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Report:

A thin layer of the ternary chalcopyrite semiconductor $CuInS_2$ grown epitaxially on a Si(001) substrate was investigated with respect to the existing phases and their lattice parameters by means of XRD. The predominant part of the sample exhibits the metastable CuAu-type ordering. Its lattice parameters are determined to be a_{ca} = 0.5565(5) nm and c_{ca} = 0.5503(3) nm, respectively. The volume fraction of the sample showing the ground-state chalcopyrite ordering is distorted in order to accommodate to the tetragonal CuAu-type structure. It is suggested that this finding is a consequence of the growth of $CuInS_2$ thin-films, where the formation of the chalcopyrite phase occurs through transformation of the primarily nucleated CuAu-type structure.

Introduction

Due to unique properties Cu-based Chalcopyrite semiconductors are nowadays willingly used as absorber layers in thin-film photovoltaic devices. A special feature of these materials has attracted some attention in recent years: the easy formation of polytypes. Here, apart from the ground-state chalcopyrite ordering, the metastable CuAu-type ordering is of high importance, especially in epitaxial and polycrystalline thin layers of the ternary semiconductor $CuInS_2$ (CIS).

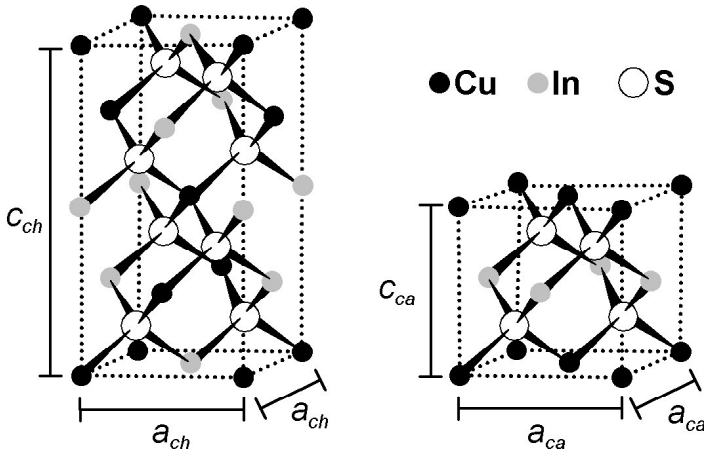

Fig. 1: Crystal structures of the chalcopyrite (left) and CuAu-type (right) phase of CIS.

Experimental

The (001)-orientation of the substrate was chosen, since it promotes the growth of the CuAu-polytype in *c*-axis direction perpendicular to the surface. The chalcopyrite(*ch*) and CuAu-type (*ca*) structures are shown in Fig. 1. These orderings can easily be distinguished in XRD if the proper reflections are chosen. Considering the selection rules for the chalcopyrite structure ($h+k+l = 2n$ and if $h = k$, then $2h+l = 4n$) and the CuAu-type structure ($h+k = 2n$, l arbitrary), it follows that the appearance of a reflection like $(001)_{ca}$ is unique for the CuAu-type structure, while the corresponding $(002)_{ch}$ reflection is forbidden for the chalcopyrite structure.

The high intensity of the synchrotron source provides the opportunity to investigate in-plane (00*l*)-reflections as well as perpendicular (0*k*0)-reflections by utilizing a reflection or transmission geometry setup, respectively. The diffraction patterns were taken in a standard Bragg-Brentano geometry with λ = 0.1032 nm.

Sample composition, homogeneity, and morphology were investigated by means of RBS: a completely homogeneous 430 nm thick film of the slightly Cu-rich composition $Cu_{1.06}In_{0.94}S_{2.0}$ with a surface roughness of 47 nm was found with no evidence for any phase segregations or inclusion of minor phases within the sample.

XRD measurements on the (00*l*) reflections (Fig. 2) reveal unambiguously the co-existence of the CuAu-type with chalco-pyrite ordering. The appearance of the $(001)_{ca}$ and $(003)_{ca}$ reflections proofs the presence of the CuAu-Type ordering in the sample, while the double-peak-like structure of the $(004)_{ch}/(002)_{ca}$ and $(008)_{ch}/(004)_{ca}$ reflections is due to the coexistence of the chalcopyrite ground state. From the peak positions within the series of (00*l*)-reflections we derived the *c*-axis parameters of the CuAu-type and the chalcopyrite ordering to be $c_{ca} = 0.5503(3)$ nm and $c_{ch} = 1.1078(7)$ nm, respectively.

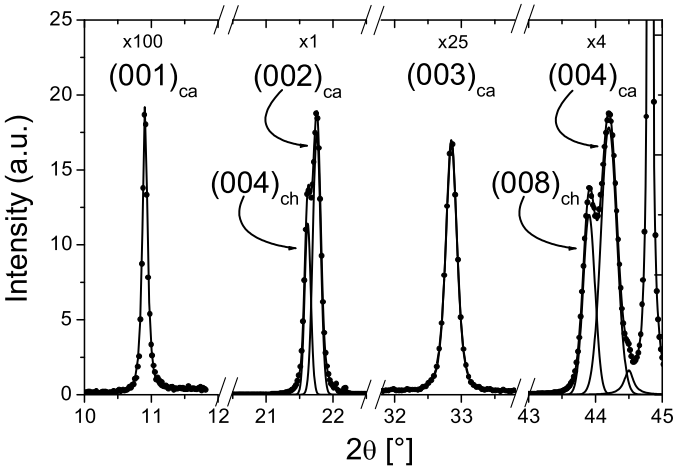

Fig. 2: XRD pattern of the (00*l*) in-plane reflections. Fitted to the spectra were mixed Lorentz/Gauß-profiles (solid lines). The high diffraction intensity around 2θ = 44.8° is due to the Si-substrate.

The ratio of the intensities of the reflections allows the direct determination of the volume fractions of the two orderings since their structure factors are equal. In the present case, the CuAu-ordering accounts for 67(3)% of the sample, while 33(3)% of the sample exhibit the chalcopyrite structure. A third net plane parallel to the surface appears in the diffraction pattern taken between 2θ = 43° and 45° by a weak shoulder at 2θ = 44.51(1)°. However, the derived lattice parameter of *c* .5468(2) nm does neither match the chalcopyrite, nor the CuAu-type ordering. Therefore, it presumably stems from a small inclusion of a third type of ordering such as the disordered zincblende structure.

Fig. 3 depicts (0*k*0)-reflections taken in transmission. The (010)- and (030)-reflections shown are forbidden for all known CIS orderings. Nevertheless, faint but sharp reflections are visible at 2θ = 10.687(4)° and 32.45(4)°. One first might suggest a small amount of *a*-axis oriented growth within the sample to be responsible for the occurrence of these two reflections. However the associated lattice parameter does not match the *c*-axis for the CuAu-type ordering and for the chalcopyrite ordering the $(002)_{ch}$ and $(006)_{ch}$ reflections are forbidden. So, the explanation of the reflections being due to *a*-axis oriented grains has to be ruled out. More likely is the occurrence of these otherwise forbidden reflections due to deviations from the ideal crystal structure for one of the present phases. The assignment of the (010)- and (030)-reflections to one of the two orderings follows from a deconvolution of the (020) and (040)-reflections.

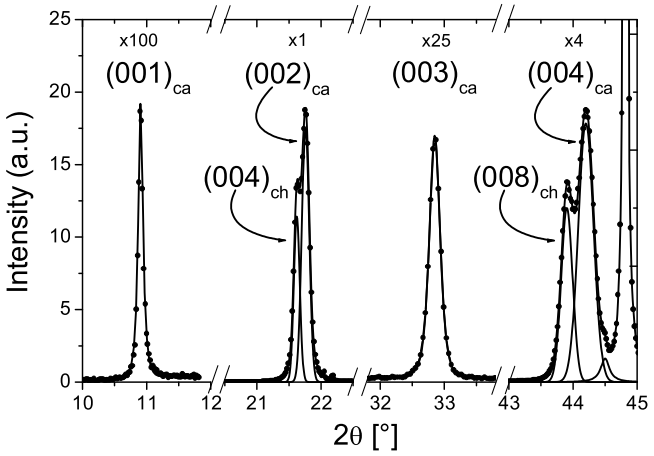

Fig. 3: XRD pattern of the (0*k*0) out-of-plane reflections as measured in transmission geometry by shining the synchrotron radiation through the Si-substrate.

Accordingly, two different net planes contribute to the respective diffraction patterns. The smaller net plane, with Bragg angles of 2θ = 21.47(1)° and 43.74(15)° matches perfectly with the lattice parameter derived from the forbidden reflections. From the ratio of the intensities in the diffraction patterns, the volume fraction of the ordering exhibiting the smaller net plane is calculated to be 35(5)%. This finding points directly towards the chalcopyrite ordering, when the results on the (00*l*)-diffraction series are considered. Hence, the larger net plane, solely showing up at Bragg angles of 2θ = 21.37(3)° and 43.54(8)°, is due to the CuAu-type ordering. Thus, we conclude, that the *a*-axis of the chalcopyrite structure amounts to $a_{ch} = 0.5541(5)$ nm, while the CuAu-type ordering has a lattice parameter of $a_{ca} = 0.5565(5)$ nm. As a consequence of this finding, the CuAu-type structure of CIS turns out to be tetragonal with a large positive tetragonal distortion of $\rho_{ca} = 1 - (c/a) = 0.02228(3)$.

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