Summary of Doctoral Dissertation

Anisotropic Growth of Metal Rods and Wires without Organic Capping Agents for Transparent Conducting Materials

有機キャッピング剤を用いない金属ロッド・ワイヤの異方性成長

および透明導電性材料としての応用

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[Background and Objectives]

This dissertation focuses on the metallic particles as transparent conducting materials for optoelectronic devices. In a typical optoelectronic device structure, bottom electrode is often TCEs while top electrode is normally an opaque metal thin film. To enhance the device performances, metallic particles as top TCEs could be integrated into the device. For the metallic particles to be used as TCEs effectively, rod and wire-shaped metallic particles are essential since they provide high electrical conductivity, transparency, and flexibility with their morphologies. However, the syntheses of these morphologies often involve in complex systems which require organic capping agents as shape-directing agents to promote the anisotropic growth of the particles. Consequently, during the fabrication of electrodes, tedious post-process is often required to remove the capping agents of the metallic particles to improve the overall electrical conductivity of the electrodes. Besides, the consideration on the post-processing is crucial especially when using metallic particles as top electrodes of the devices which contain chemical or heat-sensitive layers. Creating metallic particles in rod or wire-shaped in micro- and nano-regime without organic capping agents is thus significant and attractive as the post-processing can be eliminated. This thesis aims at the synthesis and study of anisotropic growth of the metallic particles into rod and wire-shaped without the need of organic capping agents and the application of such particles as top electrodes in optoelectronic device.

[Experimental methods]

In Chapter 2, the silver nanowires (Ag NWs) were synthesized based on a modified polyol method, with ethylene glycol (EG) as the solvent, $Fe(NO_3)_3$ and NaCl as the mediating agents, and $AgNO_3$ as silver precursor. The solution consists of all reactants was reacted at 110 °C for 15 h to grow Ag NWs. The reacted solution was purified by centrifugation at 5000 rpm for 30 min and the obtained Ag NWs were dispersed in IPA for further characterization.

In Chapter 3, Ag NWs were dispersed in IPA to form dispersion with concentration of 1.22 mg/mL prior use. To fabricate a photodiode, a commercial ITO-coated glass substrate (7-15 Ω/sq) was used as bottom electrode. The photodiode consisted of a layer of CBP with an inorganic layer of MoO_3 as active layers and Ag NWs as top electrode. The active layers were deposited using thermal evaporation method, while Ag NWs electrodes were prepared by drop-casting method.

In Chapter 4, first Cu-EG complex was prepared as copper (Cu) precursor in an EG solution, followed by the reduction of the complex into Cu particles with NaCl as the mediating agent and ascorbic acid as the reducing agent. The solution consists of all reactants was heated at 70 °C and left reacted for 20 h. The reacted solution was purified by centrifugation at 3000 rpm for 10 min. The purified Cu particles were dispersed in MeOH for further characterization.

[Results and Discussion]

The anisotropic growth of Ag NWs without the organic capping agents was studied in Chapter 2. The Ag NWs were successfully synthesized in EG with the presence of Cl^- and Fe^{3+} ions. It is found that the growth of Ag NWs correlated with the concentrations of Fe^{3+} ions. Fe^{3+}/Fe^{2+} ions and Cl^-/O_2 pairs in the reaction system controlled the kinetic growth of Ag by hindering the addition of Ag atoms on (100) facets, in return allows the continuous growth on (111) facets, leading to the formation of NWs. It is observed that at the optimal concentration of of Fe^{3+} ions (80 mM), Ag NWs with aspect ratio of as high as 1156 were obtained. The synthesis procedure could be scaled up and produce Ag NWs with a higher aspect ratio of 2820 (Figure 1(a)). This is thought to be caused by larger sizes of AgCl seeds formed in large scale synthesis. The electrical and optical properties of the Ag NWs were examined and found to be suitable for using as TCEs, particularly the transparency in UV region is similar with that of ITO electrodes.

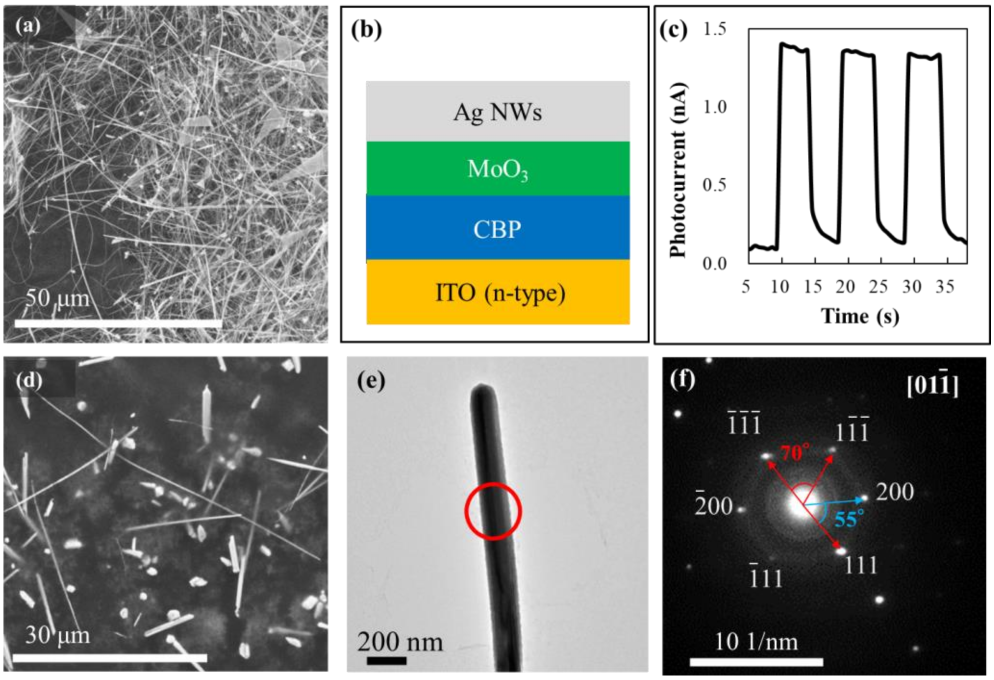

Figure 1. (a) SEM image of synthesized Ag NWs, (b) device structure of photodiode using Ag NWs as top electrodes, (c) switching behaviors of the photodiode, (d) SEM image of synthesized Cu rods, (e) TEM image of Cu rod, and (f) the corresponding SAED pattern of Cu rod taken at the area marked with a circle in the TEM image.

The application of Ag NWs, which were synthesized without organic capping agents in chapter 2, as top electrode in a fully transparent, inverted photodiode were explored for the first time. The photodiode had an inverted structure (Figure 1(b)) with CBP/MoO_3 as active layers and ITO as the bottom TCE. Since the Ag NWs were deposited by drop-casting on the top of the active layers, no post-processing was needed. It is found that the photodiode using Ag NWs as top electrode showed the highest responsivity at 340 nm which is the responsive wavelength for active layers and good switching behaviors (Figure 1(c)).

The anisotropic growth of Cu rods without organic capping agents were investigated in Chapter 4. Figure 1(d) shows the synthesized Cu rods. It is found that Cl^- ions are needed for the anisotropic growth of Cu rods. The rods have the long axis along [011], (111) facets as the tip, and (100) facets as the side surface (Figure 1(e)-(f)). By increasing the concentration of Cl^- ions, more Cu atoms contributed to the formation of Cu rods and the kinetic growths of the length and the diameter of the rods were varied. The results suggest that Cl^- ions have preferential adsorption on (100) Cu surfaces compared to (111) facets to promote the anisotropic growth of Cu along [011], thereby longer rods were obtained at higher Cl^- concentrations. Meanwhile, the adsorption of Cl^- to both (111) and (100) surfaces at high Cl^- concentration could reduce the relatively faster growth of the particle length compared with the diameter, resulting in thicker Cu rods.

[Conclusions]

Chapter 2 demonstrations the ability for the synthesis of Ag NWs to be scaled up which is beneficial and preferable for industrial production. Chapter 3 shows the simplicity of deposition and the elimination of complicated post-processing which are important and attractive for industrial production. Besides, the demonstration on using Ag NWs as top electrode in a photodiode also showed the promising potential of such Ag NWs to be used as top electrodes in full inverted structure optoelectronic devices in the future. The findings in chapter 4 provides a deep comprehension on the growth of ligand-free Cu rods with control in their aspect ratios.

In overall, this research provides (1) an improved procedure for producing high aspect-ratio, surfactant-free Ag NWs by varying the concentrations of Fe^{3+} ions and increasing the scale of the synthesis, (2) first demonstration on applying the high aspect ratio, surfactant-free Ag NWs as top electrodes without any post-processing needed in a fully transparent, inverted structure photodiode and (3) a new approach for growing surfactant-free Cu rods by varying the concentrations of Cl^- ions in the system. Studies presented in this dissertation bring a new insight and better knowledges on the anisotropic growth of metallic rods and wires without organic capping agents for using as transparent conducting materials. The findings are significant to control the growth of metallic particles and further widen their advanced applications.