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Parameter-controllable microchannel reactor for enhanced deposition of copper sulfide thin films

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ABSTRACT

A microchannel reactor was designed and fabricated based on the unique fluid-flow and mass transfer characteristics in a closely parallel channel for the deposition of copper sulfide (Cu_xS) thin films. The configuration of the microchannel allows the flow pattern to be confined uniformly across the channel width and length, thereby resulting in a uniform deposited thin film covering the whole surface of the substrate. A parametric study of the deposition of Cu_xS thin films was performed, including the effects of deposition time (2–10 min), flow rate (2–6 ml/min) and reaction temperature (60–80 °C). It was observed that the basic characteristics of Cu_xS films, such as morphology, film thickness, film composition and optical band gap, were highly affected by all deposition parameters. We were able to attain smooth, dense and adherent Cu_xS film with homogeneous grains at a high growth rate of 1.8 μm/h, by optimizing the controllable parameters. The optimized condition was at temperature of 80 °C, flow rate of 6 ml/min and deposition time of 4 min. The results showed that the film formation by heterogeneous nucleation and growth on the substrate is promoted over homogeneous reaction in the solution phase, which is strongly due to the incorporation of the optimal channel design in a micro-scale structure together with the controlled deposition parameters. This method can overcome the issue of the deposition in limited area and can be scaled for large-area substrates with good uniformity of Cu_xS films.

1. Introduction

Semiconductor thin films, especially metal chalcogenides such as Cu_xSe, Cu_xS, ZnS, SnS and CdS, have received considerable interest in the past two decades due to their excellent physical and chemical properties in a wide range of applications in various fields [1–2]. Among these, copper sulfide (Cu_xS) thin films have become one of the promising alternative candidates for *p*-type semiconductors because of their diverse stoichiometric compositions, resulting in a variation in optical and electrical properties [3]. The characteristic features of copper sulfide are known to exist in at least five phases at room temperature ranging from copper-poor to copper-rich copper sulfides, including CuS (covellite), $Cu_{1.12}S$ (yarrowite), $Cu_{1.75}S$ (anilite), $Cu_{1.8}S$ (digenite), $Cu_{1.95}S$ (djurleite) and Cu_2S (chalcocite). For this reason, Cu_xS thin films have been widely considered in many potential applications such as solar cells, gas sensors, cathode materials in lithium batteries, photo catalysts, solar control coatings, *etc.* [4–8].

So far, there have been numerous deposition methods to prepare Cu_xS thin films, which are based on both gas-phase and liquid-phase processes, such as electrodeposition [1], photochemical deposition [5], chemical bath deposition [7], sputtering [3,9], atomic layer deposition [10], spray pyrolysis [2,11–13] and chemical vapor deposition [14]. Among these, solution-based processes have many advantages in terms of cost effectiveness, simplicity of equipment and mild operating conditions. While gas-phase techniques offer a high deposition rate, large area uniformity and large scale production, however they require vacuum equipment and high-energy consumption. Thus, seeking for an enhanced deposition method that combines all of the advantages of solution-based techniques and those of gas-phase techniques will be an attractive alternative for the deposition of reproducible high quality Cu_xS thin films.

One potential deposition method to overcome all of the inherent drawbacks associated with the conventional gas-phase and liquid-phase deposition techniques is to utilize a microchannel reactor system. Theoretically, micro-scale reactors provide high surface-to-volume ratio which is the main key in defining fluid-flow characteristics [15]. Based on the microchannel environment, the very short diffusional distance within the channel leads to a superior mass and heat transfer of reacting species towards the reaction sites (substrate). Therefore, an undesirable particle formation that occurs from the homogeneous bulk precipitation and degradation of the film quality can be significantly reduced. According to these benefits, the structure of microchannel reactor enables

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the heterogeneous nucleation and growth to become favorable on the substrate surface, resulting in a high deposition rate [16–17]. In recent years, several researchers have explored various aspects of continuous flow microreactor to produce nanomaterials such as CdS thin films [18–20], flower-like ZnO structure [21], ZnO nanocrystals [22] and $Cd_{1-x}Zn_xS$ thin films [23]. These previous studies demonstrated that the microreactor approach could be adopted for the film deposition at low temperatures with improved control of reaction parameters, subsequently improving film growth and film morphology. For Cu_xS thin film deposition in particular, a microreactor-assisted solution deposition technique was utilized in the previous study, where the precursor solution was mixed through a micromixer, passed through a micro-scale tubing, and impinged onto the substrate, which was placed on a tilted heated metallic plate [24]. A variation in process parameters were investigated to obtain a particle-free flux in solution. However, the deposition by this method could only be done in a limited area of the substrate because the mixed solution is deposited drop by drop continuously on the surface of the substrate.

In this work, we therefore designed and fabricated a simple and facile microchannel reactor for a continuous flow deposition of Cu_xS thin films, where the precursor solution flows through a closely parallel channel uniformly across the width and length of the substrate and rapidly proceeds to the nucleation step at the desired temperature. The goal of this study was to control the key parameters that are associated with heterogeneous and homogeneous reactions within the microchannel to achieve high quality of Cu_xS thin films. Influences of deposition parameters including deposition time, flow rate and temperature were investigated on resulting film morphology, film thickness, film composition and optical properties.

2. Experimental procedure

2.1. Fabrication of microchannel reactor

The purpose of fabrication of microchannel reactor is to obtain high quality Cu_xS thin films with enhanced deposition rate, film uniformity, and full coverage under the condition of laminar flow throughout the whole surface of the substrate. Therefore, the reactor design requires an efficient control of the collision between reacting species in the precursor solution and the chemical surface reactions that involve nucleation and growth within the closely spaced channel. The deposition system consists of a syringe pump and the fabricated microchannel reactor, connected with a small inlet port to prevent a dead volume prior to the deposition, and a large outlet port to minimize backpressure on the top as shown in Fig. 1(a).

In terms of the channel design, Fig. 1(b) depicts a geometry and dimension of the microchannel made by an aluminum plate, where it accommodates a 25 mm (width) × 50 mm (length) × 1 mm (thickness) glass slide substrate in the center. The heating system underneath the substrate provides uniform temperature control across the deposited area. The deposition channel was designed to be 1 mm in height to offer a rapid mixing and high mass and heat transfer rates, as a result of a short diffusional distance. The inlet and outlet headers of the channel were designed as a triangular shape so that a uniform flat flow profile across the channel width could be obtained. The top and bottom plates with a gasket (1 mm thick) in between were mounted together with nuts and washers. Then, the leakage was tested prior to Cu_xS deposition.

2.2. Cu_xS thin film fabrication

According to the previous study on the deposition of Cu_xS thin films by microreactor-assisted solution deposition technique (drop-by-drop deposition process), the concentration of reactant ratio $[CuSO_4]$:[NaOAc]:[TEA]:$[NH_3]$:$[SC(NH_2)_2]$ of 1:1:7.55:8.21:0.56 resulted in a particle-free flux in solution, in which a heterogeneous surface reaction

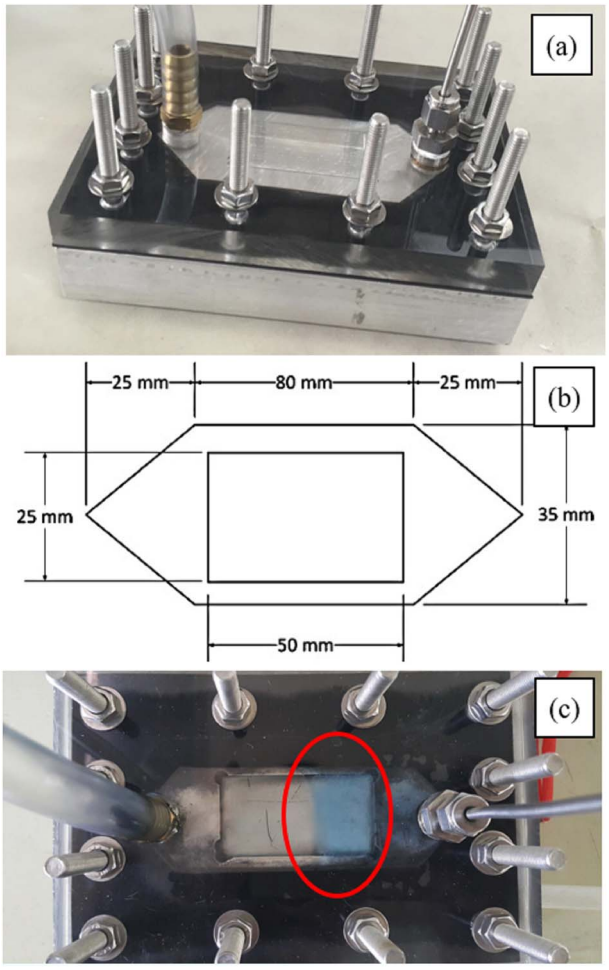

Fig. 1. (a) Fabricated microchannel reactor for Cu_xS thin film deposition, (b) Schematic drawing geometry and dimension of the channel (image not to scale) and (c) Flow distribution in the channel.

was favored over a homogeneous particle formation [24]. Therefore, in this work Cu_xS thin films were deposited on glass slide substrates from aqueous solutions using the same molar ratio, including 0.02 M of copper sulfate ($CuSO_4$), 0.02 M of sodium acetate (NaOAc), 0.151 M of triethanolamine (TEA), 0.164 M of ammonia (NH_3) and 0.011 M of thiourea ($SC(NH_2)_2$). Glass slides were cleaned with a detergent, acetone, methanol, and deionized (DI) water, and then dried under a stream of nitrogen gas prior to the deposition. The precursor solution was premixed and pumped through 1/8″ tubing which was connected to the inlet port of the microchannel reactor. A uniform profile of reactant mixture flows across the substrate and exits through 3/8″ tubing. Once the reaction was completed, the substrate was removed, washed with DI water, and dried under a stream of nitrogen gas. The variation of experimental conditions is as follows. The effects of different reaction temperatures (60, 70, and 80 °C), flow rates (2–6 ml/min) and deposition times (2–10 min) on film thickness, surface morphology, film composition and optical properties were investigated.

2.3. Characterization

The Cu_xS thin film morphologies and compositions were characterized by field emission scanning electron microscopy (FESEM, Hitachi SU8230), coupled with energy dispersive X-ray spectroscopy (EDS). The phase and crystal structure of the as-prepared thin film was examined by X-ray diffraction (XRD, Bruker D8 Advance AXS), operating at 40 kV and 30 mA, and Raman spectroscopy (NTEGRA Spectra, with a 473 nm wavelength). The optical properties were measured