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Atomic layer deposition of copper sulfide thin films

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ABSTRACT

Atomic Layer Deposition (ALD) of copper sulfide (Cu_xS) thin films from $Cu(acac)_2$ (acac = acetylacetonate = 2,4-pentanedionate) and H_2S as Cu and S precursors is reported. Typical self-saturated reactions ("ALD window") are obtained in the temperature range T_{dep} = 130–200 °C for an average growth per cycle (GR) = 0.25 Å/cycle. The morphology, crystallographic structure, chemical composition, electrical properties and optical band gap of thin films were investigated using scanning electronic microscopy (SEM), X-ray diffraction under Grazing Incidence conditions (GI-XRD), X-ray reflectivity (XRR), energy dispersive spectrometry (EDS), Hall effect measurements, and UV–vis spectroscopy. The obtained copper sulfide films are heavily p-doped (charge carrier concentration ~ 10^{21}–10^{22} cm^{-3}) with optical band gaps in the range of 2.2–2.5 eV for direct and 1.6–1.8 eV for indirect band gaps. Depending on the number of ALD cycles, multiphase compounds (made of digenite $Cu_{1.8}S$, chalcocite Cu_2S, djurleite $Cu_{31}S_{16}$ and covellite CuS) or single-phase digenite $Cu_{1.8}S$ films are obtained via a growth mechanism that involves in-situ copper reduction and loss of sulfur by evaporation.

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1. Introduction

Different strategies of thin-film solar cells have been elaborated to develop inexpensive and efficient systems for large scale production, such as the use of innovative materials or the device manufacturing via low-cost methods [1,2]. CIGS ([$Cu(In,Ga)(S,Se)_2$] absorber) solar cells are a well-established technology, with record cell efficiencies up to 21.7% [3]. A major challenge in this field is the reduction of their indium content [4]. A solution could be the "economy of atoms" by the development of ultra-thin solar devices (absorber thickness as low as 0.1 μm). In such architectures, as a back contact reengineering with optical confinement techniques is necessary [5], the process conditions have to be soft to allow the direct deposition of the absorber without damaging engineered substrates.

Atomic Layer Deposition (ALD) is a method of choice to fill all these requirements (thickness and composition control, soft deposition conditions). Indeed, ALD is a thin-film deposition method based on sequential, self-limited surface chemical reactions in the gaseous phase that allows the synthesis of films with an excellent control of the thickness and of the atomic composition at relatively low deposition temperature [6,7]. These unique features make ALD a very attractive technique for many solar cell designs that require thin layers [8–11]. The deposition of quaternary materials by ALD is very challenging, and only few examples have been reported in the literature [12–16] and are usually based on the combination of binary growth cycles that are independently understood and controlled. Thus, Cu_xS is a required binary material to achieve the ALD of a quaternary CIGS absorber. Furthermore, Cu_xS is a very interesting material per se, which has been widely considered for Li-batteries [17], and as absorber in Cu_2S – In_2S_3 heterostructure [18], Cu_2S/CdS [19] and $Cu_2S/Cd_{1-x}Zn_xS$ [20] solar cells [21]. It is known to form five solid phases at RT: chalcocite (x = 2), djurleite (x = 1.96), digenite (x = 1.8), anilite (x = 1.75), and covellite (x = 1) [22], and its synthesis by ALD has been previously reported with two different sets of precursors, $Cu(thd)_2/H_2S$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) by Johansson et al. [23] and $Cu_2(dba)_2/H_2S$ (dba = N,N′-di*sec*-butylacetamidinato) by Martinson et al. [24]. Depending on the deposition conditions (precursor, temperature), different stoichiometries and compositions were obtained. Indeed, a key parameter in an ALD growth process is the nature of the precursors as those have consequences not only on the deposition conditions, but also on the surface-reaction involved [25] and eventually on the film properties [26,27]. As we recently reported the suitability of acac-metal sources to grow $CuInS_2$ films by ALD at temperature as low as 150 °C [28], we report herein a new ALD process for the synthesis of copper sulfide films, based on $Cu(acac)_2$ as Cu source, and explore its influence on the film growth and properties.

2. Experimental

2.1. Thin-film fabrication

The depositions were carried out in a F-120 ALD reactor (ASM Microchemistry Ltd.), where the two 5 cm × 5 cm substrates are located face to face within a distance of 1 mm, on borosilicate glass and Si wafer substrates. The source materials for copper and sulfur were copper(II)

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acetylacetonate ($Cu(acac)_2$, 98%, Alfa Aesar) and H_2S (99.5%, Air Liquide). Nitrogen (N_2, 99.9999%, Air Liquide) was used as both carrier and purging gas. The Cu source was placed in a quartz boat inside the furnace and heated at $T_{Cu(acac)2} = 130$ °C while other reactants were kept at room temperature. Cu_xS films were deposited with the ALD program: n {$Cu(acac)_2$ pulse/N_2 purge/H_2S pulse/N_2 purge}, with n = number of cycles = 200–8000 at deposition temperature $T_{dep} = 130$–220 °C. The pressure in the reaction chamber was kept in the range 1–5 mbar.

2.2. Thin-film characterization

Transmittance and reflectance spectra were obtained using a Perkin Elmer Lambda 900 spectrophotometer with a PELA-1000 integrating sphere. X-ray diffraction (XRD) studies were performed under Grazing Incidence X-ray Diffraction conditions with a PanAnalytical Empyrean diffractometer using Cu–Kα radiations for crystallinity determination and XRR for thickness measurements of films <50 nm. Samples deposited on Si wafer substrates were used to determine their thickness. Thin-film compositions and morphologies as well as thickness of films >50 nm were determined with a Magellan 400L Scanning Electron Microscope provided by FEI, equipped with an Energy Dispersive X-ray Spectroscopy detector. All EDS measurements were carried out using Si (100) substrates and the reported values are atomic percentages (at.%). The SEM accelerating voltage was kept at 5 keV for all EDS measurements in order to suit the integration volume to the thickness of the films and measure atomic values with small errors. Electrical measurements were performed at room temperature using an ECOPIA HMS-3000 Hall effect measurement system with a permanent magnet of 0.5 T. Borosilicate glass samples of 6 cm^2 were used to determine the electrical properties. Values of resistivity, carrier concentration, and electron mobility chosen were the average of three measurements.

3. Results

3.1. ALD timing sequence and deposition temperature

To ensure self-limiting surface reactions, the ALD timing sequence $t_1 - t_2 - t_3 - t_4$, where t_1 is the exposure time for the $Cu(acac)_2$ pulse, t_2 the N_2 purge time following the $Cu(acac)_2$ exposure, t_3 the exposure time for H_2S, and t_4 the N_2 purge time following the H_2S exposure, was evaluated. At $T_{dep} = 150$ °C, for a constant number of cycles n = 400, each t was varied while other time values were kept constant, and plotted versus the growth rate (GR) of the resulting films (Fig. 1). The GR is mostly independent of the precursor pulse duration for 0.1 s < t < 0.3 s, which is characteristic for a surface-limited process. Some deviation occurs for longer Cu precursor pulse time that could indicate an accumulation or a moderate decomposition of the precursor species [29]. With regard to the purge pulse time effect, the GR is almost independent of its duration for 0.25 s < t < 6 s. However, the GR decreases for longer purge times after H_2S pulses (>12 s). From these results, the base line ALD program 0.3–0.5 – 0.3 – 0.5 (s) was chosen and has been used in the rest of the study. The dependence of the growth rate on the deposition temperature is presented in Fig. 2[a]. Temperature-independent surface-controlled growth ("ALD window") was obtained in the temperature range 130–200 °C for an average GR of 0.25 Å/cycle, while higher GR values were obtained at higher temperatures, indicating CVD-like growth or a decomposition process. The dependence of Cu_xS film thickness on the number of growth cycles (n) at $T_{dep} = 150$ °C is presented in Fig. 2[b]. Typical film thickness values are 10.1 nm for 400 cycles and 275 nm for 8000 cycles. A linear dependence, typical for the ALD process, is observed.

3.2. Compositional, structural, and morphological properties of the films

EDX analyses have been carried out on films corresponding to the experiments presented in Figs. 1 and 2. For Cu_xS films deposited at

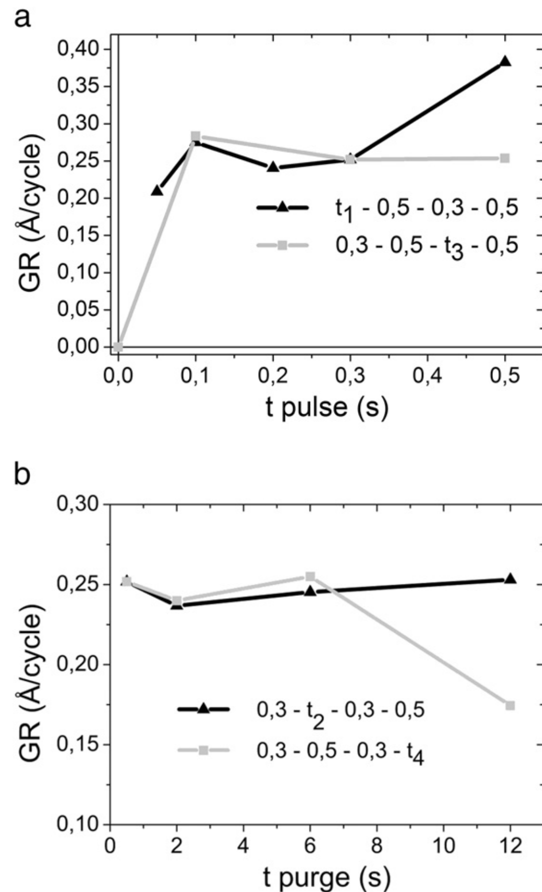

Fig. 1. Determination of the ALD timing sequence $t_1 - t_2 - t_3 - t_4$ (t_1 = t pulse $Cu(acac)_2$, t_2 = t N_2 purge, t_3 = t pulse H_2S and t_4 = t N_2 purge) at $T_{dep} = 150$ °C with n = 400: growth rate (GR in Å/cycle) dependence on the [a] pulse times and [b] purge times.

$T_{dep} = 150$ °C, only a weak dependence of pulse parameters on the composition is observed, which corresponds to x values of 1.5–1.6. However, an increase of x toward the 1.9–1.95 range is observed when the thickness is increased (n = 4000, n = 8000). When films are deposited at different temperatures, for a constant number of cycles n = 400, the composition remains constant and corresponds to a value of 1.5–1.6 for x.

Fig. 3 presents the XRD patterns under grazing-incidence conditions of Cu_xS films deposited at 150 °C for different cycle numbers on borosilicate glass. For the highest cycle number (n = 8000), the films appear as highly crystalline digenite $Cu_{1.8}S$. The diffraction peaks at 26.6, 29.7, 35.0, 42.3° indicate that it crystallizes in a rhombohedral phase (reference pattern 00-047-1748), rather than cubic phase as reported by others [30], in a favored (0 1 20) orientation. For thinner films (n = 800, 4000), films appear as multiphase compound comprising digenite, chalcocite (Cu_2S, pattern reference 00-046-1195), djurleite ($Cu_{31}S_{16}$, pattern reference 00-034-0660), and covellite (CuS, reference pattern 020-006-0464) phases. The large FWMH and low intensity values of the peaks suggest a poor crystallinity. The mean size of the ordered crystalline domains of the films has been determined using the Debye–Scherrer formula, Eq. (1) [31].

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the mean size of the crystalline domain, K is the Scherrer constant and taken equal to 0.9, λ is the wavelength of the Cu–Kα radiation, β is the Full Width at Half Maximum (FWHM) of the X-ray peak in radians and θ is the Bragg angle. The ordered crystalline domain

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