Synthesis of large-area and aligned copper oxide nanowires from copper thin film on silicon substrate

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Synthesis of large-area and aligned copper oxide nanowires from copper thin film on silicon substrate

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Abstract
Large-area and aligned copper oxide nanowires have been synthesized by thermal annealing of copper thin films deposited onto silicon substrate. The effects of the film deposition method, annealing temperature, film thickness, annealing gas, and patterning by photolithography are systematically investigated. Long and aligned nanowires can only be formed within a narrow temperature range from 400 to 500 °C. Electroplated copper film is favourable for the nanowire growth, compared to that deposited by thermal evaporation. Annealing copper thin film in static air produces large-area, uniform, but not well vertically aligned nanowires along the thin film surface. Annealing copper thin film under a N_2/O_2 gas flow generates vertically aligned, but not very uniform nanowires on large areas. Patterning copper thin film by photolithography helps to synthesize large-area, uniform, and vertically aligned nanowires along the film surface. The copper thin film is converted into bicrystal CuO nanowires, Cu_2O film, and also perhaps some CuO film after the thermal treatment in static air. Only CuO in the form of bicrystal nanowires and thin film is observed after the copper thin film is annealed under a N_2/O_2 gas flow.

1. Introduction

Nanostructures have received steadily growing interest because of their fascinating properties and various applications as compared to their bulk or microsized counterparts. Recently, one-dimensional (1D) nanostructures such as wires, belts, rods, and tubes have become one focus of intensive research as a result of their unique properties and potential usages [1]. Among the various 1D nanostructures, nanosized copper oxides, usually cupric oxide (CuO) and cuprous oxide (Cu_2O), have attracted much attention due to their interesting applications. Copper oxides have been widely used in many areas such as in heterogeneous catalysts [2], anode electrodes for batteries [3], magnetic storage media [4], and high temperature superconductors [5]. More recently, nano-CuO has been employed to realize nanoenergetic material because of the high energy release when combining with nanoaluminium [6]. Different approaches have been employed to synthesize 1D copper oxide. Xu *et al* manufactured CuO nanorods by thermal decomposition of CuC_2O_4 precursor [7]. Cu_2O nanowires were fabricated by reducing copper sulfate with hydrazine in a basic solution in [8]. Nanowires containing both Cu_2O and CuO were formed while Cu_2S nanowires were heated under oxygen at and above 300 °C [9]. Hsieh *et al* proposed a self-catalytic process for the growth of CuO nanofibre arrays [10]. Chen *et al* realized CuO nanobelts by immersing a copper foil into a water solution composed of NaOH and $(NH_4)_2S_2O_8$ [11]. Compared to the above-mentioned relatively complicated synthesis methods, a simple approach was demonstrated in [12], where CuO nanowires were prepared by directly heating copper substrates (foils, grids, and wires) in air.

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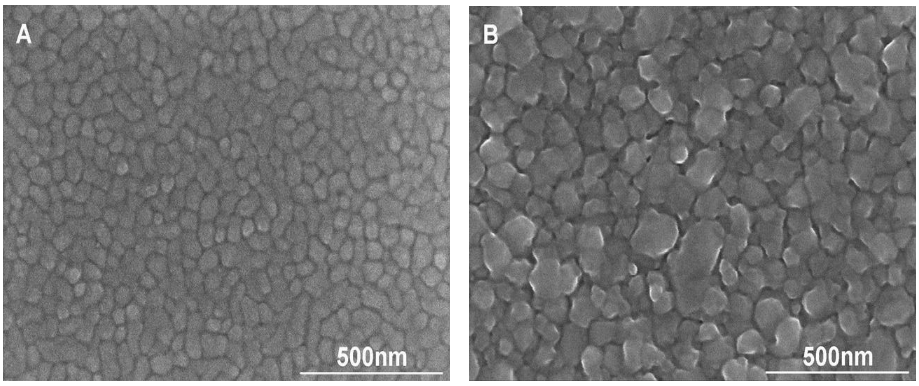

Figure 1. SEM images of the deposited 0.5 μm thick copper films onto silicon: (A) film from thermal evaporation and (B) film from electroplating.

Following this pioneering work, more studies were performed on growing CuO nanowires by annealing copper plates in air [13, 14]. Besides growing free-standing copper oxide nanowires or aligned nanowires on copper substrate, it will be interesting to realize aligned copper oxide nanowires on silicon substrate, that is a basic material for microelectronics and microsystems. This will therefore open the door to integrating the nanowires into microelectromechanical systems (MEMS), thus leading to nanobased functional structures, and, for instance, nanoenergetic material based high performance igniters as suggested in [15, 16].

According to previous investigations, it seems very difficult to grow aligned metal oxide nanowires from pure metal thin films just by thermal annealing as mentioned in [17, 18] and no approach is reported in the literature for growing aligned copper oxide nanowires on silicon substrate. In this study, we propose a simple process for growing large-area and aligned CuO nanowires by thermal annealing copper thin film deposited onto silicon substrate. We present the process optimization to overcome two well-known difficulties. The first one is the difficulty of getting large-area and uniform nanowire networks: the nanowires synthesized by annealing copper substrates appear to be straighter, much longer, and more uniform at the edges as compared with those formed in the inner areas [12]. Second, it is well known that thermal stress that might cause thin film cracks is one of the serious problems in the fabrication of thin film layered structures [19]. The experimental processes are first presented. Different parameters that affect the growth of CuO nanowires are studied. The nanowires realized are then characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and x-ray diffraction (XRD).

2. Experiments and results

Copper thin films are deposited onto silicon substrate by both thermal evaporation and electroplating. For the thermal evaporation, a 30 nm thick titanium film is first deposited onto silicon to serve as the adhesion layer, between copper and silicon. Then a 500 nm thick copper film is deposited onto the substrate. For the electroplating, a 30 nm titanium film is deposited onto silicon and this is followed by a 50 nm copper film deposition. The 50 nm copper film acts as the electrical conducting layer for the following electroplating. Copper films with the thicknesses of 500, 1000, and 1500 nm are then deposited by electroplating. All of the substrates are cut into small chips for subsequent processes. The chip is cleaned for 20 s in a solution composed of 10 ml HCl (37%) and 120 ml DI water. And then it is adequately rinsed with DI water and blow-dried with N_2. The chip is put onto a clean silicon wafer that is placed onto a quartz boat. The quartz boat is positioned in the centre of a quartz tube (100 cm in length, 17 cm in diameter) that is mounted in the middle of a horizontal tube furnace. Both static air and a N_2/O_2 gas flow are employed for the experiments. For static air, one end of the furnace is opened to the atmosphere in a class 100/1000 cleanroom. For the N_2/O_2 gas flow, a flow of high purity N_2 is first introduced into the quartz tube at a flow rate of 2000 sccm for 20 min to remove air from the system, and then this is adjusted to 200 sccm, accompanied by an O_2 flow at a rate of 50 sccm. The tube furnace is heated to the set-point temperatures (350, 400, 450, 500, 550, and 600 °C at atmospheric pressure). After being held at the set-point temperature, the O_2 flow is stopped with only N_2 being kept flowing. The system is allowed to cool naturally to room temperature to prevent the thin film from cracking, caused by thermal stress if the chip is directly taken out of the high temperature furnace. The chip is pulled out of the furnace for further analysis. The copper thin film surface is tarnished after the annealing both in static air and under a N_2/O_2 gas flow at elevated temperature. The as-prepared products on the silicon substrate are directly subjected to characterizations by SEM and XRD. For TEM and HRTEM observations, nanowires are manually separated from the silicon substrate, mixed with ethanol, and deposited onto carbon-coated copper girds.

2.1. Effect of the thin film deposition method

Figures 1(A) and (B) show the SEM images of the 0.5 μm thick copper thin films deposited onto silicon substrate by thermal evaporation and electroplating, respectively. As can be seen, the electrochemically deposited copper film is less compact compared to that deposited by thermal evaporation. The measured roughness of the electroplated copper thin film is of ±200 Å and the grain size is between 50 and 100 nm. The copper thin film deposited by thermal evaporation as shown is

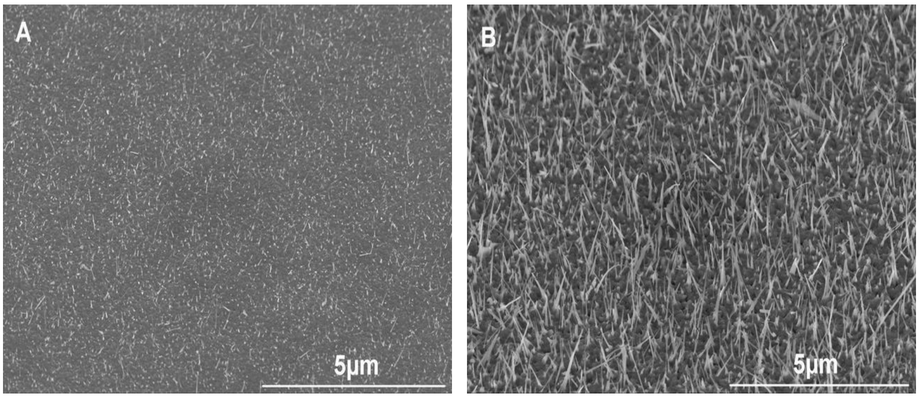

Figure 2. SEM images of the 0.5 μm thick copper films annealed in air at 500 °C for 4 h: (A) film from thermal evaporation and (B) film from electroplating.

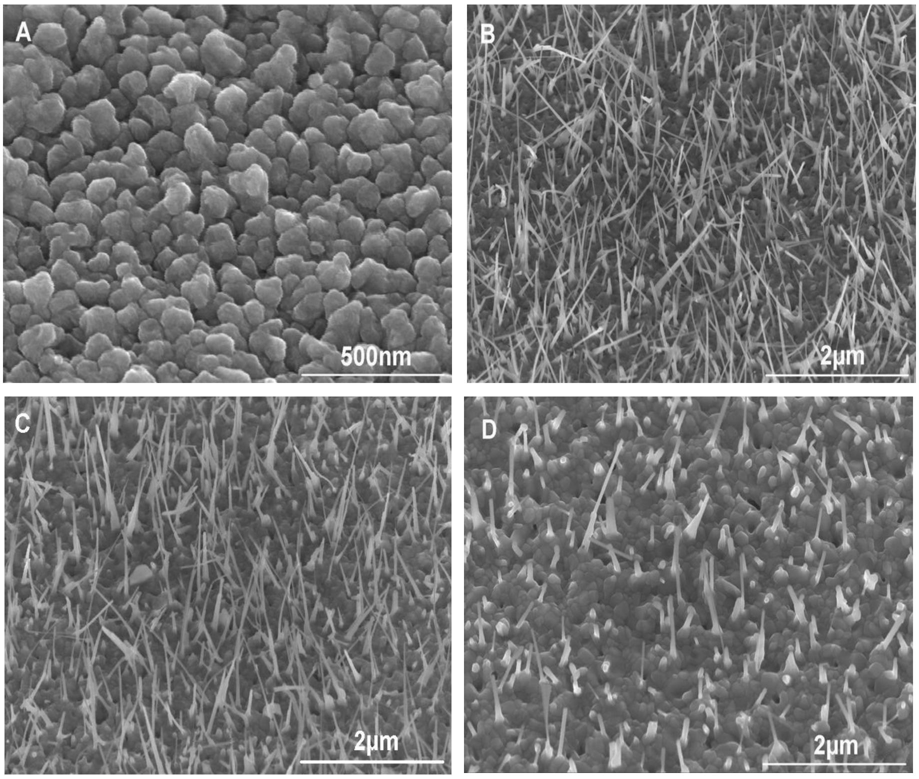

Figure 3. SEM images of the 0.5 μm thick electroplated copper film annealed for 4 h in static air at various temperatures: (A) 350 °C, (B) 450 °C, (C) 500 °C and (D) 550 °C.

denser and its measured roughness is of ±20 Å and grain size is about 20–50 nm.

Figures 2(A) and (B) show the 30° tilted view SEM images of 0.5 μm thick copper films after being annealed in static air at 500 °C for 4 h. For the copper thin film deposited by thermal evaporation (figure 2(A)), it can be seen that there is a very small amount of nanowire formed after the thermal treatment. However, as shown in figure 2(B), large amount, long and uniform nanowires are formed on the copper thin film deposited by electroplating after thermal annealing. We can conclude that the copper thin film surface morphology has a great effect on the growth of nanowires. The high porosity characteristic of the electroplated copper thin film is favourable for the growth of nanowires.

2.2. Effect of annealing temperature

Figures 3(A)–(D) show the 30° tilted view SEM images of the 0.5 μm thick electroplated copper film annealed for 4 h in static air at various temperatures. Long and uniform CuO nanowires with an average diameter of 40 nm can only be formed in a narrow temperature range from 400 to 500 °C (see figures 3(B) and (C)). When the temperature is equal to or lower than 350 °C, no nanowires are formed and the film surface is essentially coated with small particles as shown in figure 3(A). As the temperature is equal to or higher than 550 °C, there is a very small amount of nanowire formed as indicated in figure 3(D). We found that there is no relation between the nanowire diameter and the annealing temperature,

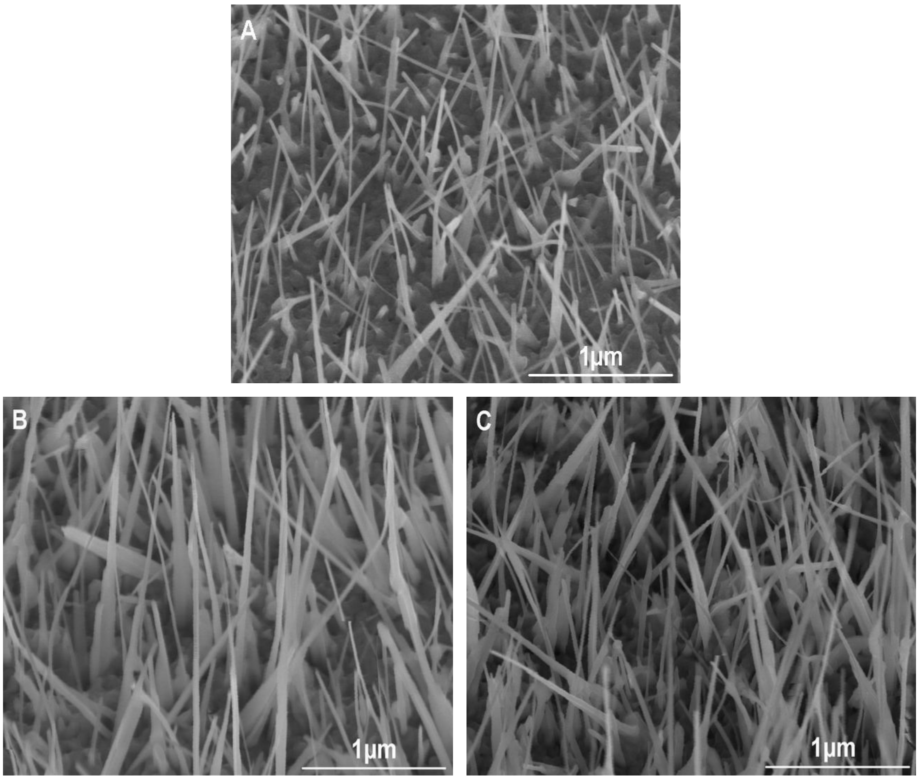

Figure 4. SEM images of the electroplated copper films annealed in air at 450 °C for 4 h: (A) 0.5 μm thick, (B) 1 μm thick, and (C) 1.5 μm thick.

whereas the authors of [12] observed that the diameter of the synthesized nanowires from copper substrates has a strong dependence on the annealing temperature. For the rest of the study, the annealing temperature will be set to 450 °C during 4 h.

2.3. Effect of thin film thickness

Figures 4(A)–(C) show the 30° tilted view SEM images of the copper films deposited by electroplating and annealed in static air at 450 °C for 4 h with different thicknesses of 0.5 μm, 1 μm, and 1.5 μm, respectively. The average diameters of the nanowires grown from 0.5 μm, 1 μm, and 1.5 μm thick copper thin films are 30 nm, 50 nm, 50 nm, respectively. Nanowires are less dense when the thin film thickness is 0.5 μm as compared to those formed when the thin film thicknesses are 1 and 1.5 μm. According to the experiments, thin films with the thickness of 1.5 μm are easier to crack than those with the thicknesses of 0.5 and 1 μm. Thick film will generate more thermal stress which is the main cause of the film cracking. In the rest of the study, 1 μm of copper thin film will be deposited by electroplating and annealed at 450 °C for 4 h.

2.4. Effect of annealing gas

As can be seen in figure 5, large-area and uniform nanowires are formed on the entire film surface after annealing the 1 μm thick electroplated copper film in static air at 450 °C for 4 h. Nevertheless, the as-prepared nanowires in static air are not well vertically aligned along the film surface. This is confirmed by the top view SEM image of the annealed copper film as shown in figure 6(A). For some applications, it is desirable to grow large-area, uniform, and vertically aligned CuO nanowires along silicon substrate—such as applications in field emission emitters [14] and realization of nano-CuO/Al based energetic materials [16]. That is why we propose to synthesize the CuO nanowires under a gas mixture flow of N_2 and O_2 to improve the alignment of the nanowires along the substrate surface. In the N_2/O_2 gas mixture flow, the O_2 concentration is set to be 20%, which is similar to that in air (21%).

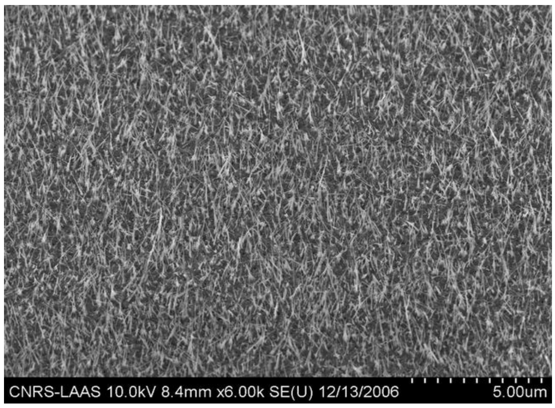

Figure 5. SEM image of the 1 μm thick electroplated copper film annealed in air at 450 °C for 4 h.

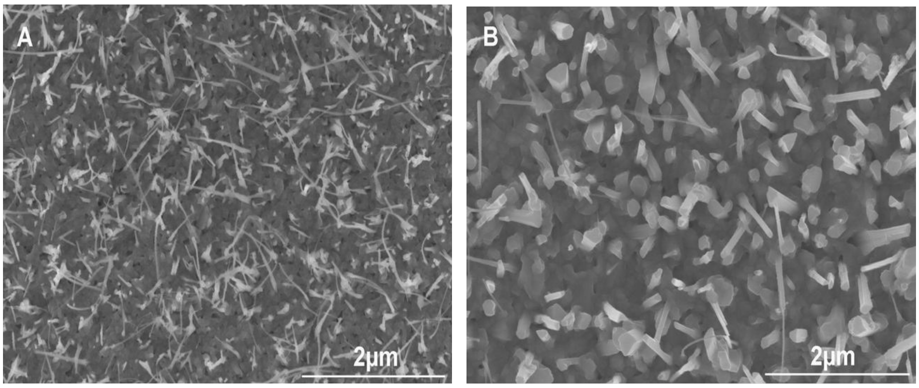

Figure 6. Top view SEM images of the 1 μm thick electroplated copper films annealed at 450 °C for 4 h: (A) in static air and (B) under a N_2/O_2 gas flow.

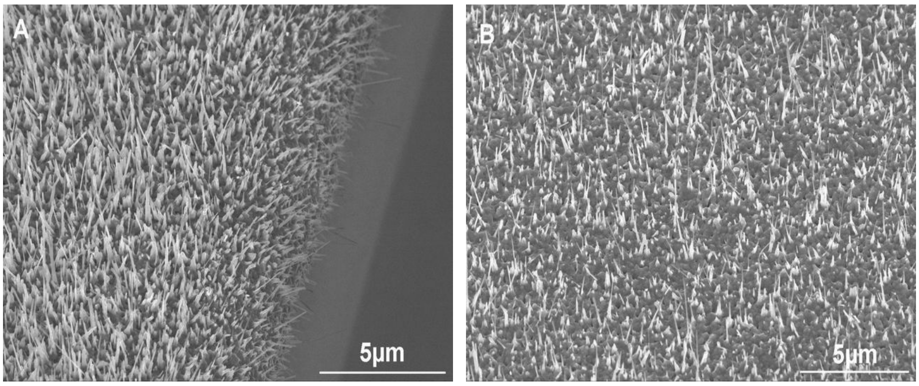

Figure 7. SEM images of the 1 μm thick electroplated copper film annealed at 450 °C for 4 h under a N_2/O_2 gas flow: (A) in film edge and (B) in film centre.

Figure 6(B) shows a top view SEM image of the 1 μm thick electroplated copper film annealed at 450 °C for 4 h in a gas mixture flow of N_2 (200 sccm) and O_2 (50 sccm). It can be seen that the resulting nanowires are mostly vertically aligned along the film surface. However, although large-area and vertically aligned CuO nanowires can grow from copper thin film on a silicon substrate under a N_2/O_2 gas flow as shown in figure 7(A), the nanowires are not uniform across the entire chip tested. Figure 7(B) is a 30° tilted view SEM image of the centre part of the same copper thin film. The nanowires appear to be longer and more uniform at the edges, as compared with those formed in the centre of the copper thin film.

2.5. *Effect of pattern by photolithography*

As mentioned in section 2.4, it is difficult to obtain large-area, vertically aligned, and also uniform nanowires. As a solution, we propose to create more edges on copper thin film by photolithography. Positive photoresist with a thickness of 2.7 μm is spin-coated onto silicon substrate and patterned using photolithography through a designed mask. A 30 nm thick titanium film is deposited onto the substrate and this is followed by a deposition of 50 nm thick copper film. Copper thin film with a thickness of 1 μm is then electroplated. After the deposition, metal Ti and Cu lift-off is performed in acetone with ultrasonics for 20 min. The silicon substrate with patterned copper thin film is cut into small chips for thermal annealing at 450 °C for 4 h under a N_2/O_2 gas flow. Figure 8(A) shows a 30° tilted view SEM image of the annealed 1 μm thick electroplated patterned copper thin film. It can be seen that large-area and uniform nanowires grow from the patterned copper thin film. Figure 8(B) is an enlarged view of the nanowires in figure 8(A). The diameters of the synthesized nanowires are in the range of 40–80 nm. A top view is shown in figure 8(C). As can be seen, most of the nanowires grow vertically along the patterned copper thin film surface.

2.6. *Solutions to thin film cracking*

As mentioned in the introduction, the high temperature annealing induced thermal stress might cause copper thin film cracks. The film cracks do occur in the early stage experiments as shown in figure 9(A). To reduce the film cracking, the film has been cooled down naturally to room temperature after the thermal annealing. Moreover, the patterning by photolithography helps in reducing the thin film stress by permitting stress release at the edges and therefore removes the cracking problem. Figure 9(B) shows a SEM image of the 1 μm thick electroplated patterned copper thin film annealed at 450 °C for 4 h under a N_2/O_2 gas flow. There is no crack in the patterned thin film after annealing.

In conclusion, the optimum process for growing large-area and uniform CuO nanowires is annealing 1 μm electroplated

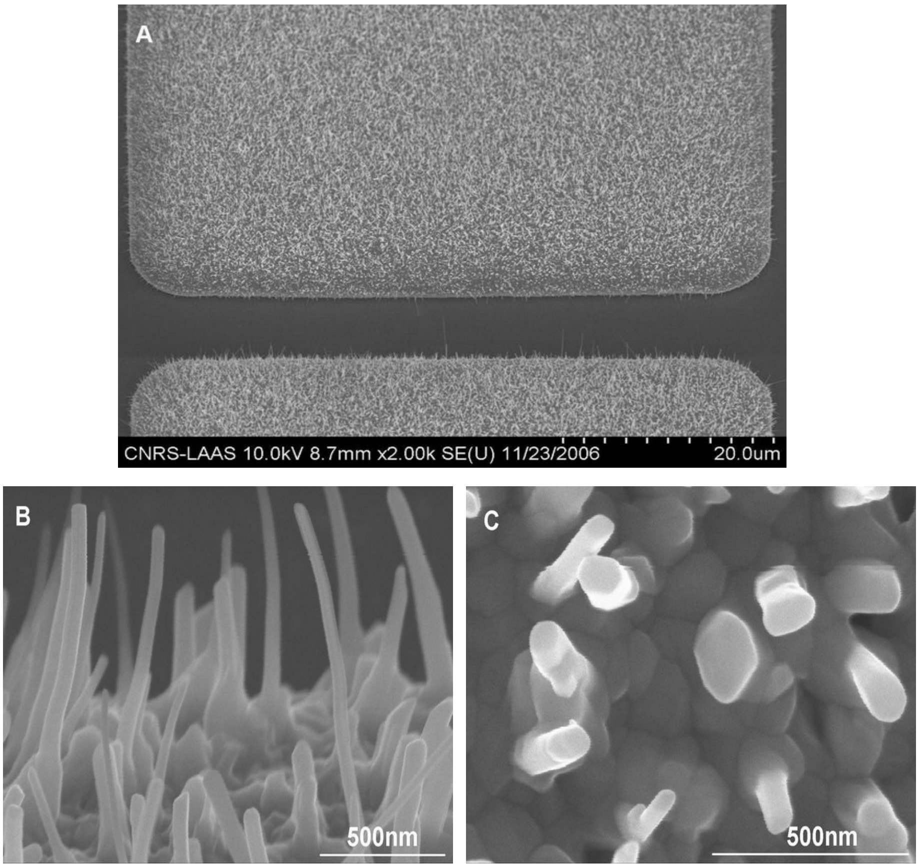

Figure 8. SEM images of the 1 μm thick electroplated copper film annealed at 450 °C for 4 h under a N_2/O_2 gas flow: (A) patterned film, (B) enlarged view, and (C) enlarged top view.

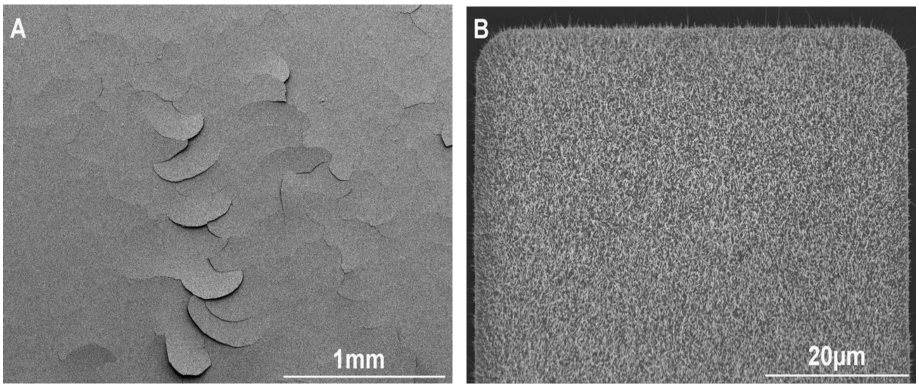

Figure 9. SEM images of the 1 μm thick electroplated copper film annealed at 450 °C for 4 h under a N_2/O_2 gas flow: (A) film without patterning and (B) patterned film.

copper thin film between 400 and 500 °C under a N_2/O_2 gas flow or in static air. The electroplated copper thin film can be deposited onto a silicon substrate and has to be patterned before annealing by photolithography to reduce film cracking.

2.7. TEM and HRTEM characterization

Figure 10(A) displays a TEM diffraction pattern of an individual nanowire from a 1 μm thick electroplated copper film annealed at 450 °C for 4 h in static air. It would be typically observed when the electron beam is focused on an individual nanowire along the [110] direction. The double diffraction is due to the twin plane within a nanowire. Figure 10(B) shows a HRTEM image of a nanowire. It can be seen that each side of the nanowire is a single crystal with a distinct fringe space pattern. The interplanar spacings for the two sides are 1.99 Å and 2.46 Å, which are similar to the spacings for {111} and {$\bar{1}$11} planes in monoclinic CuO [20]. This further confirms the bicrystallinity of the as-prepared nanowires.

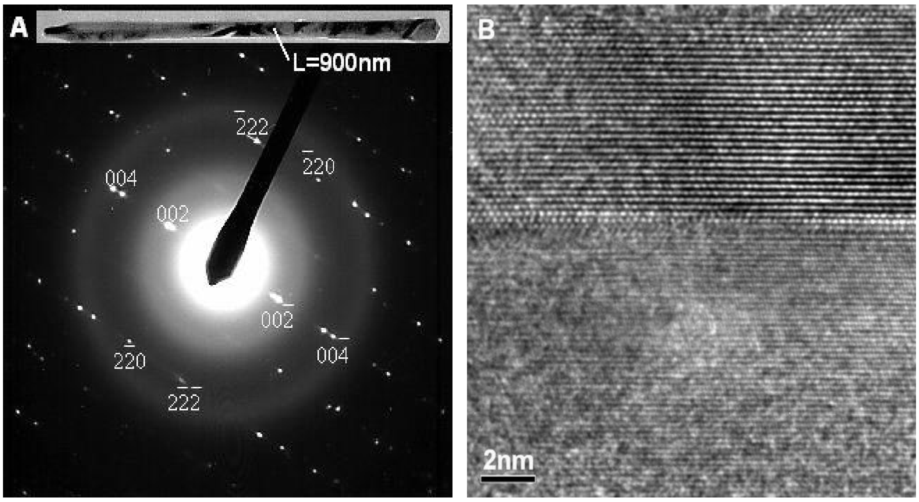

Figure 10. TEM and HRTEM images of an individual nanowire from the 1 μm thick electroplated copper film annealed at 450 °C for 4 h in static air.

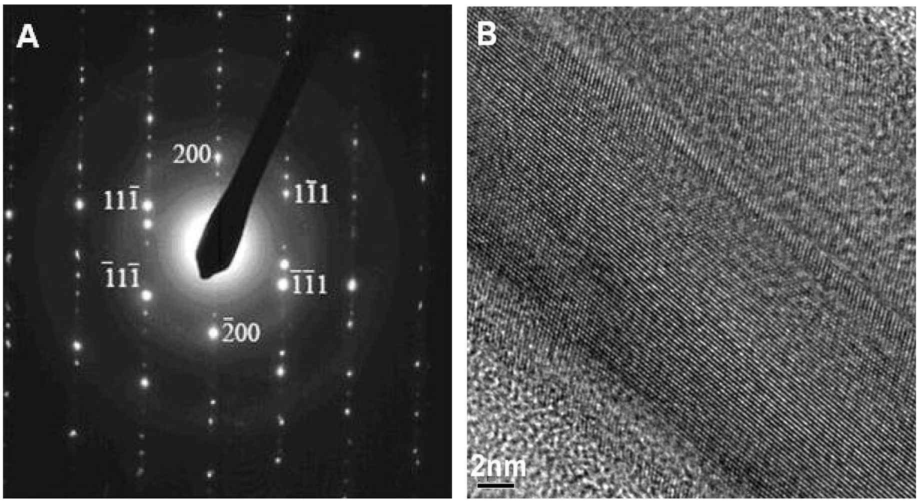

Figure 11. TEM and HRTEM images of an individual nanowire from the 1 μm thick electroplated copper film annealed at 450 °C for 4 h under a N_2/O_2 gas flow.

Figure 11(A) shows a TEM diffraction pattern of an individual nanowire from a 1 μm thick electroplated copper film annealed at 450 °C for 4 h under a N_2/O_2 gas flow. The electron beam is focused on an individual nanowire along the [011] direction. Similarly, the double diffraction is caused by the twin plane within the nanowire. Figure 11(B) is a HRTEM image of a nanowire that also confirms the formation of a bicrystalline structure within each nanowire. The interplanar spacings for the two sides are 1.98 Å and 2.35 Å.

2.8. XRD characterization

Figure 12 shows the XRD pattern of the 1 μm thick electroplated copper thin film annealed at 450 °C for 4 h in static air. As reported in [12, 13], both Cu_2O and CuO phases are present when copper substrates are annealed in static air. In this study, both Cu_2O and CuO are also observed as shown in figure 12. The deposited copper thin film is converted

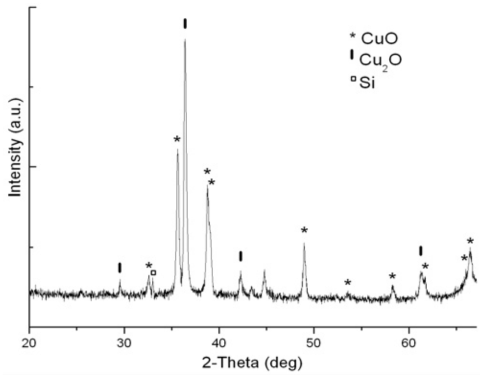

Figure 12. XRD pattern of the 1 μm thick electroplated copper film annealed at 450 °C for 4 h in static air.

into CuO nanowires, Cu_2O thin film, and also perhaps some CuO thin film. However, as shown in figure 13, only CuO

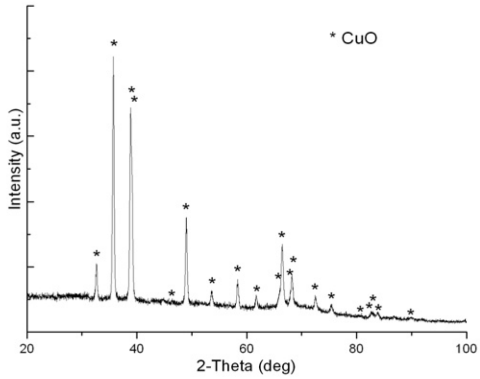

Figure 13. XRD pattern of the 1 μm thick electroplated copper film annealed at 450 °C for 4 h under a N_2/O_2 gas flow.

is observed after the 1 μm thick electroplated copper film is annealed at 450 °C for 4 h under a N_2/O_2 gas flow. The deposited copper thin film is all converted into CuO in the form of both nanowires and thin film. When static air is used, the O_2 concentration decreases locally with the reaction near the thin film surface because the oxidation rate is larger than the diffusion rate. Employing a N_2/O_2 gas flow one is able to keep a relatively high O_2 concentration near the film that helps to convert the entire copper thin film into CuO.

3. Conclusions

Large-area and aligned CuO nanowires have been successfully synthesized simply by thermal annealing of copper thin film (0.5, 1, 1.5 μm) electroplated on a silicon wafer. To get long and uniform CuO nanowires, the electroplated copper thin film has to be annealed in a narrow temperature range from 400 to 500 °C. Compared with annealing in air, annealing the copper thin film under a N_2/O_2 gas flow results in more vertically aligned nanowires along the film surface. But the as-prepared nanowires appear to be much longer and more uniform at the edge as compared with those formed in the centre. The patterning by photolithography not only can help grow large-area and uniform nanowires, but also can help to moderate the film cracking problem. Our experimental investigation concluded that the optimum thin film thickness is 1 μm for obtaining dense nanowires with the average diameters of 30–60 nm in static air and 40–80 nm under a N_2/O_2 gas flow. TEM, HRTEM, and XRD results show that the copper thin film is converted into bicrystal CuO nanowires, Cu_2O thin film, and also perhaps some CuO thin film when annealing in static air. Only CuO in the form of bicrystal nanowires and thin film is observed after the copper thin film is annealed under a N_2/O_2 gas flow. The method developed in this study is MEMS compatible, low cost and easy synthesis of ordered nanowires of copper oxide on silicon substrates. We anticipate that this method could be employed to grow other metal oxide nanowires. This will probably open the door to integrating the nanowires into MEMS, thus leading to nanobased functional structures.

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