

MATERIAL PROPERTIES AND APPLICATION ISSUES OF CuGa_xSe_y THIN FILMS GROWN BY NOVEL CHEMICAL TRANSPORT TECHNIQUE

S. Lehmann, S. Doka, J. Hofstetter, D. Fuertes-Marrón, M. Rusu, R. Würz, K. Lips,
 Th. Schedel-Niedrig, M. Ch. Lux-Steiner
 Hahn-Meitner Institut, Glienicker Straße 100 and Kekuléstrasse 5, 14109 and 12489 Berlin,
 Germany

This contribution reports on the recent activities carried out at the Hahn-Meitner-Institut Berlin related to (i) an innovative growth system for chalcopyrite materials – chemical close-spaced vapor transport (CCSVT), (ii) to the growth of ordered defect compound thin films, (iii) to ion-implanted CuGaSe_2 thin film properties and (iv) to the surface oxidation behavior of CuGaSe_2 thin films.

The aim of the innovative growth system is the development of a non-vacuum, low-temperature technology for the fast, large-area deposition of high-quality thin films on the basis of (I-III-VI₂) semiconductors for photovoltaic applications. The common concept of the new deposition techniques is based on chemical vapor transport (CVT). The novel non-vacuum CCSVT has been used for the growth of thin polycrystalline films of CuGaSe_2 by halogen-assisted transport of Ga_2Se_3 onto metallic thin film Cu-precursors deposited on Mo-coated plain soda lime glass substrates. The final film composition can be controlled ranging from single phase 1:1:2 up to 1:3:5 and 1:5:8 by adjusting process parameters [1, 2].

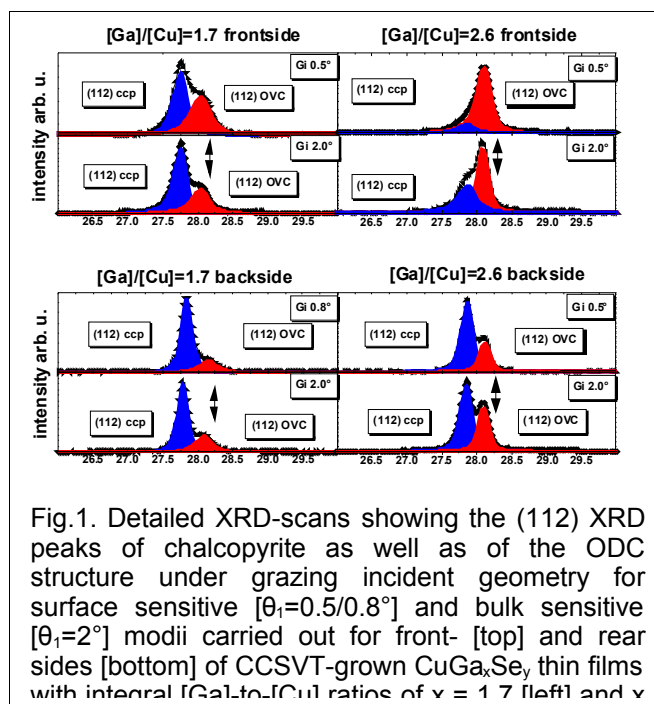


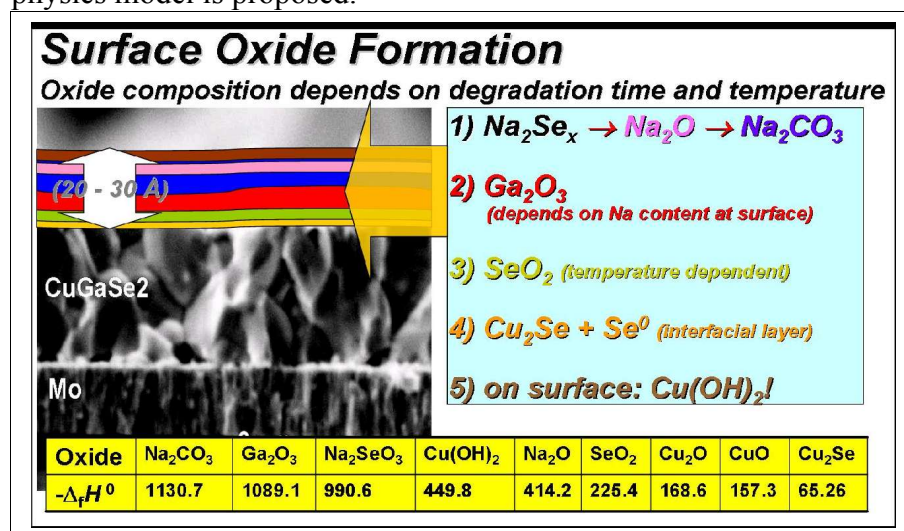
Fig.1. Detailed XRD-scans showing the (112) XRD peaks of chalcopyrite as well as of the ODC structure under grazing incident geometry for surface sensitive [$\theta_i=0.5/0.8^\circ$] and bulk sensitive [$\theta_i=2^\circ$] modii carried out for front- [top] and rear sides [bottom] of CCSVT-grown CuGa_xSe_y thin films with integral [Ga]_{to}[Cu] ratios of $x = 1.7$ [left] and $y = 2.6$ [right].

Structural and electronic properties have been monitored for thin films showing different [Ga]/[Cu] ratios as a function of processing parameters. Surface sensitive analytical tools (GI-XRD, XES, XPS) and bulk-sensitive techniques (microscopic and optical studies) have been used to characterize the thin films also for the top and the rear side. A growth model of the (1:3:5) formation will be presented based on these results [2]. CuGa_xSe_y thin films were grown in a compositional range of $1 < x < 3$ and $2 < y < 5$. For the analysis of the rear side a glass substrate was glued with silver-epoxy on the top side of the layer of selected structures (CuGa_xSe_y / molybdenum/soda-lime glass). Afterwards the layer was lifted-off [3] under inert N_2 -atmosphere. XRD-diffraction data were recorded in geometries of incident angles of $\theta_i=0.5^\circ-2^\circ$ yielding surface and bulk sensitive

structural information. The existence of two solid state phases within the thin film -chalcopyrite (CCP) [blue] and the (1:3:5) ordered defect compound (ODC) [red]- can be seen due to the occurrence of additional peaks for the ODC (see Fig.1) related to space groups which is known to be $I\bar{4}2d$ for CCP and proposed as $I\bar{4}2m$ for CuIn_3Se_5 [4].

The development of solar cells with high efficiency based on CuGaSe_2 material has inspired research thrust towards doping techniques using extrinsic dopants. Since technological applications of semiconductors depend critically on the ability to dope them, the control of the effects related to the doping has become an important task over years. It is apparent that the ion implantation process produces defects, which in turn affect the structural properties, surface states densities and recombination probabilities of the host material. On one hand CuGaSe_2 polycrystalline thin films were prepared using CCSVT technique and afterwards, the near surface region was modified by

means of Ge- implantation, on the other hand CuGaSe₂ crystals were prepared by Chemical Vapor Transport (CVT) with 1% weight Ge and Iodine as transport agent [5]. Continuous-wave electron spin resonance (cw ESR) and photoluminescence (PL) methods have been used to investigate the defects induced by Ge- incorporation into CuGaSe₂ thin films and crystals [6]. Ge elemental depth profiling and concentration in thin films have been measured by SIMS (Secondary Ion Mass Spectroscopy) and SNMS (Secondary Neutral Mass Spectroscopy) respectively, while Energy Dispersive X-ray Analysis has been used to evidence the presence of Ge in the crystal. In both CuGaSe₂ polycrystalline and crystalline additional to the Cu⁺² ESR signal, a narrow and isotropic ESR line has been found around 336.5 mT. A correlation of the Ge concentration with the intensities of this narrow ESR line has been made for the films and its dependence with temperatures exhibits the Curie paramagnetism due to localized magnetic moments, likely electrons trapped by donors. Recent X-ray absorption fine structure data have been detected in order to obtain information on the local bonding situation of incorporated Ge-atoms in the host lattice of chalcopyrite. These results have been compared with PL spectra and a comprehensive defects physics model is proposed.



In this contribution we will also present in more detail the formation of thermal and native oxides on poly- and single crystalline CuGaSe₂ studied by means of surface-sensitive photoelectron spectroscopy and bulk-sensitive low temperature electron paramagnetic resonance (EPR) [7]. In-situ detected spectra will be compared with those measured ex-situ under vacuum

conditions [8]. The thermal and native oxidation of CuGaSe₂ thin films was studied by in-situ X-ray photoelectron spectroscopy (XPS). The special design of the XPS chamber allowed to measure XP-spectra under oxidizing gas atmospheres at pressures of up to 5mbar (in-situ) or in ultra high vacuum (UHV). During thermal oxidation, the formation of predominantly Ga₂O₃ and some amount of SeO₂ were observed, but no copper oxides could be detected in the near surface region of the thin films. The same oxides were found after native oxidation in air under ambient conditions. Only after long term native oxidation for longer than four months Cu(OH)₂ was detected. An additional sodium oxide compound formed at the thin film surface, Na_xO and Na₂CO₃ after thermal and native oxidation, respectively. The amount of these sodium oxide compounds depends on the Na content on the as prepared surface. The formation of SeO₂ under humid conditions at 100°C was found to depend on the surface composition of the thin film. A simplified model for the oxidation process will be proposed [7,8].

- [1] M. Rusu, Th. Schedel-Niedrig *et al.*, Thin Solid Films **451-452** (2004) 556.
- [2] S. Lehmann, D. Fuertes-Marrón, Th. Schedel-Niedrig *et al.*, Thin Solid Films (2005) in press.
- [3] D. Fuertes Marrón, A. Meeder, Th. Schedel-Niedrig, *et al.*, Journ. Appl. Physics **97** (2005) 094915.
- [4] T. Hanada, *et al.*, Jpn. J. Appl. Phys. **36**(1997) L1494.
- [5] S. Doka, Th. Schedel-Niedrig *et al.*, Mat. Res. Society Symposium Proceedings Vol. 865 (2005) F5.27.1- F5.27.5.
- [6] S. Doka, Th. Schedel-Niedrig, K. Lips, J. Appl. Phys. (in preparation).
- [7] R. Würz, Th. Schedel-Niedrig, K. Lips *et al.*, Physical Review B **70** (2004) 205321.
- [8] R. Würz, Th. Schedel-Niedrig, *et al.*, Surface Science **580** (2005) 80-94.