

21 Copper Nanowires Prepared by the Treatment of the Cu₂S Nanowires in a Radio-frequency Hydrogen Plasma

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1 INTRODUCTION

The coinage metal nanostructured materials have been a research focus in recent years due to their potential applications in micro-electronics fabrication, biotechnology, and catalysis (Whetten, 1999). As one of the most abundant coinage metal on the earth, copper has been extensively used in chemical and biological industries. Copper nanoparticles have also attracted much attention after their successful preparation using colloidal and other methods. Here we report a novel method for the preparation of copper nanowires. Our synthetic method uses the straight and uniform nanowires of Cu₂S as a template. By treating the Cu₂S nanowires in a radio frequency (RF) hydrogen plasma under appropriate conditions, the sulphur atoms are removed as a H₂S gas, leaving behind the copper atoms in the as-prepared Cu₂S nanowires, eventually forming copper nanowires.

2 EXPERIMENTAL SECTION

The copper sulphide nanowires with a diameter of ~60 nm were prepared using the procedure reported previously (Wang, 2000). Briefly, a copper substrate surface was exposed to a mixture of hydrogen sulphide and oxygen with a molar ratio of ~2 at room temperature. The gas-solid reaction lasted for 8 h. The Cu₂S nanowire samples were transferred onto a silicon slide, which was then placed in a hydrogen plasma generator of a RF plasma asher system (Model PE-120, Denton) (Wang, 2001). The total gas pressure (95% He and 5% H₂) was kept at 500 mtorr during the reduction process. After the hydrogen plasma treatment, the samples were quickly transferred into a glass container filled with argon to avoid oxidation. The copper nanowire samples were then stored for SEM, EDX, and TEM measurements. The SEM and EDX measurements were performed on a Joel 6300 instrument, with an operating voltage of 20 kV. The TEM images and electron diffraction patterns were recorded using a Philips CM20 instrument, with an operating voltage of 200 kV.

3 RESULTS AND DISCUSSION

Shown in Figure 1 are typical SEM images of the samples. Overall, the wire morphology is preserved after the conversion from Cu_2S to Cu. However, the surfaces of the nanowires became rough due to the abstraction of S by H atom in the RF hydrogen plasma. The roughness of the Cu nanowires thus obtained is dependent on the forward RF power of the hydrogen plasma. At high forward powers (e.g., 25-30 W), Cu_2S nanowires were etched rapidly and even many holey features in the copper wires can be clearly seen (Figure 1A). When the RF forward powers of the hydrogen plasma are relatively low (e.g., 10 W), however, the shape of the nanowires is better preserved after the transformation from Cu_2S to Cu. Even after the low power RF hydrogen plasma treatment, the surface of the nanowires is still somewhat rough (Figure 1B). This can be attributed to the S-abstraction reaction itself and to the plasma etching effect on the surface of the nanowires. Therefore, in order to produce high quality Cu nanowires from Cu_2S , one should use a low forward power of the RF hydrogen plasma, and correspondingly, a longer RF hydrogen plasma treatment time to ensure a complete conversion from Cu_2S to Cu. It is noteworthy from Figure 1 that the Cu nanowires are significantly thicker than the original Cu_2S nanowires. In addition, the thickness appears to increase with the increasing RF forward power of the hydrogen plasma. This can be partially explained by the porous nature of the Cu nanowires. As will be shown below, the Cu nanowires are actually polycrystallites, and this also causes the thickening of the Cu nanowires.

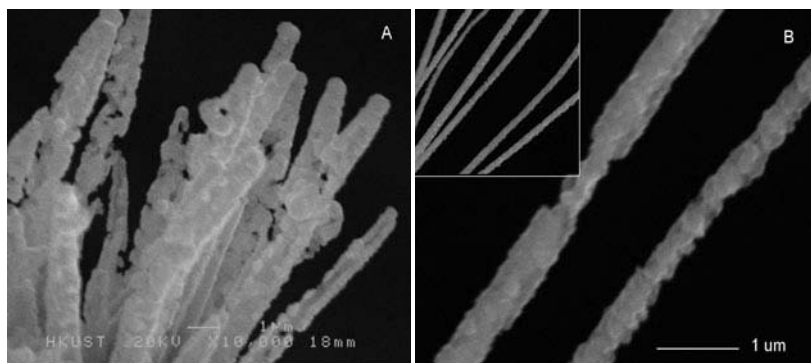


Figure 1 SEM images of the Cu nanowires produced from the reduction of Cu_2S nanowires under different R.F. hydrogen plasma conditions. The reduction time and the forward RF power are (a) 1 hour and 25-30 W, and (b) 2 h and ~10 W, respectively.

Figure 2 shows the EDX spectra of the Cu nanowire samples corresponding to the SEM images in Figures 1A and 1B, respectively. Clearly, no sulphur signal was detected in the sample after treatment at a high RF hydrogen plasma power (e.g., 25-30 W) for ~1 hour (Figure 2A). This indicates that nearly all the Cu_2S nanowires have been reduced to Cu through the reaction: $\text{Cu}_2\text{S} + 2\text{H} \rightarrow \text{Cu} + \text{H}_2\text{S}$. The generated gaseous H_2S was carried away by helium through pumping. However, when the sample was treated for 2 h at a low RF hydrogen plasma forward power (e.g., 10 W), sulphur, although depleted significantly, was still

detected (Figure 2B). Note that oxygen was detected from both samples treated with the RF hydrogen plasma. The oxygen can be attributed to copper oxides on the surfaces of these Cu nanowires, which are probably due to the oxidation by air during the transfer from the RF plasma generator to the sample preparation container for the EDX measurement. The existence of the copper oxides is understandable given the fact that the reduced atomic Cu nanowires are expected to be highly sensitive to oxygen and it is very difficult to avoid even a trace amount of O₂ during the sample transfer.

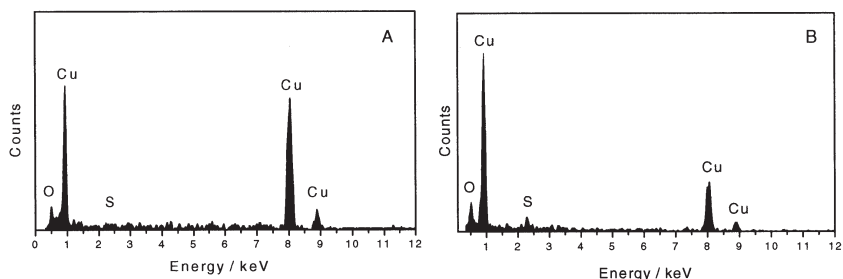


Figure 2 EDX analysis performed with the Cu wire samples treated under different RF hydrogen plasma conditions. The reduction time and the RF forward power are (a) 1 hour and 25-30 W, and (b) 2 h and ~10 W, respectively.

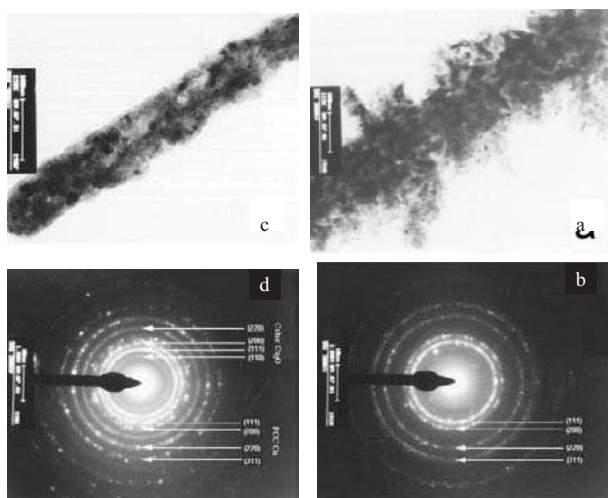


Figure 3 TEM images and selected area electron diffraction patterns of the Cu wires. (a) and (b) were taken from the fresh sample. (c) and (d) were taken from the sample after exposure to air for 24 h. The samples were prepared with a reduction time of 1 h and a forward RF power of 10 W.

TEM images of the Cu nanowires were taken both immediately after preparation and after exposure to air for 24 h (Figures 3a and 3c). The corresponding selected area electron diffraction patterns are presented in Figures 3b and 3d, respectively.

These Cu nanowires were obtained after treatment in the RF hydrogen plasma (10 W) for 1 h. It can be seen clearly from Figure 3 that the Cu nanowires are polycrystalline and consist of many small Cu particles with an average diameter of ~7 nm. The polycrystalline electron diffraction rings of the Cu wires can be attributed to the fcc structure of bulk copper (Figures 3b and 3d). For the fresh copper nanowire sample, the diameter seems to be larger and many Cu nanoparticles stick out from the wire surface (Figure 3a). When exposed to air, the Cu wires were oxidised and fcc Cu₂O nanoparticles were formed on the copper wire surfaces, as shown by the electron diffraction pattern in Figure 3d. In addition, the Cu wires became thinner and more compact (Figure 3c). This is because the fresh Cu particle aggregates on the Cu wire are fluffy (Figure 3a), but they shrank towards the Cu wire surface during the oxidation reaction, making the Cu wire structure more compact (Figure 3c).

The conversion of Cu₂S to Cu is realised by the surface reactions with the reductive species H⁺, H₂⁺, H₃⁺, H as and H in the RF plasma, which extract S to form H₂S. An analogous approach for the reduction of copper oxide films to Cu films has been reported recently (Sawada, 1999). Considering the etching effect on the surface of Cu₂S nanowires, the formation of the sponge-like Cu nanowires after the RF hydrogen plasma treatment is understandable.

4 SUMMARY AND CONCLUSIONS

In conclusion, we have demonstrated a novel method for the preparation of copper nanowires by using the straight and uniform nanowires of Cu₂S as a template. Our approach involves the extraction of the sulphur atoms from Cu₂S under a reductive atmosphere of an RF hydrogen plasma. The surface morphology of the copper nanowires could be controlled by varying the RF hydrogen plasma conditions. Owing to the etching effect of the plasma on the nanowire surfaces, a sponge-like Cu nanowires were formed after the reductive treatment. These metallic nanowires are expected to have large surface areas, a feature that is important for many practical applications such as in catalysis.

ACKNOWLEDGEMENT

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