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Scanning electrochemical microscopy studies of micropatterned copper sulfide (Cu_xS) thin films fabricated by a wet chemistry method

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ABSTRACT

Patterned copper sulfide (Cu_xS) microstructures on Si (1 1 1) wafers were successfully fabricated by a relatively simple solution growth method using copper sulfate, ethylenediaminetetraacetate and sodium thiosulfate aqueous solutions as precursors. The Cu_xS particles were selectively deposited on a patterned self-assembled monolayer of 3-aminopropyltriethoxysilane regions created by photolithography. To obtain high quality Cu_xS films, preparative conditions such as concentration, proportion, pH and temperature of the precursor solutions were optimized. Various techniques such as optical microscopy, atomic force microscopy (AFM), X-ray diffraction, optical absorption and scanning electrochemical microscopy (SECM) were employed to examine the topography and properties of the micro-patterned Cu_xS films. Optical microscopy and AFM results indicated that the Cu_xS micro-pattern possessed high selectivity and clear edge resolution. From combined X-ray diffraction analysis and optical band gap calculations we conclude that Cu_9S_5 (digenite) was the main phase within the resultant Cu_xS film. Both SECM image and cyclic voltammograms confirmed that the Cu_xS film had good electrical conductivity. Moreover, from SECM approach curve analysis, the apparent electron-transfer rate constant (k) in the micro-pattern of Cu_xS dominated surface was estimated as 0.04 cm/s. The SECM current map showed high edge acuity of the micro-patterned Cu_xS.

1. Introduction

Copper sulfide (Cu_xS, $1 \le x \le 2$) thin films have been found to have very useful electrical and optical properties and have attracted great interest for their potential use in energy applications, such as applications in achievement of solar cells and in photochemical conversion of solar energy as solar absorber coating [1,2], as selective radiation filters on architectural windows for solar control in warm climates [3], and as electroconductive coatings deposited on organic polymers [4]. At room temperature, there are five stable copper sulfide phases. Copper-rich phases exist as chalcocite (Cu_2S), djurlite ($Cu_{1.95}S$), digenite ($Cu_{1.8}S$) and anilite ($Cu_{1.75}S$), while the sulfur-rich phase exists as covellite (CuS). Mixed phases with intermediate compositions are also known. Copper sulfide (Cu_xS) usually exhibits semi-metallic properties, intrinsic semi-conductivities and in some cases, ductility [5–7]. It forms a p-type transparent film, and although transparent p-type materials generally have inferior conductivities to the widely used transparent n-type conducting materials such as ITO (In_2O_3:Sn) [8], FTO (SnO_2:F) [9], etc. [10,11], we show here that Cu_xS has semi-metallic conductivity.

Previous studies have mainly focused on the preparation of bulk Cu_xS film and numerous techniques have been investigated, such as vacuum evaporation [12], activated reactive evaporation [13], reactive magnetron sputtering [14], spray pyrolysis [15,16], slurry technique [17], and chemical bath deposition [18]. The sulfur source agents reported included thiourea, sodium sulfide and sodium thiosulfate, while copper ions were complexed by triethanolamine, ammonia, ethylenediaminetetraacetate (EDTA), citric acid or 1,4,8,11-tetrazacyclo-tetradecane. However, the production of patterned Cu_xS microstructure on a solid surface has not been reported. Patterning surfaces leads to the creation of physicochemical heterogeneities (e.g. surface energy, chemical reactivity, conductivity, topography and so forth), which are an important issue in the design of complex components used in high-tech technologies [19]. Furthermore, the creation of micro-patterned semiconductor materials has become an important subject in many areas, including microfluidics, optics, biosensors, electronics, and information storage [20–23].

A number of techniques have been successfully demonstrated for making patterned micro-features on various substrates, such as deposition by scanning electrochemical microscopy, screen printing, micromolding in capillaries (MIMIC), photolithography, laser writing, surface-templated deposition, microcontact printing and so on [24–28]. Among these methods, photolithography is one of the best-established technologies for micro-patterning and has

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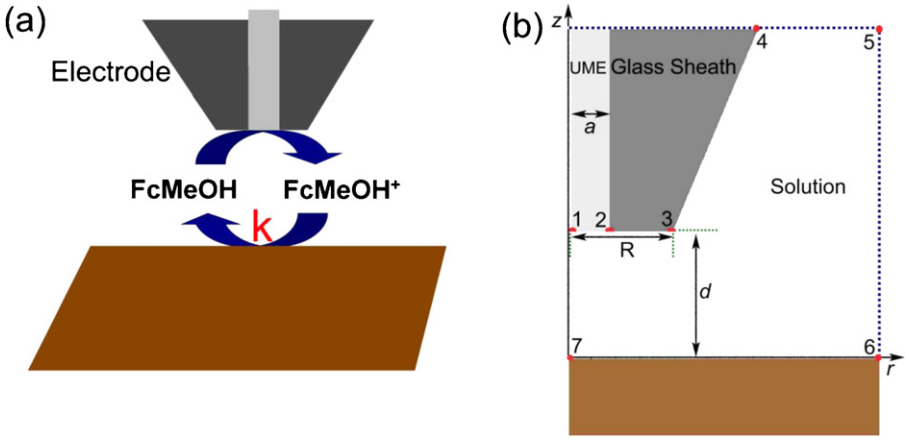

Fig. 1. (a) Diagram of SECM feedback mode on Cu_xS substrate and (b) geometry of simulation model.

found wide applications in the microelectronics industry because of advantages such as large-scale production and simple processing [29]. In this method, the pattern is produced by exposing a thin film of photoresist, light-sensitive polymer, or self-assembled monolayer (SAM) to UV light through a photomask. Either the patterned photoresist film or SAM has been used as a template for the subsequent deposition or etching. Some semiconductor microstructures have been prepared by photogenerated carriers without using photoresist or SAM, as reported in our previous study [30]. 3-Aminopropyltriethoxysilane (APTES) is a silane coupling agent which has been commonly used to provide surface protection. APTES is comprised of two reactive functional groups. The amino tail is able to form a strong covalent bond to a variety of metals such as Ag, Au and Cu. The ethoxy headgroup ($-OC_2H_5$) can undergo hydrolysis and bind to surface groups such as silanols on oxidized silicon.

In the present work, we report preliminary results on the patterning of Cu_xS films, which combines UV-photolithography and area-selective deposition. It provides a convenient, low-cost, stable method for forming patterned microstructures of copper sulfide semiconductor on solid substrates. The morphology and structure of the resultant Cu_xS patterning were characterized by optical microscopy, atomic force microscopy (AFM), and X-ray diffraction. Optical absorption and scanning electrochemical microscopy (SECM) were employed to investigate the corresponding optical band gap and electrochemical properties.

2. Simulation

The COMSOL multiphysics software (version 3.4) was employed to investigate the electrical property of the synthesized Cu_xS substrate by simulating the probe approach curves (PACs) above the Cu_xS substrate [31], which is similar to the work done by Cornut and Lefrou who reported an infinite substrate in the simulation model [32]. The redox mediator, ferrocenemethanol (FcMeOH), can be oxidized to $FcMeOH^+$ at the surface of ultramicroelectrode (UME) (radius of a) which is sealed in glass capillary (Rg radius) and positioned above the substrate with a distance of d at a biased potential of 0.4 V *vs.* Ag/AgCl:

$$FcMeOH - e^- \rightarrow FcMeOH^+ \quad (1)$$

$FcMeOH^+$ can be reduced back to FcMeOH at the Cu_xS substrate with the apparent electron-transfer rate constant of k (Fig. 1a):

$$FcMeOH^+ + e^- \xrightarrow{k} FcMeOH \quad (2)$$

$FcMeOH^+$ generated at the electrode surface can diffuse through the solution and was reduced at Cu_xS substrate (the line between points 6 and 7 in Fig. 1b) under the kinetic control. The flux of FcMeOH can be expressed as [33]:

$$D\left[\frac{\partial c(r,z)}{\partial z}\right]_{z=-d} = k[c_0 - c(r,-d)] \quad (3)$$

where D is the diffusion coefficient of FcMeOH ($7 \times 10^{-10}\ m^2/s$) [34], r and z are the coordinates shown in Fig. 1, $c(r, -d)$ is the local concentration of FcMeOH and c_0 is the bulk concentration of FcMeOH ($0.9\ mol/m^3$). Other simulation conditions can be found in the supporting information. A series of approach curves is calculated for fixed values of k by computing normalized current at 22 discrete normalized tip-substrate separation distances. The value of k at Cu_xS substrate was obtained from the simulated PAC that overlapped the experimental one.

3. Experimental

3.1. Materials

The substrates were (1 1 1)-oriented single crystal silicon wafers, with a thickness of about 0.5 mm and a diameter of 125 mm, purchased from GRINM Semiconductor Materials Co. Ltd., Beijing. The as-received wafers, polished on one side and doped as n-type, were cut to a size of 2 cm × 2 cm. 3-Aminopropyltriethoxysilane (APTES, 99%) was purchased from Aldrich (USA) and used as-received. $CuSO_4 \cdot 5H_2O$ (Fluka, USA), $Na_2S_2O_3 \cdot 5H_2O$ (Sigma–Aldrich, USA), EDTA (Sigma–Aldrich, USA), H_2SO_4 (Sigma–Aldrich, USA), H_2O_2 (Merck, Germany), KNO_3 (Sigma–Aldrich, USA) and ferrocenemethanol (FcMeOH) (Aldrich, USA) were used directly without further purification.

3.2. Preparation of patterned SAM

The silicon wafers were first cleaned by ultrasonicating in acetone, then in Milli-Q water, and then immersed in freshly prepared piranha solution (a mixture of 7:3 (v/v) 98% H_2SO_4 and 30% H_2O_2) at 90 °C for 1 h to remove organic residues and complete hydroxylation (*Caution: piranha solution reacts violently with many organic compounds and should be handled very carefully!*). The wafers were then rinsed thoroughly with Milli-Q water, placed into the APTES solution of $5.0 \times 10^{-3}\ mol\ dm^{-3}$ in a solvent of hexane, and held there for 3 h. The target monolayer of APTES was thus formed on the hydroxylated silicon surface. After rinsing with Milli-Q water, the APTES-coated silicon substrates were put into the chamber of UV/O_3 surface decontamination (Bioforce UV/Ozone ProCleaner Plus, USA) and irradiated for 1 h through a photomask consisting of