

Structural, chemical and optical properties of the polyethylene–copper sulfide composite thin films synthesized using polythionic acid as sulfur source

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ABSTRACT

Synthesis and properties of thin copper sulfide films deposited on polyethylene were explored for the development of low cost hybrid organic–inorganic photovoltaic materials. Polyethylene was used as a model organic host material for thin copper sulfide film formation. Adsorption–diffusion method was used which utilized consecutive exposure of polyethylene to polythionic acid followed by aqueous Cu(II/I) solution. Several crystalline copper sulfide phases were obtained in synthesized samples and elucidated using X-ray diffraction. Surface chemical composition determined using X-ray photoelectron spectroscopy showed the presence of copper sulfides in combination with copper hydroxide. Thickness of the composite material films ranged from several microns to $\sim 18 \mu\text{m}$ and depended on the Cu(II/I) exposure time. Bandgap of the materials obtained was measured and ranged from 1.88 to 1.17 eV. Importantly, heating these complex copper sulfide crystalline phase containing films at 100°C in inert atmosphere invariably resulted in a single copper sulfide, anilite ($\text{Cu}_{1.75}\text{S}$), phase. Anilite possesses a bandgap of 1.36 eV and has demonstrated excellent photovoltaic properties. Thus, the method described in this work can be used for a low cost large scale composite thin film photovoltaic material deposition based on anilite as photoactive material.

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1. Introduction

Copper sulfides are of great interest in numerous fundamental and industrial applications due to the wide range of stoichiometric compositions, particle morphologies, complex and diverse electronic properties [1,2]. As an intrinsic p-type semiconductor, copper sulfide has recently attracted considerable interest as a promising material with potential applications in solar cells, optical filters, nanometer-scale switches, thermoelectric and photoelectric transformers, gas sensors and photocatalysts [3–7]. Light harvesting properties are of particular interest since copper sulfide is comprised of earth abundant, environmentally benign elements [3,8]. Due to their unique optical and electrical properties, they are also widely used in thin film and composite material manufacturing [9].

One of the most interesting copper sulfide properties is its various stoichiometries with a total of fourteen different identifiable

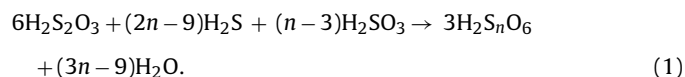
crystalline phases [10]. The copper–sulfur system has wide variety of non-stoichiometric and mixed phases from Cu_2S at copper-rich side to CuS_2 at the copper-deficient side including $\text{Cu}_{1.96}\text{S}$, $\text{Cu}_{1.94}\text{S}$, $\text{Cu}_{1.8}\text{S}$, $\text{Cu}_{1.75}\text{S}$, $\text{Cu}_{1.12}\text{S}$ and $\text{Cu}_{1.106}\text{S}$ [5,11,12]. Such varying stoichiometries and valence states greatly affect the structural, optical, and electrical properties of these copper sulfides [7]. For example, CuS exhibits p-type semiconducting properties or metallic conductivity and transforms into a superconductor at 1.6 K, which makes it useful for solar cells, optical filters and superionic materials [11,13]. On the other hand, anilite phase copper sulfide, $\text{Cu}_{1.75}\text{S}$, is a thermodynamically stable crystalline phase that was suggested to replace for $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$ (CIGS) for photovoltaic applications [14]. Furthermore, hybrid organic–inorganic materials comprised of organic photovoltaics and tunable absorption inorganics are of high potential for solar light harvesting but the conversion efficiencies are still low and CdS is state of the art material used [15]. Environmentally friendly sulfides, including copper compounds, can potentially be used as a viable substitute.

A variety of routes for obtaining of copper sulfide thin films have been developed so far, including chemical bath deposition (CBD) [16], chemical vapor deposition (CVD) [17], spray pyrolysis

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[18], electrochemical methods [19], successive ionic layer adsorption and reaction (SILAR) [20], atomic layer deposition (ALD) [21], spray-ion layer gas reaction (ILGAR) [22], most of the utilizing vacuum and/or high temperatures. The adsorption–diffusion method of obtaining copper sulfide layers is a new technology during which, after the adsorption of the sulfuration agent, a polymer surface is treated with copper salt containing aqueous solution. This method has previously been used to deposit semiconducting and conducting metal sulfide layers on non-conducting surfaces of polyethylene, polyamide and porous silica [6,23–25]. As a sulfuration agent, it utilizes polythionic acids having generic formula of $H_2S_nO_6$ ($n \geq 3$). These are analogous to sulfanes, $H-S_n-H$, where the hydrogen atom is substituted for HSO_3^- groups resulting in $HO_3S-S_{n-2}-SO_3H$ molecular structure. Highly sulfurous $H_2S_nO_6$ ($n > 6$) was first obtained by Raschig [26] from thiosulfate in acidic medium. Later, Kurtenacker and coworkers obtained polythionic acids with 10 sulfur atoms [27,28], while Janickis obtained polythionic acid with 14 sulfur atoms using fuming HCl [29]. Further increase in the sulfur chain length up to 18 atoms was performed by Janickis et al. [30] using H_2S interactions with sulfurous and thiosulfuric acids according to (1)



When synthesized, these polythionic acids gradually decompose [30]

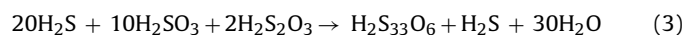


and serve as excellent proxies of sulfur for metal sulfide film synthesis. In the present study, polythionic acid ($H_2S_{33}O_6$) aqueous solutions were used as the polymer sulfuration agent. Hydrophobic polyethylene absorbs elemental sulfur from $H_2S_nO_6$ solutions which can further react with Cu aqueous solutions to form variety of crystalline copper sulfides, further denoted as Cu_xS . Layer formation proceeds not only on the very surface of the polymer, but via the diffusion of the precursor solutions into the polymer. While of significant importance as an alternative low temperature method of copper sulfide layer formation, the corresponding structure–property relationships of Cu_xS filmed are not well understood. In this work, we employed a combination of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and ultraviolet–visible spectroscopy (UV–vis) measurements to elucidate the physicochemical properties of the Cu_xS formed from polythionic acid.

2. Experimental

2.1. Cu_xS film deposition

Polythionic acid ($H_2S_{33}O_6$) aqueous solutions were used as sulfuration agent and the conditions are shown in Table 1. 2 mmol/L solutions of higher polythionic acid were synthesized according to (3) using the procedure describe before [31]



Films of low density polyethylene (PE) films were used as substrates and were cut into rectangular pieces of 15 mm × 75 mm. Before sulfuration, pieces of polyethylene film were cleaned in a 4% solution of a non-ionic surfactant (Prewocell WOF-100), degreased with benzene and washed in distilled water. Prewocell WOF-100 is a nonionic surface active material of generic formula $R-CH_2-O-(CH_2CH_2CH_2O)_x-(CH_2CH_2O)_y$ where x – is the number of ethylenoxo functional groups and y – propylenoxo functional groups. Non-ionic surfactants have previously been used to

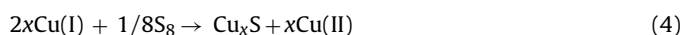
Table 1

Experimental conditions of Cu_xS thin film deposition on polyethylene (PE)^a.

Sample	Exposure time (min)	
	2 mmol/L $H_2S_{33}O_6$	0.34 M Cu(II) and 0.06 M Cu(I)
PE- Cu_xS -1	30	1
PE- Cu_xS -2	30	5
PE- Cu_xS -3	30	10
PE- Cu_xS -4	30	20
PE- Cu_xS -5	60	1
PE- Cu_xS -6	60	5
PE- Cu_xS -7	60	10
PE- Cu_xS -8	60	20
PE- Cu_xS -9	120	1
PE- Cu_xS -10	120	5
PE- Cu_xS -11	120	10
PE- Cu_xS -12	120	20

^a Samples were consecutively exposed to $H_2S_{33}O_6$ at 60 °C followed by Cu(II/I) solution treatment at 60 °C.

improve adsorption of metallic films on polymer surface [32]. Samples of polyethylene were treated in a thermostatic vessel using a continually stirred polythionic acid solution at 60 °C. At certain time intervals, samples were removed from the polythionic acid solution, rinsed with distilled water, dried using filter paper and then dried over $CaCl_2$ for 24 h. The samples were then treated with a Cu(II/I) salt solution at 60 °C, rinsed with distilled water, dried over $CaCl_2$ and analyzed using XRD, XPS, SEM and UV–vis. Depending on the initial concentration of sulfur formed in PE and the extent of the polymer treatment with copper salt solution, brown or black copper sulfide layers on the polymer surface were obtained. Copper sulfide layers formed as a result of heterogeneous redox reactions between Cu(I) and S_8



0.4 mol/L aqueous solution of $CuSO_4$ with a 0.1 mol/L of a reducing agent, hydroquinone, were used since Cu(I) salt solution alone is unstable. A mixture of univalent and divalent copper ions is present in this solution independent of temperature with the concentrations of 0.34 M Cu(II) and 0.06 M Cu(I) [33].

2.2. XRD characterization

X-ray diffraction analysis Cu_xS thin films deposited on polyethylene surface was performed using a DRON-6 diffractometer equipped with a special device for beam limitation at low and medium diffraction angles using graphite-monochromatized $Cu-K\alpha$ radiation source ($\lambda = 1.541 \text{ \AA}$) operating at 30 kV and a current of 30 mA. The XRD patterns were recorded with a step size of 0.05° from $2\theta = 25$ to 70° . X-ray diffractograms were processed using the software packages Search Match, ConvX, Xfit and Microsoft Office Excel.

2.3. XPS characterization

Surface elemental analysis of the PE- Cu_xS was performed using a custom-designed Kratos Axis Ultra X-ray photoelectron spectroscopy system [34]. The surface analysis chamber is equipped with aluminum K_{α} X-ray gun and 500 mm Rowland circle silicon single crystal monochromator. The X-ray gun was operated using a 15 mA emission current at an accelerating voltage of 15 kV. Low-energy electrons were used for charge compensation to neutralize the sample. High-resolution spectra were acquired in the region of interest using the following experimental parameters: 20–40 eV energy window; pass energy of 20 eV; step size of 0.1 eV, and dwell time of 1000 ms. One sweep was used to acquire a survey spectrum of all binding regions. The absolute energy scale was calibrated to the $Cu2p_{2/3}$ peak binding energy of 932.6 eV using an etched copper

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