Growth of Cu-Oxide Nanowires on Cu Substrates by Thermal Annealing*

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The CuO/Cu2O nanowire axial heterostructures were fabricated by a thermal oxidation technique in air. These nanowire structures resulted from CuO nanowire growth followed by Cu2O formation. These nanowires were divided into two regions. One is the top half part of the nanowire with CuO domains, and the other part is the bottom half of the wires with Cu2O domains. The structural property of the CuO/Cu2O nanowire axial heterostructures was clarified in detail. Both the CuO and the Cu2O have domain boundaries parallel to the growth direction. The specific relationship of the crystalline orientation between the CuO and Cu2O shows that CuO [110] or [110] is nearly parallel to Cu2O [110] mostly along the growth directions. The growth condition dependence of the morphological structure was also examined. A simple axial nanowire heterostructure fabrication technique using the compositional modification was developed. [DOI: 10.1380/ejssnt.2012.175]

Keywords: Copper oxides; Oxidation; Scanning transmission electron microscopy; Nano-wires, quantum wires, and nanotubes; Diffusion and migration

I. INTRODUCTION

Recently, one-dimensional (1D) nanostructures have attracted tremendous attention due to their advanced properties as compared to those of bulk materials. In addition, it is expected that 1D nano-devices with heterostructures should provide a wider range of functionalities, and improve device performance with respect to the assembly of the nanowires into more complex superstructures.

The fabrication of semiconductor nanowire heterostructures by the “top-down” process has been widely reported. However, this process induced damage that degraded the device performance of the nanowire heterostructures [1]. Thus, “bottom-up” growth of axial nanowire heterostructures has been developed using a vapor-liquid-solid (VLS) mechanism [2]. Nowadays, oxide heterostructures are also extensively fabricated for optoelectronic device applications, and oxide axial nanowire heterostructures have been fabricated, such as ZnO/ZnInO [3] and ZnS/ZnSnO4 [4].

Cu-oxide is a class of oxide semiconductors, and has been intensively studied because of its abundance and safety. Cupric oxide (CuO) and cuprous oxide (Cu2O) are semiconductors and have energy band gaps of 1.2 and 2.1 eV, respectively. While, intrinsic CuO and Cu2O are p-type semiconductors, the n-type Cu2O growth and electrical control of Cu2O have also been reported [5]. The oxides are expected to be used not only as catalyst, magnetic storage media and superconductors, but also energetic materials for photovoltaic devices, such as solar cells [6–8]. It is reported that the CuO/Cu2O heterojunction, which consists of Cu2O and CuO grains layers, has been fabricated for optoelectronic applications [9]. In addition, various CuO nanowires have been currently synthesized by the oxidation of a copper foil. The detailed structure and the growth mechanism of the CuO nanowire have been investigated [10–19]. On the other hand, the growth of a Cu2O nanowire has only been rarely reported [11, 20, 21], and the growth mechanism of the Cu2O nanowire has not been clarified. In addition, the nanowire heterostructures composed of both CuO and Cu2O have not yet been fabricated. It is expected that the formation of CuO/Cu2O axial nanowire heterostructures will lead to improvement of its properties and its modification of the optoelectronic properties of the CuO/Cu2O heterojunction.

In this study, Cu-oxide nanowires were grown by the direct thermal oxidation of Cu substrates in air to fabricate CuO/Cu2O axial nanowire heterostructures, and the morphological and structural properties of the heterostructure were examined. In addition, the growth condition dependence of the structural properties of the nanowires is shown, and the growth evolution of the Cu-oxide nanostructures is discussed in order to clarify the growth mechanism of the Cu2O nanowires.

II. EXPERIMENTAL

Cu-oxide nanostructures were synthesized by the thermal oxidation of copper substrates in air. The substrates were placed in a quartz tube, which was loosely sealed at 1 atmosphere of air. The nanostructure growth was performed by exposure of the copper substrates to air in a loosely sealed tube under the following temperature profile. The Cu substrates were heated to the elevated temperature range of 773-973 K within 30 min (pre-thermal treatment time, t_p), and were maintained for several seconds to several hours (main thermal treatment time, t_m). Thereafter, the substrates were allowed to naturally cool to room temperature. It is noted that the nanostructures started to grow during the t_p, then further elongated during the t_m. The structural and morphological properties of the Cu-oxide nanostructures were characterized by

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FIG. 1: (a) SEM image of Cu-oxide nanowires on the Cu substrate thermally treated at 873 K for the $t_m$ of 1 h. (b) Enlarged SEM image of the nanowires shown in (a). (c) XRD spectrum of the Cu-oxide nanowires.

TABLE I: Chemical compositions of Cu-oxide nanowires measured by EDS point analyses for the positions shown in Fig. 2(a).

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<th>Position</th>
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III. RESULTS AND DISCUSSION

Figure 1(a) shows an SEM image of the Cu-oxide nanowires on a Cu substrate thermally treated at 873 K for the $t_m$ of 1 h. High density nanowires with the average length of about 10 $\mu$m were observed. Figure 1(b) shows an enlarged SEM image of the nanowires shown in Fig. 1(a). It is noted that each nanowire is divided into two regions. One is the top half part of the nanowire with the diameter of about 100 nm, and the other part is the bottom half of the wires with diameters of several hundred nm, the features of which are shown by the arrows in the figure. An XRD spectrum of the nanowires is shown in Fig. 1(c), which revealed the simultaneous formation of both the CuO and Cu$_2$O phases.

Figure 2 shows STEM images and the corresponding EDS mappings of one of the nanowires shown in Fig. 1. It was found that O atoms are homogeneously distributed throughout the nanowire as shown in Fig. 2(b). On the other hand, high density Cu atoms are distributed in the bottom half part of the nanowire, while lower density Cu atoms are detected in the top half part of the nanowire as shown in Fig. 2(c). Table I shows the results of point analyses of the chemical compositions shown in Fig. 2(a), and it was found that the chemical compositions of the top and bottom half parts of the nanowire are CuO and Cu$_2$O, respectively. The nanowire consists of two regions. Namely, one is the top half part of the nanowire with thin CuO, and the other part is the bottom half of the wires with thicker Cu$_2$O. The CuO/Cu$_2$O interface is clearly seen at the middle part of the nanowire as shown in Fig. 2(d).

Figure 3(a) shows an enlarged TEM image of the top of the CuO region. The Cu-oxide nanowires were grown on the Cu substrate at 873 K for the $t_m$ of 1 h. It was found that the CuO region consists of two domains divided by a boundary parallel to the longitudinal axis along the growth direction. It has been reported that the bi-crystal CuO nanowire is composed of two domains divided by (111) interfaces of CuO [9].

Figures 3(b) and (c) show high resolution TEM (HRTEM) images of domains A and B shown in Fig. 3(a), respectively. The Fast Fourier Transformation (FFT) patterns of the images and corresponding crystalline orientations of the domains are shown in each figure. CuO has a monoclinic structure with $a = 0.4668$ nm, $b = 0.3442$ nm, $c = 0.5131$ nm and $\beta = 99.506$ degrees. As shown in Fig. 3(b), the interplanar spacings for the two lattice planes are 0.31 and 0.26 nm, corresponding to the (101) and (111) planes of the monoclinic CuO, respectively. The FFT pattern of domain A is specified as a monoclinic CuO structure with a zone axis perpendicular to the (1¯11) plane. The bi-crystal (111) domain boundary is inclined by about 57 degrees from the electron beam direction to the side wall of the nanowire along the growth direction.

On the other hand, for domain B in Fig. 3(c), the electron beam is focused in a direction perpendicular to the (111) plane. The crystalline orientations of domains A and B are rotated by 180 degrees along the [100] direction to each other. The bi-crystal (111) plane of domain B faces the (111) plane of domain A at the grain boundary. The extra FFT spot slightly observed in the fig-
FIG. 3: (a) Enlarged TEM image at the top of the CuO region. (b) and (c) HRTEM images of domains A and B shown in (a), respectively. FFT patterns of the images and corresponding crystalline orientations of the domains are shown in the inset. (d) Schematic illustration of crystallographic configurations of the CuO nanowire shown along the growth direction. (e) and (f) Pole figures of domains A and B along the electron beam direction, respectively.

Figure 4(a) shows a TEM image of a part of the Cu$_2$O region, and Figs. 4(b) and (c) show enlarged HRTEM images of the square parts shown in Fig. 4(a). The Cu$_2$O nanowires were grown on the Cu substrate at 873 K for the $t_m$ of 1 h. The FFT patterns of the images and corresponding crystalline orientations of the domains are shown in the inset. Cu$_2$O has a cubic structure with the lattice constant of 0.4217 nm. The growth direction of the Cu$_2$O shown in Fig. 4(b) is [110] and the electron beam is along the [001] direction. On the other hand, the growth direction of the Cu$_2$O mostly shown in Fig. 4(c) is [110], where the electron beam is along the [112] direction. In addition, a long-range periodicity of the moire fringe along the diameter direction of the nanowire of about 1.4 nm is observed, which is caused by an interference between ($d = 0.26$ nm) and ($d = 0.30$ nm). This means that the two domains of the Cu$_2$O are overlapped along the electron beam direction in the area shown in Fig. 4(c). The crystallographic configuration of the Cu$_2$O region is schematically illustrated as shown in the figure. As a result, it was determined that the Cu$_2$O nanowires were formed on the lower part of the CuO nanowires accompanied by the formation of domains rotated around each other along the growth direction. Based on the results mentioned above, it was found that CuO/Cu$_2$O nanowire axial heterostructures were grown with a specific crystalline orientation relationship between the CuO and Cu$_2$O domains.

Figure 5(a) shows the main thermal treatment temperature dependence of the growth morphology of the CuO nanowires grown for the $t_m$ of 1 h. At the low main thermal treatment temperature of 773 K, thin CuO nanowires are predominantly grown. As the temperature increased, thicker Cu$_2$O domains are formed from the bottom of the nanowire. However, a thin CuO domain remains on the top half of the nanowire, as already mentioned. With the increasing temperature, thick Cu$_2$O nanowires are predominantly grown at the main thermal treatment temperature of 873 K. Figure 5(b) shows the $t_m$ dependence of the growth morphology of the CuO-nanowire axial heterostructures.

Table II: Chemical compositions measured by EDS point analyses for the positions of the Cu-oxide nanowires thermally treated at 873 K for the $t_m$, of 5 seconds shown in Fig. 5(b).

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FIG. 5: (a) Main thermal treatment temperature dependence of the growth morphology of the Cu-oxide nanowires grown for the $t_m$ of 1 h. (b) $t_m$ dependence of the growth morphology of the Cu-oxide nanowires grown at the main thermal treatment temperature of 873 K. The chemical compositions of the nanowires thermally treated for the $t_m$ of 5 seconds are shown in Table II.

nanowires grown at the main thermal treatment temperature of 873 K. For the nanowires thermally treated for the $t_m$ of 5 seconds, the nanowires were mainly grown during the $t_p$. Table II shows the results of EDS point analyses of the nanowires. It was found that the chemical compositions of all parts of the nanowire are CuO, and the nanowire is single phase CuO. As the $t_m$ increased, thin CuO nanowires are mostly grown as shown for the $t_m$ of 0.5 h. In addition, with the further increasing $t_m$, thick Cu$_2$O nanowires are predominant.

The growth mechanism of the CuO nanowires has been investigated, and discussed as follows. Due to the existence of the grain boundary parallel to the growth direction, the nanowire growth occurs via the short-circuit diffusion of Cu ions along the bi-crystal grain boundary [15, 17]. In addition, it was reported that CuO nanowires are grown when sufficient oxygen is supplied to the nanowires. However, Cu$_2$O is the main oxidation product when the oxygen is deficient, as discussed on a thermodynamic basis [10]. Based on these discussions, the structural property and growth evolution of the CuO/Cu$_2$O nanowires can be explained as follows.

The growth evolution of Cu$_2$O nanowires through the CuO nanowires is schematically illustrated in Figs. 6(a)-(c). During the initial growth stage of the nanowire, CuO is nucleated and forms the single phase CuO nanowires with a diameter of about 100 nm during the $t_p$. At a low temperature, the growth of CuO is more preferable than that of Cu$_2$O [15]. The gradual increase in the substrate temperature causes the preferable CuO nanowire formation. With the increasing main thermal treatment temperature, the Cu diffusion is enhanced, and then the Cu$_2$O domains grow from the bottom of the nanowire. On the other hand, with the increasing $t_m$, thin, dense and elongated CuO nanowires are grown. However, oxygen is consumed in the limited space of the reaction tube. After the CuO nanowire growth, additional Cu atoms diffused into the CuO nanowires from the bottom of the wires to form the Cu$_2$O domains due to the oxygen deficiency. Thus, the CuO/Cu$_2$O axial nanowire heterostructures are fabricated.

Moreover, a specific relationship of the crystalline orientations between the CuO and Cu$_2$O is observed, as already mentioned. A possible structural model of the CuO/Cu$_2$O crystallographic configuration is shown in Fig. 6(d). The growth directions of the CuO nanowire are mostly along [110] or [110], and that of the Cu$_2$O domain is [110]. It is considered that the preferential growth direction of Cu$_2$O [110] enhances the crystal growth in the Cu$_2$O [110] direction along the nanowire [22]. In addition, the bi-crystal structure of CuO affects the structural property of the Cu$_2$O nanostructures. During the formation of Cu$_2$O, polycrystalline growth is possible, however, the
small lattice mismatch \( f \) between CuO and Cu\(_2\)O along the specific growth directions leads to the growth [110] direction of Cu\(_2\)O, as examples, CuO(111)/Cu\(_2\)O(111) \((f = -0.32)\), CuO(002)/Cu\(_2\)O(111) \((f = -0.032)\), CuO(200)/Cu\(_2\)O(111) \((f = 0.063)\), etc. Assuming the CuO/Cu\(_2\)O crystallographic configuration mentioned above, Cu\(_2\)O \{111\}, \{100\} grows along the radial directions of the nanowires as shown in the figure. In this case, Cu\(_2\)O \{111\} is nearly parallel to the Cu\(_2\)O\{011\}, the configuration which is observed in Fig. 4.

As a simple and scalable growth method, the oxidation behavior of metals has been typically conducted for the nanostructure growth of metal oxides. In other words, the possible control of the oxidation behavior of metals leads to artificial structural modifications of the oxide nanostructures. It was found in this study that the CuO/Cu\(_2\)O axial nanowire heterostructures were fabricated through the CuO nanowire formation followed by the additional diffusion of Cu atoms into the CuO nanowires from the Cu substrates. The axial nanowire heterostructure is simply designed by only a compositional modification along the growth direction. It is expected that further precise sequential control of the growth conditions will lead to the synthesis of more refined or sophisticated nanostructures, for example, a multilayered nanowire heterostructure.

IV. CONCLUSIONS

In this study, CuO/Cu\(_2\)O nanowire axial heterostructures were fabricated by a thermal oxidation technique in air using a loosely sealed quartz tube. The gradual increase in the substrate temperature as the pre-thermal treatment is employed to make certain the preferable CuO formation during the initial stage of the nanowire growth. The morphological structure and growth mechanism of Cu\(_2\)O nanowires are clarified as mentioned below. The nanowires were divided into two regions. One is the top half part of the nanowire with thin CuO, and the other part is the bottom half of the nanowire with thicker Cu\(_2\)O. The bi-crystal structure of CuO affects the structural property of the Cu\(_2\)O nanostructures. The CuO nanowire is divided by the (111) interface boundary parallel to the longitudinal axis along the growth direction. The crystalline orientations of the domains in CuO are rotated by 180 degrees to each other along the [100] direction. Both the CuO and the Cu\(_2\)O have domain boundaries parallel to the growth direction. The specific relationship of the crystalline orientation between CuO and Cu\(_2\)O shows that CuO [110] or [110] is nearly parallel to Cu\(_2\)O [110] mostly along the growth directions. The axial nanowire heterostructure fabrication technique using a compositional modification will provide a simple fabrication procedure for nano-scale semiconductor engineering.