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Synthesis of CuO Quadrilateral Nanoplate Thin Films by Controlled Crystal Growth in A Two-dimensional Micro Space †

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Abstract: Thin films consisting of quadrilateral nanoplates of CuO on the surface of a Cu plate were successfully synthesized in a two-dimensional micro space by the hydrothermal oxidation of a Cu plate using aqueous $(NH_4)_2S_2O_8$ solution as the oxidizer. Selective crystal growth was clearly observed in the two-dimensional micro space formed between the Al_2O_3 and the Cu plates, and a highly crystalline CuO quadrilateral nanoplate thin film was formed on the surface of the Cu plate that faced the Al_2O_3 plate. Similar experiments were performed by replacing the Al_2O_3 plate by Cu, Ti, or SUS316L plates as the substrate, to investigate the effect of the substrate facing the Cu plate. Using different substrates resulted in significant differences in the morphology of the CuO thin film on the Cu plate facing the substrate. The present study demonstrates that the use of a two-dimensional micro space can be extremely effective in controlling the nanostructure of thin films.

Keywords: CuO; Thin film; Crystal growth; Two-dimensional micro space

1. Introduction

Recently, cupric oxide (CuO) has been actively researched for use in a number of applications, in sensor materials [1], catalyst materials [2], lithium-ion secondary batteries [3], optoelectronic materials [4], pseudocapacitor electrode materials [5], and superhydrophobic materials [6], as well as for As(III) removal [7], hydrogen production [8], and photocatalytic water splitting [9]. Previous studies have shown that the properties of CuO are greatly influenced by its nanoscale morphology and the exposed crystallographic faces on its surface. Hence, to optimize the properties of CuO nanoparticles, it is important to avoid random aggregation and fabricate thin films wherein the morphology, arrangement, and aggregation of the nanoparticles are precisely controlled. Syntheses and applications of precisely controlled nanostructured CuO thin films have been reported by several groups [3,5,8,9]. The synthesis of ceramic nanoparticle thin films on metals (i.e., nanostructured ceramic thin film/metal composites) has become an active research area, because these composites are extremely promising functional materials that combine the excellent mechanical properties and conductivity of the metal with the specific physical and chemical properties of the ceramic nanoparticles. Nanostructured CuO thin film/Cu composites have been synthesized by aqueous solution techniques [10–15] and thermal oxidation processes [16–22]. There are several reports on the uses of nanostructured CuO thin film/Cu composites as electrochemical sensors for detecting H_2O_2 [13], glucose [13], and H_2S [21]; field emission materials [18,20]; antimicrobial materials [15]; and cathodes in dye-sensitized solar cells [10].

Nanoparticles with specific morphology and structure can be synthesized using micro-reactors [23,24], where a tube of micrometer sized diameter is used as the one-dimensional reactor. The effective control of crystal growth in micro space has been reported;

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however, this method cannot be used to synthesize thin films. In the present study, we have developed a novel method that uses a two-dimensional space that has a thickness of micrometers with lengths and widths of the order of cm, (i.e., a two-dimensional micro space) for the synthesis of nanostructured ceramic thin films. This method allows controlling the structures of ceramic thin films on the nanoscale by confining the reaction in the micro space. It is expected that using this method, new nanostructured ceramic thin film/metal composites with previously unreported nanostructures and morphologies with unique chemical and physical properties can be formed due to the effect of the two-dimensional micro space reaction. In particular, the present work is focused on the attempt to synthesize a nanostructured cupric oxide thin film on the surface of a copper plate by hydrothermal reaction in a two-dimensional micro space, using an aqueous solution of $(NH_4)_2S_2O_8$ as the oxidizer. This reaction yielded CuO quadrilateral nanoplate thin film/Cu composites, the unique structure of which could be attributed to the controlled crystal growth in the two-dimensional micro space. The effect of the substrates used for creating the two-dimensional micro space was also examined with respect to the crystal structure and nanomorphology of the CuO thin films.

2. Methods

A two-dimensional micro space was formed on a Cu plate (20 × 20 × 0.3 mm) by constructing a reaction field, as shown in Figure 1. A SUS316 wire with 200 μm external diameter was wound over an Al_2O_3 plate (20 × 20 × 1 mm). The Al_2O_3 plate and the Cu plate were arranged to face each other and fixed using the SUS316 wire. Fixing these two plates created a 200 μm gap (i.e., a two-dimensional micro space). The fixed plates were soaked in a mixture of 1 mol/l $(NH_4)_2S_2O_8$ (2 ml), 10 mol/l NaOH (4 ml), and distilled water (9 ml), and allowed to react hydrothermally at 120 °C for 20 h. After the reaction, the Cu plate was repeatedly washed with distilled water and characterized. In the characterization experiments, the surface of the Cu plate that faced the Al_2O_3 plate was designated as surface A, while the surface of the Cu plate that faced away from the Al_2O_3 plate was designated as surface B. A similar reaction was carried out without using the Al_2O_3 plate, i.e., only the Cu plate was used. The surface of this Cu plate was designated as surface C. The effect of the composition of the substrate (that faced the Cu plate) on the crystal structure and morphology of the thin film was examined using respectively, a Cu plate, a SUS316L plate, or a Ti plate instead of the Al_2O_3 plate, for the hydrothermal synthesis experiment. A Hitachi S-3000N microscope was used to acquire scanning electron microscopy (SEM) images. A Shimadzu XRD-6100 instrument with CuKα radiation was used to obtain X-ray diffraction (XRD) patterns.

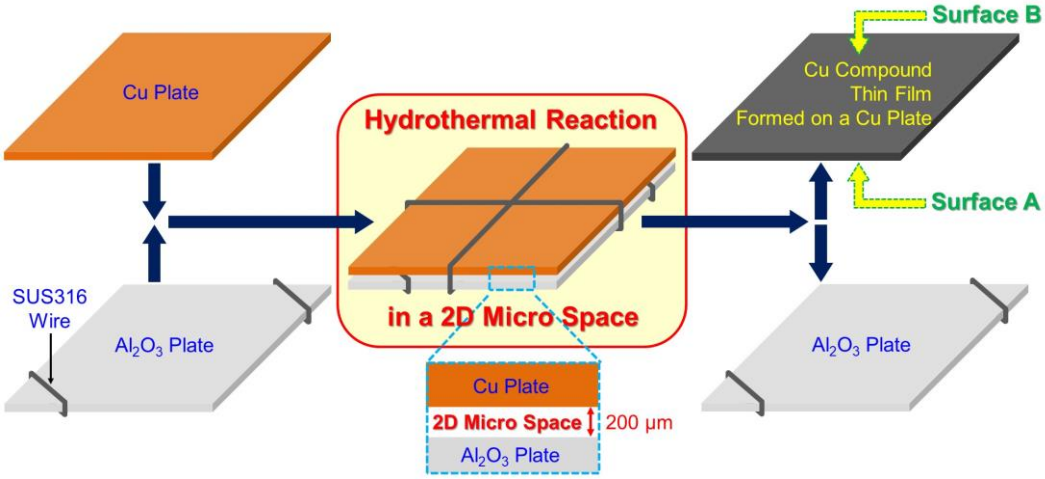

Figure 1. Schematic representation of the formation of a two-dimensional micro space.

3. Results and Discussion

A surface of the raw Cu plate was all smooth. Figure 2 shows the results obtained using the Al_2O_3 plate as the substrate. As shown in Figures 2a and 2b, a black thin film composed of quadrilateral nanoplates with side dimensions of approximately 0.6-2.3 μm (an average side dimension of 1.43 μm) and an average thickness of ca. 160 nm was synthesized on surface A. In contrast, the surface B was coated by a thin film composed of lamellar structures with sizes of approximately 1 μm or less, with uneven edges and irregular shapes (Figure 2c and 2d). The SEM images of the surface C (Figure 2e and 2f) were similar to those of surface B. The XRD pattern of surface A (Figure 3a) showed nine sharp diffraction peaks attributed to monoclinic CuO, along with diffraction peaks from the Cu substrate. Two diffraction peaks attributed to Cu_2O were also observed, although their intensities were extremely low. Therefore, it was concluded that the principal crystallographic phase of the nanoplate thin film was CuO. Liu et al. [12] have studied the reaction between Cu and $(NH_4)_2S_2O_8$ aqueous solution in the presence of NaOH, and have reported the following scheme of reactions:

$$Cu + 2NaOH + (NH_4)_2S_2O_8 \rightarrow Cu(OH)_2 + Na_2SO_4 + (NH_4)_2SO_4$$

$$Cu(OH)_2 + 2OH^- \rightarrow [Cu(OH)_4]^{2-}$$

$$[Cu(OH)_4]^{2-} \rightarrow CuO + 2OH^- + H_2O$$

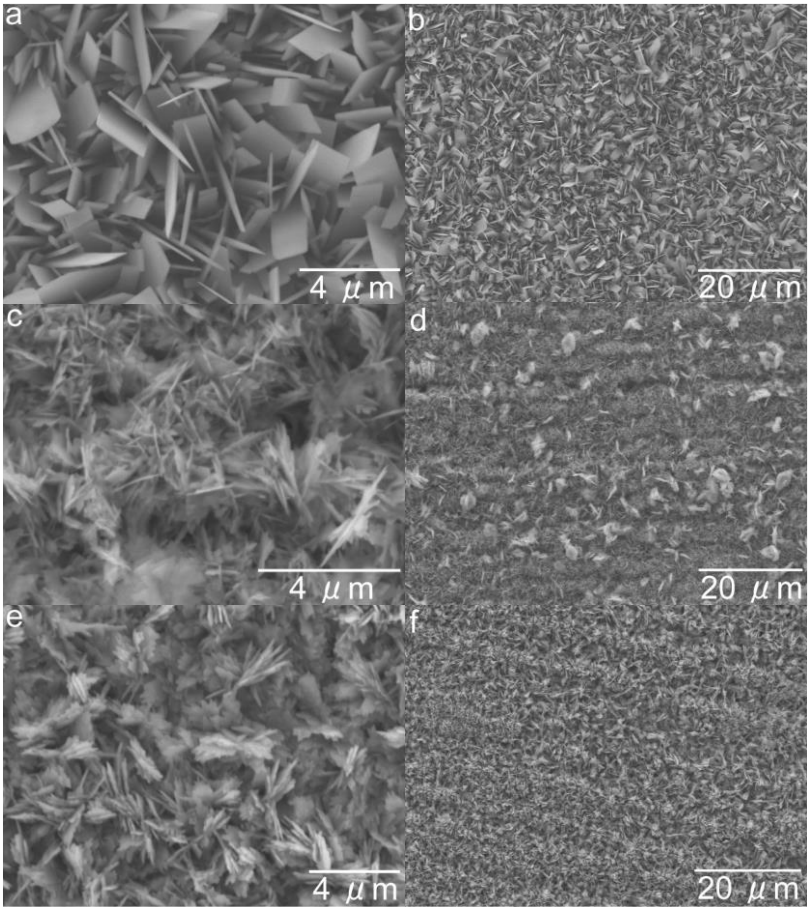

Figure 2. SEM images of thin films formed on the surfaces of the Cu plate obtained using Al_2O_3 plate as the substrate; (**a** and **b**): surface **A**, (**c** and **d**): surface **B**, and (**e** and **f**): surface **C**.

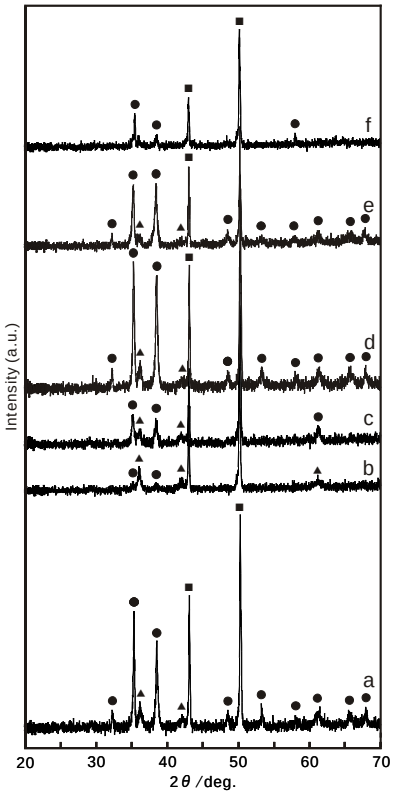

Figure 3. XRD patterns of thin films formed on the surfaces on the Cu substrates obtained using (a, b, and c) Al_2O_3, (d) Cu, (e) SUS316L, and (f) Ti plate, as the substrate; (a, d, e, and f), surface **A**, (b), surface **B**, and (c) surface **C**. Peak assignment: ●: CuO, ■: Cu, ▲: Cu_2O.

In the present study, ions such as $[Cu(OH)_4]^{2-}$ generated near the surface of the Cu plate were deposited onto the surface A of the Cu plate as CuO quadrilateral nanoplates that form the CuO thin film. XRD patterns of the thin films synthesized on surfaces B and C (Figure 3b and 3c) showed diffraction peaks attributed to CuO, but only a few peaks were observed and their intensities were markedly lower than those observed on surface A. On surface B, the intensities of the CuO peaks were lower than the intensities of the peaks from Cu_2O. On surface C, the intensities of the diffraction peaks attributed to CuO were slightly higher than those from Cu_2O. Therefore, it is obvious that a selective crystal growth of CuO occurred in the two-dimensional micro space formed between the Al_2O_3 plate and the Cu plate, and a highly crystalline CuO quadrilateral nanoplate thin film, which has not been reported previously, was synthesized. In the past, in the syntheses of nanostructured ceramic thin films, structure control at the nanoscale was achieved by controlling the composition, the concentrations of the precursor solutions and the reaction temperature, or by using structure directing agents such as surfactants. The present study revealed that a two-dimensional micro space can be extremely effective for the controlled synthesis of nanostructured materials. The possible sequence of events in this process of crystal growth in a two-dimensional micro space can be described as follows: (1) the two-dimensional micro space moderately inhibited the diffusion of the raw material, and the generation and diffusion of CuO precursor ions near the Cu plate surface, (2) the rates of nucleation and crystal growth decreased, and (3) quadrilateral nanoplates with uniform sizes and shapes were selectively synthesized. Zou et al. [25] reported the formation of well-aligned arrays of monoclinic CuO nanoplatelets on the walls of a teflon container, but the corresponding SEM images were significantly different from those observed in our case. It was explained that this particular morphology was the result of a preferred orientation of the nanoplatelets along the [010] direction. Moura et al. [26] reported aggregates of monoclinic CuO plates with quadrilateral shapes and elucidated that CuO crystals grow preferentially along the [100] and [010] to form plates. Taking into account the

two reports, we suppose that in our study, CuO crystals grew from the Cu substrate along the [010] direction vertically aligned with the Cu substrate and in the [100] direction when aligned parallel to the Cu substrate. On surfaces B and C, in the absence of a two-dimensional micro space, the diffusion of the raw material, and the generation and diffusion of CuO precursor ions near the Cu plate surface readily occurred. Consequently, the rate of nucleation and crystal growth increased, resulting in the synthesis of thin films composed of poorly crystallized CuO and Cu_2O nanoparticles with different shapes with two-dimensional morphology.

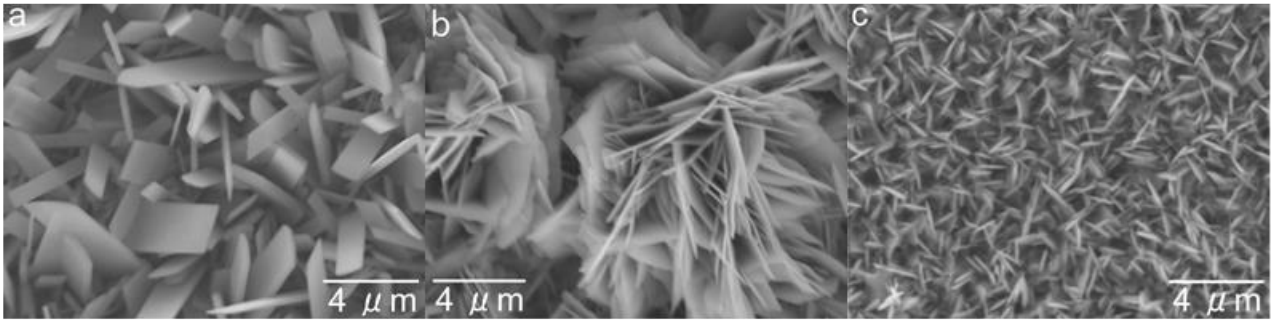

Figure 4. SEM images of thin films formed on surface **A** of the Cu substrates obtained using (**a**) Cu, (**b**) SUS316L, and (**c**) Ti plate, as the substrate instead of the Al_2O_3 plate.

Similar experiments were conducted by substituting the Al_2O_3 plate by a Cu, Ti, or SUS316L plate as the substrate, to investigate the effect of the nature of the substrate facing the Cu plate. All these substrates showed significant differences in morphology between the surfaces of the Cu plate facing the substrate (surface A) and the other surface (surface B). Figure 4 shows the SEM images of surface A of the Cu plate obtained while using these alternative substrates. These images indicate the preferential formation of thin films composed of particles with a two-dimensional morphology on surface A, clearly demonstrating a selective crystal growth in the two-dimensional micro space. However, the two-dimensional morphology differed greatly depending on the nature of the substrate used. Formation of a two-dimensional micro space using two Cu plates gave rise to thin films composed of quadrilateral nanoplates of approximately 0.8–2.4 μm (an average dimension of 1.41 μm) on each side of the surface A (Figure 4a), which are similar to those (Figure 2a and 2b) on obtained surface A using the Al_2O_3 plate. The average thickness of the quadrilateral nanoplates, ca. 280 nm, synthesized using the Cu plate as the substrate, was slightly larger than of that synthesized using the Al_2O_3 plate as the substrate (ca. 160 nm). This thickness difference is probably due to the larger number of complex ions generated by the CuO precursor in the two-dimensional micro space between the two Cu plates than between the Al_2O_3 and Cu plates. Using the SUS316L plate resulted in the synthesis of a thin film composed of thin quadrilateral nanoplates on surface A (Figure 4b). The quadrilateral nanoplates obtained using the SUS316L are larger and thinner than those obtained using the Al_2O_3 and Cu plates. Although SUS316L is a corrosion-resistant substance used in biomaterials, trace elements eluted from SUS316L into the NaOH solution during the hydrothermal reaction may have a slight influence on the growth of CuO crystals. The silver color of the SUS316L plate changed to brown after the reaction. The XRD patterns (Figure 3d and 3e) of surface A obtained using the Cu and SUS316 plates were similar to that on surface A obtained using the Al_2O_3 plate (Figure 3a), which confirmed the formation of highly crystalline CuO. Using the Ti plate resulted in thin films composed of plates of ca. 1.0 μm with bulky particles of several μm or more in size (Figure 4c). The XRD patterns of this thin film (Figure 3f) revealed diffraction peaks attributed to CuO. The intensities of these diffraction peaks were markedly lower than the CuO peaks in the XRD patterns of the quadrilateral nanoplate thin film (Figures 3a, 3d and 3e), indicating

the extremely low crystallinity of CuO in the plates. Ti plate is known to react with aqueous NaOH solution to form sodium titanate. In the present study, during the reaction, a large amount of Ti chemical species generated from the Ti plate adsorbed onto the CuO surface due to which the crystal growth of CuO was inhibited to some extent and resulted in the CuO plates with low crystallinity. These results suggest that by changing the nature of the substrate in the formation of the two-dimensional micro space on the surface of the Cu plate, a precise control of the nanostructure of CuO thin films can be achieved.

4. Conclusions

In the present study, the use of a two-dimensional micro space as a reaction field resulted in the successful synthesis of a thin film composed of quadrilateral CuO nanoplates on the surface of a Cu plate. This thin film combines the excellent mechanical properties and conductivity of the Cu plate, and the particular chemical properties related to the controlled morphology of the CuO quadrilateral nanoplates. Hence, this composite material has potential applications as a material for sensors, catalysts, and batteries. The synthetic strategy developed in the present study, where a two-dimensional micro space was used as a reaction field, can be applied for the synthesis of novel ceramic thin film/metal composites with a variety of tailored nanostructures.

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