

Phase composition of Cu_xS thin films: spectroscopic evidence of covellite formation

ILARIA BENCISTÀ¹, FRANCESCO DI BENEDETTO^{1,*}, MASSIMO INNOCENTI^{1,2}, ANTONIO DE LUCA¹,
GABRIELE FORNACIAI¹, ALESSANDRO LAVACCHI², GIORDANO MONTGROSSI³, WERNER OBERHAUSER²,
LUCA A. PARDI⁴, MAURIZIO ROMANELLI¹, FRANCESCO VIZZA² and MARIA LUISA FORESTI¹

¹ Dipartimento di Chimica, Università di Firenze, via della lastruccia 3, Sesto Fiorentino 50019, Italy

*Corresponding author, e-mail: francesco.dibenedetto@unifi.it

² Istituto di Chimica dei Composti OrganoMetallici, Consiglio Nazionale delle Ricerche (CNR), via Madonna del Piano
10, Sesto Fiorentino 50019, Italy

³ Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche (CNR), via G. La Pira 4, Firenze 50121, Italy

⁴ Istituto per i Processi Chimico-Fisici, Consiglio Nazionale delle Ricerche (CNR), via Moruzzi 1, Pisa 56010, Italy

Abstract: Transition metal sulphides, grown in alternate layers by Electrochemical Atomic Layer Deposition (ECALD) to form thin films, are relevant candidates as photovoltaic materials for solar-cell production. However, the knowledge of the phase composition of the deposited sulphide, which is a fundamental information to assign and predict its effective semiconducting properties, is often hindered by the limited amount of material and by its morphological constraints. In the present study, an X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) investigation of a copper sulphide thin film, synthesised according to the ECALD method, is proposed as an alternative and efficient way to identify the deposited semiconductor. The detailed XPS analysis of the Cu and S contents in the film points to a 1:1 stoichiometric ratio, corresponding to the CuS compound. Moreover, Cu is observed only as monovalent, and the possible co-existence of sulphide ions and of disulphide units is inferred. Accordingly, the attribution of the structure of the thin film to covellite, CuS, is proposed, as being the only one able to account for all experimental evidences. We suggest that the covellite structure can be set up by spontaneous rearrangement starting from a wurtzite-type CuS deposit, driven by the negative Gibbs energy involved in the formation of the compound from the elements. Finally the morphological characterisation of the film confirms its spatial homogeneity, thus making the covellite film a potential candidate for solar-cell applications.

Key-words: CuS, XPS, AFM, covellite, thin film, photovoltaic material.

1. Introduction

Concerns linked to the transgression of environmental planetary boundaries (Rockström *et al.*, 2009) are presently focussed on the accumulation of Green House Gases in the atmosphere due to the consumption of fossil fuels driven by the ever growing demand for energy. These environmental concerns combined with increased consciousness of the limited availability of base and trace metals (Bihouix & de Guillebon, 2010) are promoting applied research to develop renewable technologies in order to satisfy the growing energy and materials demand through an efficient use of natural resources.

Solar energy is the most abundant renewable source: the radiant power intercepted by our planet is ~ 175 PW, four orders of magnitude larger than the present global average power demand of 15 TW (BP, 2011). The increasing interest in photovoltaic technology is thus fully justified. Beyond the actual commercial technologies, mainly

based on silicon and on CIGS (Copper Indium Gallium sulphides/selenides), binary, ternary and quaternary chalcogenides are considered in numerous studies as semiconducting substrates able to capture and convert solar energy (*e.g.*, Araki *et al.*, 2008; Oishi *et al.*, 2008; Scragg *et al.*, 2008; Mellikov *et al.*, 2009; Zhang *et al.*, 2009).

The conversion efficiency of a material resides on its structural and crystal chemical properties (Schorr, 2007). Accordingly, a fundamental step in exploring if a material is suitable for photovoltaic purposes consists in the determination of its mineralogical composition, namely in its applicative form (*e.g.*, substrate, thin film, nanoparticles, . . .). This determination is often difficult, due to the limited amount and to the spatial organisation of the photovoltaic substrate.

In a previous study (Innocenti *et al.*, 2011), an extensive electrochemical characterisation has been carried out on copper sulphide thin films, Cu_xS , grown on a Ag (111) surface through electrochemical deposition (ECALD). Preliminary X-ray Photoelectron Spectroscopy (XPS)

surveys pointed out the absence of divalent Cu in a deposit having CuS stoichiometry, thus rising questions on the achievement of charge balance. The present study is undertaken to provide an answer through the determination of Cu and S valence states and of the mineralogical composition of CuS, by an accurate XPS and Atomic Force Microscopy (AFM) characterization.

2. Experimental procedures

2.1. Growth of copper sulphide thin films

The sample investigated in this study consists in a thin film of copper sulphide deposited onto a single crystal of Ag (111) electrode, through an electrochemical procedure named ECALD (Electro Chemical Atomic Layer Deposition, Gregory & Stickney (1991)). This technique allows a layer-by-layer growth of the compound based on the alternate surface limited deposition of S and Cu, according to the scheme shown in Fig. 1.

The copper sulphide layers are obtained from Merck CuCl_2 and Aldrich Na_2S dissolved in ammonia buffer at $\text{pH} = 9.6$, prepared with HClO_4 (Merck) and NH_4OH (Merck). All reactants were analytical grade. A completely automated apparatus, designed and set up in the Electrochemical Laboratory at the Department of Chemistry of Florence University, was used to build the sample. This apparatus allows one to deposit single element monolayers in a pre-ordered sequence. Details of the technique, of the automated apparatus and of the deposition procedure are described in Innocenti *et al.* (2011). All potentials in the present study are referred to $\text{Ag}/\text{AgCl}/\text{sat. KCl}$ electrode.

In Fig. 2a the cyclic voltammogram of 0.5 mM Na_2S on Ag (111) is shown, as recorded from -1.1 to -0.60 V. In the anodic scan, the peak at -0.73 V (solid line) is referred to UPD (Under Potential Deposition) of S on Ag (111), whereas the bulk deposition (dashed line) occurs at -0.61 V. In the cathodic scan, there are two stripping peaks: the peak of the previously deposited bulk S (dashed line) occurs at -0.74 V and the peak of the first layer deposited on Ag (solid line) occurs at -0.81 V. Hence, a controlled deposit of a monolayer of S on Ag (111) can be obtained by exploiting a UPD of sulphide at -0.68 V for 60 s.

Figure 2b shows the cyclic voltammogram of CuCl_2 on a S-covered Ag (111). The presence of a surface limited deposition confirmed the possibility of depositing a controlled amount, namely a monolayer, of copper on the S-covered Ag. This deposit can be performed maintaining a

potential of -0.38 V for 120 s. The reader is referred to the study of Innocenti *et al.* (2011) for a more detailed interpretation of the peaks of the voltammogram of Fig. 2b.

Samples of Cu_xS deposited on Ag (111) were obtained by choosing the proper potentials for the deposition of each element and alternating the inlet of the solutions in the cell by the automated apparatus. The investigated sample, Cu_xS , is formed by 20 copper sulphide layers, as summarized in Table 1. The ECALD cycle for the binary compound deposition is schematically sketched in Fig. 2c.

2.2. Characterisation of thin film samples

The XPS measurements were performed in a Ultra High Vacuum (UHV) chamber capable of a minimal operating pressure of $\sim 10^{-10}$ torr, using a VSW HAC 5000 system equipped with a hemispherical electron analyser and a single-channel electron multiplier. A conventional, non-monochromatized Al K (1486.6 eV) primary excitation source was used. Survey and detailed scans were carried out with pass energies of 90 and 44 eV, respectively. Thus, the overall resolution resulted to be 1.2 eV as measured on a pure silver calibrating sample for the Ag $3d_{5/2}$ signal.

Surface topography of the films was measured *ex situ* in a dry nitrogen atmosphere, using a Molecular Imaging AFM (PicoSPM, Molecular Imaging) operating in contact mode, with a commercial Si_3N_4 cantilever (Nanosensors, Wetzlar-Blankenfeld). The samples were characterized by non-filtered 512×512 pixel images.

3. Results

3.1. XPS investigations

The survey scan, performed over the whole available range of binding energies, allowed to assess the presence of silver (due to the Ag electrode), carbon (due to contamination), oxygen, sulphur and copper. High-resolution scans were thus performed for all elements in the sample.

The high-resolution XPS spectrum in the S 2p region (Fig. 3a) does not allow the resolution of the two $2p_{3/2}$ and $2p_{1/2}$ components: a single broad peak is observed. The binding energy of the peak (162.1 eV) allows one to assign sulphur to the form of sulphide (Wagner *et al.*, 1979). Moreover, a shoulder at lower binding energy (~ 161.0 eV) may be identified. This spectral feature was already described by Patrick *et al.* (1997), investigating a sample of unoxidised covellite, CuS. These authors attributed the two components, in an approximate intensity ratio of 2:1,

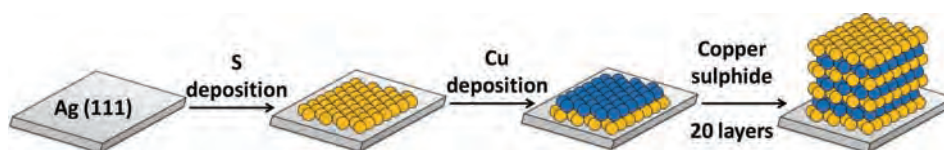


Fig. 1. Schematic representation of the procedure of deposition of copper sulphide sample on Ag(111) by ECALD.

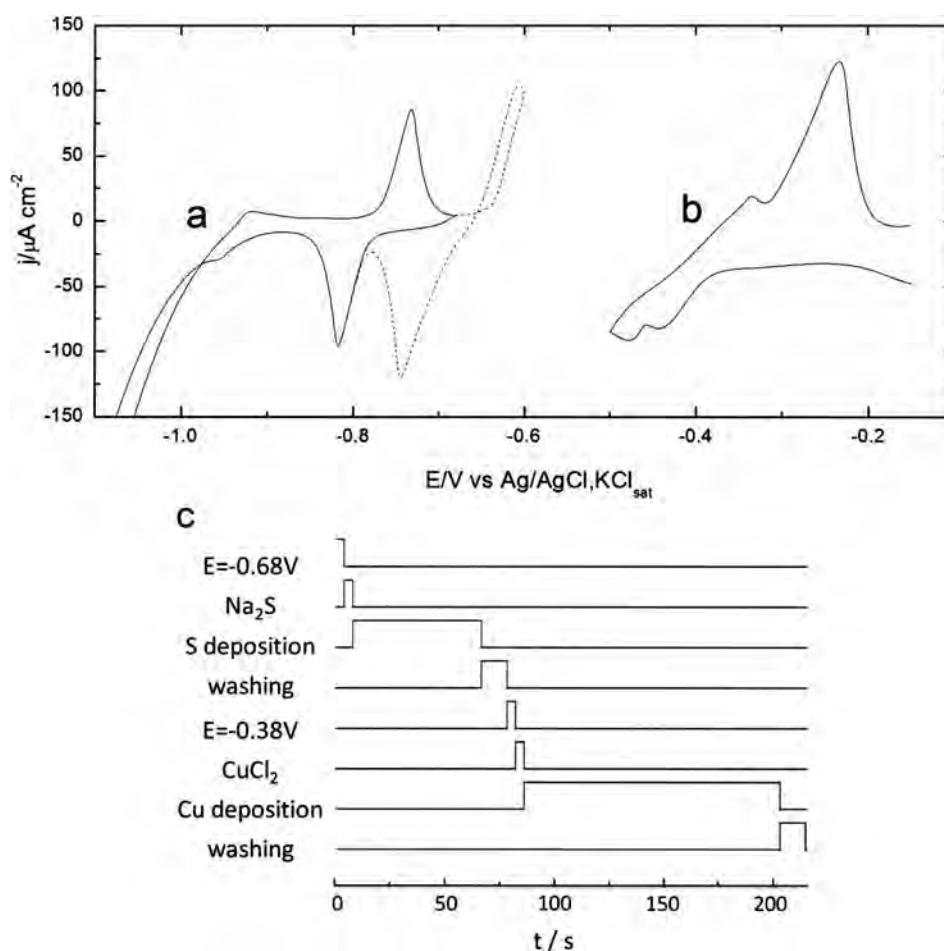


Fig. 2. Cyclic voltammograms of 0.5 mM Na₂S on Ag (111) (a) and 0.5 mM CuCl₂ on a S-covered Ag (111) (b). Scan rate 50 mV s⁻¹. (c) Diagram of a single ECALE cycle for copper sulphide deposition.

Table 1. Programme of the operations, potential and time of deposition in the preparation of the copper sulphide sample.

Sequence of deposition: Ag/S/(Cu/S) ₂₀		Potential (V)	Time (s)
Stage 1	Deposition of S	-0.68	60
	Washing in ammonia buffer	-0.68	10
Stage 2 (20 times)	Deposition of Cu	-0.38	120
	Washing in ammonia buffer	-0.38	10
	Deposition of S	-0.68	60
	Washing in ammonia buffer	-0.68	10
	Deposition of S	-0.68	60
	Washing in ammonia buffer	-0.68	10

to the well known presence of S²⁻ and S₂²⁻ species in the covellite structure (Evans & Konner, 1976).

The XPS spectrum in the Cu region reveals two well-defined peaks, attributed to the 2p_{3/2} to 2p_{1/2} components of copper. Since the peaks of Cu(I) and Cu(II) in sulphides occur at about the same energy values (Patrick *et al.*, 1997), the binding energy analysis does not allow a safe discrimination between the two valence states (Fig. 3b). A reliable attribution of the valence state can be fostered by noting that the shake up peaks (*i.e.* satellite peaks due to energy-loss processes, Wagner *et al.*, 1979) are absent in

the spectrum. Accordingly, only Cu(I) is occurring in the sample. Again, this evidence is in excellent agreement with the experimental findings of Patrick *et al.* (1997).

The C 1s XPS region shows the presence of contamination carbon with the main peak assumed to be 284.8 eV. The peak also reveals the occurrence of higher binding energy components, which can be ascribed to oxygenated carbon compounds. The O 1s peak culminating at 532.0 eV resulted from the convolution of the signals of the oxygenated carbon compounds and oxide/hydroxide species.

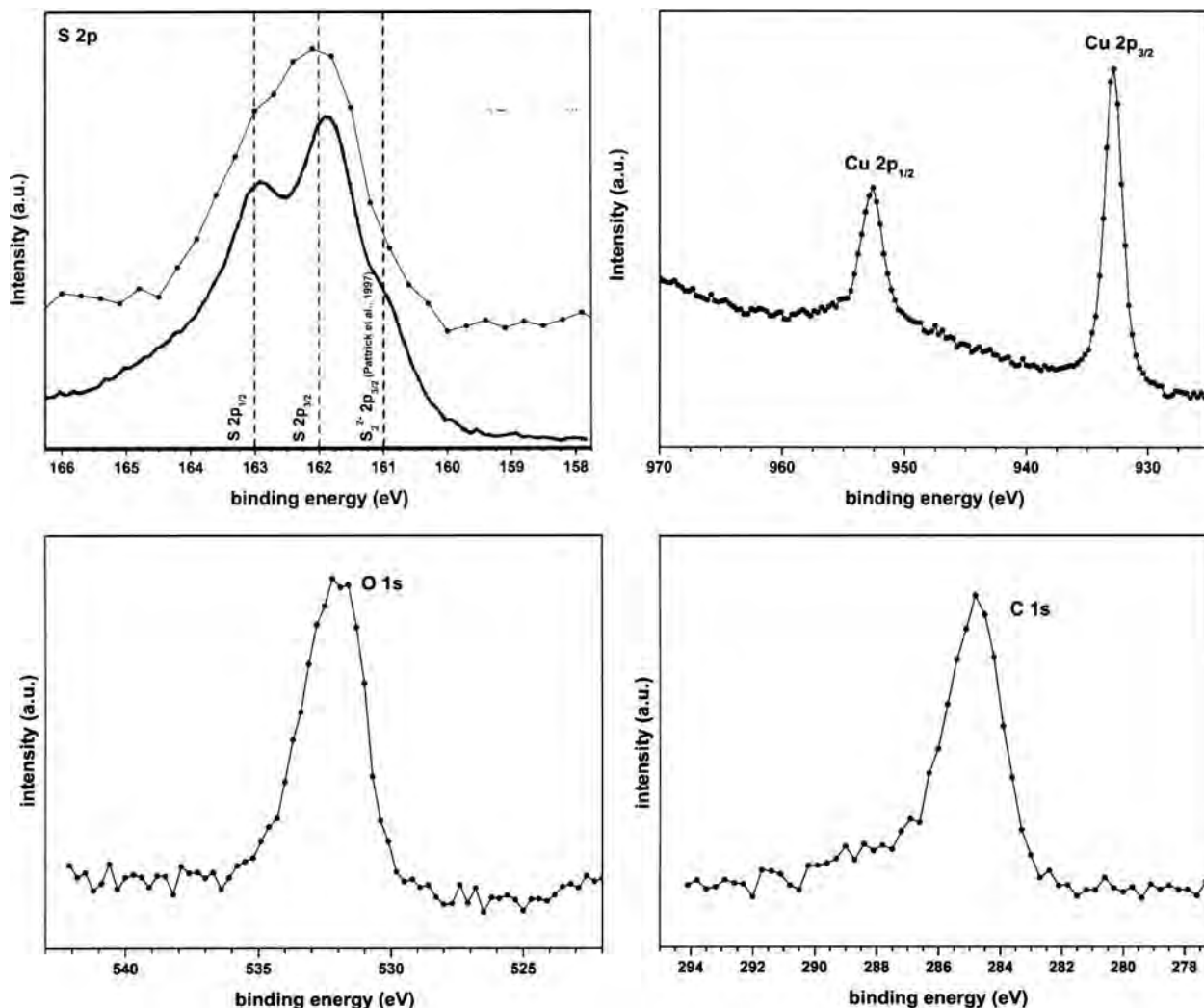


Fig. 3. High-resolution XPS spectra of the S 2p (a), Cu 2p (b), O 1s (c) and C 1s (d) regions. In the graph (a), the continuous line refers to Patrick *et al.*'s (1997) data on covellite. Modified from Patrick *et al.* (1997). The vertical dashed lines in graph (a) refer to the literature's values of the $2p_{3/2}$ and $2p_{1/2}$ binding energies.

Quantitative analysis of the relative proportions of the copper, sulphur and oxygen signals were performed to sort out the bulk composition of the sulphide thin layer. On the basis of the atomic sensitivity factors reported in Wagner *et al.* (1981), the ratio between the copper and the sulphide species is 0.9:1. According to these values, the CuS formula is confirmed, within the accuracy limit of the employed technique.

The attribution of oxygen, present in the survey scan, is controversial. This element does not certainly arise from the synthesis of the film, and it can belong to at least three phases: C-, O-bearing impurities (the most probable), the surface oxidation of the electrode and/or the film. In these latter cases it should be bound to Ag or to Cu. We compared the relative intensities of S and O signals. Even if all the oxygen detected were assigned only to the copper species, the atomic ratio between the copper involved in the oxide and sulphide phases would be lower than 0.2. Accordingly, the fact that some Cu could be bound to

O instead of S would obviously affect the Cu/S ratio, but this change is of minor importance.

3.2. Morphological characterization

The $10 \times 10 \mu\text{m}$ AFM three-dimensional micrograph of the thin film of CuS obtained after 20 deposition cycles is shown in Fig. 4b, compared to the micrograph of the Ag (111) substrate alone (Fig. 4a). The AFM images show a very similar morphology, as expected for a layer by layer deposition technique. The surface roughness R_{RMS} is defined as

$$R_{\text{RMS}} = \sqrt{\frac{\sum_{k=0}^{M-1} \sum_{l=0}^{N-1} \left(Z_{k,l} - \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} Z_{k,l} \right)^2}{MN}},$$

where $Z_{k,l}$ is the height of the (k,l) th pixel, and MN is the total number of pixels. A small R_{RMS} increase from 2.1 nm

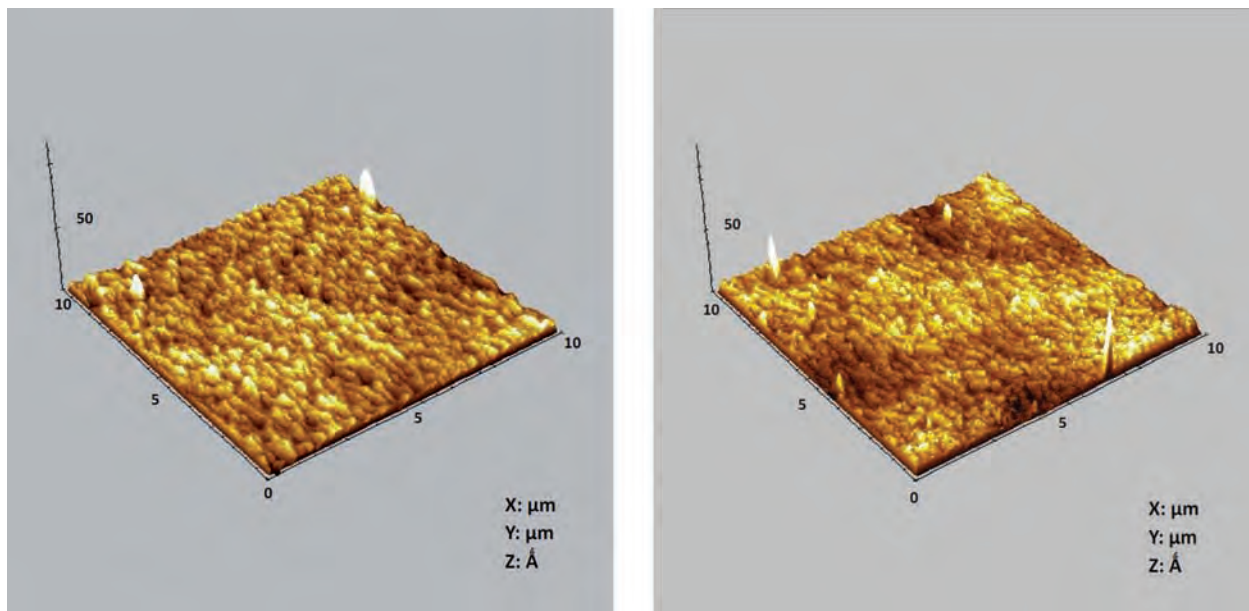


Fig. 4. Three-dimensional $10 \times 10 \mu\text{m}$ AFM micrographs of a sample of Ag (111) before (a) and after 20 cycles of deposition of Cu_xS (b).

for pure Ag (111) to 2.5 nm for CuS/Ag (111), can be observed but is almost within experimental error (~ 0.3 nm). The observed small change of R_{RMS} is quite similar to that reported in the growth of CdS by Innocenti *et al.* (2002).

4. Discussion

The present XPS results point to two main pieces of evidence:

- (1) the deposit consists in equimolar Cu and S (within the accuracy of the method), thus supporting CuS as its formula composition;
- (2) the valence states of Cu and S are Cu(I) and S(-II), respectively, although a possible fraction of S(-I) in the form of disulphide anion cannot be ruled out.

In the Cu-S system, several phases having intermediate composition between the two end terms are known: Cu_2S , chalcocite; $\text{Cu}_{1.97}\text{S}$, djurleite; $\text{Cu}_{1.8}\text{S}$, digenite; $\text{Cu}_{1.75}\text{S}$, anilite; $\text{Cu}_{1.6}\text{S}$, geerite; $\text{Cu}_{1.39}\text{S}$, spionkopite; $\text{Cu}_{1.12}\text{S}$ yarrowite; CuS , covellite; CuS_2 (Patrick *et al.*, 1997). Among them, only four are thermodynamically stable at environmental conditions, namely chalcocite, djurleite, anilite and covellite (Cipriani & Di Benedetto 2005). Digenite and Cu disulphide are stable at non-environmental conditions, and geerite, spionkopite and yarrowite are metastable (Patrick *et al.*, 1997). Accordingly, the experimental Cu/S ratio observed in the present XPS characterisation can be attributed with a good reliability to the covellite or to the yarrowite phase. Since the yarrowite phase appears less favoured due to its intrinsic metastability, and due to the experimental Cu/S ratio that is slightly < 1 , we propose that the CuS deposit crystallised with the

covellite structure. In any case the structural similarity between covellite and yarrowite would not change significantly the conclusions.

The conflict between the 1:1 stoichiometry and the valence states of Cu and S is resolved by the proposed attribution to covellite. According to Patrick *et al.* (1997), in fact, the valence states of covellite can be described as $\text{Cu(I)}_3\text{S}_2^{2-}\text{S}^{\bullet-}$, where the symbol $\bullet$ indicates a positive hole. The hole, necessary to achieve the charge balance, represents an electron deficiency stabilised through the whole lattice (Nakajima *et al.*, 1970; Patrick *et al.*, 1997). This deficiency, in turn, behaves as a population of partly free carriers, which were revealed by Di Benedetto *et al.* (2006). Similar considerations were also proposed in an EPR spectroscopic study by Borgheresi *et al.* (2006), which confirmed the absence of Cu(II) in covellite.

Accordingly, by using the Patrick *et al.*'s (1997) formula, all pieces of evidence are accounted for: the monovalence of Cu, the presence of the disulphide groups, and the presence of the sulphide fraction.

The attribution to the covellite structural model of the CuS thin film needs some more consideration about the phase formation starting from a layer-by-layer deposition. The negative Gibbs energy involved during the formation of the copper sulphide is available to drive the rearrangement of the layers towards the most stable compound under the chosen conditions (Loglio *et al.*, 2008). It should be expected, in the present case, that a wurtzite-type structure could be formed, as observed, *e.g.* in the case of (Zn, Cd)S thin layer deposition (Loglio *et al.*, 2008).

On the contrary, the fact that covellite is present in the film, in spite of its high level of structural complexity, agrees with one of the two formation processes of covellite from solution proposed by Patrick *et al.* (1997). These authors proposed that the covellite structure could be

originated from an initial wurtzite-type one, through a two-step rearrangement driven by the redox potentials of Cu (II) in sulphidic environment and by the electron densities in the intermediate structure.

5. Conclusion

The present study solves the conflict between the experimental 1:1 stoichiometry and the ions valence states in a CuS thin film grown on Ag (111). The solution relies in the fact that CuS crystallises as covellite, where positive holes allow Cu ions to be stabilised in their monovalent state.

This result confirms that covellite-type materials can be easily deposited as thin film on Ag surfaces, and that they grow with the same structure as the substrate and with high homogeneity (the roughness R_{RMS} remains constant in the different areas of the sample, as shown by the AFM investigations). This level of quality is compatible with the requirements in photovoltaic technology.

Finally, we propose that the rearrangement mechanism proposed by Patrick *et al.* (1997) is operative during the sulphide formation, driving an initial wurtzite-type deposit to the final covellite-type material.

Acknowledgements: The authors are grateful to Ferdinando Capolupo for his technical assistance and acknowledge the financial support from the MIUR (Italy) for the PRIN 2008 project prot. 2008N7CYL5.

References

- Araki, H., Mikaduki, A., Kubo, Y., Sato, T., Jimbo, K., Maw, W.S., Katagiri, H., Yamazaki, M., Oishi, K., Takeuchi, A. (2008): Preparation of $\text{Cu}_2\text{ZnSnS}_4$ thin films by sulfurization of stacked metallic layers. *Thin Solid Films*, **517**, 1457–1460.
- Bihouix, P. & de Guillebon, B. (2010): Quel futur pour le métaux? EDP Sciences, Paris. 299 p, ISBN: 978–2–7598–0549–5.
- Borgheresi, M., Cipriani, C., Di Benedetto, F., Pratesi, G., Romanelli, M. (2006): Revisione delle collezioni del Museo di Mineralogia di Firenze: le covelline. *Museol. Sci.*, **21**, 317–328.
- BP (2011): Available at the web site: http://www.bp.com/assets/bp_internet/globalbp/globalbp_uk_english/reports_and_publications/statistical_energy_review_2011/STAGING/local_assets/pdf/statistical_review_of_world_energy_full_report_2011.pdf
- Di Benedetto, F., Borgheresi, M., Caneschi, A., Chastanet, G., Cipriani, C., Gatteschi, D., Pratesi, G., Romanelli, M., Sessoli, R. (2006): First evidence of natural superconductivity: covellite. *Eur. J. Mineral.*, **18**, 283–287.
- Evans Jr., H.T. & Konner, J.A. (1976): Crystal structure refinement of covellite. *Am. Mineral.*, **61**, 996–1000.
- Gregory, B.W. & Stickney, J.L. (1991): Electrochemical atomic layer epitaxy (ECALE). *J. Electroanal. Chem.*, **300**, 543–561.
- Innocenti, M., Cattarin, S., Cavallini, M., Loglio, F., Foresti, M.L. (2002): Characterisation of thin films of CdS deposited on Ag(111) by ECALE. A morphological and photoelectrochemical investigation. *J. Electroanal. Chem.*, **532**, 219–225.
- Innocenti, M., Bencistà, I., Bellandi, S., Bianchini, C., Di Benedetto, F., Lavacchi, A., Vizza, F., Foresti, M.L. (2011): Electrochemical layer by layer growth and characterization of copper sulfur thin films on Ag (111). *Electrochim. Acta.*, **58**, 599–605.
- Loglio, F., Telford, A.M., Salvietti, E., Innocenti, M., Pezzatini, G., Cammelli, S., D'Acapito, F., Felici, R., Pozzi, A., Foresti, M.L. (2008): Ternary $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ deposited on Ag (1 1 1) by ECALE: electrochemical and EXAFS characterization. *Electrochim. Acta*, **53**, 6978–6987.
- Melikov, E., Meissner, D., Varema, T., Altosaar, M., Kauk, M., Volobujeva, O., Raudoja, J., Timmo, K., Danilson, M. (2009): Monograin materials for solar cells. *Sol. Energy Mater. Sol. Cells.*, **93**, 65–68.
- Nakajima, T., Isino, M., Kanda, E. (1970): Non linear pressure dependence of the superconducting transition temperature of Copper Sulfide CuS. *J. Phys. Soc. Jpn.*, **28**, 369–374.
- Oishi, K., Saito, G., Ebina, K., Nagahashi, M., Jimbo, K., Maw, W.S., Katagiri, H., Yamazaki, M., Araki, H., Takeuchi, T. (2008): Growth of $\text{Cu}_2\text{ZnSnS}_4$ thin films on Si(100) substrates by multisource evaporation. *Thin Solid Films*, **517**, 1449–1452.
- Patrick, R.A.D., Mosselmans, J.F.W., Charnock, J.M., England, K.E.R., Helz, G.R., Garner, C.D., Vaughan, D.J. (1997): The structure of amorphous copper sulphide precipitates: an X-ray absorption study. *Geochim. Cosmochim. Acta*, **61**, 2023–2036.
- Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin III, F.S., Lambin, E.F., Lenton, T.M., Scheffer, M., Folke, C., Schellnhuber, H.J., Nykvist, B., de Wit, C.A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P.K., Costanza, R., Svedin, U., Falkenmar, M., Karlberg, L., Corell, R.W., Fabry, V.J., Hansen, J., Walker, B., Liverman, D., Richardson, K., Crutzen, P., Foley, J.A. (2009): A safe operating space for humanity. *Nature*, **461**, 472–475.
- Schorr, S. (2007): Structural aspects of adamantite like multinary chalcogenides. *Thin Solid Films*, **515**, 5985–5991.
- Scrugg, J.J., Dale, P.J., Peter, L.M. (2008): Towards sustainable materials for solar energy conversion: preparation and photoelectrochemical characterisation of $\text{Cu}_2\text{ZnSnS}_4$. *Electrochem. Commun.*, **10**, 639–642.
- Wagner, C.D., Riggs, W.M., Davis, L.E., Moulder, J.F., Muilenberg, G.E. (1979): Handbook of X-ray photoelectron spectroscopy. Perkin Elmer, Eden Prairie, MN.
- Wagner, C.D., Davis, L.E., Zeller, M.V., Taylor, J.A., Raymond, R.M., Gale, L.H. (1981): Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis. *Surf. Interface Anal.*, **3**, 211.
- Zhang, X., Shi, X., Ye, W., Ma, C., Wang, C. (2009): Electrochemical deposition of quaternary $\text{Cu}_2\text{ZnSnS}_4$ thin films as potential solar cell material. *Appl. Phys. A Mater.*, **94**, 381–386.

Received 24 October 2012

Modified version received 24 December 2012

Accepted 24 April 2012