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Characterization of $Cu(In/Ga)S_2$ thin films epitaxially grown on Si(111)

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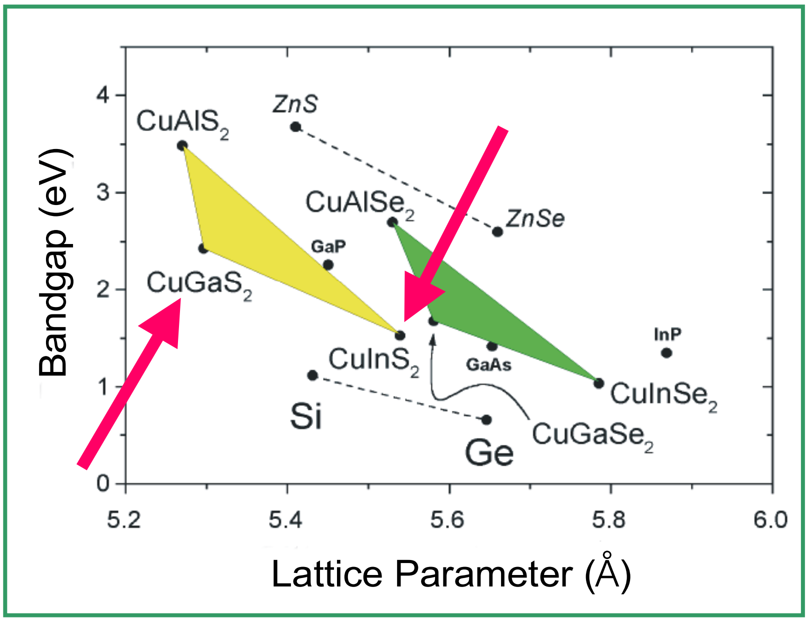
Within the chalcopyrite family the sulphur based compounds $CuMS_2$ (M=In, Ga, Al) have attracted much interest in recent years because they show a **direct** wide band-gap covering from E_{gap} = 1.53 eV ($CuInS_2$) over E_{gap} = 2.43 eV ($CuGaS_2$) to E_{gap} = 3.49 eV ($CuAlS_2$) [Fig.1]. Therefore they are particularly suitable for optoelectronic as well as photovoltaic applications. The epitaxial growth of $CuInS_2$ (**CIS**) on Si(111) and Si(001) was already demonstrated [1,2] while $CuGaS_2$ was hitherto grown epitaxially on GaAs(001), GaP(001) and Si(001) only [3,4]. Recently, our group demonstrated the epitaxial growth of $CuGaS_2$ (**CGS**) thin films on Si(111) substrates using the three-sources-molecular beam epitaxy (MBE) [5]. Our recent work focused on the heteroepitaxial growth of quaternary $CuIn_{(1-x)}Ga_xS_2$ (**CIGS**) thin films on Si(111) substrates by means of molecular-beam epitaxy. By variation of the Ga/In contents, evaluated by *x*, a nearly perfect lateral lattice match between epitaxial layer and substrate can be achieved [Fig. 2][6]. The *in situ* analysis of the growing thin film using electron diffraction via LEED or RHEED already indicates the epitaxial growth of $CuIn_{(1-x)}Ga_xS_2$. However, more detailed information concerning the structural perfection of the grown layers will be won using the *ex situ* methods of high-resolution transmission electron microscopy (HRTEM) and x-ray diffraction (HRXRD).



Lattice Parameter

a_{CGS} = 5.3474 Å
c_{CGS} = 10.4743 Å
→ c/a = 1.9588

a_{CIS} = 5.5228 Å
c_{CIS} = 11.1329 Å
→ c/a = 2.0158

a_{Si} = 5.43098 Å

Fig. 1: Bandgap versus. lattice parameter for the chalcopyrite family $CuMS_2$ (M=In, Ga, Al).

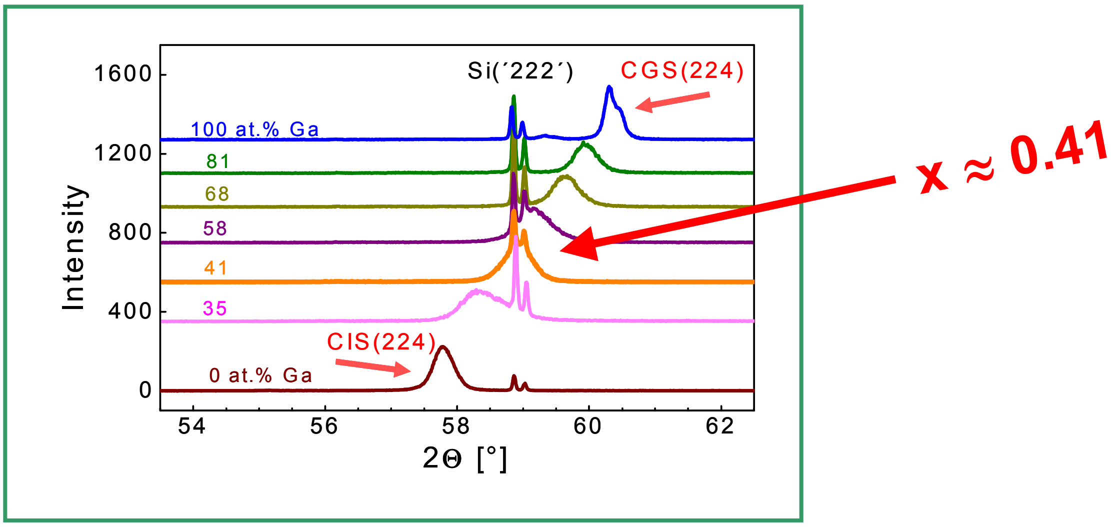


Fig. 2: XRD Θ-2Θ scans of epitaxial $CuIn_{(1-x)}Ga_xS_2$ films on Si(111) in vicinity of the forbidden 222-reflection of Si. The 224-film-reflections shift to higher scattering angles with increasing Ga content x. For x ≈ 0.41 the reflections of the film and substrate coincide. The diffraction pattern series were recorded with a conventional homebound x-ray diffraction set-up using CuKα1,2 radiation. Therefore the double $K\alpha_{1,2}$ peaks of the forbidden 222-reflection of Si arise.

X-ray diffraction executed in the usual Θ/2Θ-mode, with a wafer orientation for the symmetric reflection on lattice planes parallel to the surface give only information concerning the lattice parameter normal to the wafer surface and therefore also to the thin film, whereas the x-ray diffraction in transmission mode give information on the crystallographic **in-plane parameters** both of the crystalline substrate and the epitaxially grown $CuIn_{(1-x)}Ga_xS_2$ thin film. In this case we have also the possibility to compare directly the adequate thin film reflections to those of the substrate, arising during the same run. This is very useful for a high precision Bragg angle calibration**.**

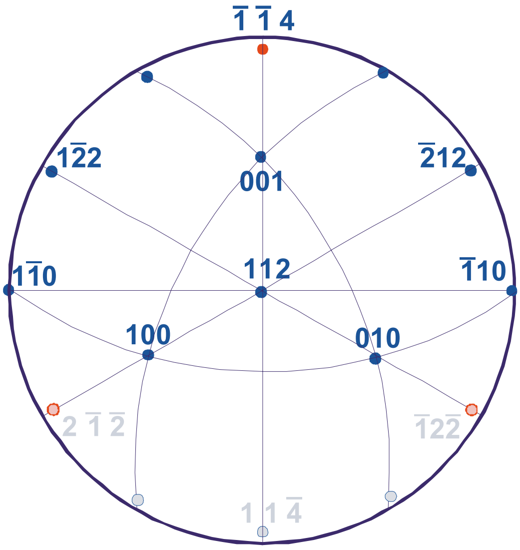


Fig. 3: Stereographic projection of CGS in respect of the [112] pole.

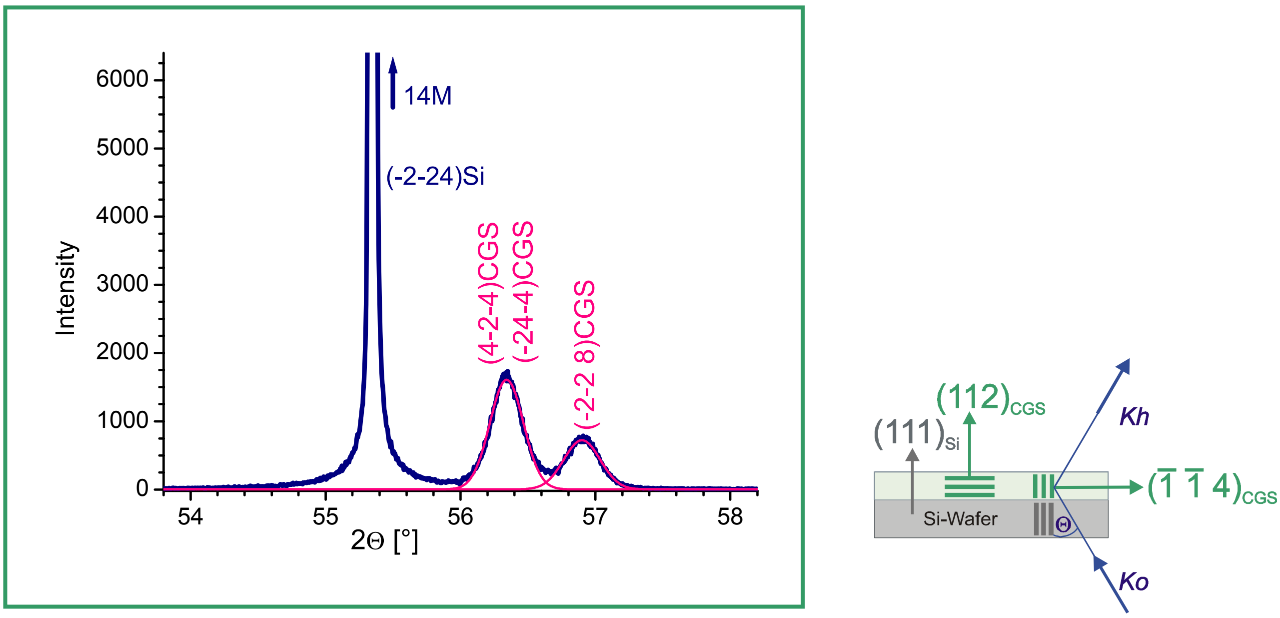


Fig. 4: HRXRD scan in transmission mode of epitaxial CGS films on Si(111). The diffractogram shows the splitting up of the adequate CGS thin film reflections. This is caused by two effects: firstly the grown CGS film is characterized by a parameter relation of $c/2 \neq a$ and secondly by a formation of 120°-rotation-twins (see Fig. 3).

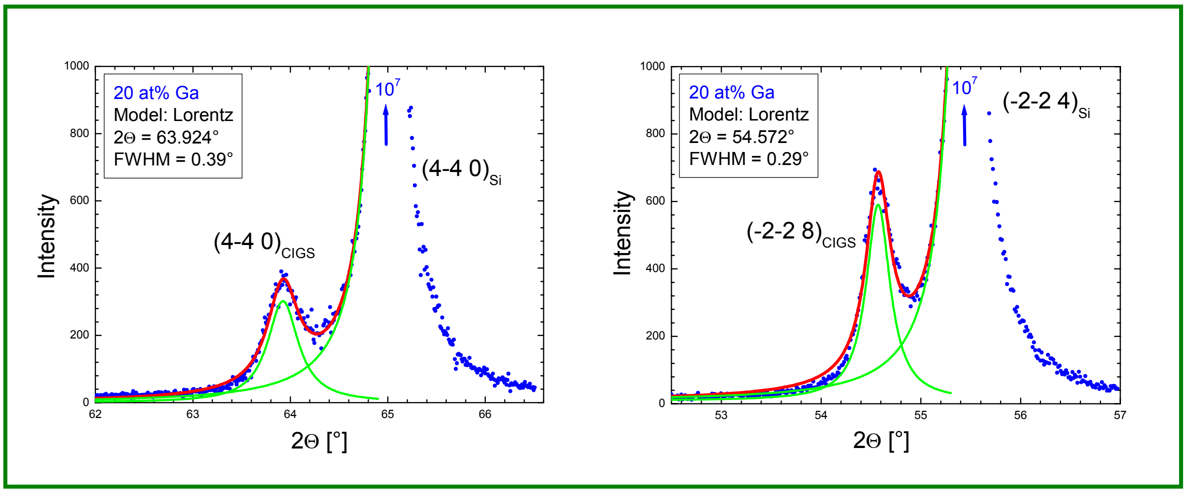


Fig. 5: HRXRD scan in transmission mode of epitaxial $CuIn_{(1-x)}Ga_xS_2$ films on Si(111). With the Ga content of x ≈ 0.20, no lateral lattice match between epitaxial layer and substrate is to be observed, as well no splitting up of the adequate thin film reflections can be recognized. Hence we have here a lattice parameter relation of c/2 ≈ a. The 4-40-reflection of CIGS results a lattice parameter $a_{CIGS(x=20)}$ = 0.5513(4) nm.

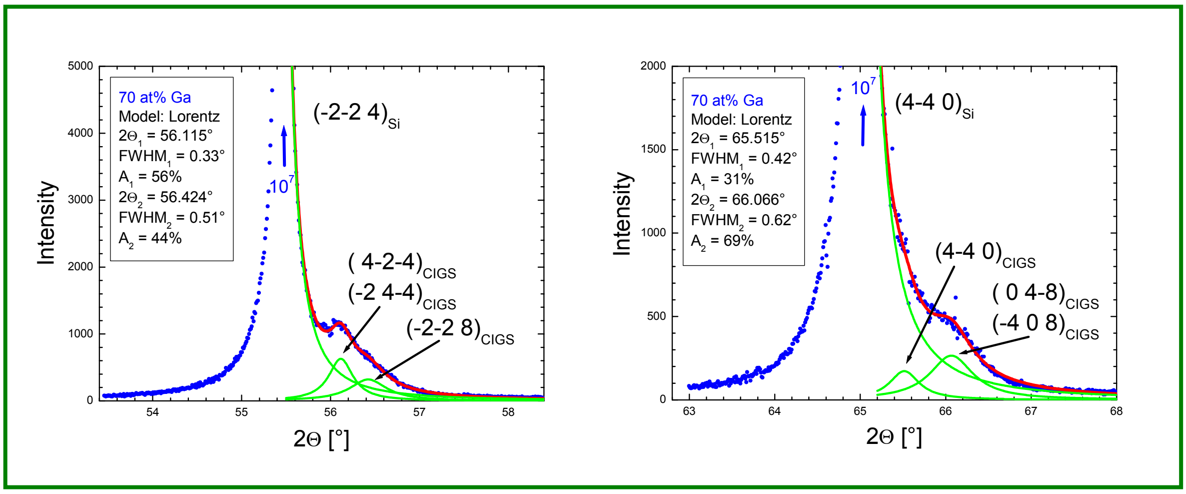


Fig. 6: HRXRD scan in transmission mode of epitaxial $CuIn_{(1-x)}Ga_xS_2$ films on Si(111). With the Ga content of x ≈ 0.70, no lateral lattice match between epitaxial layer and substrate is to be observed. Here however, the profile analysis of the measured reflection results in a splitting up of the adequate thin film reflections (see also Fig. 4). Hence, we have here once again a lattice parameter relation of c/2 ≠ a. The 4-40-reflection of CIGS results a lattice parameter $a_{CIGS(x=70)}$ = 0.5390(4) nm.

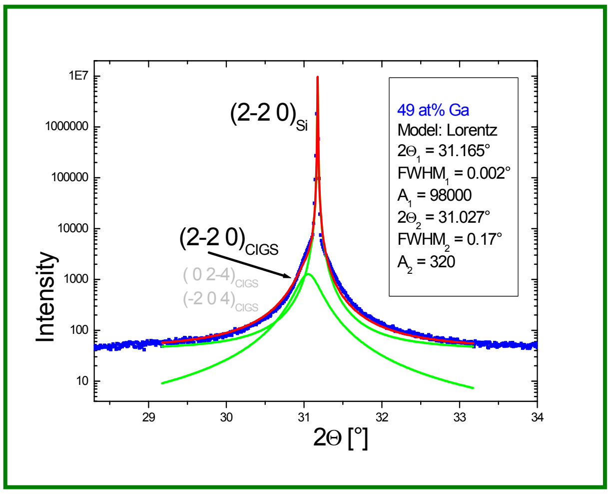


Fig. 7: HRXRD scan in transmission mode of epitaxial $CuIn_{(1-x)}Ga_xS_2$ films on Si(111). With the Ga content of $x \approx 0.49$, no separation of the thin film and substrate reflections is to be observed. Hence, we have also in plane a lattice match between the epitaxially grown CIGS thin film on the Si(111) substrate. However, in this case it is nearly impossible to evaluate significant in-plane lattice parameters of the grown CIGS thin film using profile analysis of the superimposed thin film and substrate reflections.
But the precise knowledge of the thin film in-plane lattice parameters depending on the depth and thickness of the grown thin film is of interest to determine the inherent strain.

We hope with HRXRD measurements in the Grazing Incidence Diffraction (GID) mode, just as well for $CuIn_{(1-x)}Ga_xS_2$ films with $x \approx 0.49$, to separate the thin film reflection from those of the substrate. Then, it will be possible to determine also the inherent strain components of the epitaxially grown CIGS thin film.

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