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Preparation of covellite and digenite thin films by an intermittent spray pyrolysis deposition method

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Abstract

Intermittent spray pyrolysis of 0.01–0.20 M aqueous solutions of CuCl (dissolved in the presence of 3-fold molar amount of thiourea) onto a heated alkali-free glass substrate in air already at 225–275°C resulted in various thin films of CuS (covellite) and/or $Cu_{1.8}S$ (Cu_9S_5, digenite). A combination of low pyrolysis temperatures (225–250°C) and low solution concentrations (0.01–0.02 M) has resulted in the formation of thin solid CuS films. At a pyrolysis temperature of 275°C $Cu_{1.8}S$ films have been obtained. The higher concentration range (0.05–0.20 M) has been found favorable for simultaneous formation of $Cu_{1.8}S$ and CuS. In the two-phase layers the crystal growth of CuS has seemed to be limited, whilst the growth of $Cu_{1.8}S$ has been preferentially favored especially on its (0 0 15) lattice plane. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Copper sulfides; Films; X-ray methods

1. Introduction

There is an increasing demand for photovoltaic compounds consisting of common and non-harmful elements, such as cuprous oxide[1] and tin sulfide,[2] and fabricated by a low cost method such as spray pyrolysis deposition (SPD), especially for the thin layers of solar cells.[3] Cuprous sulfide (Cu_2S, chalcocite) films were well-known from the history of the first all-thin-film solar cells (CdS/Cu_2S), and even nowadays, several trials have been carried out to prepare various films containing Cu and S elements. Recently especially p-type semiconductor thin films[4,5] and powders[6] of CuS (covellite), thin films of CuInS2[7–9] and Cu_2ZnSnS_4[10] were deposited by using spray pyrolysis.

Spray-solutions of the copper and sulfur constituents are often prepared by dissolving Cu(II) chloride or nitrate salts, and thiourea in water.[4–9] The addition of thiourea to the Cu(II) solutions results at least partly in a reduction of copper to Cu(I) which is kept in the aqueous solutions by its complex formation with the excess of thiourea.[11,12] Nevertheless, formation of CuS films are reported from binary solutions of thiourea and Cu(II) salts.[4,5]

Here we report the formation of both covellite (CuS) and digenite ($Cu_{1.8}S$) films deposited in air by using our intermittent spray pyrolysis method, aqueous solutions of CuCl (instead of $CuCl_2$) and thiourea with a molar ratio of 1:3, and heated alkali-free glass substrate. The effects of various substrate temperatures, solution concentrations and various waiting times between repetition of short sprays, on the phase-composition of the Cu–S thin films obtained have been studied by X-ray diffraction.

2. Experimental

An aqueous solution of CuCl and thiourea in a molar ratio of 1:3 was supplied to a pneumatic spraying system[2,3,9] described earlier. The concentrations of the CuCl solutions were 0.01, 0.02, 0.05, 0.10 and 0.2 mol dm^{-3}. The nozzle worked with 0.3 MPa of compressed air, and the droplets were sprayed onto a non-alkaline glass substrate (Corning 1737, 25×25×1 mm^3) at a distance of 300 mm. The glass substrate placed on a

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cordierite holder were temperature-controlled. The spraying rate and time were 0.5 ml/s and 0.5 s, respectively. Between two sprays a 1- or 3-min break was inserted to let the substrate temperature recover (it is lowered because of the evaporation of spray-droplets) and to let further time to the decomposition reactions to take place. Twenty sprays were carried out at substrate temperatures of 225, 250 and 275°C using various concentrations of a solution of CuCl.

3. Results and discussion

3.1. Thin films prepared by spray pyrolysis deposition

As a result of intermittent spray pyrolysis depositions an almost exclusive thin film formation of CuS (covellite, JCPDS 6-464) with a greenish color was observed at 225 and 250°C from 10 and 20 mM solutions of CuCl with a 3-fold amount of thiourea (Fig. 1). XRD reflection from the following lattice planes of CuS was observed (1 1 0), (0 0 6), (1 0 3), (1 0 2) and (101) at 2θ angles of 47.9, 32.8, 31.8, 29.3 and 27.7°, respectively. Single phase digenite $Cu_{1.8}S$ (Cu_9S_5, JCPDS 23-962) thin films were found to be formed at 275°C (Figs. 1 and 2). XRD reflection from the following rhombohedral lattice planes of $Cu_{1.8}S$ was observed (0 0 1 5), (1 0 1 0) and (0 1 2 0) at 2θ angles of 27.8, 32.15 and 46.2°, respectively.

Digenite phase accompanied with covellite also occurred at 225 and 250°C by using spray-solutions of CuCl with a concentration of higher than 20 mM, especially when 3 min waiting time was applied between the individual sprays (Fig. 3). Using 100 or 200 mM solutions of CuCl, a formation of digenite with unusually increased intensity of the (0 0 1 5) reflection was observed, indicating a preferable growing orientation of digenite crystallites. (Figs. 2 and 3).

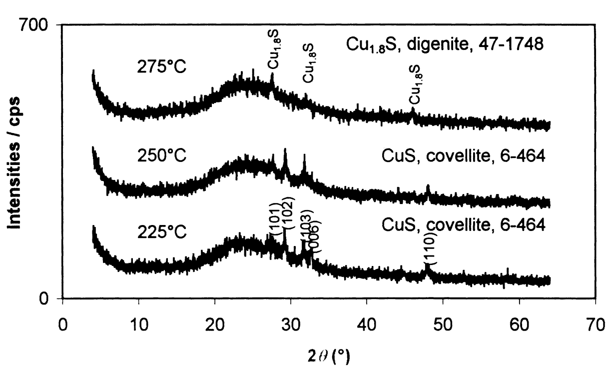

Fig. 1. Covellite and digenite thin films obtained by spraying of 10 mM CuCl solutions (with 3-fold amount of thiourea) onto alkali-free glass substrate with temperature of 225, 250 and 275°C. Waiting time $t=60$ s, 20 sprays applied. XRD reflection from the following lattice planes of CuS was observed (1 1 0), (0 0 6), (1 0 3), (1 0 2) and (1 0 1) at 2θ angles of 47.9, 32.8, 31.8, 29.3 and 27.7°, respectively.

3.2. Role of circumstances for the formation and stability of various species of copper sulfide in comparison with the literature records

When a spraying process started from the solutions of Cu(II) salts, some ions may remain in the form of Cu(II) despite the reductive effect of thiourea. Thus, it seems to be reasonable that CuS (covellite) can also be formed from such solutions,[4-6,11] even if we take into account that the structure of CuS covellite is best represented as mixed sulfide–disulfide of mixed valence copper $Cu^{I}_{4}Cu^{II}_{2}(S_2)_2S_2$.[13,14] On the other hand Lenggoro et al.[6] have observed the occurrence of both digenite and covellite submicron particles at certain concentration-ratios of Cu(II): thiourea and temperatures high enough, when spraying 0.05 M Cu(II) solutions in nitrogen atmosphere.[6] Digenite formation was observed after annealing at 500°C of some amorphous Cu_xS films obtained by chemical bath deposition from thiourea solutions of Cu(II), as well.[15] Here we used Cu(I) containing solutions, and both covellite and digenite formation has been achieved by intermittent SPD, which can be explained with an easy conversion of covellite into digenite.

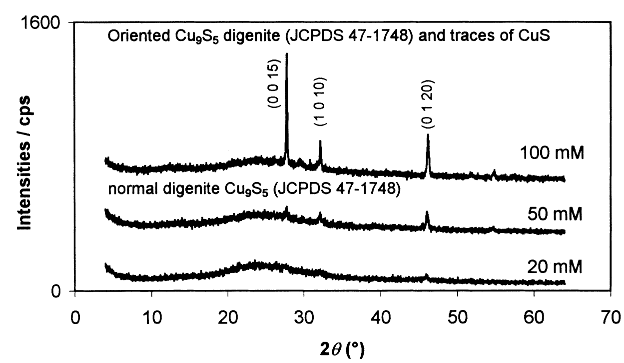

Fig. 2. Digenite films deposited at 275°C from 20, 50 and 100 mM solutions of CuCl with three fold amount of thiourea. Waiting time $t=3$ min, 20 sprays. XRD reflection from the following rhombohedral lattice planes of $Cu_{1.8}S$ was observed (0 0 1 5), (1 0 1 0) and (0 1 2 0) at 2θ angles of 27.8, 32.15 and 46.2°, respectively.

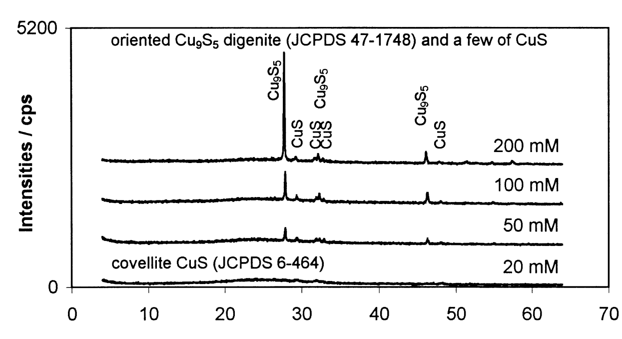

Fig. 3. XRD profiles of depositions obtained at 250°C by spraying 20, 50, 100 and 200 mM solution of CuCl (with 3-fold amount of thiourea). Waiting time $t=3$ min, 20 sprays. Oriented digenite phase and some covellite can be identified.

There are reports on conversion of covellite (CuS) into digenite ($Cu_{1.8}S$) and djurleite ($Cu_{1.96}S$) at elevated temperatures, at 300 and 400°C in nitrogen,[16] and at 250 and 300°C in air,[17] respectively. The thermodynamic equilibrium between covellite and digenite has been also examined below 100°C.[18] Above 77°C the high temperature modification of digenite can coexist together with covellite over a wide range of composition according to the Cu–S phase diagram.[19] We also think that the simultaneous occurrence of the digenite phase, between 225–275°C, is driven by increasing temperatures and waiting time used in our spraying experiments. The increasing concentration of spray solution seems to help the formation of more or less preferentially oriented digenite phase. We think that the crystal growth of CuS is kinetically hintered, whilst the growth of $Cu_{1.8}S$ crystals is favored especially on its (0 0 1 5) lattice plane. It can be significant when the spray droplets has material sufficiently enough for a growth process, i.e. when higher solution concentrations are sprayed.

The effect of spraying atmosphere and the type of solvent used may also be important. Some reports indicate an oxidative thermal decomposition of CuS in air in the temperature range of 250–260°C.[20] A detailed thermoanalytical study on the oxidation of covellite is also in preparation.[21] According to others, in the above temperature range a loss of S can occur to yield more stable copper-rich forms (anilite,[22] digenite[23]) or in vacuum, finally chalcocite.[24] Spraying of CuCl and thiourea dissolved in a molar ratio of 2:1 in acetonitril, is the only case when a very close composition to Cu_2S (chalcocite) was reported and used for solar cell fabrication by spray pyrolysis deposition.[25]

4. Conclusions

The intermittent spray pyrolysis depositions using 10 and 20 mM solutions of CuCl dissolved by using 3 fold molar amount of thiourea onto heated glass substrates have resulted already at 225 and 250°C in sulfur rich covellite (CuS), whilst at 275°C in digenite ($Cu_{1.8}S$) thin films. In general, the usage of higher substrate temperatures and longer waiting times between sprays have been found favorable to the formation of digenite. In several cases both covellite and digenite simultaneously have been formed. More concentrated spray-solutions of CuCl, favored a crystal growth process of digenite along with its (0 0 1 5) plane.

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