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Nano-particulate CuI film formed on porous copper substrate by iodination

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Abstract

A nano-particulate thin CuI film is fabricated by iodination of a porous copper substrate that was prepared by using an alumina mask and characteristic properties of these films are studied.

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1. Introduction

Nano-particulate semiconductor thin films which present restricted size and regular space distribution have been extensively studied [1,2]. Copper iodide (CuI) is one of a few kinds of p-type high band gap materials, which has been identified in the fabrication of conductive transparent thin films. In Particular, nano-particulate CuI thin films have potentiality for application in different kinds of electronic devices. Various techniques have been used to prepare such a structure, including radio frequency/direct current (rf–dc) coupled magnetron sputtering [3], pulse laser deposition (PLD) [4], hybrid electrochemical/chemical synthesis [5], and others [6–8]. It is well known that semiconductor thin films can be prepared using porous anodic alumina (PAA) as a template. As a typical self-assembly film, PAA holds nearly parallel nanoporous structure [9–13], thus functional materials are usually deposited into its pores to form nanostructured composite films [14–16]. Additionally, however, PAA film could also be utilized as a mask for the underlying substrate to prepare certain nanostructures. In this Letter, we describe a novel and facile method to fabricate a nano-particulate CuI film by iodination of a porous copper substrate, which was prepared by using a PAA mask. To the best of our knowledge, there are few reports relating to the preparation of semiconductor thin films by this method until now. The formation process, morphology, and corresponding properties of the prepared CuI films are investigated.

2. Experimental

2.1. Synthesis of nano-particulate CuI thin film

A copper plate was mechanically polished and ultrasonically cleaned with a detergent. After removing the grease and the native oxidation layer, highly pure aluminum film (99.99%) with a thickness of about 400 nm was deposited on the pretreated copper plate using the electron beam evaporation technique. The vacuum chamber was maintained under a pressure of 2.5×10^{-6} Pa. The accelerating voltage of the electron beam is kept constant near 10 kV and the electron gun current of 0.5 A. The surface of Al film deposited on Cu substrate does not exhibit any cracks or pinholes, and was directly used for anodization.

The anodization process was conducted at a constant cell potential in a 15 wt% sulfuric acid electrolyte at room temperature (25 °C). The prepared Al/Cu plate

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was used as the working electrode in the electrochemical cell. Only the Al surface of Al/Cu plate contacted the electrolyte in order to avoid anodizing the Al-absent copper face in the acid solution. The distance between the Pt counter electrode and the Al/Cu working electrode was kept at 2 cm. The voltage was set at a constant DC 5 V, allowing for copper's good conductivity. Synchronous current-time (*I–t*) curve during the anodizing process was recorded to characterize the formation of both PAA mask and porous Cu surface. The as-treated Cu plate with porous surface was washed and dried for the following iodination reaction [17].

After washed with 2-propanol, the Cu plate sample was kept suspended in a chamber, where it reacted with the iodine vapor mixed with 2-propanol gas carried over by N_2 steam (50 ml min^{-1}) for 5 min. A CuI thin film was formed and its thickness is about 400 nm determined by a chemical method [17]. The synthetic procedure of the nano-particulate CuI thin film grown on the surface of Cu plate is shown in Scheme 1. For comparison, copper plate not treated by PAA mask was also anodized in acid solution and then used to prepare CuI film by the same method mentioned above.

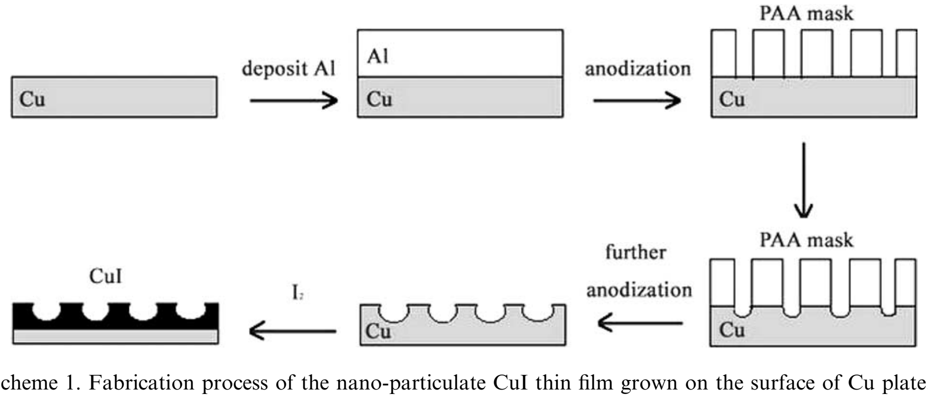
2.2. Instruments and measurements

The microstructures of the prepared specimens were observed by a scanning electron microscope (Hitachi X650), and an atomic force microscope (Nanoscope IIIa), respectively. Elemental analysis was made by X-ray energy dispersive spectroscopy (EDAX PV9100) equipped on SEM. The phase identification was characterized by X-ray diffraction patterns (SHIMADZU XD-3A diffractometer) with a Cu Kα radiation source (35 kV) and X-ray photoelectron spectra (ESCALab MK2 photoelectron spectrometer) using Al Kα as the exciting source. Emission studies of the films were carried out by a photoluminescence measurement (FluoroMax-2 spectrometer) with a Xe lamp as the excitation light source at room temperature. The excitation wavelength of the samples was 340 nm.

3. Results and discussion

Fig. 1 presents typical anodization *I–t* curves of aluminum layer deposited on substrates copper (a) and silicon (b), respectively. The shapes for both of the curves in A–C range are very similar to that of bulk Al plate [18], because at this stage the electrolyte only contacts the Al film and the substrate only works as an anode. With the exhaustion of Al film (around point C), the alumina barrier layer will become thinner. When the electrolyte passes through the porous layer of PAA film and gradually extends to the aluminum/substrates interface, different processes will take place, which depends on the various types and/or properties of the substrates. In case of chemically stable Au [19] or indium tin oxide (ITO) [20], the substrates will just act as the conductive media layer for the growth of PAA film. If the substrate is metal Ta [21] or semiconductor Si [22,23], the PAA film produced in the former stage will function as a mask for the local anodization of the underlying materials. As a result, pillared Ta_2O_5 [21], porous silicon nanostructures [22], and/or nanoscaled island-shaped SiO_2 films [23] have been acquired by this way. For our Al/Cu system, since the Cu substrate contacts the electrolyte after point C, the current gradually increases, as shown in curve a. At the same time, the copper crystals at the bottom of PAA pores are locally oxidized. The formed copper ions depart from the Cu substrate and enter the solution, leaving many fallings on the Cu surface. With these fallings extending, the PAA mask will peel off and the current intensity will further increase. At this stage the anodization process is ended (around point D). Therefore, we can detect and control the growing process of porous Cu substrates by using the *I–t* curve. For the Al/Si system (curve b), silicon crystals at the bottom of PAA pores are locally oxidized into SiO_2, thus the current for curve b is evidently reduced after point C.

Fig. 2a shows the SEM image of the Cu plate surface anodized without PAA mask. It is observed that the copper plate forms a continuous mountain-like surface. CuI film was then produced on this copper surface by



Scheme 1. Fabrication process of the nano-particulate CuI thin film grown on the surface of Cu plate.

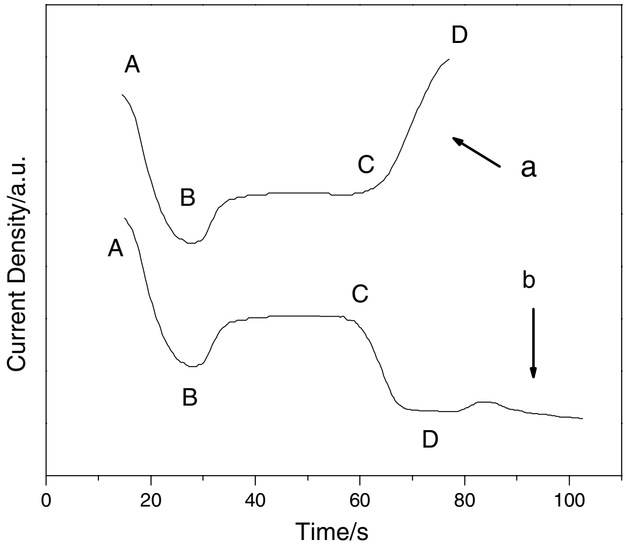


Fig. 1. Current density vs time (*I*–*t*) curve during anodization. (a) Al/Cu system, (b) Al/Si system.

the interfacial iodination reaction: $Cu + I_2 \rightarrow 2CuI$. The existence of 2-proganol vapors in mixed I_2 gas can lower the vapor pressure of the iodine, which may assist the formation of a uniform CuI layer [17]. After reaction, a shallow-white thin layer could be found on the Cu surface. As observed from SEM image of Fig. 2b, average size of CuI particles in the prepared film is about 300–400 nm and the particle shape is very irregular.

For the Cu film treated with PPA mask and its corresponding CuI film prepared by subsequent iodination reaction, no Cu or CuI grains were observed even at the maximum enlargement power of SEM. Thus, AFM measurements were employed to detect their surface morphology. Fig. 2c exhibits a typical three-dimensional AFM picture of the Cu surface treated with PAA mask, from which a homogeneous and uniform structure appears on Cu substrate. Each isolated Cu grain has an average diameter of about ~40 nm. The corresponding X-ray energy dispersive spectroscopy (XEDS) analyses prove that this surface is composed only of the element Cu, not the residues of the peeled PAA film. It is noticeable that some fallings are clearly seen among the Cu grains. It might be supposed that each PAA pore originally occupied the position of each falling. Therefore, the PAA mask ought to be responsible for the formation of the porous Cu substrate. From Fig. 2d, it can be seen that the CuI film prepared through the mask route exhibits distinct packed nano-particulate structure with an average diameter of about ~40 nm.

The phase of the CuI film prepared through the PAA mask route was checked by X-ray diffraction (XRD)

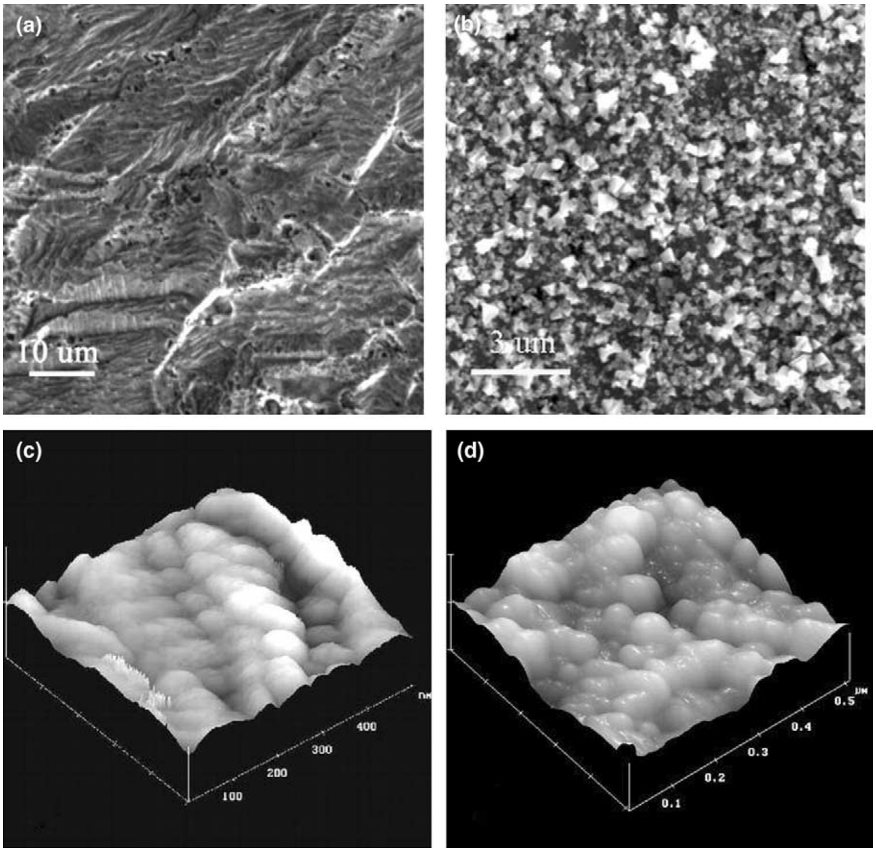


Fig. 2. SEM images of Cu plate anodized in acid solution without PAA mask (a) and CuI grains grown on the untreated Cu substrate surface (b). Typical 3D AFM images of Cu plate treated by PAA mask (c) and CuI grains grown on the treated Cu substrate surface (d).

pattern. As shown in Fig. 3a, three characteristic peaks at 42.9, 49.9 and 73.8 ° are attributed to Cu (1 1 1), (2 0 0), and (2 2 0) reflections, respectively. Except for the peaks originating from Cu substrate, a new and well-resolved pattern appears due to the formation of a γ-phase of CuI crystals. The peak at $2\theta = 25.2°$ is assigned as the (1 1 1) reflection line. Meanwhile, no peaks from other species were observed. The inset of Fig. 3a shows CuI (1 1 1) reflection of the samples fabricated without (curve 1) and with (curve 2) the PAA mask. Curve 2 affords an obvious broad reflection for the (1 1 1) plane of CuI crystals, which indicates the formation of ultra fine CuI grains through the mask route. The average particle size is estimated to be 36 nm by the Scherrer equation, conforming to the results of AFM observations.

XPS spectra were also used to determine the chemical composition of the prepared CuI film. The C1s peak located at 284.6 eV was taken as the internal standard and different peak positions were normalized with respect to it. All the observed peaks could be assignable to Cu, I, C, or O and no traces of other ions are revealed (this figure is not shown in the text). The presence of C is attributed to gaseous molecules adsorbed on the film surface. Fig. 3b exhibits the higher-resolution spectra of the Cu and I regions of the CuI film prepared with the PAA mask (curve 2). The corresponding spectra for the CuI film prepared without the PAA mask is also shown as a reference (curve 1). From a quantitative standpoint for both of the samples, the observed Cu $2p_{1/2}$ photoemission peak is at around 954.0 eV and the I $3d_{5/2}$ photoemission peak is at 619.3 eV. All of those observed peaks match those of the standard and are in good agreement with the values of 952.9 and 620.0 eV reported for CuI film prepared by other methods [3]. In addition, obvious shake-up peaks appear in curve 1 at the position with the energy 8–10 eV higher than that of Cu $2p_{3/2}$ or Cu $2p_{3/2}$, but no such a phenomenon appears in curve 2, which demonstrates that an amount of Cu^{2+} (i.e., CuO) might exist in the CuI film prepared without the PAA mask [24]. The absence of Cu^{2+} in the sample with the PAA mask may be attributed to the porous structure of Cu substrate, which could control crystal growth of CuI, thus making the iodination reaction moderate and protecting Cu near the surface from oxidizing under the fierce reaction conditions. However, Cu^0 from the substrate and Cu^+ from CuI cannot be distinguished by the XPS data because their photoemission lines are very close. Thus, we cannot obtain the actual ratio of Cu/I for the prepared film by comparing their corresponding peak areas.

Photoluminescence spectrum of the sample prepared with the PAA mask was shown as curve a in Fig. 4. For comparison, the PL spectrum of CuI film converted from the Cu substrate without the PAA mask was also determined (curve b). Both of the samples present a characteristic emission peak at the position of 411 nm (3.0 eV), which is located at lower energy position compared to a previously reported bandgap of CuI (about 3.1 eV) [5]. This observed emission peak might be due to the surface trapping sites (~0.2 eV higher the valence band edge of CuI) created by adsorbed iodine because samples of CuI always contain a stoichiometric excess of iodine [25]. At the same time, it can be found that the emission intensity from the CuI film grown on the Cu surface treated by PAA is higher than the one from reference. Though the amount of excess iodine in CuI films might influence the PL intensity of CuI [25], formation of ultra fine CuI grains may be another important reason. It can be suggested that the porous Cu substrate should hold larger surface areas compared to the untreated Cu surface. So, the fabricated CuI film will

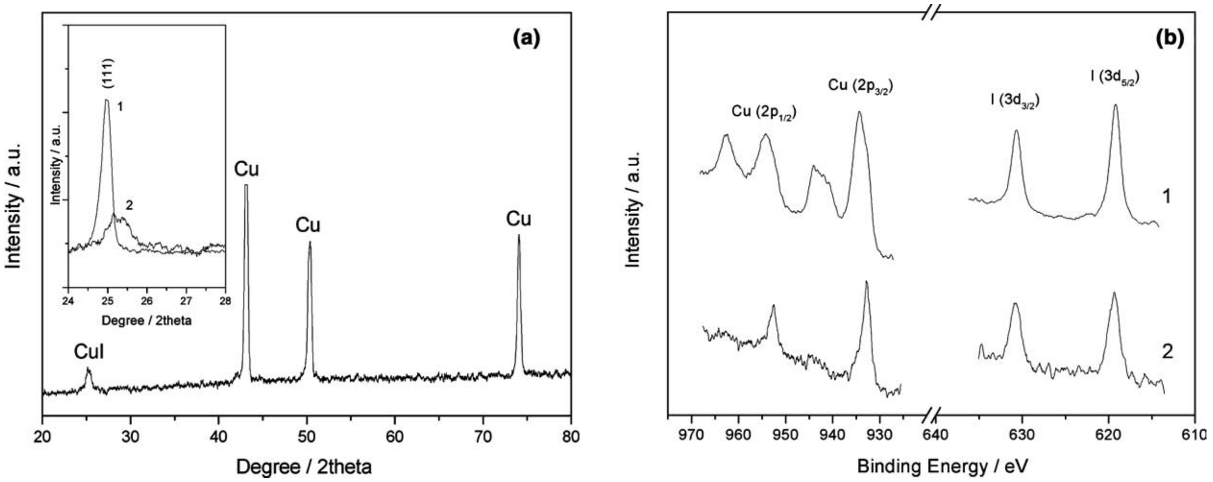


Fig. 3. (a) X-ray diffraction pattern of CuI film produced on the surface of Cu plate treated with the PAA mask. Inset is CuI (1 1 1) reflection of CuI film prepared without (1) and with (2) the PAA mask. (b) XPS close-up survey spectrum of Cu 2p and I 3d cores of CuI film prepared without (1) and with (2) the PAA mask.

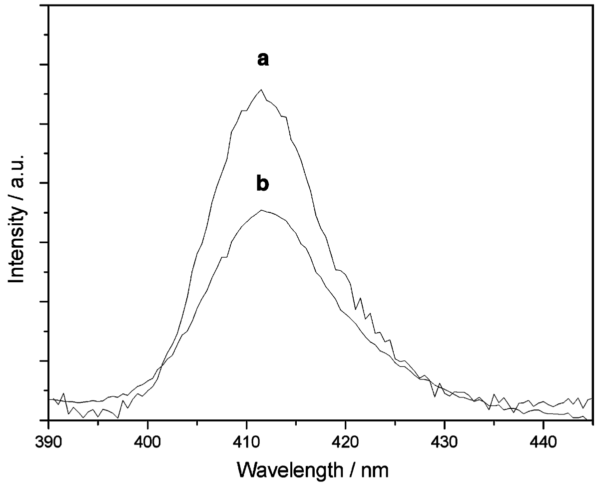


Fig. 4. Room-temperature PL spectra of CuI films prepared under the same experimental conditions on the Cu substrate treated with (a) and without (b) PAA mask.

have a larger luminescence area, which may also lead to the increase of PL intensity.

4. Conclusions

In this study, we provide a novel process to fabricate nano-particulate CuI thin films. A porous Cu substrate was first prepared using PAA as a mask, and then the nano-particulate CuI film was formed by a subsequent iodination reaction. Compared to the conventional electron beam (EB) lithography, this molding process by PAA mask is simple and convenient and is promising for application to the other substrates. Additionally, the dimensions of pore and unit cell of the PAA mask can be readily controlled and adjusted by appropriate choice of electrolyte, anodizing time, temperature, voltage or current density. Thus, the parameters of the produced nano-particulate structure will be tunable according to the experimental conditions, which is of great importance in practical applications.

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