

Cu oxide nanowire array grown on Si-based SiO₂ nanoscale islands via nanochannels

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Abstract

Cu oxide nanowire array on Si-based SiO₂ nanoscale islands was fabricated via nanochannels of Si-based porous anodic alumina (PAA) template at room temperature under a pulse voltage in a conventional solution for copper electrodeposition. X-ray diffraction and X-ray photoelectron spectroscopy showed that the main composite of the oxide nanowire is Cu₂O. The nanowires had a preferential growth direction (1 1 1) and connected with the nanoscale SiO₂ islands, which was confirmed by Transmission Electron Microscopy (TEM). Such Si-based nanostructure is useful in the nanoelectrics application. The growth mechanism of Cu oxide nanowires in Si-based PAA template was discussed. The formation of Cu₂O is due to the alkalinity of the anodized solution. However, the oscillations of the potential and current during the experiment trend to bring on a small amount of copper and CuO in the nanowires.

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1. Introduction

Porous anodic alumina (PAA) film with highly ordered pore arrangement, controllable pore diameter, channel length, and fine insulating property [1–3] is widely used as template to grow nanowires or nanotubes [4,5], since the pioneering work of Martin's groups [6]. However, most of work on the fabrication and characterization of the nanomaterials formed in the nanopores of PAA templates is based on bulk aluminum. On the other hand, PAA film can be formed onto other substrates such as silicon wafer. Silicon-based nanowire and nanotube may have a great nanoelectrics applica-

tion potential [7] since it is compatible with Si-based microelectronics fabrication processes.

Currently, cuprous oxide has attracted much interest because Cu₂O is a p-type semiconductor with a direct band gap of 2 eV [8] and a typical type of exciton materials [9]. Cu/Cu₂O layered nanostructures with optoelectronic properties have been fabricated by electrodeposition [10]. By a reduction route, crystalline Cu₂O nanowires were synthesized in the presence of the surfactant [11]. Among those fabrication methods, chemical method is the main method because of low cost and easy controlling. However, during the growth process, the temperature of reaction solution could be raised up to as 60 °C [11]. At this high temperature, the template such as porous alumina could be affected seriously [12]. Thus, low temperature even room temperature during electrodeposition is needed for semiconductor oxide nanowire

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(such as ZnO, Cu₂O) fabrication via PAA template, especially via Si-based template with thin thickness.

Recently, we had fabricated a Si-based SiO₂ nanoscale island array using PAA template [13,14]. Ge⁺ implantation and subsequent annealing lead to the formation of a Si-based nanoscale light source array, which was useful in nano-optoelectronics [13]. Well-aligned CNT array on Si-based nanoscale SiO₂ islands was produced at low temperature by microwave plasma-enhanced chemical vapor deposition (MW-PECVD) [14]. Here, we utilize PAA template to fabricate ordered Cu oxide (in which the main composite is Cu₂O) nanowire array on Si-based SiO₂ nanoscale islands at room temperature under a pulse voltage in a conventional solution for copper electrodeposition. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) results show that Cu oxide nanowire array was produced by electrodeposition. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) observations confirmed that nanowires were imbedded into nanopores of PAA template and connected with nanoscale SiO₂ islands.

2. Experimental procedure

The substrates used in our experiment were p-type <100>-oriented silicon wafers with a resistivity of 5 Ω cm. A layer of Al film with the thickness of 500 nm and the purity of 99.99% was deposited onto Si wafer by electron beam evaporation (called as Al/Si system). Si-based PAA template was fabricated by two-step process which was similar to the Masuda's work [16]. Anodization with a platinum plate as a cathode was carried out in the oxalic acid of 0.5 M under a constant dc

voltage of 40 V. By monitoring anodic *I*-*t* curve, anodization of Al/Si system can easily be controlled in situ. In additions, Si-based nanoscale SiO₂ island array at the bottoms of the nanopore channels of PAA template could be fabricated when the excess anodization process was adopted [13]. In order to remove the barrier layer, anodization time was prolonged and subsequently the samples were immersed into a 5 wt% phosphoric acid solution for several minutes. During electrodeposition process, a two-electrode arrangement had been used, where Si-based PAA template was served as an anode and platinum plate was as a cathode. Electrodeposition was conducted under a pulse voltage ($V_{\max} = -5.1$ V, $V_{\min} = -0.1$ V, Duty ratio = 30 ms:1000 ms) at room temperature in a conventional solution (Cu₂P₂O₇, 55 g/L; K₄P₂O₇, 210 g/L; KNO₃, 4 g/L; NH₃ · H₂O, 6 ml/L) [15] for 9 min. The SEM images of PAA template surface were obtained on JSM-6335 equipment of JEOL company. A monochromatic Al Kα excitation line (1486.6 eV) has been used for the XPS measurements. TEM images were acquired on CM20 at 120 kV (Philips).

3. Results and discussion

The complexity of the two-step anodization process is the controlling conditions between steps on Si-based Al film with thin thickness of about 500 nm in our experiment. The problem can be fixed by careful adjusting and monitoring the time-dependent current through out the whole anodization process. Fig. 1(a) shows the SEM image of Si-based PAA template fabricated by two-step method. PAA template has smooth surface and uniform, locally ordered nanopore arrangement.

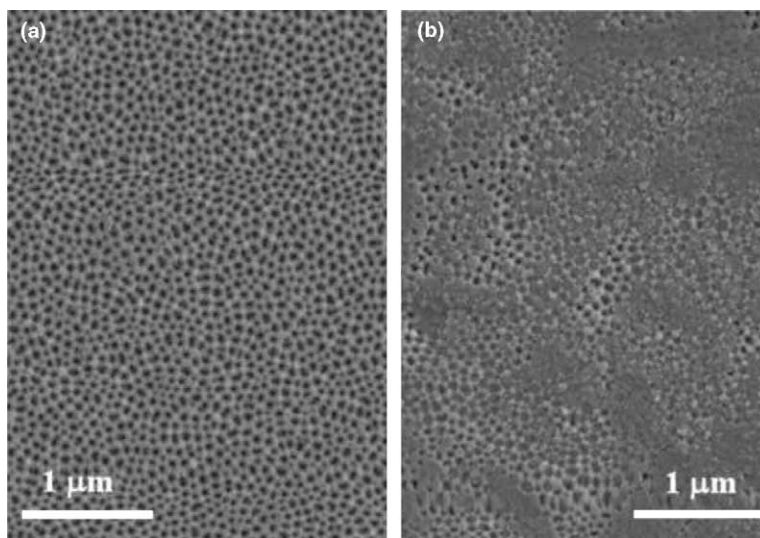


Fig. 1. SEM images of: (a) Si-based PAA template formed in oxalic acid solution of 0.5 M under a constant DC voltage of 40 V and (b) Cu oxide nanowire array, which were embedded into nanopores of Si-based PAA template.

The mean diameter of nanopores is about 50 nm and the distance between two nanopores is about 80 nm. Fig. 1(b) demonstrates the SEM image of Cu oxide nanowire array embedded into nanopores of PAA template. However, the nanopores are not fully embedded by nanowires and in some regions; the growth rate of the nanowires seems to be a little lower than other area so that the nanopores are not completely filled. Both two phenomena agree with the electrochemical process. As every nanopore corresponds to one nano-electrode [17], the process for every nanopore is different from each other during either anodization or electrodeposition. During deposition, the potential or current of the nano-electrode has a little variation which is critically dependent on the localized environment such as the size of nanopores, thickness of barrier layer if it has not been removed completely, and thickness of nano-scale SiO_2 islands. All these micro-phenomena are undoubtedly influential to the deposition of materials into nanopores via PAA template.

Fig. 2 shows the XRD pattern of Cu oxide nanowire array containing several clearly distinguishable peaks [18]. The strongest peak (36.426°) is due to Cu_2O (1 1 1) while the other weak peaks are due to Cu_2O (2 0 0), Cu_2O (2 2 0), and Cu_2O (3 1 1). In addition, two other peaks can be observed as illustrated in the inset of Fig. 2 they are corresponding to Cu (1 1 1) and CuO (1 1 1) even though their intensities are very weak. By fitting the area of each peak, the fractions of Cu and CuO in the nanowires are about 13% and 6%, respectively. Obviously, the main compound of the nanowires is Cu_2O and it has the preferential (1 1 1) orientation.

XPS result in Fig. 3 further discloses the formation of Cu_2O in the nanowires. The Cu $2p_{3/2}$ core level and its corresponding shake-up satellites can be deconvoluted with Gaussian lines into 4 distinct peaks. Peak 1 is

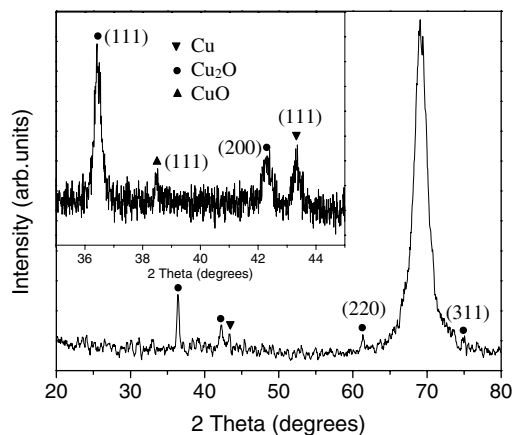


Fig. 2. XRD pattern of Cu oxide nanowire array embedded into nanopores of Si-based PAA template; the inset is the fine XRD pattern concentrating on the (1 1 1) orientation of Cu, Cu_2O , CuO.

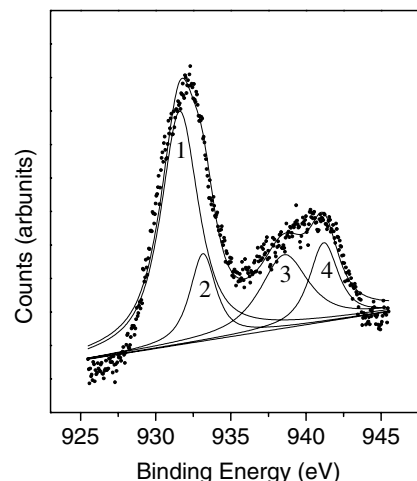


Fig. 3. XPS spectrum of Cu $2p$ core level of Cu oxide nanowire.

assigned to the Cu (+1) state while peaks 2–4 are assigned to the Cu (+2) state [11,19,20]. The ratio of area sum of peaks 2–4 to that of peak 1 is used for measuring the relative amount of Cu (+2) to Cu (+1) on the surface. In our results, the relative amount of Cu (+2) to Cu (+1) on the surface in XPS measurement is a little bit higher than the relative amount of CuO to Cu_2O in XRD measurement and it may be due to the measurement is focused on the surface of sample and Cu_2O is unstable in air and easily be oxidized at the surface [21].

So far, the Cu oxide (mainly is Cu_2O) nanowire array had been formed in Si-based PAA template and it has been confirmed by XRD and XPS measurements. The structure of the nanowires in the nanopores has been further disclosed using electron microscopy. The nanowires are formed in the nanopores and they are directly connected with the nanoscale SiO_2 islands as shown in Fig. 4. Fig. 4(a) and (b) show the cross-sectional SEM and TEM images of Si-based Cu oxide nanowire array. The thickness of SiO_2 island is about 10 nm, which is much thinner than that of the insulating alumina. The resistivity of nano-scale island is much different from the bulk SiO_2 . So Cu oxide nanowires can grow onto nanoscale SiO_2 islands. Its diameter is about 30 nm and the length is about 250 nm as indicated by the arrow in Fig. 4(b). During electrodeposition, Cu oxide nanowire grown along the wall of nanopore as seen in Fig. 3(a). We consider that the large bias (5.1 V) applied between anode and cathode induced the fast growth along normal direction. The nanopore could not be filled at same time. So the diameter of nanowire was smaller than that of nanopore. The novel structure obtained in our experiment as illustrated in the schematic diagram of Fig. 4(c) is extremely useful to be applied in nanoelectronics and nano-optoelectronics [13] since the fabrication method via Si-based template is easily compatible with Si-based microelectronics [22].

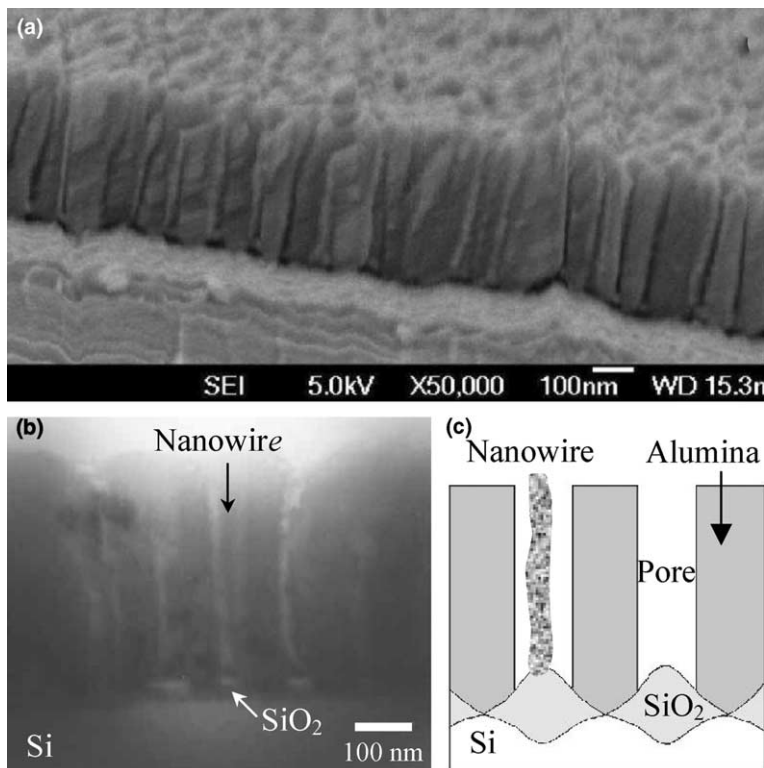


Fig. 4. Cross-sectional SEM (a) and TEM (b) images of Si-based Cu oxide nanowire array grown on Si-based SiO₂ nanoscale islands. (c) Schematic diagram of Si-based nanostructure in which nanowire is connected with Si-based SiO₂ nanoscale island via nanochannel of Si-based PAA template.

4. Growth mechanism

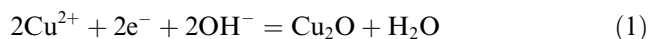
Cu₂O is usually generated during the deposition of copper [23,24]. Chemical composition electrodeposited under a constant voltage can be transited certain ratio of Cu and Cu₂O due to the migration rates of the anions and the hydrogen ions [25]. At the same time, Cu₂O may bring on the color change of the deposit during the dynamic morphological transition in quasi-two-dimensional electrodeposition. The growth velocity is determined by the migration rate of the anions, while the hydrogen ions are responsible for the chemical front coming from the anodic region. During the electrodeposition, Cu²⁺ ions are driven to the cathode by electric field and then they are reduced and diffuse on the deposit surface. The deposition of Cu and Cu₂O always exist because the equilibrium electrode potential for Cu₂O is higher than that for Cu [23]. As the Cu²⁺ is consumed in the front of the growing interface and the concentration of Cu²⁺ usually fluctuates, it affects the equilibrium electrode potential of Cu. Once the equilibrium electrode potential becomes lower than the actual electrode potential, the deposition of metal copper stops while the deposition of Cu₂O remains. So Cu₂O can be mostly observed during the deposition of copper.

In our experiment, a conventional solution is used for through-hole deposition of copper [15]; the content of Cu₂O is much higher than that of Cu or CuO as deduced

by XRD analysis. While in the previous works about copper electrodeposition [23,24], the content of metal copper is always more than that of Cu₂O, and no CuO can be observed. For special environment of nanopore, Cu²⁺ is not easy to arrive at the growing interface but the pulse voltage setup in our experiment may compensate this effect. The subsequent time (970 ms) after deposition time (30 ms) in one period (1000 ms) is long enough for Cu²⁺ to reach the growing interface since the growth rate is low (about 0.46 nm/period). However, the formation of CuO is not so obvious and it cannot be explained by the above mechanism.

Another possible growth mechanism for Cu₂O is a later overgrowth mechanism [25], which involves an initial electroless deposition of Cu₂O growth seeds in contact with the nanoscale SiO₂ islands. Electrochemical deposition of Cu₂O processed on the seeds seems that it can be used to explain the growth mechanism in our works because SiO₂ islands were formed previously. However, it should be impossible that copper and CuO can be observed by this mechanism [25]. But there exist pure copper and CuO in our works.

So neglecting the complexity of the reaction and the complexation of copper by anion, we consider a simplified representation of the reactions occurring at the working nano-electrodes [10,26].



This reaction agrees with the alkalinity of the solution for electrodeposition, which is about 8.2–9.0 [15]. The formation of copper and CuO in the nanowires may be due to potential and current oscillations in the electrochemical deposition system [27]. The oscillations are often attributing to the adsorption and dissolution of a passivating film [28]. The equilibrium electrode potential for Cu is lower than that for Cu₂O [23]. Therefore, a small amount of Cu is formed in the nano-electrode system when the potential oscillates. For a reverse process, CuO is formed.

5. Conclusion

Cu oxide (mainly Cu₂O) nanowire array on Si-based SiO₂ nanoscale islands is fabricated via Si-based PAA template at room temperature under a pulse voltage in a conventional solution electrodeposition for copper. The nanowires have a preferred growth direction (1 1 1) and connect with the nanoscale SiO₂ islands as confirmed by TEM observation. The formation of Cu₂O is due to the alkalinity of the solution. However, the potential and current oscillation may bring on small amount of Cu and CuO while the mechanism may be helpful to grow other semiconductor oxide film or nanomaterials.

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