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Growth of conductive copper sulfide thin films by atomic layer deposition

Johanna Johansson, Juhana Kostamo,† Maarit Karppinen‡ and Lauri Niinistö*

Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology,
P. O. Box 6100, FIN-02015 Espoo, Finland. Fax: +358 9 462373; E-mail: lauri.niinisto@hut.fi

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Copper sulfide thin films were deposited on soda lime glass and Si(100) substrates by atomic layer deposition (ALD) using the β-diketonate-type volatile Cu compound $Cu(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) and H_2S as precursors. Depositions were carried out in the temperature range 125–250 °C. The film growth was surface-controlled in the temperature ranges 125–140 °C and 125–160 °C on glass and silicon substrates, respectively, growth rate being approximately 0.3 Å $cycle^{-1}$ on both substrates for films of a thickness above approximately 50 nm. For thinner films the growth rate was higher, approximately 0.5 Å $cycle^{-1}$. The deposited Cu_xS thin films were characterized by X-ray diffraction (XRD), time-of-flight elastic recoil detection analysis (TOF-ERDA), atomic force microscopy (AFM) and four-point resistivity measurements to determine crystallinity, chemical composition and surface morphology as well as surface resistivity (1×10^{-4} Ω cm), respectively.

Introduction

Due their optical and electrical properties copper sulfide (Cu_xS) thin films find uses in many photovoltaic and photothermal applications. The interest in Cu_xS thin films was previously focused mostly on their possible use in solar cells,[1–5] but more recently their application in solar control coatings for architectural and automobile glazings,[6,7] in transparent and conductive coatings, and as elastic thin film Cu sensor electrodes[8] have also been considered. Lately Cu_xS thin films have also shown promise as gas sensor material in room temperature solid-state gas sensors for ammonia.[9,10] The most striking benefit obtained by utilizing Cu_xS as sensor material is the low working temperature of the sensor. Most sensor materials are based on oxides that typically demand temperatures of at least a few hundred degrees to achieve good gas sensing properties, while a gas sensor based on Cu_xS is effective already at room temperature.[9,10] In addition to ammonia, the Cu_xS sensor could also detect other molecules containing the NH_n moiety as well as acetone and ethanol.

Copper and sulfur form five solid and stable phases at room temperature, of which two are stoichiometric, *i.e.* Cu_2S (covellite) and CuS (chalcocite), while the remaining three are non-stoichiometric, *viz.* $Cu_{1.75}S$ (anilite), $Cu_{1.8}S$ (digenite) and $Cu_{1.96}S$ (djurleite). Besides these five stable phases copper and sulfur also form a number of mixed phases. The properties of copper sulfide are affected by the accurate stoichiometry, which depends on the preparative conditions used for the thin film deposition. Both gas-phase and liquid-phase methods have been employed in the deposition of Cu_xS thin films. Gas-phase deposition techniques include vacuum evaporation,[11] flash evaporation,[12] activated reactive evaporation (ARE),[13] sputtering[14,15] and chemical vapor deposition (CVD),[16–18] whereas the liquid-phase deposition techniques are chemical bath deposition (CBD),[8,19–21] spray pyrolysis,[22] electrodeposition, electroless deposition[23] and successive ionic layer adsorption and reaction (SILAR) methods.[24]

Here we report for the first time on the deposition of copper sulfide thin films by the atomic layer deposition (ALD) technique, also referred to as atomic layer epitaxy (ALE) or atomic layer chemical vapor deposition (ALCVD). The ALD process has certain unique features when compared to conventional thin film deposition techniques.[25,26] It is a surface-controlled chemical vapor-deposition technique that is based on sequential, self-limiting adsorption of gaseous precursors.[26] Gaseous precursor pulses are applied and separated by nitrogen or argon purging gas pulses. After each precursor pulse the surface is saturated with the chemisorbed precursor. This enables a controlled layer-by-layer growth with the growth rate proportional to the number of reaction cycles instead of the intensity of reactant fluxes. This in turn leads to excellent thickness control and uniform film growth, even on large area substrates and porous supports with nanometer-scale cavities and variable surface geometries.[27]

Experimental

The Cu_xS thin film depositions were carried out in a commercial flow-type F-120 ALE reactor manufactured by ASM Microchemistry Ltd (Espoo, Finland).[28,29] The precursor vapors were alternately introduced into the reactor while nitrogen (purity 99.999%) was used as a carrier and purging gas. The precursor materials for copper and sulfur were the volatile copper(II) β-diketonate $Cu(thd)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptanedione) and hydrogen sulfide (Messer, Krefeld, Germany, no. 30335, purity class 5.0), respectively. The copper precursor $Cu(thd)_2$ was synthesized from analytical grade $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) and Hthd (Merck-Schuchardt) applying the method described by Eisentraut and Sievers,[30] and purified by vacuum sublimation. The $Cu(thd)_2$ precursor was evaporated at 115 °C and the H_2S gas was delivered into the reactor at a flow rate 10 cm^3 min^{-1} with an absolute pressure of about 800 mbar. The total reactor pressure was approximately 2 mbar during the deposition of thin films. The

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†Present address: ASM Microchemistry Ltd., P. O. Box 132, FIN-02631 Espoo, Finland
‡Present address: Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

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$Cu(thd)_2$ pulse time was varied between 0.8 and 2.0 s and the H_2S pulse time between 0.1 and 2.0 s. Nitrogen gas pulses of 1.5 s duration were used for purging the reactor between the successive precursor pulses. One growth cycle is thus determined as the sequence of a $Cu(thd)_2$-pulse, a first purge pulse, an H_2S-pulse and a second purge pulse. The Cu_xS films were deposited onto fine polished soda lime glass (Grade LCD, Tosoh Corp., Japan) and Si(100) substrates (Okmetic, Finland) measuring 5×5 cm^2 at deposition temperatures of 125 to 250 °C. Four substrates were used in each deposition and in most of the experiments both silicon (100) and glass substrates were used in the same batch. This enabled us to evaluate the effect of substrate under strictly identical conditions as well as to check the deposition profile over a total length of 10 cm. The total number of cycles was varied between 500 and 9000 leading to thin films of approximately 25 to 220 nm thickness, respectively.

The volatility of the $Cu(thd)_2$ precursor and its thermal stability were evaluated by simultaneous thermogravimetric/differential thermal analysis (TG/DTA) measurements (Seiko SSC 5200) in the temperature range 30 to 300 °C. A pressure of approximately 2 mbar and a small nitrogen (purity 99.999%) flow were used to simulate the growth conditions in an ALD reactor. The heating rate was 10 °C min^{-1} and the sample weight was *ca.* 13 mg.

The crystallinity of the copper sulfide thin films was determined by X-ray diffractometry (XRD) in a Philips PW 1830 instrument. The XRD patterns were recorded using CuKα radiation (1.54 Å). The 2θ range of 10–80° was covered with a step length 0.020° and a measurement time of 1 s step^{-1}. Surface morphologies of the films were determined in tapping mode by a Nanoscope III Multimode SPM atomic force microscope (Digital Instruments) using 1 Hz scanning and a scanning area of either 2×2 μm^2 or 10×10 μm^2.

Cu_xS thin film thicknesses were determined by profilometry (Sloan Dektak 3030ST Auto I Surface Texture Profiler) using a 900 μm scan length and tip force of 20 mN. The steps were etched by aqua regia protecting the thin film sample parts with photoresist (Hoechst, AZ 1350 H). The thicknesses of the thinnest films were also determined by X-ray reflectometry using CuKα radiation and a 2θ range of 0–3°.

The thin film composition and stoichiometry were determined by time-of-flight elastic recoil detection analysis (TOF-ERDA). In this ion beam method of analysis heavy ions are used as projectiles which hit the sample and generate forward recoiling sample atoms.[31] For each recoil the velocity and energy are determined using timing gates and a charged particle detector, respectively. By use of these two signals different masses can be separated. The heavy recoil energy spectra are obtained from the TOF signals but for hydrogen the charged particle detector is used. Using a known measurement geometry, stopping powers and scattering cross sections depth profiles were deduced for each element. In this study the sample surface was tilted 20° and recoils were detected at 40° with respect to the incoming ion beam. The 53 MeV ^{127}I ion beam used for TOF-ERDA was obtained from a 5 MV EGP-10-II tandem accelerator at the Accelerator Laboratory of the University of Helsinki.

The resistivities of the Cu_xS thin films were determined by *ex situ* four-point resistivity measurements (Cascade Microtech Inc.) using a CPS probe station and a Keithley Sourcemeter.

Results and discussion

Simultaneous TG/DTA measurements revealed an essentially complete (98.5%) volatility of the $Cu(thd)_2$ precursor in a single step. The TG curve onset was at about 120 °C. The TG measurement was used to select the evaporation temperature of the precursor for the subsequent ALD depositions. The optimal temperature for the source was found to be 115 °C since at this temperature about 0.2 mg $Cu(thd)_2$ was consumed per growth cycle; this precursor amount was sufficient to coat all four substrates used in one deposition batch and keep the thin film growth rate constant.

The dependence of the growth rate on the deposition temperature is shown in Fig. 1. Temperature-independent surface-controlled growth ('ALE window')[25,26] was obtained in the temperature range 125–140 °C on single crystal silicon substrates and in the temperature range 125–160 °C on glass substrates. Temperature range for surface-controlled growth might possibly extend to still lower temperatures but temperatures less than 125 °C could not be studied because a sufficient temperature gradient is necessary between the precursor and deposition sections of the reactor in order to guarantee successful material transport and thin film deposition. The growth rate was about 0.3 Å cycle^{-1} on both glass and silicon substrates. However, thickness measurements for films grown at deposition temperatures above 140 °C or 160 °C onto silicon and glass substrates, respectively, could not be accurately performed by profilometry. At these high temperatures the films showed thickness variations of several hundreds of nanometers within a substrate length of some tens of micrometers, probably due to gas-phase decomposition reactions or nucleation, *cf.* AFM data (Fig. 4), which show a distinct change in crystallite size and morphology at temperatures above 150 °C.

After the temperature range for surface-controlled growth (125–140 °C or 125–160 °C depending on the substrate) had been found, the effect of precursor pulse times was studied. These depositions were performed at the optimal deposition temperature of 130 °C. The growth rate of Cu_xS was found to depend on both $Cu(thd)_2$ and H_2S pulse times when the pulse time was less than 0.5 s. For longer pulse times the growth rate was almost constant. The effect was more evident for films grown on glass substrates since silicon was used as front substrate and glass as rear substrate. A shortage of precursor was therefore first seen on glass substrates.

The dependence of Cu_xS film thickness on the number of deposition cycles at 130 °C is presented in Fig. 2. Depositions carried out with the total number of deposition cycles exceeding about 1000 (film thickness above 50 nm) resulted in a linear dependency of the film thickness on the number of deposition cycles, typical for an ALD/ALE process.[25] The growth rate (0.3 Å cycle^{-1}) on both glass and silicon substrates is much less than one monolayer per cycle (approximately 0.15 ML) since the $Cu(thd)_2$ precursor molecule is bulky and adsorption is limited by steric hindrance. Also the density of available adsorption sites on the surface affects the growth rate. For very thin films (< 50 nm), however, the growth rate was appreciably higher than for thicker films, *i.e.* approximately 0.5 Å cycle^{-1}. As a consequence the line depicting the dependence of film thickness on the number of growth cycles intersects the *y*-axis above the origin in Fig. 2. Higher growth

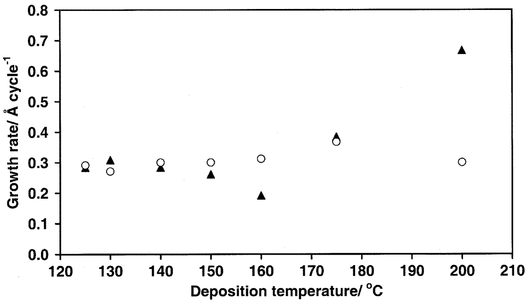

Fig. 1 Averaged growth rate of copper sulfide on single crystal silicon (100) (▲) and glass (○) substrates as a function of deposition temperature.

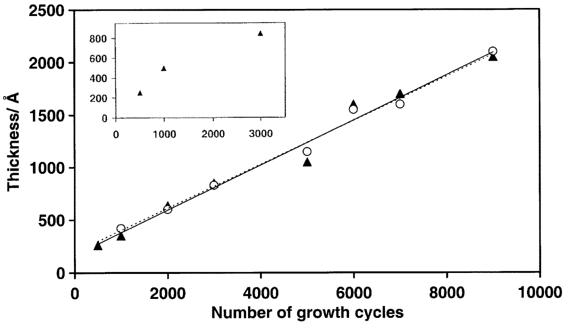

Fig. 2 CuS film thickness as a function of the number of deposition cycles. The thin films were grown at 130 °C on single crystal silicon (100) (▲) substrates and glass (○) substrates. The inset graph presents the dependence of the film thickness on the number of deposition cycles when the films were grown at 130 °C on single crystal silicon.

rates for thinner films have been observed in previous ALD studies on the deposition of cerium dioxide[32] and titanium dioxide[33,34] thin films. Generally, changes in the growth rate appear to be related to changes in the surface morphology during the growth process.[33,34] Surface roughening caused by *e.g.* changes in the film crystallinity increase the surface area and thus the number of available precursor adsorption sites leading to an enhanced growth rate. Correspondingly, when the number of available adsorption sites decreases due to changes in the growth process, the growth rate diminishes.

XRD measurements carried out for thin films grown on both substrates showed that the films were polycrystalline hexagonal CuS with the major orientation depending on deposition temperature. Films grown at lower temperatures (125–160 °C) showed a preferred (102) orientation (Fig. 3), whereas films grown at higher temperatures (175–225 °C) were preferably (101) oriented. Deposition temperatures above 225 °C led to amorphous films for which no XRD reflections could be observed. The film thickness variations in the controlled growth regime (ALE temperature window)[26] were relatively small within the total substrate length of 10 cm.

AFM images taken from films grown on silicon substrates at four different temperatures (125–175 °C) are presented in Fig. 4. The measurements show that films grown at temperatures of surface-controlled growth are uniform with only small thickness variations, whereas films grown outside the range for surface-controlled growth show larger roughness. The roughness (root mean square, rms) of films grown in the so-called ALE-window, *i.e.* temperature range for controlled growth,[26] was about 2–5 nm. Between 150 °C and 175 °C the growth mode appears to change from spherical particles to much higher pillar-like crystallites. Larger roughness (rms) at higher temperatures is probably due to reactions in the gas phase leading to film growth which is not surface-controlled.

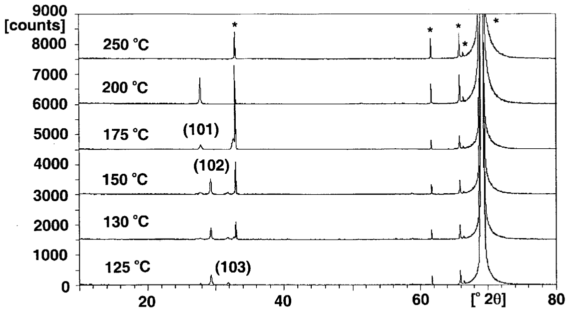

Fig. 3 X-ray patterns of CuS thin films grown on silicon (100) at different deposition temperatures. The number of deposition cycles was 3000 in all cases. Peaks marked with an asterisk are due to the silicon substrate.

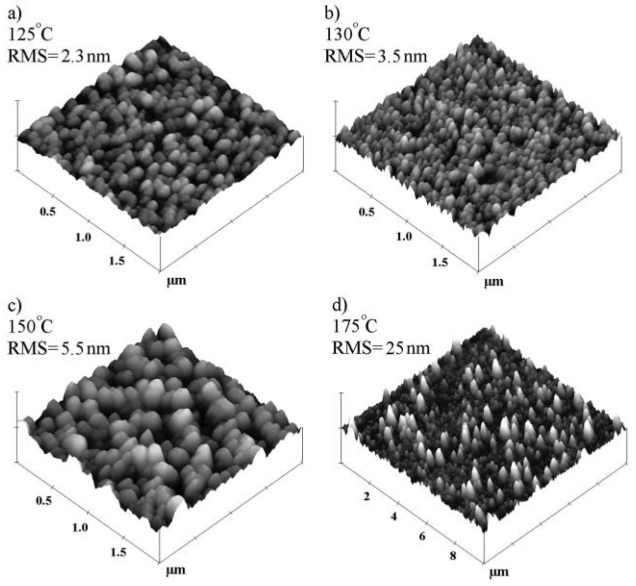

Fig. 4 AFM images of CuS thin films grown at different temperatures: (a) 125 °C, (b) 130 °C, (c) 150 °C and (d) 175 °C. The Cu(thd)$_2$ pulse time was 0.8 s, the H$_2$S pulse time 1.5 s and the number of cycles 3000 in all cases. The *z*-axis of images (a), (b) and (c) is 50 nm, while the *z*-axis of image (d) is 300 nm.

Stoichiometry of the copper sulfide films was measured from a sample deposited at 130 °C using optimised parameters. The TOF-ERDA measurement showed that the Cu : S stoichiometry of the film was 1 : 1 within the range of measurement error. The TOF-ERDA measurement also showed that there were only minor impurities in the film. Carbon, hydrogen and oxygen contents were all less than 0.2 atom% with the exception for the surface and the film/substrate interface. A further proof of the 1 : 1 stoichiometry is the lack of luminescence in our copper sulfide thin films. Jiang *et al.*[35] have showed that both nanocrystalline Cu$_7$S$_4$ and Cu$_9$S$_8$ (particle sizes 25.3–27.4 nm) are luminescent in the spectral range 400–700 nm whereas nanocrystalline CuS (particle size 26.8 nm) is not. We measured the optical properties of the Cu$_x$S films with a fluorescence spectrometer (FS 900, Edinburgh Analytical Instruments), but observed no luminescence in the range 200–700 nm. The crystallite sizes in our samples varied mostly from 20 to 80 nm as calculated from XRD data using the Scherrer equation.

The conductivity of these films was excellent. The room-temperature resistivity values were about 1×10^{-4} Ω cm for the films grown in the temperature range for the surface-controlled growth (Fig. 5). Films grown at higher deposition temperatures were more resistive with the resistivity increasing as a function of deposition temperature. Generally, the resistivity of Cu$_x$S films greatly varies depending on the stoichiometry and fabrication method (Table 1). As a rule, the film resistivity increases when the copper content increases. Resistivities of copper sulfide films fabricated by liquid-phase methods have

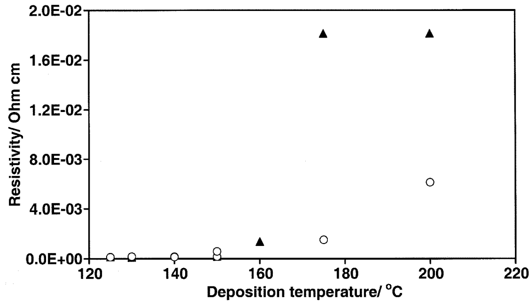

Fig. 5 CuS film resistivity as a function of the deposition temperature for films grown on silicon (▲) and glass (○) substrates.

Table 1 Surface resistivities at room temperature for copper sulfide films prepared by different methods

Deposition method	Deposition temperature/°C	Stoichiometry	Surface resistivity/Ω cm	Ref.
CBD[e]	60	Cu_xS	0.0001	36
CBD	30	CuS	0.01	37
CBD	24	CuS	1 (0.002[a])	38
CBD	not mentioned	~CuS	10 000	39
Electroless deposition	50	CuS	0.00095 (0.0004[b])	19
rf sputtering[f]	not mentioned	Cu_xS[c]	0.0001–100 (⩾0.005[d])	12
MOCVD[g]	300–500	$Cu_{1.96}S\cdots CuS$	0.032	18
ALD[h]	130	CuS	0.0001	present study

[a] After annealing at 150 °C. [b] After annealing at 130 °C. [c] The copper sulfide film consisted of $Cu_{1.96}S$, CuS and Cu. [d] After annealing at 200 °C. [e] CBD = chemical bath deposition. [f] rf = radio frequency. [g] MOCVD = metal organic chemical vapor deposition. [h] ALD = atomic layer deposition.

usually been in the range 1×10^{-4} to10 Ω cm,[18,36–38] but even values of about 1×10^{4} Ω cm have been obtained for amorphous films.[39] In some cases the conductivity has been improved by some orders of magnitude by annealing, but resistivities less than 1×10^{-4} Ω cm have not been obtained for copper sulfide films as far as we are aware. Films grown by gas-phase methods have also shown resistivities ranging from 1×10^{-4} to 1×10^{2} Ω cm[14,18] depending on the exact film stoichiometry. The films fabricated in this study are therefore among the most conductive copper sulfide thin films reported. They also show *p*-type conductivity as expected on the basis of the literature.[18,22] The measurement was performed by the thermoelectric probe method where the conductivity type is determined by the sign of the thermal emf generated by a temperature gradient.

Conclusions

The present study shows that CuS thin films can be grown by atomic layer deposition using a volatile copper β-diketonate complex [$Cu(thd)_2$] and H_2S as precursors. The thin film growth is surface-controlled in the temperature range 125–140 °C or 125–160 °C on silicon and glass substrates, respectively. After optimisation of the $Cu(thd)_2$ and H_2S precursor pulse lengths, homogenous depositions over the 10×5 cm^2 substrate area were observed with only small thickness variations. The growth rate at 130 °C was approx. 0.3 Å cycle^{-1} on both soda lime glass and Si(100) substrates. The growth rate was much less than a monolayer because of steric hindrance caused by the bulky $Cu(thd)_2$ precursor molecule and the availability of adsorption sites. The relationship between the number of cycles and the thickness of the deposited films at 130 °C was perfectly linear throughout the deposition range studied (500 to 9000 cycles) resulting in Cu_xS film thickness of 25 to 220 nm, respectively.

The CuS thin films deposited within the temperature range of surface-controlled growth were polycrystalline with (102) as the major orientation. The 1 : 1 (Cu : S) stoichiometry was confirmed by TOF-ERDA measurements. According to AFM measurements the films showed low roughness with rms values of only 2–5 nm for 90 nm thick films grown on silicon substrates at 125–150 °C. The conductivity of the Cu_xS film was among the best values reported in the literature for copper sulfide films,[14,18,19,36–39] the resistivity of our films being approximately 1×10^{-4} Ω cm.

The present study demonstrates for the first time that ALD/ALE can be used to deposit copper sulfide in a surface-controlled manner at relatively low temperatures. The resulting films on glass and silicon substrates are polycrystalline exhibiting excellent conductivity and only small thickness variations.

Most of the earlier ALD research has been focused on oxide materials,[40] binary sulfides having been studied only in a few cases most notably in connection with electroluminescent flat-panel display development and manufacturing.[41] The present study, however, is an additional proof that sulfides as well can be deposited in a controlled and reproducible way.

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