offer a good signal-to-noise ratio. Previously, a similar approach has been reported by bridging ZnO nanowire [9-12]. However, these approaches are relatively complex, expensive, and time consuming for fabrication such as metal coating sputtering system, plasma system and photolithography process, which will limit for practical application in nanowire based gas sensor. To conquer the limitations of nanolithography, it is required to develop a convenient approach to fabricate the nanowire based chemical sensor. In this study, we report a new method, which is cost-effective, time-saving, and highly reproducible process to synthesis multiple CuO bridged nanowires with their electrical contacts by one step thermal treatment. The gas sensing capability, sensitivity, and noise properties of the CuO nanowire-bridge device are demonstrated and their chemical-sensing mechanism are also discussed.

2. EXPERIMENTAL

Prior to the growing of CuO nanowire-bridges, a 3-cm-long 99.999% pure Cu wire with a diameter of 0.1 mm was first rinsed in HCl and vibrated ultrasonically for 60 seconds. The chemically cleaned Cu wire was subsequently rinsed with de-ionized water and then dried by N_2 flow. To grow the nanowire-bridges, firstly, the two Cu wires were twisted together, as shown in Fig. 1(a). And then we inserted the twisted Cu wires into a quartz tube with a conventional horizontal furnace under atmospheric pressure to thermally treat at 500^{o}C for 2 hours. After this process, surface morphology of the sample was characterized by a Hitachi S-4700I field-emission scanning electron microscope (FESEM) operated at 15kV. Crystallographic and structural properties of the thermally treated sample were characterized by a Siemens D5000 X-ray Diffraction (XRD) system and a Philips FEI TECNAI G^2 high resolution transmission electron microscopy (HRTEM) operated at 200kV.

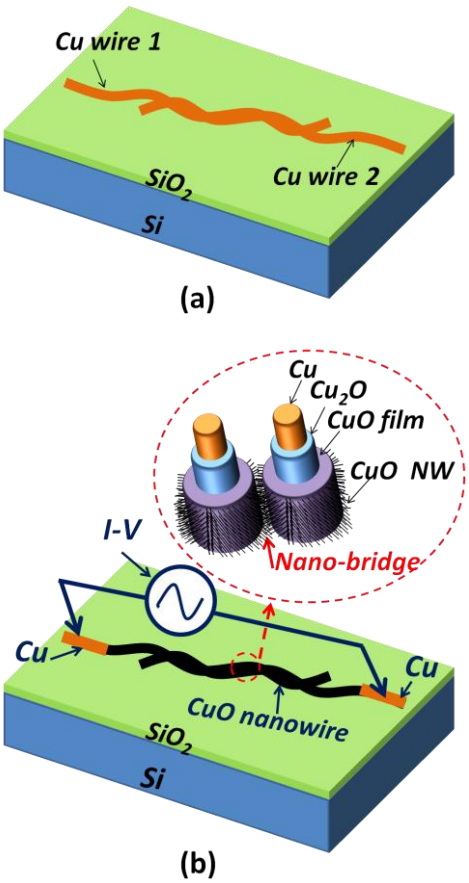

Figure 1. schematic of growth the CuO nanowires-bridges by (a) before and (b) after the thermally treatment.

For the fabrication of the nanowire-bridge chemical sensor, we placed the thermally treated sample on the SiO_2 (300nm)/Si substrate and used the Cu core on each end side of the wires as electrodes, as shown in Fig. 1(b). Fig. 1(b) inset shows schematic of the CuO nanowire-bridges structure. The sample was subsequently placed in a high vacuum chamber for Current-voltage (I-V) characterization. The sample was then measured by contacting the two electrodes using a Keithley 4200-SCS semiconductor analysis system. The resistance of the CuO nanowire-bridges was measured at 1V bias varying oxygen pressures for chemical sensor application.

3. RESULTS AND DISCUSSION

Fig. 2(a) depicts top-view FESEM image of the CuO nanowire-bridges array grown on the two Cu wires by the thermally treated process. It can be seen clearly that large area, high-density, and well-aligned CuO nanowires were grown on the both Cu_2O/Cu wire template. Fig. 2(a) inset shows an enlarged FESEM image between two Cu wires, which can be found many nanowire/nanowire junctions as seen in red circles mark. These networking junctions on two CuO nanowires, which have

grown on both Cu wires as shown in Fig. 2(b) will serve as electrical transport path while Current-voltage (I-V) measuring in chemical sensor applications.

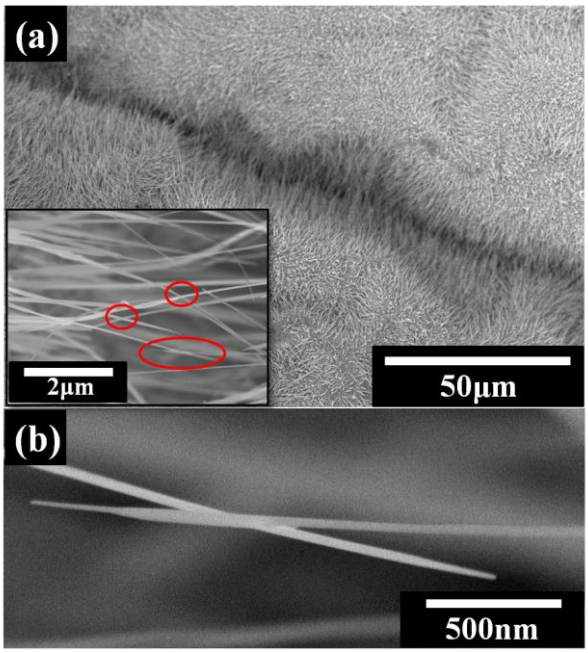

Figure 2. (a) Top-view and inset enlarged FESEM images of the thermally treated sample. (c) High magnification FESEM images of the CuO nanowire-bridges.

This CuO nanowire-bridge device is very easy and efficient fabricated compared to other growth method reported by some research group [9-12]. In addition, the SEM image of the CuO film and growth phenomena was shown on Fig. S1 (supporting information). In our work, the nanowire-bridges are self-assembled on the two twisted Cu wires during the one step thermal treatment process. Note that, in other research reports, the nanowire-bridge based devices are generally fabricated by dreary and complex processing steps such as a series of processes involving mask lithography to define the electrical contacts and to synthesis nanowire, or photolithography technique [13].

Fig. 3(a) shows the XRD spectrum of the thermally treated sample of the CuO film and CuO nanowire. It was found that both the film and the nanowire sample were display very sharp Cu_2O and CuO related peaks and could be well indexed from JCPDS (No. 45-0937, 05-0667). The result shows only Cu and O involved element in the nanowires and film, and indicates highly crystalline structure, which also agrees with the XRD analysis. It is worth to mention that the CuO nanowire-bridges were self-grew on the two twisted Cu wires by one step thermal treatment process in the air ambient and catalytic free in our chemical sensor fabrication method. The formation of CuO can be investigated by two chemical reaction equations as following while the thermal treating process [14]:

$$4Cu + O_2 \rightarrow 2Cu_2O \quad (1)$$

$$2Cu_2O + O_2 \rightarrow 4CuO \quad (2)$$

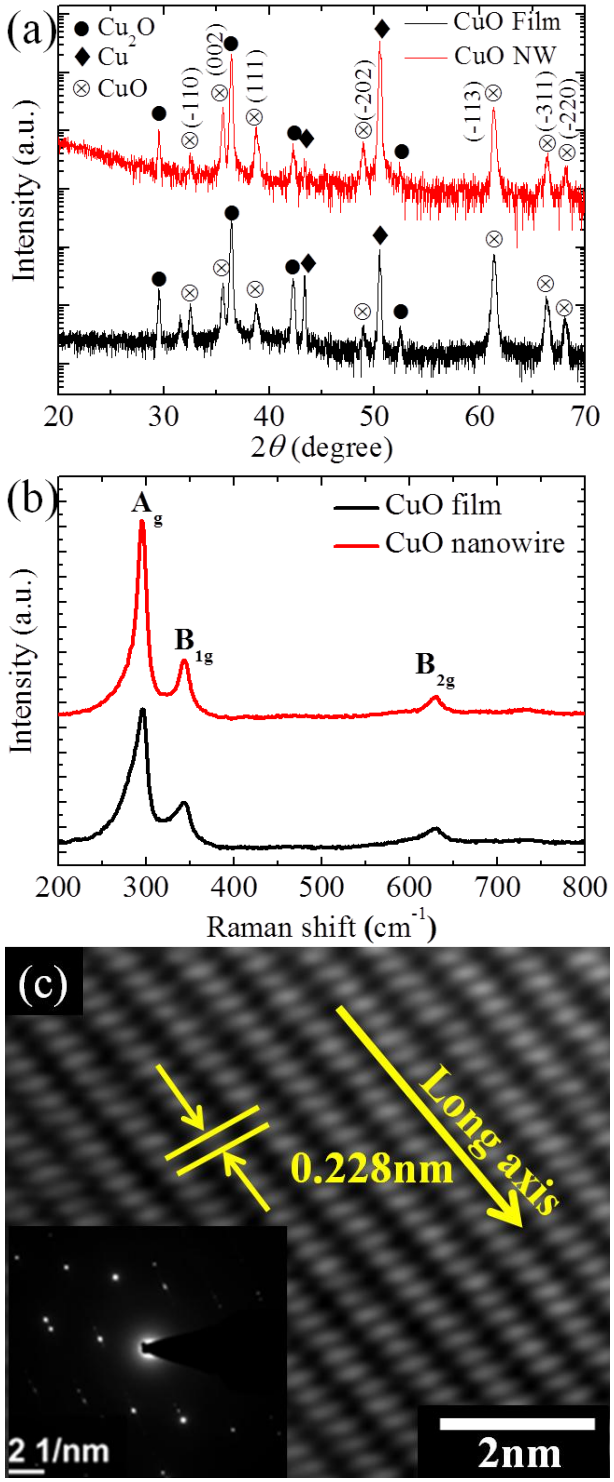

Figure 3. (a) XRD patterns and (b) Room temperature Raman spectra for the CuO film and the CuO nanowire-bridges. (c) High magnification TEM images of the

We believe that the similar mechanism of the continuously oxidized the Cu wires could also occur as our thermally treated in the air. As a result, we observed the tri-layer core-shell wire covered with numerous nanowires as illustrated on Fig. 1(b) inset.

Fig. 3(b) depicts room temperature Raman spectrum of the CuO film and CuO nanowires. We observed that both film and nanowires show three main peaks, located at 298, 348 and 630 cm^{-1}, corresponding to the Raman active optical phonon modes of A_g, B_{1g} and B_{2g} symmetries, respectively [15]. The results of these three strong peaks suggest that both the CuO film and nanowires are highly good quality sample for chemical sensor applications.

Fig. 3(c) shows the HRTEM image and its corresponding selected-area electron diffraction (SAED), which taken from a randomly picked nanowire on the sample. It was confirmed that the CuO nanowire is single crystalline with no observable defect in this region and the lattice spacing was observed to be 0.228 nm corresponding to the (-2 0 2) plane of the CuO crystal. Fig. 3(c) inset depicts the SAED pattern of the sample, which can be seen clearly that the pairs of reciprocal lattice peaks existed along two different lattice directions [16]. Such a pattern suggests the twin plan exists in the CuO nanowires, and implies the nanowires are dual-phased monoclinic CuO [17].

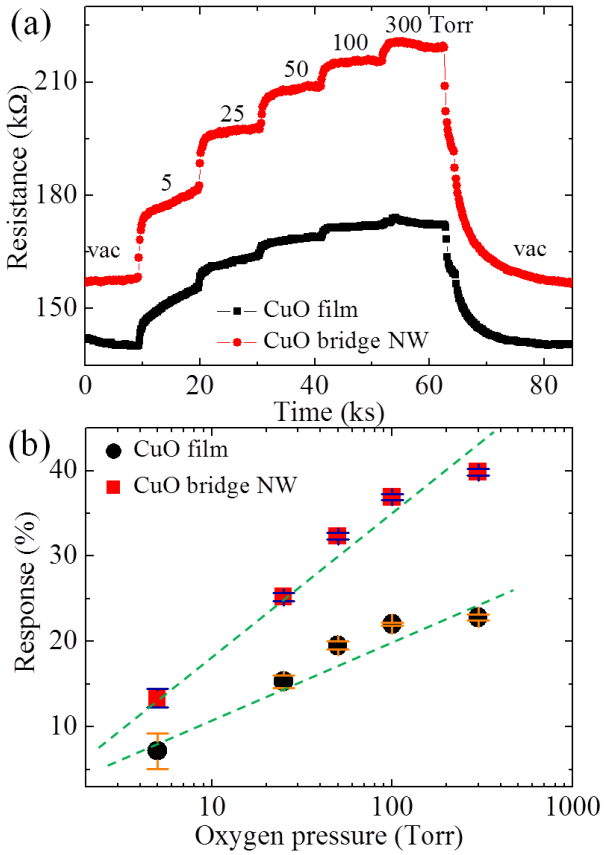

Figure 4. (a) Measured resistance as a function of time sensing response for the CuO film and the CuO nanowire-bridges. (b) Measured response (%) as a function of the oxygen pressures.

The oxygen molecules sensing responses of the CuO film and the CuO nanowire-bridge devices with varying gas pressures in room temperature were measured at 1V bias, and the results are shown in Fig. 4(a). It can be found that both resistances of the CuO film and the CuO nanowire-bridge devices are increased, while enhancing the oxygen pressure. Moreover, to quantitatively determinate

the O_2 sensing response, the response equation of the CuO film and the CuO nanowire-bridge devices was described as the following

$$response = \frac{R_g - R_a}{R_a} \times 100 \ = S * \log[P] + A \tag{3}$$

Where R_g denotes the sensor resistance in the oxygen gas and R_a denotes that under vacuum. S is sensitivity, P is the oxygen gas pressure in the chamber, and A is constant. Fig. 4(b) shows the response of the sensor devices as a function of oxygen pressure. As can be seen in Fig. 4(b), the CuO film device shows an obvious change of response, and its sensitivity is 0.09. In addition, the response of the CuO nanowire-bridge device is much larger than that of the CuO film device. Moreover, it can be found that sensitivity of the CuO nanowire-bridges is 0.155, which is about 2 times higher than that of CuO film device.

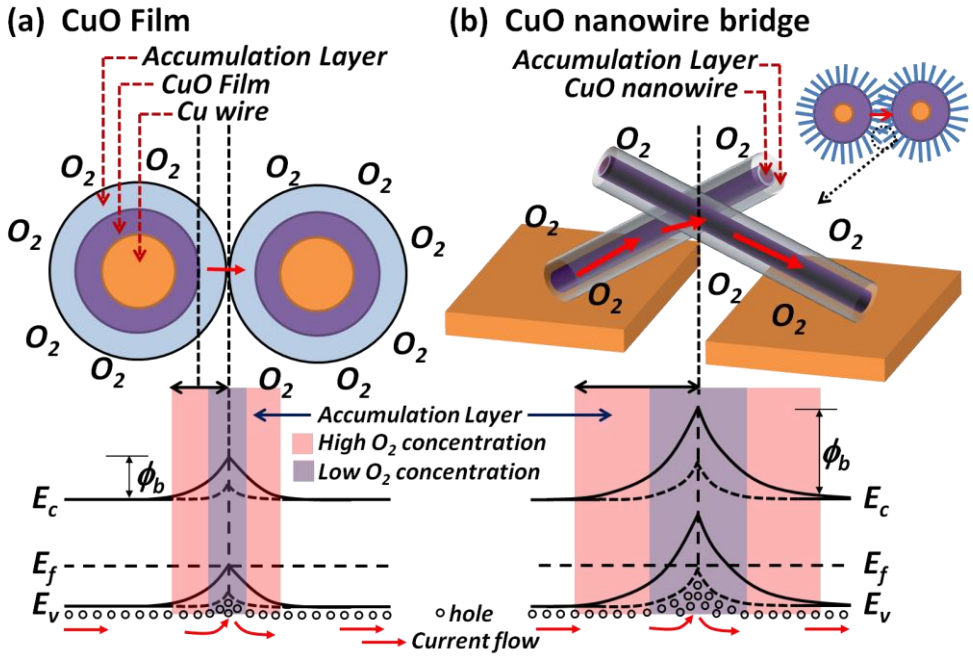

Figure 5. Schematic of the electron transport processes in the sensing layer (top) and the corresponding energy bands representation (bottom) for (a) the CuO film and (b) the CuO nanowire-bridges.

This result also indicates that the oxygen molecular sensing performance of the CuO nanowire-bridges can be improved by large surface-area-to-volume effect.

The mechanism of the enhanced oxygen sensitivity between the CuO nanowire-bridges and the CuO film device is illustrated qualitatively in Fig. 5(a), the CuO film, and Fig. 5(b), the CuO nanowire-bridges. It is well known that CuO is a p-type semiconductor which the copper vacancies provide the acceptor levels as the synthesis in progress [18,19]. While the oxygen sensing, the O_2

molecules will be adsorbed on CuO surface and create surface states of electron trap, which leads to the energy band bend upwards at the surface forming an accumulation layer with majority carriers of holes [20]. This reaction process can be described by the following equation [21]:

$$O_2 \leftrightarrow O_2^- + \text{VacancyCu}_2^+ + 2h \qquad (4)$$

As the oxygen sensing, the holes (*h*) will accumulate near the surface of the CuO to form the hole accumulation layer due to surface band bending effect, which will lead to decrease the overall conductance of the device. This means that the accumulation layer/barrier height (ϕ_b) can be modulated by oxygen concentration, which will induce the device to change its conductance. Fig. 5(a) depicts the cross-section schematic diagram of the CuO film that both surfaces of the CuO films are connected together (Fig. 5(a) top), and it corresponds the real-space energy band diagram (Fig. 5(a) bottom). In the CuO film case, the electron transport flowed through the contact area of both surfaces of the CuO films. Therefore, the contact area plays a dominant role in conduction. Moreover, the transport properties of CuO film are similar to the bulk CuO material, in which surface states and surface barrier height (ϕ_b) are relatively less than that in the nanostructure. That will result in fewer oxygen molecules available in surface states, which will limit sensing sensitivity of the device. In the CuO nanowire-bridge case, owing to the large surface-to-volume ratio, the sensing performance of the device is expected to be strongly affected by surface states. Fig. 5(b) depicts the schematic diagram of the CuO nanowire-bridges, Fig. 5(b) top, and the real-space energy band diagram, Fig. 5(b) bottom. As the CuO nanowire-bridges do not expose in oxygen molecule, the current flow through networking points connecting by two CuO nanowires as a conductive nano-bridge. As the CuO nanowire-bridges exposes in oxygen molecule, the surface of each nanowire adsorbed oxygen molecule will significantly increase both the accumulation layer and barrier height (ϕ_b) in the networking junctions. Therefore, the electrical transport properties of the CuO nanowire-bridges are strongly influenced by the networking junctions. As a result, the enhanced sensitivity of our CuO nanowire-bridge device can be ascribed as high density of surface states of the CuO nanowires, which will induce large tunable surface band bending with barrier height (ϕ_b) by oxygen molecule in the each networking junction.

The noise property is a very important parameter for the actual application of a gas sensor. Because the low-frequency noise property contains information about the charge fluctuations, it will determine the reliability of the gas-sensing device. Fig. 6 shows measured noise power spectra of both CuO film and the CuO nanowire-bridges, respectively. We applied forward bias of 1V with bandwidth from 1 Hz to 1000 Hz at room temperature while noise measuring. According to the Hooge's empirical model, the noise power spectrum of low-frequency was given by the equation [22, 23]

$$S_n(f) = S_o \frac{I_d^{\beta}}{f^{\alpha}} \qquad (5)$$

where $S_n(f)$ is the spectral density of the noise current, I_d is the dark current of the detector, f is the frequency, S_o is a bias-independent constant, α and β are two fitting parameters. Note that the noise

spectra shown 1/*f*-type (α=1) fluctuations is widely found in nature. This behavior of the noise power spectra at low-frequencies *f* have been observed in physics, technology, biology, condensed matter and electronic devices [24], which represents low noise signal in the device.

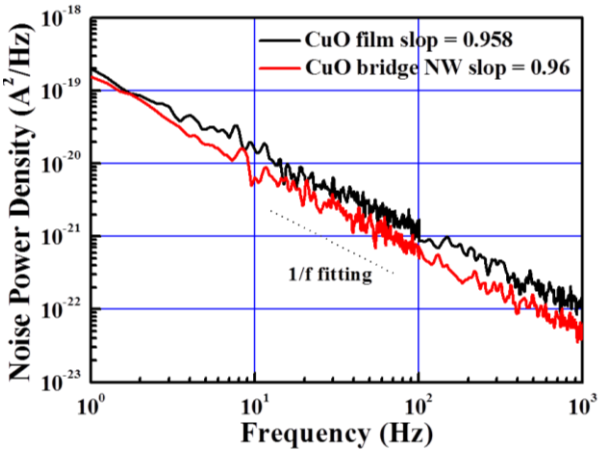

Figure 6. Measured noise power spectra of the fabricated CuO film and CuO nanowire-bridges device.

In the measured curves, the fitting parameters α of the CuO film and the CuO nanowire-bridges were found to be 0.956 and 0.958 (near α=1). As a result, we can conclude that the low-frequency noise in our devices is dominated by 1/*f* type noise [22]. Such a result also suggests that this CuO film and CuO nanowire-bridge device has a good gas-sensing reliability.

4. CONCLUSION

In this study, we have introduced a direct growth of CuO nanowire-bridge device fabrication by one step thermal treatment. It is found that the nanowire-bridges are self-assembled during the nanowires growing. The XRD, micro Raman, and HRTEM measurements indicate that the CuO nanowires are single crystalline with high crystal quality. The sensing response of the CuO nanobridges reinforces linearly while logarithmic O_2 pressure increases at room temperature. It is also found that the sensitivity of CuO nanowire-bridge device for sensing oxygen molecule is about 2 times higher than that of the CuO thin film on the same measuring condition. The enhanced sensitivity of the nanowire-bridges should be attributed to the higher surface band bending, which due to the large potential barrier interacts as the accumulation layer at nanowire/nanowire junction in each nanowire. Furthermore, the electrical noise properties of both the CuO film and the CuO nanowire-bridges are followed Hooge's 1/f-type fluctuations model, which suggests a good reliability of the gas-sensing device. This one step fabrication method in the CuO nanowire bridging can provide a new type sensing application such as chemical/bio sensors, nanomechanical resonators and photodetector to enhance their capability.

ACKNOWLEDGEMENTS
This work was supported in part by the Center for Micro/Nano Science and Technology, National Cheng Kung University (NCKU), Taiwan (D97-2700), and in part by the Advanced Optoelectronic Technology Center, NCKU. This work was also supported in part by the Center for Condensed Matter Sciences (CCMS), National Taiwan University, and National Science Council of Taiwan under grant No. NSC-100-2221-E-158-002

References

1. J.W. Yu, C.K. Li, C.Y. Chen, Y.R. Wu, L.J. Chou and L.H. Peng, *Appl. Phys. Lett*., 99 (2011) 152108
2. L. Li, Y.X. Zhang, X.S. Fang, T.Y. Zhai, M.Y. Liao, H.Q. Wang, G.H. Li, Y. Koide, Y. Bando and D. Golberg, *Nanotechnology*, 22 (2012) 165704
3. Y.Q. Cong, Z. Li, Q. Wang, Y. Zhang, Q, Xu and F.X. Fu, *Acta Phys.-Chim. Sin*., 28 (2012)1489
4. S.A. Anggraini, V.V. Plashnitsa, P. Elumalai, M. Breedon and N. Miura, *Sens. Actuator B-Chem.*, 160 (2011) 1273
5. J. Zhang, X.H. Liu, S.H. Wu, B.Q. Cao and S.H. Zheng, *Sens. Actuator B-Chem*., 169 (2012) 61
6. C.M. Chang, M.H. Hom, and I.C. Leu, *RSC Advances*, 2 (2012) 2469
7. H. Kim, C. Jin, S. An and C. Lee, *Ceram. Int*., 38 (2012) 3563
8. J. Pan, R. Ganesan, H. Shen and S. Mathur, *J. Phys. Chem*. C, 114 (2010) 8245
9. M.W. Ahn, K.S. Park, J.H. Heo, D.W. Kim, K.J. Choi and J.G. Park, *Sens. Actuator B-Chem*., 138 (2009) 168
10. A. Menzel, K. Subannajui, F. Gueder, D. Moser, O. Paul and M. Zacharias, *Adv. Funct. Mater*., 21 (2011) 4342
11. Y. Li, A. Paulsen, I. Yamada, Y. Koide and J.J. Delaunay, *Nanotechnology*, 21 (2010) 295502
12. Lu Yuan and Guangwen Zhou, *J. Electrochem. Soc*, 159 (2012) C205
13. R.R. He, D. Gao, R. Fan, A.I. Hochbaum, C. Carraro, R. Maboudian, P.D. Yang, *Adv. Mater*., 17 (2005) 2098
14. X. Jiang, T. Herricks, and Y. Xia, *Nano Lett.*, 2 12 (2002) 1333
15. J. Chrzanowski, J.C. Irwin, *Solid State Commun*., 70 (1989) 11
16. S.B. Wang, C.H. Hsiao, S.J. Chang, K.T. Lam, K.H. Wen, S.C. Hung, S.J. Young and B.R. Huang, *Sens. Actuator A-Phys*., 171 (2011) 207-211
17. L. Zhang, C. Rossi, C. Tenailleau, P. Alphonse, J.Y. Chane-Ching, *Nanotechnology* 18 (2007) 275607
18. F.D. Koffyberg, F.A. Benko, *J. Appl. Phys.* 53 (1982) 1173
19. Y.K. Jeong, G.M. Choi, *J. Phys. Chem. Solids*, 57 (1996) 81
20. M. Hubner, C.E. Simion, A. Tomescu-St˘anoiu, S. Pokhrel, N. Barsana, U. Weimar, *Sens. Actuator B-Chem.*, 153 (2011) 347
21. V. F. Kiselev and O. V. Krylov, *Adsorption and Catalysis on Transition Metal and Their Oxides* ed Robert Gomer, New York: Springer (1989)
22. P. Dutta, and P. M. Horn, *Rev. Mod. Phys*., Vol. 53 (1982) 497
23. H. T. Hsueh, S. J. Chang, W. Y. Weng, C. L. Hsu, T. J. Hsueh, F. Y. Hung, S. L. Wu, and B. T. Dai, *IEEE Tran. Nanotechnol.*, 11 (2012) 127
24. http://www.scholarpedia.org/article/1/f_noise#1.2Ff_noise_in_solids.2C_con

Supporting information:

The CuO film was growth by a conventional horizontal furnace under atmospheric pressure at 400^{o}C in air for 2 hours as shown in Fig S1.

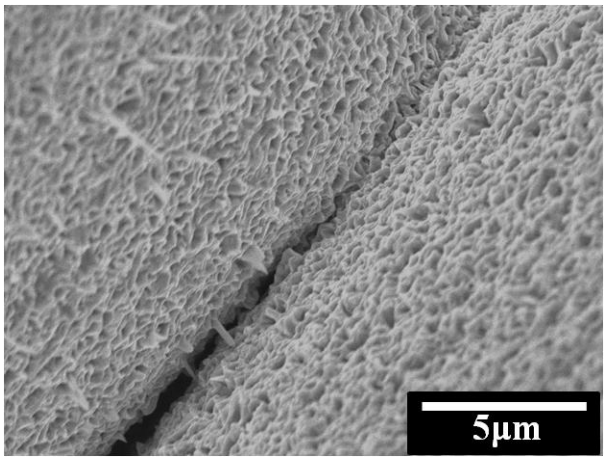

Figure S1. Top-view FESEM image of the CuO film by thermal treatment sample at 400 ^{o}C.