



Facile vapor-phase synthesis of copper nanostructures on cuprous iodide films



Yasuhiro Seguchi^{*}, Tetsuro Soejima

Department of Applied Chemistry, Faculty of Science and Engineering, Kindai University, 3-4-1 Kowakae, Higashi-osaka, Osaka 577-8502, Japan

ARTICLE INFO

Article history:

Received 20 April 2017

Received in revised form

15 July 2017

Accepted 17 July 2017

Available online 18 July 2017

Keywords:

Copper

Cuprous iodide

Vacuum evaporation

Nanowire

ABSTRACT

One-dimensional growth of copper (Cu) is observed when Cu is deposited on cuprous iodide (CuI) films at elevated temperatures by thermal evaporation in high vacuum. The morphology, crystallinity, and chemical composition were examined for the samples using scanning electron microscopy, transmission electron microscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. Straight single-crystalline Cu nanowires can be formed on polycrystalline CuI films at 200 °C. Anisotropic growth of Cu in one-dimension was promoted by enhancing grain growth and continuity of CuI films. At a lower temperature of 100 °C, fuzzy branching nanowires were grown on the surface of CuI films, enabling to simply fabricate a self-supporting, highly porous film of Cu. It is revealed that a CuI film serves as a functional substrate to synthesize nanostructured Cu at low temperatures. Possible growth processes are proposed to explain the observed morphology evolution of Cu with respect to synthesis conditions. The characterization of water wettability showed that the hydrophobicity was remarkably enhanced due to the formation of nanostructured Cu on the CuI films.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

One-dimensional (1D) metal nanostructures have been extensively investigated and expected to apply in diverse fields due to their attractive properties. Among them, nanostructured copper (Cu) has started to gain considerable attention for future low-cost nanoscale materials and devices [1]. Many studies on Cu nanowires have demonstrated their potential for various applications, e.g., transparent conductive electrodes [2–5], high sensitive substrates for surface-enhanced Raman scattering [6], field-emission display [7], sensor [8], surface fastener [9], and thermal interface material [10]. On the other hand, the instability of nanostructured Cu under ambient conditions remains one of the problems to be solved for practical applications. For such a drawback of nanostructured Cu, possible solutions have recently been emerged; that is, their stability can be improved by the use of corrosion protectors [11–16]. In some cases, easy oxidation of nanostructured Cu is possibly utilized for expanding the areas of potential applications, since the resulting copper oxides have a variety of interesting properties that have been reviewed in recent articles [17,18].

A number of synthetic methods have been exploited to fabricate 1D nanostructures based on different strategies for achieving 1D growth, which has been typically described for chemical approaches by Xia et al. [19]. As for vapor-phase synthesis, various deposition methods with or without an intentional introduction of inert gas have been employed for nanowire growth of Cu [20–28] and some of other metals [27–37]. However, as described below, it is not fully understood yet how the nucleation and 1D growth of Cu are related to the synthesis conditions, such as the deposition geometry associated with the apparatus, the type and temperature of the substrate. Cu nanowires have been synthesized in inert atmosphere on Si substrates at temperatures in the range of 250–400 °C [20–22]. Growth of Cu nanorods/nanowires has also been observed under high-vacuum conditions in several studies [23–28], which are of particular interest in relation to the present work. When a Cu grid was heated (~800–920 °C) or a Cu powder charge was irradiated with electron beam in a transmission electron microscope (TEM), evaporated and/or migrated Cu atoms have been formed into nanorods/nanowires on a carbon film [23–25]. Instead of a TEM chamber, a high-vacuum evaporator has been employed to synthesize Cu nanorods on an amorphous carbon film at about 500 °C [26], and Cu nanowhiskers on partially carbon-coated Si wafers at 650 °C [27]. Suzuki et al. have reported the growth of Cu nanowhiskers on SiO₂ substrates at relatively low

^{*} Corresponding author.

E-mail address: seguchi@apch.kindai.ac.jp (Y. Seguchi).

temperatures in the range of ~280–420 °C [28]; however, they needed to deposit Cu at a glancing angle. One sees that the reported growth temperature of Cu nanorods/nanowires has widely ranged from 250 to 920 °C for vapor phase deposition [20–28]. The substrates used for 1D Cu growth are limited to carbon, Si, and silicon oxide; occasionally, Si and its oxide have been unfavorable for 1D growth of Cu [24,26].

In this work, Cu nanowires were found to grow on cuprous iodide (CuI) films at the lowest temperature ever reported through thermal evaporation, in which the incident vapor flux of Cu was about in the direction to the film normal. The obtained results evidently show that the CuI film used as the substrate is crucial for 1D Cu growth. Straight well-crystallized Cu nanowires were observed to grow on polycrystalline CuI films at the temperature as low as 200 °C. Interestingly, fuzzy branching nanowires of Cu were also synthesized at an unexpectedly low temperature of 100 °C, leading to a successful fabrication of nanowire-based, self-supporting porous films of Cu. The observed low-temperature growth of Cu nanostructures would be a key to gaining insight into their possible growth mechanism unique to the Cu/CuI system.

2. Experimental section

2.1. Synthesis of Cu nanostructures

In a typical procedure, deposition of Cu was carried out twice per sample via thermal evaporation of high-purity Cu from a resistively heated tungsten boat: one is in the preparation process of a CuI film and the other is for the synthesis of nanostructured Cu on the CuI film. A Cu film with a thickness (d_{Cu}) of 5–50 nm was first deposited on the major part of a wafer of p-type Si(100) at ambient temperature. Si wafers were cleaned with deionized water, acetone (ultrasonication for 10 min), and ethanol before being loaded in a vacuum chamber. Instead of Si wafers, air-cleaved thin plates of NaCl(100) were used in some experiments. The deposition of Cu was done at a rate of $\sim 0.1 \text{ nm s}^{-1}$ and in a pressure of $\sim 10^{-3} \text{ Pa}$. The nominal thickness and the deposition rate of the Cu film were measured by a quartz crystal monitor. CuI films were prepared by a chemical reaction of Cu films with iodine vapor; the obtained CuI film and pieces of iodine were placed inside a Petri dish, which was then covered with a lid. For a typical Cu film of 50 nm thickness, iodization duration of 10–20 min was enough Cu/Si(100) to convert into CuI/Si(100) with a homogeneous color at room temperature. In order to synthesize Cu nanostructure, a CuI film thus prepared on a Si wafer was fixed on a substrate holder with a ceramic heater and a thermocouple (type K), so as to face down to the evaporation source of Cu in another high-vacuum chamber. Subsequent deposition of Cu was conducted on the substrate that was held at the desired temperature in the range of 100–250 °C. The amount of nanostructured Cu on a CuI film was monitored by measuring the nominal film thickness (50–400 nm) using a quartz crystal oscillator, as well as the Cu film on the bare Si substrate. The pressure during the deposition and the deposition rate were $\sim 10^{-4} \text{ Pa}$ and $\sim 0.1 \text{ nm s}^{-1}$, respectively. After the deposition of Cu, samples were naturally cooled down to room temperature in vacuum.

2.2. Characterization

Field-emission scanning electron microscope (Hitachi, S-4800) operated at an accelerating voltage of 10 kV was used for the morphology observations of the samples. X-ray diffractometer (Rigaku, MiniFlex II) with Cu K_α radiation generated at the power of 30 kV–15 mA was employed for their structural analyses. The crystallinity and the chemical composition of nanowires were examined using transmission electron microscope (JEOL, JEM-

2100F) equipped with an energy-dispersive X-ray spectrometer. X-ray photoelectron spectrometer (Shimadzu-Kratos, Axis-Nova) with a monochromatic Al K_α source operated at 15kV–10mA was used for the characterization of the sample surface. Structural micrographs and elemental analysis data were acquired under the operation at 200 kV for the specimens that were transferred onto a carbon-coated TEM grid from the Cu/CuI surface by a careful scratching. Surface wettability was characterized by measuring static contact angle(CA) at ambient temperature. The measurements using a deionized water droplet with a volume of $\sim 5 \mu\text{L}$ were done for five different spots for each sample surface; then, an average value was evaluated from the CA values obtained by a half-angle method.

3. Results and discussion

3.1. Growth of straight Cu nanowires on CuI films

We first show the results of morphological and structural characterizations that were performed for the samples with 50 nm-thick Cu deposited at 200 °C. The obtained results confirm that both the deposition of Cu and a CuI film as the substrate are indispensable to the formation of Cu nanowires. Scanning electron microscopy (SEM) images were taken for three kinds of areas, i.e., CuI/Si(100), Cu/CuI/Si(100), and Cu/Si(100), which are obtained after the Cu-deposition schematically illustrated in Fig. 1(a). Growth of free-standing straight nanowires was observed on the Cu-deposited surface of the CuI film as shown in Fig. 1(c) and (f). The average diameter of nanowires is roughly estimated to be about 200 nm from high-magnification images shown in the insets of these figures. The maximum length of straight nanowires amounts to $\sim 9 \mu\text{m}$. On the contrary, nanowires grew neither on the CuI surface covered with a shadow mask nor on the Cu-deposited surface of Si wafer, as seen in Fig. 1(b), (d), (e), and (g).

The iodized film in this sample was grown from a Cu film of 50 nm in thickness ($d_{\text{Cu}} = 50 \text{ nm}$). The observed SEM image showed that the resultant CuI film is continuous and polycrystalline in structure with the grain size of ~ 100 – 300 nm (Fig. 1(b) and (e)). The film growth during iodization of the Cu film proceeded upward without changing the film area, which seems to have induced a columnar structure of the CuI film (Fig. 1(e)). The thickness estimated from the cross-sectional view of Fig. 1(e) approximately corresponds to $4.7 d_{\text{Cu}}$ ($\sim 240 \text{ nm}$) that is expected from the increase of molar volume through the vapor iodization of the Cu film: growth of a film of γ -CuI phase with zinc-blende structure (ICDD, PDF No. 06-0246) from a Cu film with face-centered cubic (fcc) structure (ICDD, PDF No. 04-0836). For convenience, we will denote below the nominal CuI thickness (d_{CuI}) of our samples as the value determined from the approximate expression of $d_{\text{CuI}} \approx 4.7 d_{\text{Cu}}$ (for the characterizations of as-prepared CuI films, see Fig. S1 in Supplementary Information).

As seen in the insets of Fig. 1(e) and (f), the interface between CuI and Si substrate remains clear irrespective of the Cu deposition on a CuI film, indicating that the reaction at CuI/Si interface could be negligible. On the other hand, the Cu deposition on the bare Si substrate gives rise to protruding products under a continuous Cu film as seen in Fig. 1(d) and (g). The inset of Fig. 1(g) clearly shows that the product is embedded in the Si substrate, which is similar to the previous observation of octahedral Cu_3Si nanocrystals grown at above 650 °C [38]. The formation of copper silicides through the Cu-Si reaction has been observed even at a low temperature of 200 °C [39]. Thus we suppose that some copper silicide may be produced in Cu-deposited area on the bare Si wafer (Fig. 1(d) and (g)).

Fig. 2 shows a typical X-ray diffraction (XRD) pattern for the Cu/

Download English Version:

<https://daneshyari.com/en/article/5468015>

Download Persian Version:

<https://daneshyari.com/article/5468015>

[Daneshyari.com](https://daneshyari.com)