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Anodic alumina template on Au/Si substrate and preparation of CdS nanowires

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Abstract

A layer of thin gold film was sandwiched between a silicon substrate and an Al film to form the Al/Au/Si structure. Subsequent anodization leads to formation of a Si-based anodic aluminum oxide (AAO) template (AAO/Au/Si structure) with ordered nanopores. This kind of template has unique electrodeposition properties and can bond well with the deposited materials. The anodic process of the Al/Au/Si structure was investigated in detail by in situ monitoring the current–time curve. As an application, CdS nanowires were fabricated on the silicon substrate using this kind of AAO templates. Light-emitting property from the CdS nanowires was observed. This kind of Si-based light-emitting nanowires are expected to have practical applications in optoelectronic integration. © 2002 Published by Elsevier Science Ltd.

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Template technique is one of the most successful approaches for obtaining size-controllable nanomaterials [1,2]. Recently, anodic aluminum oxide (AAO), a typical self-organized porous template, has attracted considerable interest in preparation of nanocrystallites for various electronic and electrochemical systems [3–6]. It is reported that photoelectric, magnetic and catalytic nanomaterials have been prepared by using AAO as template [7–10]. In our previous work, the template technique has been transferred onto silicon wafer to obtain Si-based AAO template (AAO/Si), which is compatible with Si planar techniques and hence can be used to fabricate various nanostructured materials on the silicon substrates [11–14]. These Si-based nanostructures are expected to have practical applications in nanooptoelectronic integration [15,16]. In this work, we propose a novel AAO/Au/Si template in which a layer of thin gold film is sandwiched between the Si substrate and the alumina layer. This template is proved to have more advantages in preparation of Si-based nanostructures.

A layer of gold with a thickness of 20 nm was deposited by electron beam evaporation onto the silicon wafer (p-type, 0.5 Ω cm, and ⟨100⟩-oriented). Then on the gold layer, aluminum (99.99%) was deposited to a thickness of 400 nm. Since the surface of the deposited Al film was smooth and clear, the samples were directly anodized without any pretreatment. The anodization process was carried out at room temperature, as reported previously [11,12]. The electrolytic solution was 15 wt% H_2SO_4 and the bias voltage was set at constant dc voltage of 40 V. The anodization time was about 90 s. After anodization, the samples were rinsed thoroughly in deionized water. Current–time (I–t) curve was obtained on a fast recorder.

Fig. 1 shows a planar view of the AAO film detached

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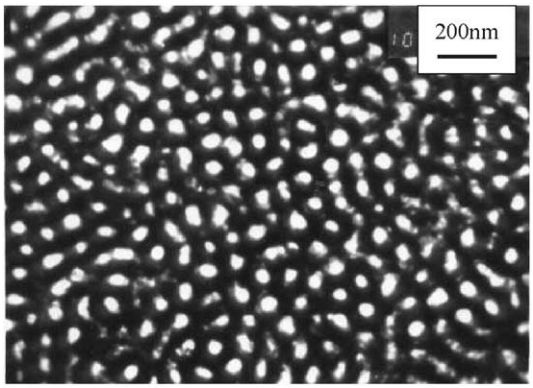

Fig. 1. Planar TEM image of AAO film detached from the Au/Si substrate.

from the substrate by JEOL JEM-2000 transmission electron microscope (TEM). It can be seen that there are many isolated circular nanopores in the film. The nanopores are uniform and locally ordered in distribution and have an average diameter of about 40 nm.

It is interesting to consider the details of anodic process for the Al/Au/Si system. A typical I–t curve of anodization for this system is shown in Fig. 2 (curve a). Compared with the I–t curves of both bulk Al (curve b) and Al film grown on silicon substrate (curve c), some new features appear. The curve a in the A–C range is the typical anodization process of Al film [17]. At this stage, the electrolyte just contacts with Al film and the Au/Si substrate only acts as an anode. With the anodization process going on, the front of the alumina barrier layer is gradually extended to the gold film. Owing to the stable chemical properties of gold, anodization process on the gold film will be hindered. With the exhaustion of Al film (at point C), the alumina barrier layer will become thinner and thinner. As a result, the current rapidly increases, as shown in the C–D range of curve a. At point D, the barrier layer has completely

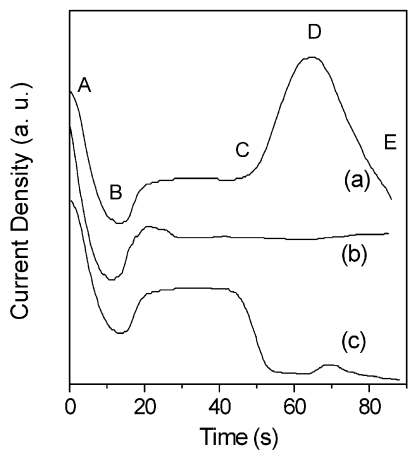

Fig. 2. Current density vs. time (I–t) curve during anodization. (a) The Al/Au/Si system, (b) bulk Al system, and (c) Al/Si system.

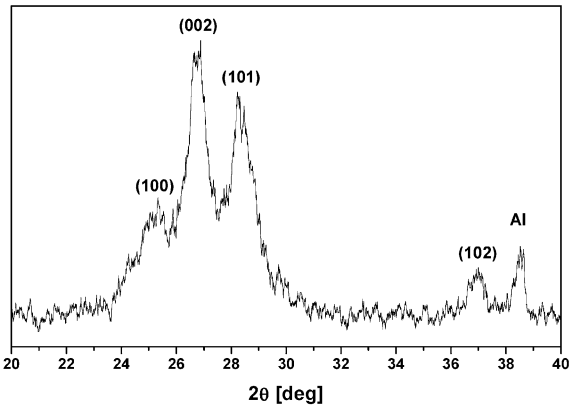

Fig. 3. X-ray diffraction pattern of the sample prepared by the AAO/Au/Si template.

vanished. Thus, the electrolyte passes porous layer of the AAO film and directly touches the gold layer. At this time, the electrolytic reaction of water takes place: oxygen gas is produced on the anode and the pores of AAO will be filled with gas bubbles, which will induce high resistance. As a result, the current is reduced in the D–E range. When the anodization process passes point D and continues for some time in the range D–E, the AAO film starts to detach from the Au/Si substrate due to the extrusion action of the gas on the alumina/gold interface. To obtain a tight AAO/Au/Si structure, anodization should be stopped at point D. The above process is different from that of Al/Si structure, for which, the current is evidently reduced after point C due to the formation of insulate SiO_2 layer.

As an application example of this template, CdS nanocrystals were prepared by electrochemical deposition in dimethyl sulfoxide (DMSO) solution composed of 0.055 M $CdCl_2$ and 0.19 M elemental sulfur [7]. The temperature was maintained at 120 °C by a thermostat. A 10 V dc voltage was applied between the AAO/Au/Si working electrode and graphite counter electrode from 5 to 20 min. A typical XRD pattern of a sample prepared by this template is shown in Fig. 3. All the diffraction peaks could be indexed to hexagonal CdS (wurtzite structure) within experimental error. The (002) diffraction peak is unusually strong compared to the bulk hexagonal CdS, indicating a preferential growth direction in the sample. The electrodeposited semiconductor CdS was freed from the AAO film by dissolving the anodic oxide in 0.1 M NaOH at 40 °C. Fig. 4(a) shows a typical TEM image of the samples electrodeposited at 120 °C for 20 min. In the image, a straight and uninterrupted wire structure of the deposited CdS may clearly be observed. A TEM image of individual CdS nanowire is presented in Fig. 4(b). The diameter of the nanowire is about 40 nm close to the pore size of the AAO/Au/Si template and it is rather uniform in different positions. The phenomenon indicates that it is the AAO template that induces the morphology of the deposited CdS nanowires.

The corresponding photoluminescence (PL) of the CdS

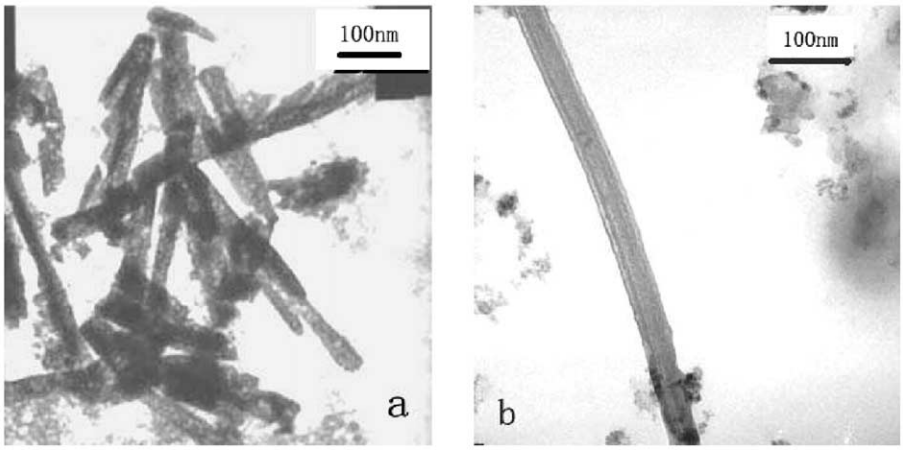

Fig. 4. (a) A typical TEM image of the CdS nanowires electrodeposited in the AAO/Au/Si film shown after the complete dissolution of anodic oxide supporting matrix in 0.1 M NaOH at 40 °C. (b) A TEM image of individual CdS nanowire.

sample is presented in Fig. 5, in which a sharp peak can clearly be observed. The position of the peak is at about 570 nm, which is related to the sulfur-deficient defects at the surfaces of CdS nanowires [17,18]. Since this CdS ordered structure is fabricated on the basis of the Si-based AAO template with ordered arrangement of the nanopores, this kind of template will be useful in fabricating Si-based nanoscaled light source. It must be noted that, in our case the arrangement order of nanopores is not very well. This is due to the limited Al thickness [19]. The small thickness of AAO template produced from the corresponding thin Al film is needed for Si planar techniques and Si-based integration. If a thick Al film is adopted, the Si planar techniques will be difficult to be applied on this kind of Si-based nanostructures. To improve the arrangement of nanopores in case of thin Al film, the SiC molding process could be employed [20].

Compared to Al/Si system, the AAO template prepared on Al/Au/Si system has obvious advantages. For the AAO directly grown on a silicon wafer, the Si substrate will inevitably be oxidized to form SiO_2 layer with high resistance, when the reaction runs to the Al/Si interface. While the Al/Au/Si system provides a stable and low resistance contact, which will play an important role in both template formation and nanodevice fabrication. For example, in order to electrodeposit the CdS nanocrystallites into the nanopores of the AAO/Si template, a higher voltage (>60 V) will be required. But in the case of AAO/Au/Si template, due to good conductivity of gold layer, the electrochemical deposition could be carried out under a lower voltage (10–20 V), which is in favor of the growth of the nanocrystallites. Furthermore, the gold film can be used as a high quality contact for nanomaterials and nanodevices. Thus the AAO/Au/Si template will be more suitable to be utilized in fabricating Si-based nanostructures in various electrochemical systems. At last, gold layer at the bottom of the luminescence structure could be regarded as high efficient reflection source, which will enhance the luminescence intensity.

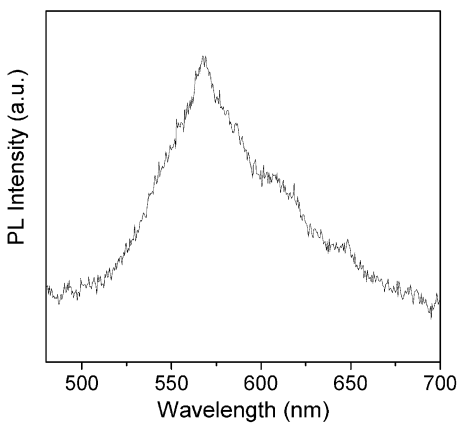

Fig. 5. PL spectrum of the CdS nanowires electrodeposited into the AAO/Au/Si template at room temperature.

In conclusion, a novel AAO/Au/Si template with ordered nanopores has been presented. This template technique and structure has unique properties, which are promising for electrochemical deposition and Si-based nanodevice fabrication. This kind of nanostructures is compatible with conventional Si planar techniques and hence can be used to fabricate Si-based nanoscaled light sources.

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