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Fabrication of coaxial p-copper oxide/n-ZnO nanowire photodiodes

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1. Introduction

ZnO is an interesting TCO material [1-3] with a room temperature energy gap of 3.37 eV and a strong exciton binding energy of 60 meV. To maximize the functionality of ZnO, we might need to pursuit ZnO-based hetero-structured p-n junction. It is known that copper oxides tend to be naturally cation deficient and hole conductors. Copper have different positive oxidation numbers, such as +1 for Cu_2O, +1.5 for Cu_4O_3, and +2 for CuO. In the Cu-O system, it is known that Cu_2O (cuprite) and CuO (tenorite) are stable under standard environment. Cu_2O is a natural p-type direct-gap semiconductor with a cubic crystal structure and room temperature bandgap energy of 2.1 eV while CuO with narrow bandgap of 1.2 eV is a p-type semiconductor with monoclinic structure. On the other hand, only few reports on Cu_4O_3 (paramelaconite) could be found in the literature. It has been shown that Cu_4O_3, could also be written as $Cu(I)_2Cu(II)_2O_3$, is a potential catalyst for oxidation. Thus, these copper oxides should be able to serve as an ideal p-type material for ZnO-based hetero-structured p-n junction.

2. Experiment

A 50-nm-thick Ga-doped ZnO film was deposited onto the glass substrate by RF sputtering. ZnO nanowires were then grown on the ZnO:Ga/glass template by VLS method. Detailed growth procedures of the n-ZnO nanowires could be found elsewhere [3]. Copper oxides were subsequently deposited by DC sputtering using Ar and O_2 as the sputtering gases. The target used to deposit copper oxide was a 99.99%-pure copper. During sputtering, we kept the Ar flow rate, base pressure, chamber pressure, DC power and substrate temperature at 15 sccm, 2×10^{-6} torr, 6 mtorr, 400 W and 25^0C, respectively. The O_2 flow rate was varied from 1 to 6 sccm. Fig. 1 schematically depicts the structure of the fabricated p-copper oxide/n-ZnO nanowire photodiode.

3. Results and discussion

Fig. 2 shows cross-sectional FESEM image of the ZnO nanowires prepared on ZnO:Ga/glass template. As shown in figure 2, it was found that average length, average diameter and density of these ZnO nanowires were 1 µm, 100 nm and 23 wires/µm^2, respectively. The inset in Fig. 2 shows XRD spectrum of these ZnO nanowires.

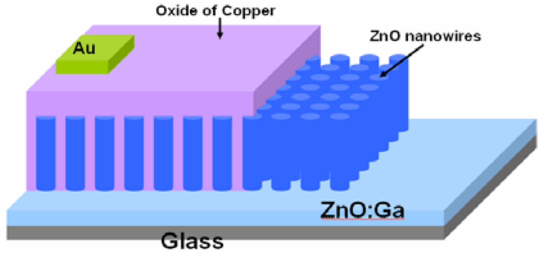

Fig. 1 Schematic illustration of the coaxial p-copper oxide/n-ZnO device.

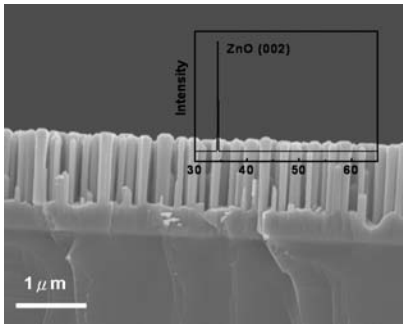

Fig. 2 Cross-sectional FESEM image and XRD spectrum of the ZnO nanowires prepared on ZnO:Ga/glass template.

Figure 3 shows the XRD spectra of these deposited copper oxides with different O_2 flow rates. For the sample deposited with an O_2 flow rate of 1 sccm, we observed two XRD peaks. One was the Cu_2O (111) peak while the other was the Cu (111) peak. As we increased the O_2 flow rate to 2 sccm, it was found that the Cu_2O (111) peak intensity became larger than that of the Cu (111) peak. As we increased the O_2 flow rate to 3 sccm, it was found that the Cu_2O (111) peak continuous to grow and became sharper while the intensity of Cu (111) peak became negligibly small. As we increased the O_2 flow rate to 4 sccm, it was found that intensities of Cu_2O-related peaks continuous to grow. Such a spectrum also suggests that the deposited copper oxide was pure crystalline Cu_2O when sputtered with an O_2 flow rate of 4 sccm. As we further increased the O_2 flow rate to 5 sccm, intensities of the Cu_2O-related peaks all decreased significantly. Instead, a strong peak located at $2\theta=36.2^o$ appeared which was labeled as Cu_4O_3 (004). As we continuously increased the O_2 flow rate to 6 sccm, the dominant peak shifted to $2\theta=35.9^o$, which was labeled as CuO (111). Such an observation suggested that most of the sputtered Cu was fully oxidized to CuO with an O_2 flow rate to 6 sccm.

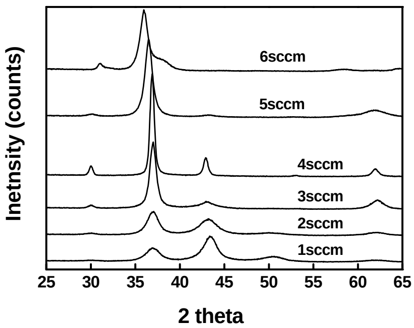

Figure 3 XRD spectra measured from the deposited copper oxides with various O_2 flow rates.

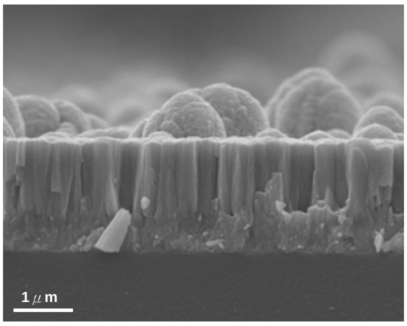

Figure 4 Cross-sectional FESEM image of the sample with Cu_2O deposited on ZnO nanowires.

Figure 4 shows cross-sectional FESEM image of the sample with Cu_2O deposited on ZnO nanowires with an O_2 flow rate of 4 sccm. We also achieved Cu_4O_3/ZnO nanowires and CuO/ZnO nanowires by increasing the O_2 flow rate during sputtering to 5 and 6 sccm, respectively.

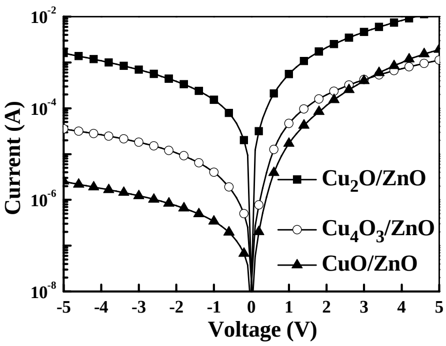

Figure 5 Dark I-V characteristics

Figure 5 shows dark I-V characteristics measured form the fabricated photodiodes. Figures 6 show dynamic photo responses measured from the fabricated Cu_2O/ZnO, Cu_4O_3/ZnO and CuO/ZnO nanowire photodiode, respectively. From the measured photocurrent, we can determine the responsivity of the fabricated photodiodes. which were 0.12, 0.40 and 1.00 A/W for Cu_2O/ZnO, Cu_4O_3/ZnO and CuO/ZnO nanowire photodiode, respectively.

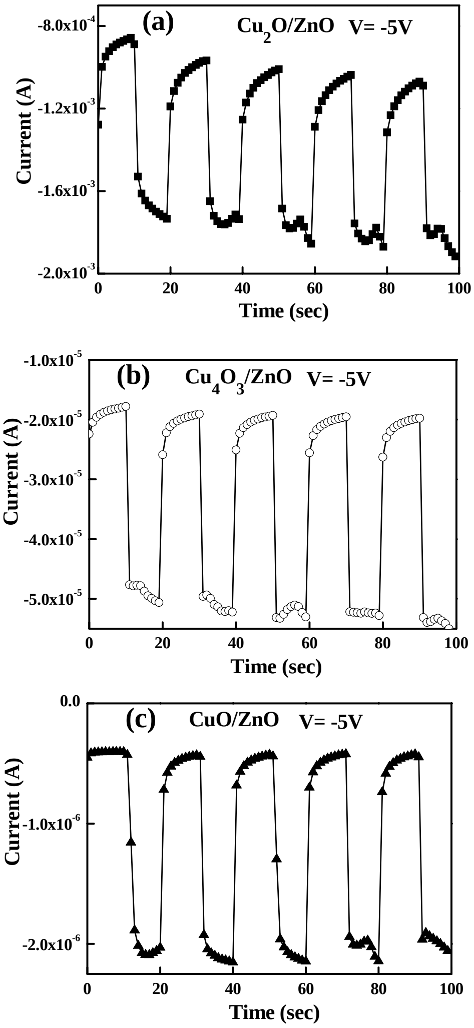

Figure 6 Dynamic photo responses measured from (a) Cu_2O/ZnO nanowire photodiode, (b) Cu_4O_3/ZnO nanowire photodiode and (c) CuO/ZnO nanowire photodiode

Reference

[1] L.S. Huang, S.G. Yang, T. Li, B.X. Gu, Y.W. Du, Y.N. Lu, S.Z. Shi, J.Cryst. Growth vol. 260, pp. 130, 2004.

[2] M. Izaki, T. Shinagawa, K. T. Mizuno, Y. Ida, M. Inaba, A. Tasaka, J. Phys. D: Appl. Phys. vol. 40, pp. 3326, 2007.

[3] C. L. Hsu, S. J. Chang, Y. R. Lin, S. Y. Tsai and I. C. Chen, *Chem. Commun.* vol. 28, pp. 3571 2005.