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CuS films grown by a chemical bath deposition process with amino acids as complexing agents

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ABSTRACT

CuS thin films were deposited by an ammonia-free chemical bath deposition process. This approach uses amino acids (alanine, glycine and serine) as complexing agents. The conditions under which amino acids form complexes and release Cu ions are discussed. All the resulting CuS films, formed by nanoflake particles, had the hexagonal crystalline structure (covellite). Moreover, the coexistence of Cu^{+} and Cu^{2+} states in these films were confirmed by X-ray photoelectron spectroscopy. Amino acids as complexing agents were then observed to affect mainly to the growth kinetics of the CuS films. Thus, thicknesses of 42, 55.4 and 70 nm were obtained for the films processed with solution reactions containing alanine, glycine and serine, respectively. The optical band gaps of the films with moderate transmittance had values in the range from 2.25 to 2.4 eV. Finally, the resulting CuS films with electrical resistivities from 1.84×10^{-3} to 2.8×10^{-3} Ω-cm showed a decrease of photosensitivity with the film thickness.

1. Introduction

Copper sulfide (Cu_xS) is a p-type semiconductor with five different stable phases at room temperature, namely, chalcocite (Cu_2S), djurleite ($Cu_{1.96}S$), digenite ($Cu_{1.85}S$), anilite ($Cu_{1.75}S$) and covellite (CuS). Depending on the stoichiometric composition, the Cu_xS band gap may vary between 1.2 and 2.53 eV [1,2]. Moreover, this semiconductor has metal-like electrical conductivity because copper vacancies act as acceptors [3]. Thus, owing to its physical, chemical, optical and electrical properties, CuS has been widely applied as an active material for supercapacitors [4], glucose sensors [5], gas sensors [6], photosensors [7], pH sensors [8], solar cells [9], Na-ion Batteries [10], among others. The preparation of CuS thin films can be performed by techniques such as successive ionic layer adsorption and reaction (SILAR) [11], atomic layer deposition [12], electrochemical deposition [13], and chemical bath deposition (CBD) [14]. Particularly, CBD is a low-temperature, simple and low-cost method for which no high pressure or vacuum equipments are required. Moreover, this method has been used for the deposition of high quality semiconductor thin films on large area substrates. Deposition parameters such as temperature, pH and chemical reagents used in the CBD process can affect the growth rate, structure, chemical composition, and physical properties of the deposited films. As study case, some authors have compared the influence of complexing agents in the chemical deposition of metal sulfide thin films observing variations in thickness, morphology and crystalline structure [15–18]. Most of these formulations use ammonia or hydrazine compounds as complexing agents which are harmful organic compounds to the environment because of its high volatility and toxicity. Alternatively, some approaches have been developed to optimize the deposition of semiconductor films with ammonia-free CBD processes. For instance, our research group has reported the deposition of CdS, $Cd_{1-x}Zn_xS$ and ZnS:(Cu, Mn) thin films using tri-sodium citrate, amino acids and ethylenediaminetetraacetic acid as complexing agents [19–22]. The ammonia-free chemical deposition of CuS films has been reported by using tri-sodium citrate as complexing agent in acidic solutions [23,24]. Recently, Flores-García et al. reported the deposition of Cu_xS films in alkaline solutions using this complexing agent [25]. The resulting films, formed by agglomerates with irregular shapes, had thicknesses in the range of 40–80 nm and resistivity values in the range of $106–10^{-2}$ Ω-cm. Alanine is an amino acid used as a stabilizing ligand for the synthesis of water soluble CuS nanoparticles by a simple colloidal route, as reported by Nelwamondo et al. [26]. The binding mode of alanine on the surface of the resulting nanoparticles was shown to be pH and temperature dependent. As it is known, the preparation of CuS films by the CBD method requires the availability of Cu ions along the deposition time through the action of complexing agents to ensure the formation of CuS particles with the available S ions and its adsorption to the substrate. The aim of this paper is to show the capability of amino

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acids to act as complexing agents for the chemical deposition of CuS films on glass substrates. This approach can be considered as an environmental friendly process because no ammonia or hydrazine compounds were used. Besides, amino acids are biodegradable organic molecules that can be reused in the CBD process. Amino acids have a basic amino group (–NH2) and an acidic carboxyl group (–COOH) that interact with metal ions to form complexes. The amino acids involved in this study were alanine (ala), glycine (gly), and serine (ser). Variations of film growth rates were observed as effect of the different complexation powers of the amino acids. Specifically, the thickness of the films labeled as a-CuS, g-CuS, and s-CuS prepared with reaction solutions containing ala, gly, and ser, respectively, was found to increase in the order a-CuS < g-CuS < s-CuS. All the films, formed by nanoflake particles, had the covellite CuS phase with the coexistence of Cu^{+} and Cu^{2+} states, as confirmed by X-ray photoelectron spectroscopy. The moderate optical transmittance and absorbance as well as the electrical resistivity, in the order of 10^{-3} Ω cm, suggest the potential application of these CuS films as counter electrodes in quantum dot sensitized solar cells.

2. Experimental details

The deposition of the a-CuS, g-CuS, and s-CuS films was carried out on glass substrates vertically immersed in a beaker with reaction solutions previously prepared, under stirring, by the addition of 2 ml of 0.25 M $Cu(NO_3)_2$, 2 ml of the desired complexing agent (1 M of ala, gly or ser) and 4 ml of 1.5 M thiourea. Deionized water was also added to complete a volume of 60 ml. Finally, the pH of the reaction solution was adjusted to 9 with some drops of KOH solution. At these conditions the Cu-amino acid complexes were appropriately formed, as demonstrated by the FTIR spectroscopy analysis. The temperature of the reaction solution was kept at 60 °C, during the films deposition, by immersing the beaker in a water bath system. The deposition time, which is considered as the time elapsed from the immersion of the beaker in the water bath until the substrates are removed from the solution, was forty minutes. The substrates with freshly deposited films were then washed with deionized water and air dried at room temperature.

Table 1
Assignment of the FT-IR features of ala, gly and ser in aqueous solutions at neutral pH.

Wave number (cm^{-1})			Assignment
Alanine	Glycine	Serine	
3086	3111	3133	$\nu_{asym}NH_3$
1599	1599	1590	δ_{asym} NH_3
1514	1506	1514	$\nu_{asym}COO$
1396	1408	1413	$\nu_{sym}COO$
1363	1337	1345	ωCH_2
1300	–	–	$tw CH_2$
1109	1100	1050	ρNH_3

ν stretching, δ bending, ω wagging, ρ rocking and *tw* twisting.

The structure of the amino acids in reaction solutions at neutral pH and its interactions with Cu ions in reaction solutions at pH9 were analyzed by a FT-IR/NIR Perkin Elmer Frontier spectrometer. The crystalline structure of the Cu films was analyzed by the X-ray diffraction (XRD) technique with a Philips diffractometer X′Pert using Cu (Kα) radiation, which has a characteristic wavelength (λ) of 1.5418 Å.

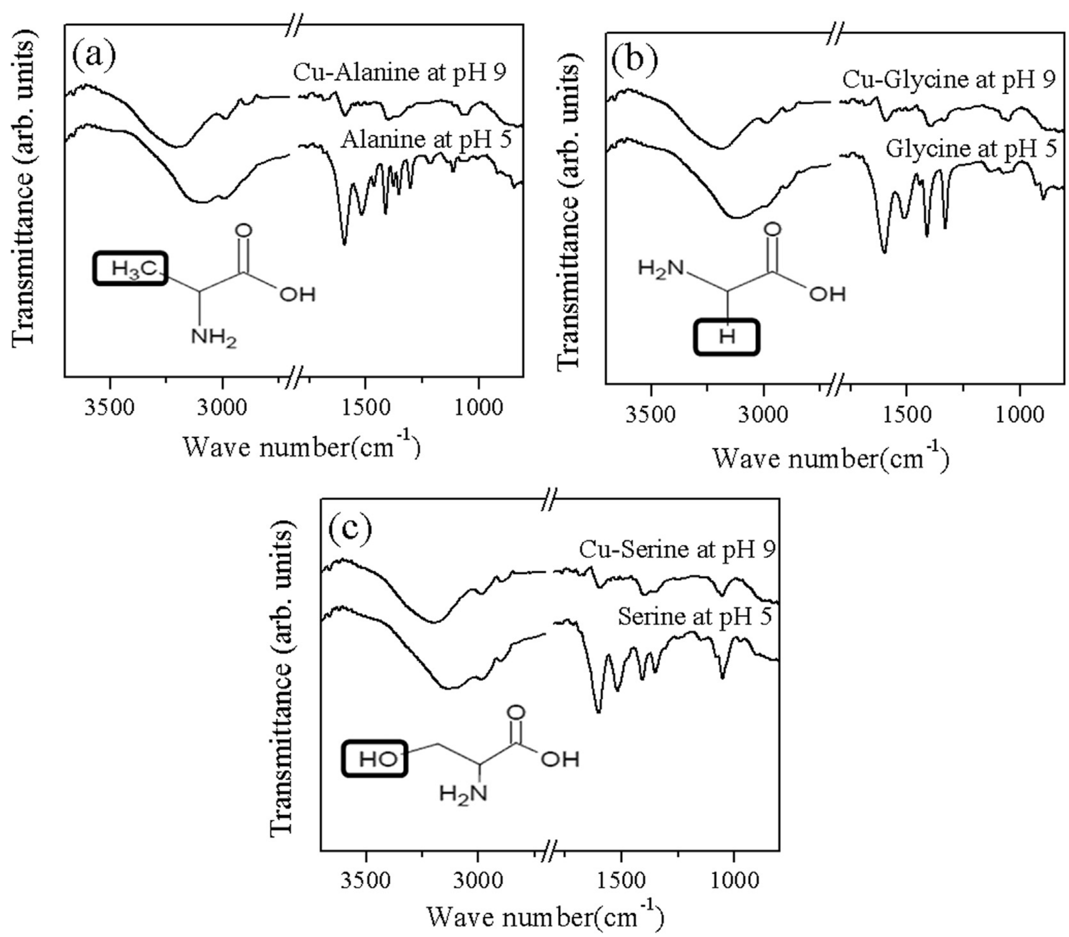

Fig. 1. IR spectra of amino acids in aqueous solutions at neutral pH (bottom curve) and its interaction with Cu ions in aqueous solutions at pH9: (a) ala, (b) gly and (c) ser.