Growth of Grass Like Architectures on Si Substrate and Its Mechanism Study

Lijiao Hu, Yang Ju*, Hosoi Atsushi

Department of Mechanical Science and Engineering, Nagoya University, Nagoya 464-8603, Japan
* Corresponding author: ju@mech.nagoya-u.ac.jp

Abstract Grass like architectures were synthesized directly on Silicon substrate by thermal oxidation method with nickel catalyst at low temperature. Humidity and catalyst played an important role in the fabrication of the grass like architectures. The morphology of the grass-like architectures was controlled by heating temperature. The grass like architectures were observed by scanning electron microscope (SEM, JSM-7000FK), Energy-dispersive X-ray (EDX) and X-ray diffraction (XRD). The grass like architectures were approximately 8-70μm in size with 1-2.5μm width leaves. The growth of grass like architectures affected by oxidation, vertical stress induced, and horizontal compressive stress was studied in details.

Keywords Grass like architectures, Thermal oxidation, Nickel catalyst, Compressive stress

1. Introduction

Cuprous oxide (Cu_2O) is a p-type semiconductor metal oxide with a direct band gap of about 2.17 eV. Due to its unique optical, electrical, and magnetic properties[1–3], and other properties such as simplicity and low cost of preparation, nontoxic nature, and abundance, it has attracted great attention and been widely applied in solar energy conversion[4], photocatalysis[5], sensors[6], negative electrode materials for lithium-ion batteries[7], electrochromism[8], and antibacterials[9]. The fundamental properties of micro/nanostructure semiconductors are found to be dependent on their architectures, including geometry, morphology, and hierarchical structures[10]. Therefore, great efforts have been devoted to artificially control the morphology of Cu_2O micro/nanocrystals in the past several years[11]. Different Cu_2O nano architectures have been synthesized, such as nanowhiskers[12], nanowires[13], nanocubes[14], nanorods[15], nanospheres[16], nanoflowers[17], nanocages[18]. A variety of methods have been reported to synthesize nanoflowers of different materials. These methods include hydrothermal synthesis[19], sol–gel method[20], chemical vapor deposition[21], ultrasonic pyrolysis[22], electrodeposition method[23], and solution routes[24].

Herein, we have developed novel syntheses of grass like Cu_2O architectures on silicon substrate with nickel-based catalyst at a low temperature. Although many studies proposed the evolution of different structures, the ability to manifest the precise growth mechanism of Cu_2O micro/nanostructures is still quite limited. In this work, the growth mechanism of Cu_2O grass-like architecture on silicon substrate was studied through the phenomenon of several contrast experiments.

2. Experiment

Commercial silicon wafer with a thickness of 0.50 mm was cut into square samples which were 20mm×20mm in size. The substrates were then ultrasonically (BRANSONIC1510) cleaned with acetone, washed with ethanol and de-ionized water sequentially to dissolve the contaminations. Nickel based catalyst used in this experiment was the high temperature electrically conductive coating material (Pyro-DuctTM 598-C, AREMCO, INC.). Catalyst was manually daubed on the silicon substrate as the shape of islands with diameter around 2-3 mm. Cu powder was dispersed around Ni on the substrate. Grass like architectures were then synthesized by heating the sample in wet air atmosphere at 200°C temperature for 3h.

After the heating process, morphologies of the oxidized specimens were characterized by the scanning electron microscopy (SEM, JSM-7000FK), Energy-dispersive X-ray (EDX) and X-ray diffraction (XRD).

3. Results and discussion

3.1. Experiment results

As shown in Fig. 1 grass like architectures, which were 8-70 μm in size with 1-2.5 μm width leaves grew mainly at the edge of the catalyst island. The contrast experiments showed that without the nickel based catalyst there would be no grass like architectures growing on the Si substrate even after the same heating process. Meanwhile, there was no grass like architectures growing on Si substrates which were heated at thermostatic drier and vacuum tank. Therefore, the catalyst, humidity and oxygen atmosphere were considered to be three of the important factors to affect the growth of grass like architectures.

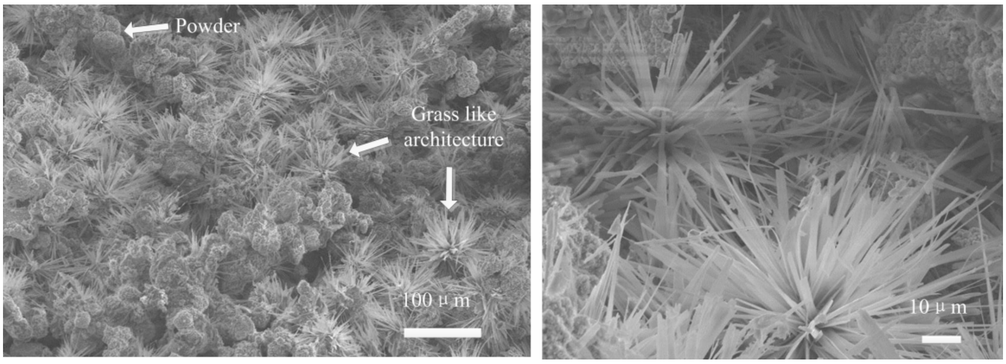
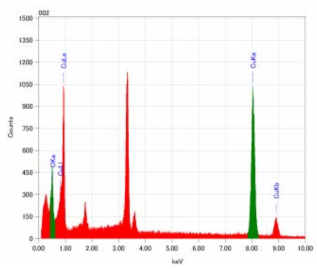


Figure 1. SEM image of grass like architectures



Element	Weight%	Atomic%
O K	12.17	35.50
Cu K	87.83	64.50
Totals	100	

Figure 2. EDX spectra of grass like architectures on Si substrate

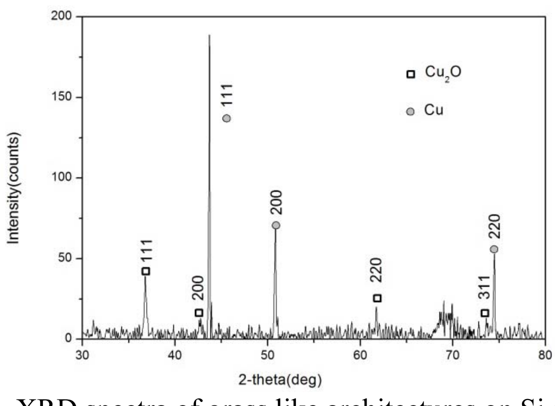


Figure 3. XRD spectra of grass like architectures on Si substrate

Energy-dispersive X-ray (EDX) analysis (Fig.2) indicates that the architectures are composed of Cu elements (35.50%) and oxygen elements (64.50%). The architecture was composed of Cu_2O

grass-like architectures, as confirmed by the X-ray diffraction (XRD) spectrum (Fig.3). The sharp diffraction peaks also indicate the sample is highly crystalline.

3.2. Discussion

The oxide formation appears to proceed via the diffusion of both copper and oxygen. Subsequently, oxidation takes place at the interface between the oxygen in the air and the Cu ions of the copper powders. Cu ions migrate from the inner of powder to the interface, according to stress induce mechanism. Meanwhile, the oxygen diffuses from outside to inside of interface in the opposite direction, according to Flick's first law[25]. As in figure 4, it was suspected that core(Cu)-shell(Cu_2O) composite structure developed in the Cu powder. It was in accord with the aforementioned EDX and XRD results, which were that the composition of grass like architectures was the Cu_2O and the powder was composed of Cu and Cu_2O.

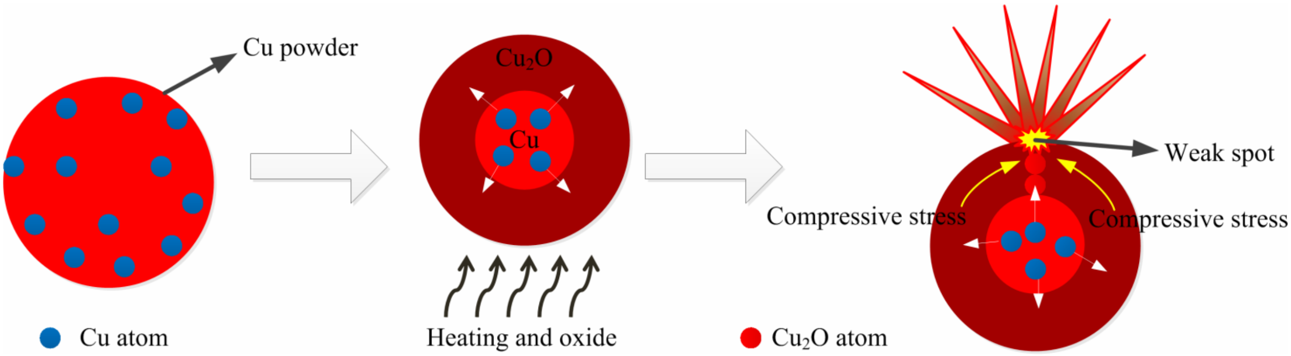


Figure 4. Schematic of atoms migration and its simplified mechanical model

Nickel based high temperature electrical conductive material played an important role in this process. It had the similar character as colloid nickel which has shown to be potential catalysts for selective hydrogenation, such as high surface-to-volume ratio for catalyst. However, colloid nickel can not resist the high temperature environment which is an essential factor for the formation of grass like architectures in our experiments. In our case, environment humidity supplied efficient water vapors from which nickel, as hydrogen absorption catalysts, would absorb hydrogen and left bivalent oxygen ions with two chemical bonds.

Normally, at 200ºC there would have nanowires generated at the surface. However, in our case it was suspected that the tangential direction compressive stress was increased by the composition effect of catalyst, humidity and oxidation during the heating process, as shown in Figure 4. The atom accumulated at the grain boundary under the oxide layer. Finally, with long enough heating time grass like architectures sprouted from the weak spots at the surface of the oxide layer.

It was suspect with longer heating time the core-shell composite structure in the Cu powder would disappear and the powder would be completely oxidized.

4. Conclusion

In summary, grass like architectures which were 8-70μm in size with 1-2.5μm width leaves has been successfully fabricated by thermal oxidation approach. The microstructures and compositions of the samples were characterized by SEM, EDX and XRD. The formation mechanism of grass like architectures were examined and proposed. The results showed that tangential direction compressive stress caused by the oxide layer of the Cu powder surface played a critical role in the formation of grass like architectures. Compared with other methods for fabricating copper oxide grass like architectures, the method proposed in the paper featured simplicity and cheapness.

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