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Long Silver Nanowires Synthesis by Pulsed Electrodeposition

Silver nanowires were pulse electrodeposited into nanopore anodic alumina oxide templates. The effects of continuous and pulse electrodeposition waveform on the microstructure properties of the nanowire arrays were studied. It is seen that the microstructure of nanowire is depend to pulse condition. The off time duration of pulse waveform enables to control the growth direction of Ag nanowires.

Keywords: *nanoporous alumina, pulse electrodeposition, silver nanowire.*

1. Introduction.

One-dimensional nanostructures have attracted extensive attention because of their unique physical and chemical properties [1] and the potential applications in nanoscale devices [2]. Controllable growth of nanostructures is of great importance for the application of nanostructures [3], [4]. The template method has proved to be a simple and versatile approach for preparing ordered nanowire or nanotube arrays since the pioneering work of Martin's group [5-7]. Possible templates include nuclear track-etched polycarbonate membranes, nanochannel glasses and self-ordered anodic aluminum oxide templates. It has been found the porous anodic alumina (PAA) template is an ideal template because it posses many desirable characteristics, including tunable pore dimensions over a wide range of diameters and lengths, good mechanical strength and thermal stability.
Electrodeposition, on the other hand, is one of the most widely used methods to fill the nanoporous template with conducting and semiconducting materials, forming continuous nanowires. Among all the metals, silver is particularly important as it possesses the highest electrical conductivity and promising potential applications in many fields, such as catalysts and electronic nanodevices [8–11]. This pattern of electrodeposition is a promising technique for fabricating nanostructures in a 'bottom-up' fashion [12].

Electrodeposition using an PAA template has been employed to fabricate silver nanowire arrays, and various other techniques such as DC deposition [13], AC deposition [14], cyclic voltammetry [15], pulsed deposition [16] and galvanostatic deposition [17-18] have been used. However, the preparation of long and continuous silver nanowires (with high aspect ratios, and with well controlled morphology and microstructures) still remains a great challenge to material scientists.

In this work Ag nanowire arrays were ac (pulse) electrodeposited into the long PAA nanostructure fabricated by hard anodization of Aluminum. The microstructures properties of the nanowires as a function of waveform in the pulse electrodeposition were investigated.

2. Experimental

Samples with a radius of 12mm were cut from a high purity foil of aluminum (99.999% purity, 0.25mm thickness), degreased in acetone, and washed in deionized water. Before anodization, the aluminum was electropolished at a constant voltage (20V) in a 1 : 4 volume mixture of perchloric acid and ethanol to diminish the roughness of the aluminum foil surface. Before the hard anodization (HA) process, at first we need to create a protective layer against burning the sample at high voltage and current so the procedure was started by mild anodization (MA) at 40V for 10 minutes. The anodization process was switched from MA to HA by increasing the anodization voltage slowly [19]. The anodization voltage was increased to a final value and kept constant. During the MA and HA processes the electrolyte temperature of all the samples was kept constant at 0 ˚C. When the current density reaches to the steady state, the anodization procedure was continued by thinning process.

Following the hard anodization, voltage was reduced systematically to promote thinning of the barrier layer. To do this, a programmable power supply was employed. The thinning voltage was adjusted according to an exponential equation as follows:

$$V_{thin=}V_{hard}\ e^{-\eta t}$$

in which: η is a constant that controls the rate of reduction of voltage; V_{thin} and V_{hard} are thinning voltage and anodization voltage in hard anodization step (130V), respectively. Accordingly, a η equal to $0.0015s^{-1}$ was employed and the thinning voltage stopped at 12V. The voltage, current and thinning process as functions of time are displayed in figure 1.

The anodized aluminum is then placed in a suitable electrolyte consisting of 25gr/l $AgNO_3$ with 40 gr/l H_3BO_3, that one desired to deposit. Alternating voltage is imposed between PAA template with Al plate as working electrode and graphite as counter-electrode at room temperature. Because PAA template conducts preferentially in only one direction (the cathodic direction), it is called a " valve metal oxide". Silver metal ions are reduced to zero-valent metal within the nanopores of

template during the chathodic half cycle of the imposed ac signal, but are not re-oxidized in the anodic half cycles. Moreover, the electric fields are greater near the pores base. Hence silver growth begins there and the pores fill from the bottom up, in this way the Ag nanowire arrays are produced.

Pulse ac electrodeposition was carried out with 18/18 V reductive/ oxidative voltage, using sine waveform. The reductive/oxidative time equal to 5ms with various off-time between pulses (t_{off} =0, 25, 50, 100 ms) were considered. A typical diagram of pulse employed in this work is shown in figure 2. For a meaningful comparison of the effects of off-time between pulses on the crystal structure, the nanowire length should be identical for samples made under differing off-time. This requirement is easily archived by controlling the magnitude of charge passed during electrodeposition, since the nanowire diameter is dictated by the predetermined pore size. Scanning electron microscopy (SEM) was used to investigate the morphology of the samples. The crystal structure of the Ag nanowire arrays was examined by x-ray diffraction (XRD).

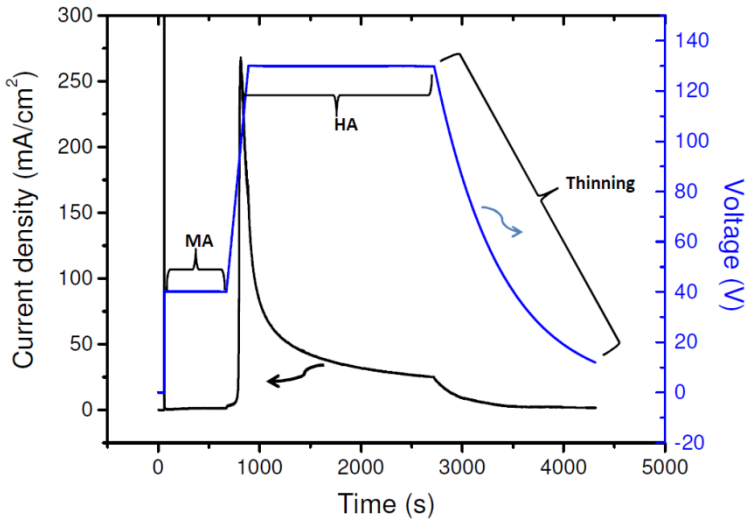

Figure 1. Voltage, current and thinning-time curves of sample made in 0.3 oxalic acid.

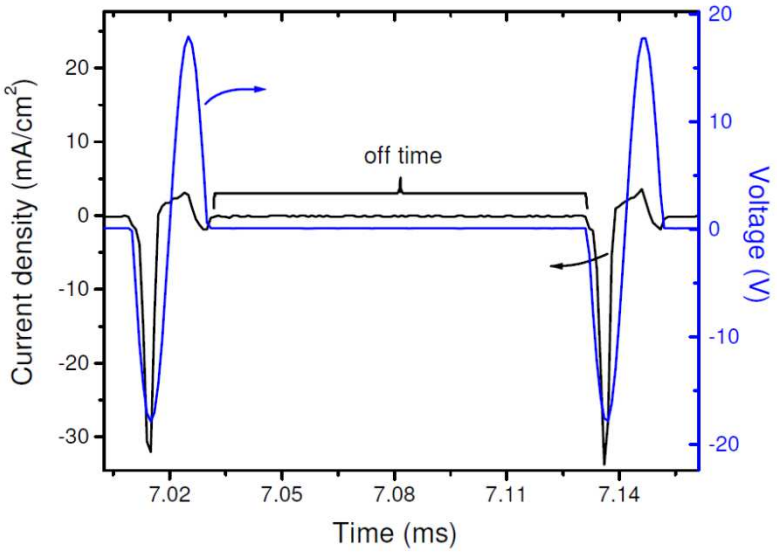

Figure 2. Current and voltage curves as a function of time in deposition process.

3. Result and discussion

Our Purpose here is to fabricate high aspect ratio Ag nanowire. For this purpose alumina nanostructure was fabricated by using hard anodization process. Figure 3(a ,b) shows the bottom view and cross-section SEM micrographs of PAA after hard anodization step. As seen in this figure hexagonal self-assembled nanopores were formed with 60 nm diameter and 260 nm inter-pore distances. After the HA process, for AC electrodeposition it is needed to decrease the barrier layer thickness. According to linier relation between barrier layer thickness and anodization voltage, it is possible to decrease the barrier layer thickness by gradually decreasing the anodization voltage, this procedure is named thinning [20]. By decreasing the voltage, the current density decreases as it is seen in figure 1. During the thinning process we increase the electrolyte temperature from 0 to 17 ˚C to prevent of rapid decreasing of anodization current. Moreover we decrease the rate of voltage reduction in lower voltage to control the current density as it is shown in figure 1. In the period of the thinning, the anodization process slowly changes from HA to MA process.

In order to gain insight in to the effect of thinning process on a structure of PAA film, we take the cross section SEM micrograph of thinned pores. As it is shown in figure 3(b) before thinning process the pores direction is straight, because during this part by attention to V- t curve the anodization voltage is constant and anodization current is in HA current order. But decreasing the voltage

and current led to the formation of dendrites at the pore bottoms and ordering in the pore bottoms is lost (see figure 3(c)).

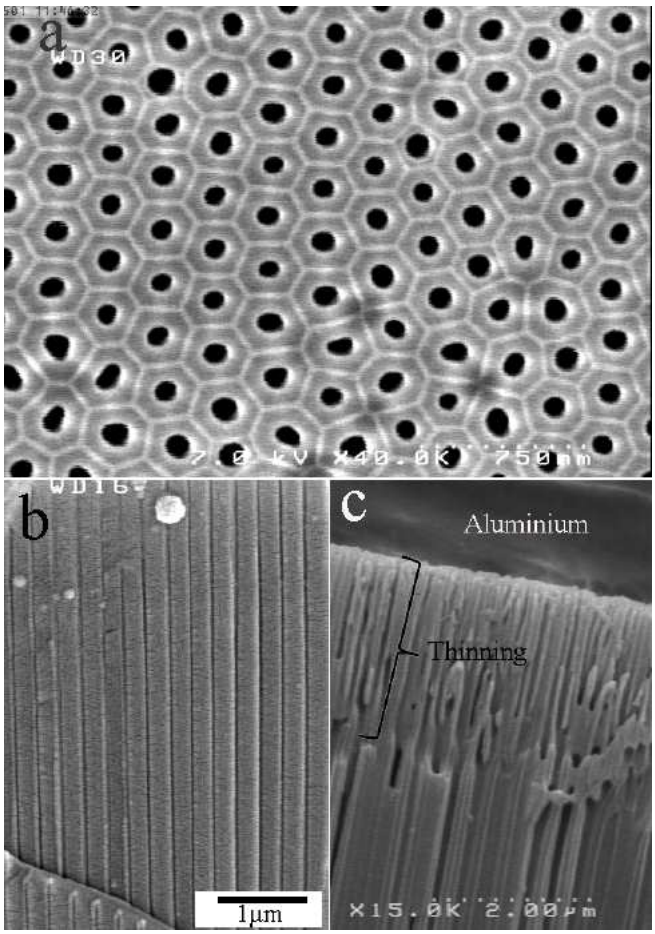

Figure 3. (a) Bottom view, (b) cross-section SEM micrograph of straight and (c) thinned part of PAA film.

The SEM micrograph of figure 4 shows Ag nanowire whit high aspect ratio. This figure demonstrates the ion electrodeposition process transform the pore profiles in to the Ag nanowire**.** The length and aspect ratio of Ag nanowires are more than 30μm and 500 respectively.

To control the microstructure of Ag nanowire the effect of pulse shape on a growth direction of silver atoms during the electrodeposition was investigated.

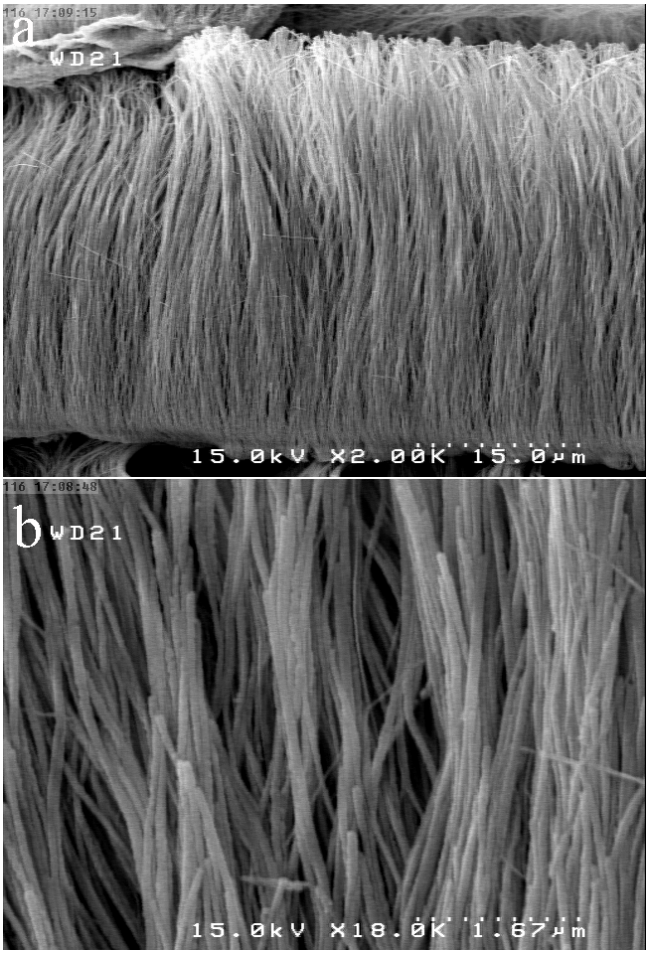

Figure 4. The SEM micrograph of high aspect ratio Ag nanowires after removing alumina template, (a) low and (b) high magnification.

In order to study the microstructures of the samples, the X-ray diffraction patterns of samples made at different off time, were compared. A Siemens D5000 X-ray diffractometer was used which utilizes a standard Cu tube source run at voltage of 40 kV and filament current of 40mA. A Cu Kα radiation of wavelength 0.1540496 nm is produced by this system. All θ–2θ scans were made from incident beam angles of 30° to around 85° of the surface with detector increments of 0.1° every 20 s.

The variation of the local pH and concentration of metallic ions at the pore bottom in the ac electrodeposition effected the crystal growth direction of metallic

nanowire [21]. Therefore to study the effect of pulse condition, four samples made at 0, 25, 50, 100 ms deposition off times, were compared. As it is seen in figure 5; off time between pulses have remarkable influence on the crystal orientation. Increasing the off time from 0 to 100 ms led to noticeable reduction of FCC (111) peak intensity and in 100 ms this peak disappears. Amplitude of FCC (220) peak at first increases by increasing of off time until 25 ms but further increases in off time causes the reduction of this peak. It is worth to mention increment of off time led to appear of hexagonal (004) peak. Therefore it is concluded that crystal orientation of Ag nanowires are dependent on the off time between pulses.

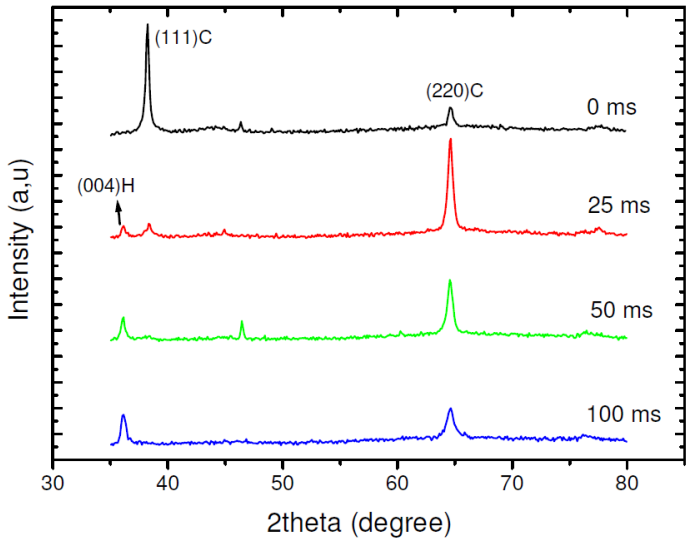

Figure 5. XRD patterns of the samples prepared with off times ranging from 0 to 100 ms.

4. Conclusions

Highly ordered PAA film with long pore length was fabricated based on hard anodization process. The ac pulse electrodeposition into PAA film was achieved through thin barrier layer obtained by an exponentially non-equilibrium anodization. Highly crystalline Ag nanowires were fabricated with different off times between pulses and led to the following results:

1. Base on hard anodization highly ordered PAA film with pore length more than 30μm was fabricated.

2. By thinning process after hard anodization, ac or ac pulse electrodeposition of ionic particle into a PAA film is possible.

3. Crystallinity and crystal orientation were found to be dependent on the off time between pulses.

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