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CuO Nanowires Grown from Cu Film Heated Under a N_2/O_2 Flow

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Pure, large-area, and aligned CuO nanowires are realized from copper thin film deposited onto silicon substrate by thermal annealing under a N_2/O_2 gas flow. The as-prepared pure and vertically aligned CuO nanowires along silicon substrate have several advantages over previous approaches such as easier integration into silicon based micro systems, more convenience for subsequent elements deposition, and higher heat of reaction for realization of CuO/Al based nano energetic materials. It is found that long and aligned nanowires can only be formed within a narrow temperature range from 400 to 500 °C. A N_2/O_2 gas flow rate of 400/100 sccm is moderate for realizing long and aligned CuO nanowires. The synthesized nanowires and thin film beneath the nanowires are confirmed to be pure CuO using X-ray diffraction. The CuO nanowires are found to be bicrystal by high resolution transmission electron microscopy.

Keywords: Pure, Aligned, CuO Nanowire, Copper Thin Film, Silicon, N_2/O_2 Gas Flow.

1. INTRODUCTION

Recently, nano copper oxides (mainly CuO and Cu_2O) have become one intensive research focus because of their fascinating properties and interesting applications compared to their bulk or micro counterparts. Copper oxides have been extensively used in various areas including battery anode electrodes, heterogeneous catalyst, magnetic storage media, high-temperature superconductors, and nano energetic materials,[1–6] where one-dimensional nano copper oxides (wires, belts, and rods) have been paid special attention. One-dimensional nano copper oxides have been realized by different methods such as thermal decomposition of CuC_2O_4 precursor, reduction of copper sulfate with hydrazine, heat treatment of Cu_2S nanowires with oxygen, self-catalytic growth, solution treatment of copper foil, and thermal annealing of copper substrates (foils, grids, and wires) in air.[7–14] In the previous approaches, free-standing copper oxide nanowires or aligned nanowires on copper substrate have been successfully synthesized. However, no approach is found in the literature to grow vertically aligned copper oxide nanowires along silicon substrate. It is very interesting to realize copper oxide nanowires on silicon substrate that is a basic and widely used material in semiconductor industry. This will possibly provide the opportunities to integrate the nanowires into silicon based micro systems, thus resulting in nano based functional devices. Nano energetic material based high temperature initiators suggested in Refs. [15–16] are typical examples for these functional nano devices. Among the above-mentioned synthesis approaches of copper oxide nanowires, the simplest way is to heat copper substrates directly in air.[12–14] By employing the similar method, it maybe possible to grow copper oxide nanowires on copper thin film deposited onto silicon substrate. However, in accordance with the literature,[17–18] it seems very hard to realize metal oxide nanowires just from pure metal thin films by thermal annealing. Furthermore, the copper oxide nanowires synthesized in static air are not well vertically aligned on the top surface,[12] which is not desirable for some special applications. For instance, it is not favorable for the nano aluminum deposition to realize CuO/Al based nano energetic materials.[16] In this study, we successfully synthesized large-area and well vertically aligned pure CuO nanowires by thermal annealing copper thin film deposited onto silicon substrate under a N_2/O_2 gas flow.

2. EXPERIMENTAL DETAILS

A 30 nm titanium film is first deposited onto a 4-inch silicon wafer followed by a 50 nm copper film deposition by thermal evaporation, where the titanium film acts as the

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adhesion layer between copper and silicon substrate and the copper film serves as the electrical conducting layer for the subsequent electroplating. Copper film with a thickness of 1 μm is deposited onto the substrate by electroplating. The substrate is cut into small chips that are then treated for 20 s in a solution containing 120 ml DI water and 10 ml 37% HCl. After being rinsed with DI water and blown-dried using N_2, the chips are placed on a clean silicon wafer. The wafer is put onto a quartz boat that is positioned in the center of a quartz tube. The quartz tube is mounted inside a horizontal tube furnace. A high-purity N_2 flow at a rate of 2000 sccm is first introduced into the quartz tube for 20 min to remove air in the system. And then the N_2 flow is reduced into 400 sccm. Simultaneously, a high-purity O_2 flow at a rate of 100 sccm is introduced into the system. The tube furnace is heated to the set-point temperatures at about 8 °C/min at atmospheric pressure. After being held for the designed time, the O_2 flow is terminated. And only N_2 is kept flowing. The furnace is cooled down naturally to room temperature. The chips are taken out of the furnace for further analysis.

3. RESULTS AND DISCUSSION

3.1. SEM Characterization

Figure 1(A) shows a 30° tilted view scanning electron microscopy (SEM) image of the annealed copper film at 400 °C for 5 h. The diameters of the as-realized CuO nanowires are in the range of 60–100 nm. The nanowires in Figure 1(A) are shown in Figure 1(B) with a lower magnification. It can be seen that large-area and uniform nanowires are grown from the copper thin film surface after the thermal treatment under a N_2/O_2 flow. The resulting nanowires are mostly vertically aligned along the film surface. This is confirmed by the top view SEM images in Figures 2(A–B). As stated in Ref. [12], the copper oxide nanowires realized in static air from copper substrate are not well vertically aligned on the top surface. The vertically aligned CuO nanowires synthesized on silicon substrate in this study have some potential advantages over the CuO nanowires prepared on copper substrate under static air in Refs. [12–14]. A typical example is that the vertical nanowires are favorable for the subsequent nano aluminum deposition so as to achieve CuO/Al based nano

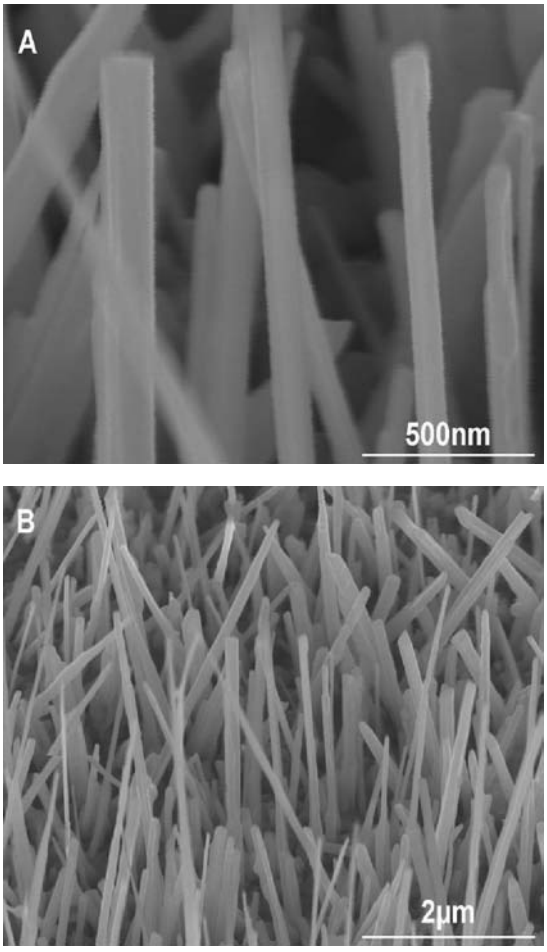

Fig. 1. 30° tilted view SEM images of the annealed copper film at 400 °C for 5 h.

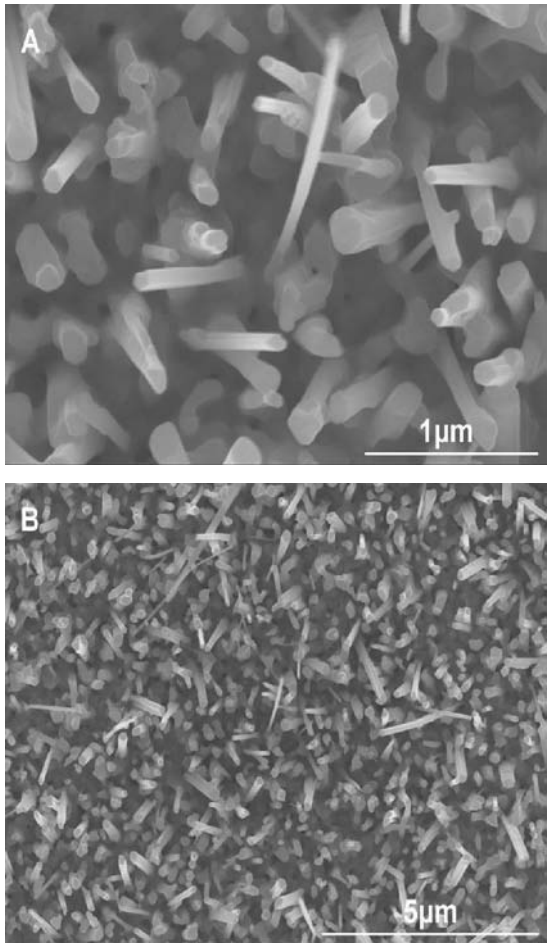

Fig. 2. Top view SEM images of the annealed copper film at 400 °C for 5 h.

energetic materials.[16] Furthermore, since the nanowires are realized onto silicon substrate, it is easier to integrate them into silicon based micro systems. This will probably lead to CuO nanowire based functional devices. According to Ref. [12], CuO nanowires were formed in a temperature range from 400 to 700 °C while copper substrates were annealed in static air. Nevertheless, in this study long and aligned CuO nanowires can only be synthesized in a narrow temperature range from 400 to 500 °C when copper thin films are heated under a N_2/O_2 gas flow. Below 350 °C, no nanowires are formed and the thin film surface is mainly covered by nano particles. When the temperature is higher than 550 °C, there is a very small amount of short nanowires formed on the thin film surface. Figures 3(A–B) shows the SEM images of the annealed copper film at 400 °C for 5 h with different N_2/O_2 gas flow rates. When the N_2/O_2 gas flow rate is very low (100/25 sccm), the as-prepared nanowires are not well vertically aligned along the substrate as shown in Figure 3(A), which is similar to those synthesized in static air. However, when the N_2/O_2 gas flow rate is too high (800/200 sccm), only very short nanowires are obtained as can be seen in Figure 3(C). The N_2/O_2 gas flow rate of 400/100 sccm found in the present study is a moderate value for realizing long and vertically aligned nanowires along the substrate.

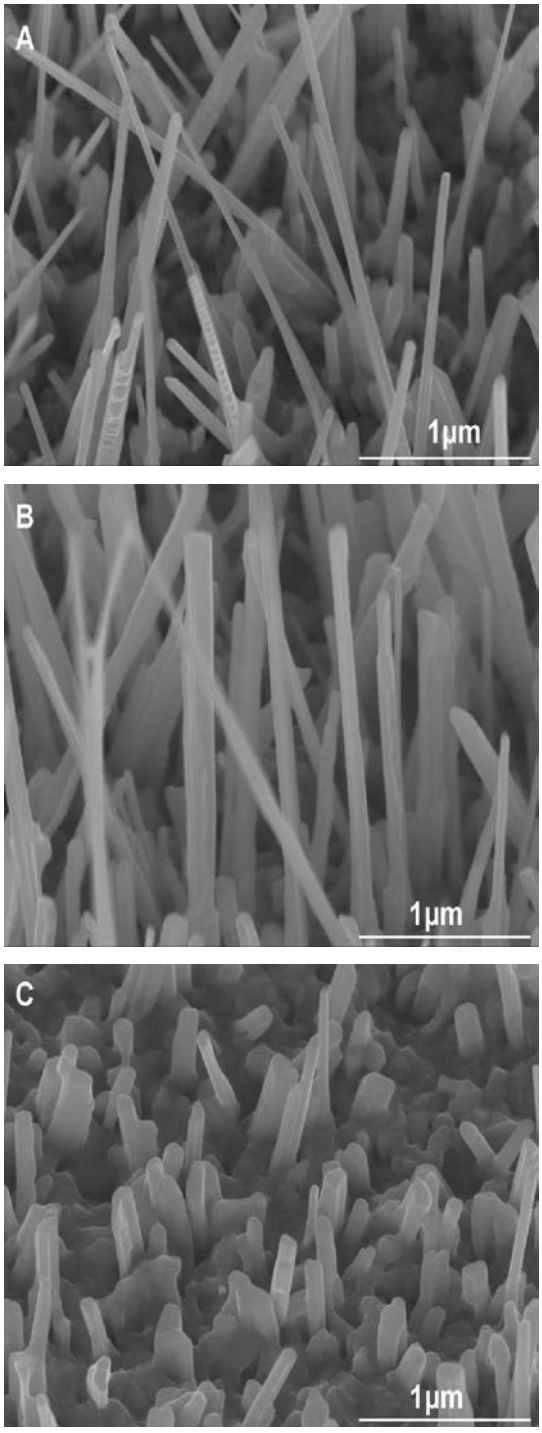

Fig. 3. 30° tilted view SEM images of the annealed copper film at 400 °C for 5 h in (A) N_2/O_2 (100/25 sccm), (B) N_2/O_2 (400/100 sccm), and (C) N_2/O_2 (800/200 sccm).

3.2. XRD Characterization

Figure 4 shows the X-ray diffraction (XRD) pattern of the annealed copper film at 400 °C for 5 h. According to the results in Refs. [12–13], both CuO and Cu_2O are observed when copper substrates are thermally treated in static air. In this study only CuO is found after copper thin film is annealed under a N_2/O_2 gas flow at 400 °C for 5 h as can be seen in Figure 4. The deposited copper thin film is all converted into CuO in the form of both nanowires and thin film. As mentioned previously, a 30 nm thick Ti film is deposited onto silicon to serve as the adhesion layer between copper and silicon. After the thermal annealing, no Ti or TiO_2 is observed from the XRD pattern. This is mainly caused by the very small Ti film thickness.

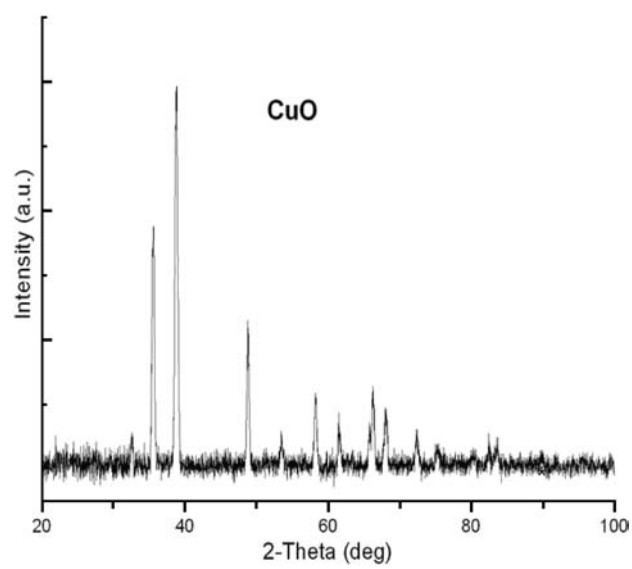

Fig. 4. XRD pattern of the annealed copper film at 400 °C for 5 h.

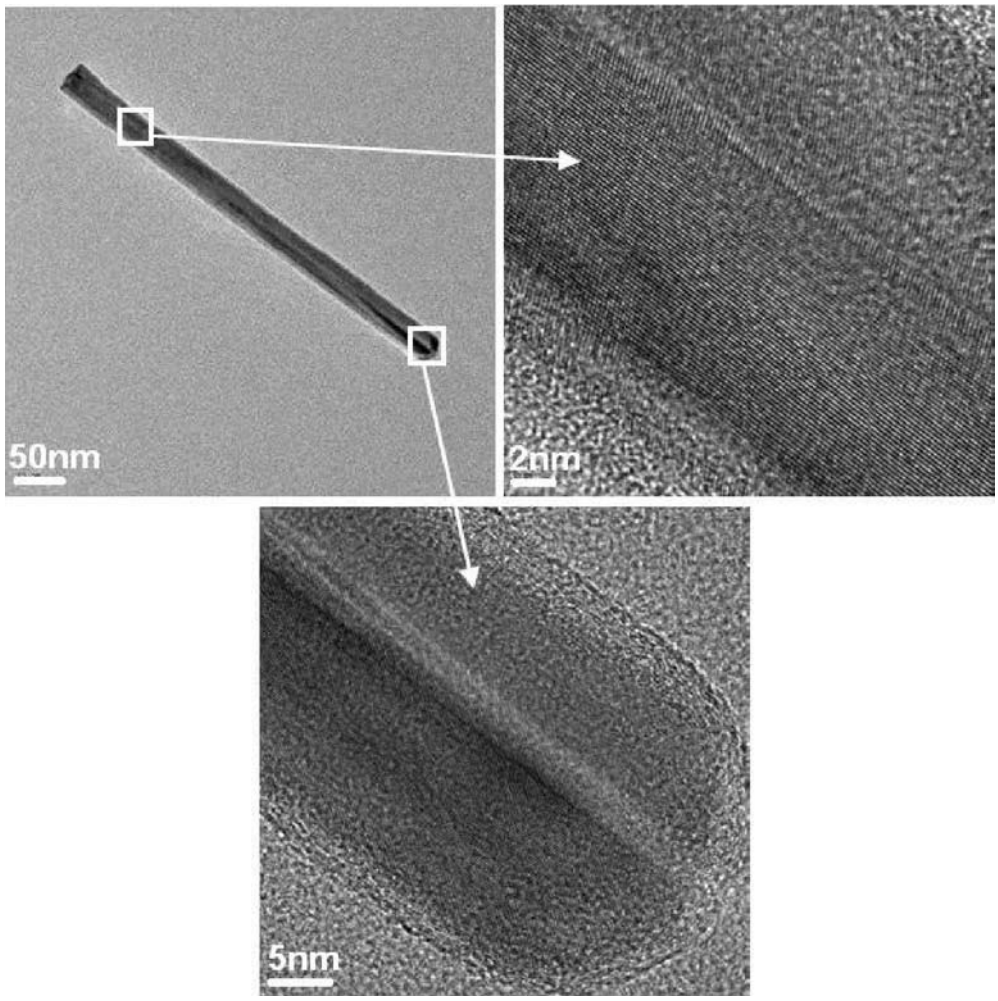

Fig. 5. HRTEM images of an individual nanowire from the annealed copper film at 400 °C for 5 h.

The obtained pure CuO is beneficial for realizing CuO/Al based nano energetic materials as suggested in Ref. [16] because the heat of reaction (4.144 kJ/g) between CuO and Al is much higher than that (2.434 kJ/g) between Cu_2O and Al.[19–20]

Vapor-liquid-solid and vapor-solid mechanisms are usually used to interpret the nanowire growth in the gas phase.[12, 13, 17] Vapor-solid mechanism is supposed to be accounted for the CuO nanowire growth because the particle-type termination of the nanowire, a most notable sign of the vapor-liquid-solid growth mechanism does not present in accordance with our SEM observations. As mentioned previously, the CuO nanowires synthesized in this study under a N_2/O_2 gas flow appear to be more vertical, denser, and thicker compared to the CuO nanowires realized in static air in Refs. [12–14]. When static air is used, the O_2 concentration decreases with the reaction near the thin film surface because the oxidation rate is larger than the diffusion rate. The locally low O_2 concentration is not beneficial for the nanowire growth. Employing gas flow increases the diffusion rate and the oxidation is no more limited by diffusion.

3.3. TEM Characterization

Figure 5 displays the high resolution transmission electron microscopy (HRTEM) images of an individual nanowire grown from the annealed copper thin film at 400 °C for 5 h. It can be seen that each side of the nanowire is a single crystal with a distinct fringe space pattern. The interplanar spacing for each side is 1.98 Å and 2.35 Å, respectively, which is similar to the spacing for {111} and $\{\bar{1}11\}$ planes in monoclinic CuO. This confirms the bicrystallinity of the as-prepared nanowires.

4. CONCLUSIONS

In this study, pure and aligned CuO nanowires have been successfully realized onto silicon substrate. The nanowires are synthesized by annealing copper thin film deposited onto silicon under a N_2/O_2 gas flow. Compared to the

CuO nanowires grown from copper substrates in static air performed by previous approaches, the nanowires achieved here are more vertical, purer, and more uniform. Therefore, they are favorable for subsequent nano Al deposition so as to realize CuO/Al based nano energetic materials. Long and aligned CuO nanowires can only be formed in a narrow temperature range from 400 to 500 °C. A moderate high N_2/O_2 gas flow rate of 400/100 sccm can help prepare well vertical and thicker nanowires along the copper thin film because the gas flow is able to keep a relatively high O_2 concentration near the thin film to support the nanowire growth. XRD and HRTEM results indicate that the entire copper thin film is converted into pure CuO in terms of both bicrystal nanowires and thin film. Because the nanowires are realized onto silicon substrate, it is supposed to be easier to integrate the nanowires into silicon based micro systems, thus probably resulting in nanowire based functional devices.

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