Fabrication of copper nanowires using overpotential electrodeposition and anodic aluminium oxide template

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Overpotential is widely used in electrodeposition of copper nanowires (Cu NWs). However, the value of >2 is harmful for nanowires formation. In this reported study, pulse technology is used to solve the problem. The authors have investigated the effects of potential and voltage mode on the formation of Cu NWs via a porous anodic aluminium oxide template using the electrochemical deposition method. Cu NWs were synthesised by electrochemical deposition in 0.2 M $CuSO_4$-based solution under different potential modes of direct current (DC) and pulse. Scanning electron microscopy and grazing incidence X-ray diffraction were used to examine the nanostructure, morphology and phase of Cu NWs. The Cu NWs deposited by pulse mode exhibited a high aspect ratio despite a high potential of 2–3 V, whereas that at higher DC potential was rather short because of hydrogen generation in reduction reaction. The hydrogen byproduct during Cu NWs synthesis can be effectively released at the off period of pulse deposition for good nanowires formation.

1. Introduction: Nanostructured copper materials have attracted much attention because of their good ductility, electrical conductivity and heat conductivity which can be used for various applications such as field emitters [1], current collectors for Li ion batteries [2], electrostatically dissipative devices [3], wire-grid polarisers [4], cooling devices [5] and interconnects [6]. Although several techniques such as photolithography and etching can fabricate these one-dimensional nanostructures, the template-assisted deposition method [7, 8] is considered one of the most prominent methods because of the advantages of controllable diameter, high aspect ratio, being economical and large area. In general, anodic aluminium oxide (AAO) films [9, 10] and polycarbonate membranes [11, 12] were commonly used as templates for manufacturing micronanostructures. Compared with polycarbonate membranes, the AAO templates show better material properties in nanopore density, arrangement, mechanical strength and chemical stability. Therefore copper nanowires (Cu NWs) deposited by an AAO template can provide promising applicability in devices. The reduction potential of Cu has been reported to be 0.099 V for a standard calomel electrode (SCE) [9]. However, overpotential was widely used in the deposition of Cu NWs. Gao *et al.* [13] reported that low overpotential from −0.15 to −0.45 V (SCE) benefited to form single-crystal Cu NWs and avoided the formation of copper oxide. Xue and Wang [14] also found that increasing applied potential to 1.8 V could increase growth rates of copper nanostructures. To our best knowledge, it has not been reported that overpotential is >2 V because the overpotential also causes production of hydrogen gas [15]. In addition, Inguanta *et al.* [16] reported DC mode deposited Cu NWs had high growth rates but less uniform lengths than those by pulse mode. In contrast, square pulse deposition mode produced lower growth rates but quite uniform lengths at −0.3 to −0.6 V (SCE). In this Letter, we focus on the comparison of DC and pulse deposition at specific higher overpotential of −1 to −3 V (SCE). The pulse electrochemical deposition with a period of zero potential is expected to solve the hydrogen problem. The Cu NWs were deposited in 0.2 M $CuSO_4$-based solution at a room temperature of 25°C. The effect of the magnitude of applied potential and duty ratio on crystallinity has been investigated. Scanning electron microscopy and grazing incidence X-ray diffraction were employed to analyse Cu NWs. The nanostructure, morphology and phase of Cu NWs are discussed and correlated.

2. Experimental procedures: The commercial AAO template (Whatman Anodisc, England) with pore diameter of about 200 nm and thickness of 60 μm was used for electrochemical deposition. The AAO template was pre-evaporated with silver for the conductive layer. The AAO template was cut into pieces of 0.9 × 0.9 cm in size and then it was mounted onto a copper foil. The electrolyte was prepared by 0.2 M $CuSO_4$ and 0.2 g/l sodium dodecyl sulphate. Before electrochemical deposition, the sample was immersed into the electrolyte for 30 min. Electrochemical deposition experiments were performed by DC and pulse modes at 25°C for 30 min. The experimental parameters were 1–3 V in DC mode. At pulse mode, the period of the pulse was 2 s. The duty cycle ($t_{on}/t_{on} + t_{off}$) is 25–75%. The applied potential was fixed at 1–3 V during the t_{on} period, whereas it was 0 V during the t_{off} period. All deposition conditions are listed in Table 1. The electrochemical deposition was performed by means of a potentiostat (Jiehan 5000, Taiwan) and the three-electrode electrochemical cell with copper foil as the working electrode, copper foil as the counter electrode and SCE as the reference electrode. After electrochemical deposition, the sample was immersed into 5 M NaOH for 20 min to remove the template. The morphology of the Cu NWs was examined by high-resolution field emission scanning electron microscopy (SEM) (JEOL, JSM-7000F, Japan). The crystal structure of the Cu NWs was investigated by a thin film X-ray diffractometer (D8 Discover, Germany). Diffractograms were obtained in the 2θ range from 20° to 80° with a scan rate of 3°/min.

3. Results and discussion: Fig. 1 shows the SEM micrographs of Cu NWs formed at 1 V by DC and pulse electrodepositions with different duty ratios for 30 min. From Fig. 1*a*, it is indicated that the Cu NWs could grow from the silver layer at DC 1 V successfully and the length of the NWs is 28.4 ± 4.2 μm. The calculated aspect ratio can reach 142 based on a pore size of 200 nm. The very high aspect ratio of the Cu NWs results in the aggregation phenomenon. Compared with DC deposition, the length of a Cu NW by using pulse potential reduces with decreasing duty ratio. The values are 26.8 ± 2.4 μm for the duty

Table 1 List of deposition parameters of Cu NWs and their corresponding measured length and aspect ratio

| Mode	Potential, V	Duty ratio, %	Time, min	Length, μm	Aspect ratio
DC	1	–	30	28.4 ± 4.2	142
DC	2	–	30	1.0 ± 0.2	5
DC	3	–	30	0.6 ± 0.1	3
pulse	1	75	30	26.8 ± 2.5	134
pulse	1	50	30	25.1 ± 2.8	125.5
pulse	1	25	30	14.7 ± 2.4	73.5
pulse	2	50	30	31.6 ± 4.2	158
pulse	3	50	30	22.7 ± 4.3	113.5
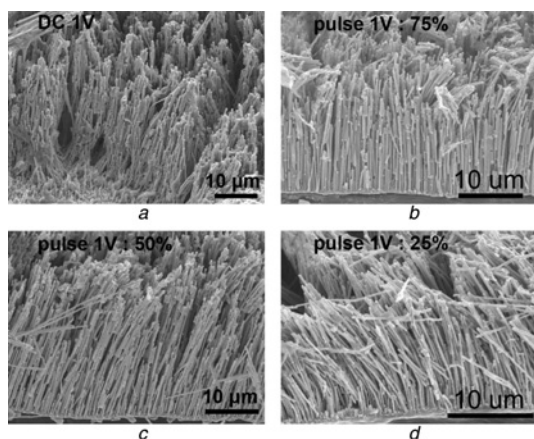
Figure 1 SEM micrographs of Cu NWs for 30 min at 25°C at applied negative potentials
a DC 1 V
b Pulse 1 V with duty ratio of 25%
c Pulse 1 V with 50% duty ratio
d Pulse 1 V with 75% duty ratio

ratio of 75%, 25.1 ± 2.8 μm for 50% and 14.7 ± 2.4 μm for 25%, respectively. On considering DC deposition at a duty ratio of 100%, it is revealed that the decrease of length at 1 V with decreasing duty ratio is attributed to the shorter total working time. However, the growth rate in pulse deposition reached 94, 88 and 52% of the one in DC when the duty ratio is 75, 50 and 25%, respectively. This result reveals high efficiency in pulse deposition. Fig. 2 shows the grazing incidence x-ray diffraction (GIXRD) patterns of Cu NWs deposited at 1 V with different pulse duty ratios. The strong intensity of the peaks at 43.3° are from the Cu(111) plane together with other two distinct peaks Cu (200) and Cu(220) at ∼50.4° and 74.1°. The diffraction peaks around 38° are because of the silver seed layer. The peak intensity increases with increasing duty ratio. It can be attributed to higher wire lengths at high duty ratio. However, it is noted that there is an increase of the intensity of copper oxide at the duty ratio of 75%. In the literature, a similar oxidation situation has occurred in DC deposition at very low potential [13]. At the high duty ratio, the formation of CuO happens during Cu NWs growth. It suggests that it is better that the duty ratio is <75% for fabricating pristine Cu NWs with a high aspect ratio. Considering the good deposition efficiency, a duty ratio of 50% is preferable to 25% at higher potentials of 2–3 V.
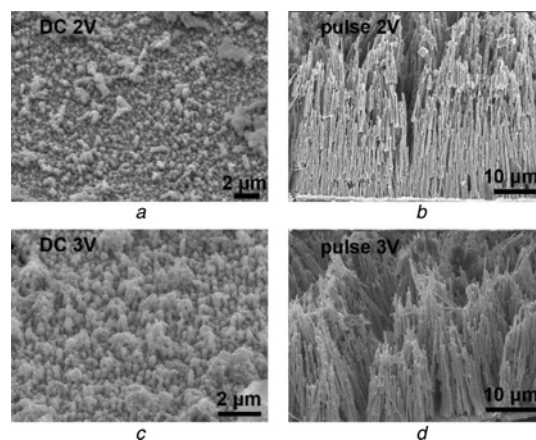
Fig. 3 shows SEM micrographs of Cu NWs by DC and pulse mode with the duty cycle of 50% for 30 min at 25 °C at high over-potentials of 2 and 3 V. In contrast to 1 V in DC deposition, Cu NWs deposited at 2 and 3 V (Figs. 3a and c) seem extremely short. The estimated lengths are 1.0 ± 0.2 μm and 0.6 ± 0.1 μm,
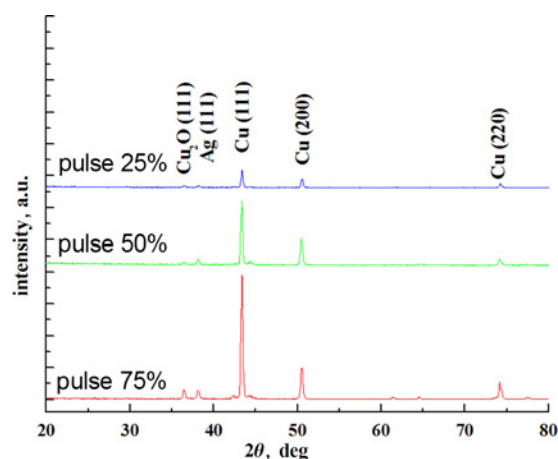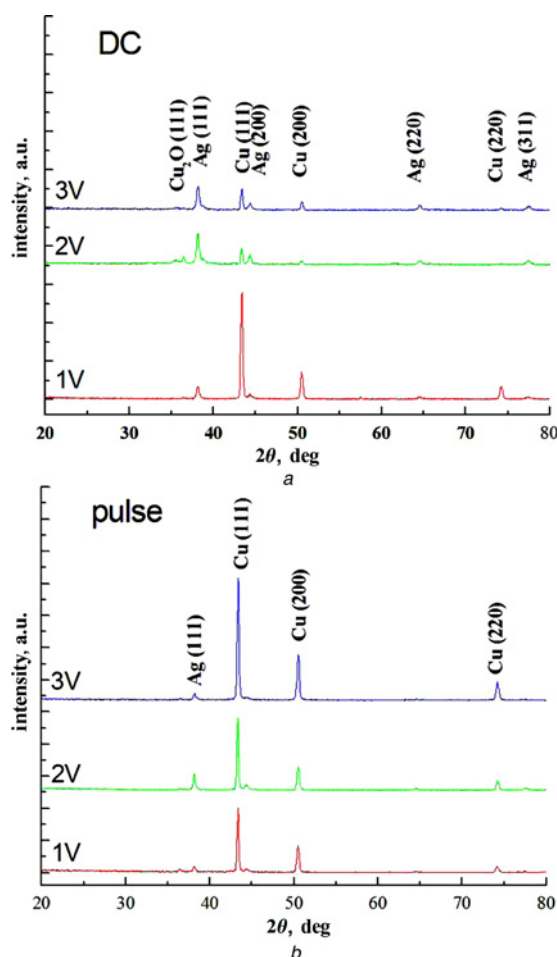

Figure 2 GIXRD patterns of Cu NWs deposited by pulse mode with duty ratio of 25–75% for 30 min at 25°C

respectively. Regarding the literature, a lot of hydrogen is produced in higher overpotential [15]. When the applied potential is larger than 1 V, a greater amount of hydrogen hinders copper ions from migrating from the surface into the nanopore of the AAO. Therefore the growth of Cu NWs in DC mode is inhibited. This is because overpotential should not be too large in the growth of Cu NWs. On the other hand, it is significant that the Cu NWs were successfully grown at high applied potential in pulse mode. The lengths of Cu NWs by pulse mode at 2 and 3 V are 31.6 ± 4.2 and 22.7 ± 4.3 μm, respectively. During the t_{off} period (0 V), excess hydrogen can be released so that the copper ion can migrate into the nanopores. Moreover, the t_{off} period is helpful for the diffusion of copper ion. When increasing applied overpotential, the reaction rate of copper ions to nanowires also increases. Therefore the length of Cu NWs at the potential of 2 V is relatively long. However, the length of Cu NWs at the potential of 3 V decreases. It is probably because of more excess hydrogen produced to diminish the migration of copper ions into the nanopore bottom.

Figs. 4a and b show the GIXRD patterns of Cu NWs deposited at 1, 2 and 3 V by DC and pulse depositions for 30 min at 25°C, respectively. It is seen that the intensity of copper oxide is not obvious at large overpotential. From Fig. 4a, it is indicated that Cu NWs at 1 V preferentially grow along the (111) plane. However, the Cu(111) peak intensity of Cu NWs at DC 2 and 3 V

Figure 3 SEM micrographs of Cu NWs by DC and pulse mode with duty cycle of 50% for 30 min at 25°C at applied negative potential
a DC 2 V
b Pulse 2 V
c DC 3 V
d Pulse 3 V

Figure 4 *GIXRD patterns of Cu NWs deposited by DC (Fig. 4a) and pulse mode for 30 min at 25°C at duty cycle of 50% at potentials of 1–3 V (Fig. 4b)*

is very weak compared with that at DC 1 V which is much longer than at DC 2 and 3 V. Therefore Cu(111) intensity at 1 V is much higher than the other two potentials. From Fig. 4*b*, it is revealed that preferential growth of Cu NWs is also along the Cu (111) plane. Cu (111) peak intensity increases with increasing potential. Compared with the above-mentioned results, the increase of intensity at the 3 V sample may not be attributed to the length of nanowires but better crystalline. This result implies that higher overpotential could enhance crystallinity because of the higher growth rate of grains than the nucleation rate. Therefore Cu(111) peak intensity is strong at the 3 V potential.

4. Conclusion: Pristine Cu NWs arrays with a high aspect ratio have been fabricated successfully via an anodic alumina template by pulse electrodeposition with a duty ratio of 50%. The length of Cu NWs at higher DC potential of 2 and 3 V is extremely short because of generated hydrogen in reduction reaction to hinder copper ion migration into porous alumina. That is, the depletion rate of copper ions is faster than the rate of mass transfer. In contrast, the pulse mode provides an idle period during electrodeposition, therefore hydrogen can be released from

nanopore channels for good nanowires formation. Higher pulse potential can promote growth of Cu NWs for prolonged Cu NWs and enhanced crystallinity. It has been found that pulse mode is a promising technology compared with DC mode for the efficiency of nanowires synthesis using an AAO template at high potential.

6 References

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