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$CuGaS_2$ thin film epitaxially grown on Si(111)

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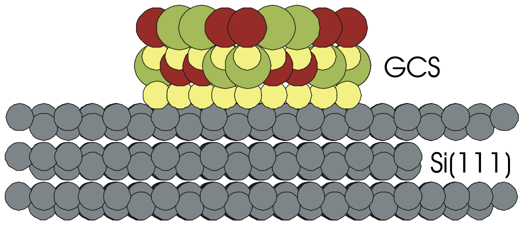
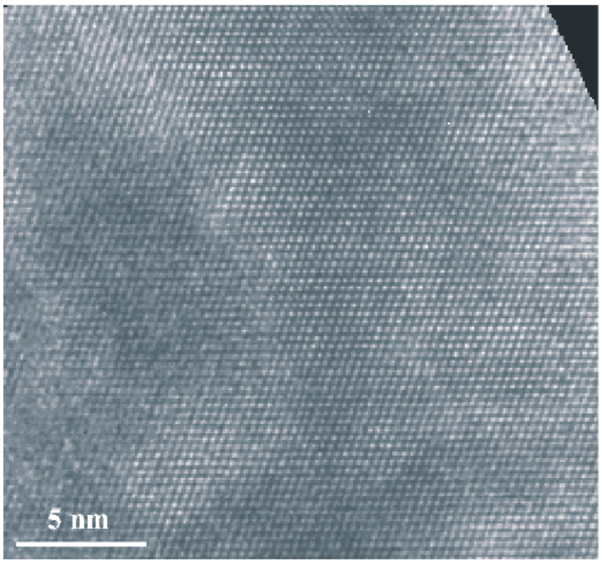
The aim of the experiment has been to characterize $CuGaS_2$ thin film epitaxially grown on Si(111) substrates by means of high resolution x-ray diffraction methods (HRXRD). Data concerning the characteristic of the epitaxial growth, the crystallographic orientation of the thin film crystallites to the substrate as well as the numerical evaluation of the in-plane lattice parameter **a** of the epitaxially grown $CuGaS_2$ are of special interest for the thin film producer to optimize the technological growth process as well as the research and development of optoelectronic devices.

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 ($CuAlS_2$). Therefore they are particularly suitable for optoelectronic as well as photovoltaic applications.

The epitaxial growth of $CuInS_2$ on Si was already demonstrated [1] while CuGaS2 was hitherto grown epitaxially on the compound semiconductor substrates GaAs and GaP only [2]. Recently, our efforts to epitaxial growth of CuGaS2 (CGS) thin films on Si(111) substrates using the three-sources-molecular beam epitaxy (MBE) were successful [3].



The structure of the grown CGS films was studied by means of high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and high resolution X-ray diffraction (HRXRD).



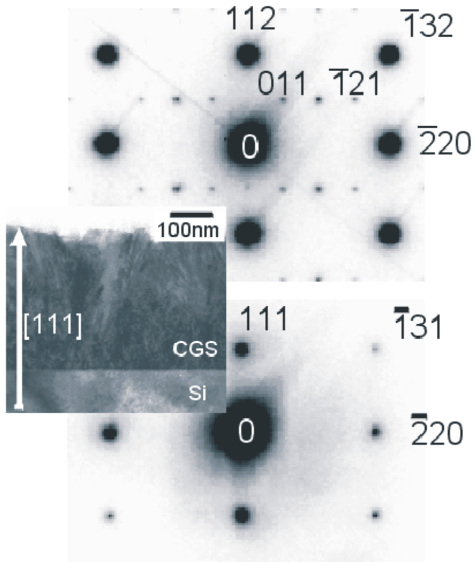


Fig. 1: [110] cross-section HRTEM image shows perfectly grown regions of CGS on Si(111)

Fig. 2: Selected area electron diffraction pattern of the [11-4]-zone axis of CGS on Si(111) shows chalcopyrite ordering (h+k+l=2n)

The XRD measurements have been carried out to check the crystallographic phase, to find out the crystallographic orientation of the grown CGS films in relation to the substrate as well as to determine the real lattice parameter **a** and **c** of the epitaxially grown $CuGaS_2$. A part of the measurements, which predominantly used the reflection mode, were accomplished at the home institute using a 18kW rotation unit x-ray generator as radiation source. Whereas the measurements, which predominantly used the transmission mode, were carried out using synchrotron radiation at the ESRF in Grenoble (CRG beamline ROBL). The used high-resolution x-ray diffractometers were equipped with an Eulerian Cradle. This made possible the X-ray diffraction investigation by using symmetric, asymmetric und oblique crystal reflection adjustments (Fig. 3,4,5).

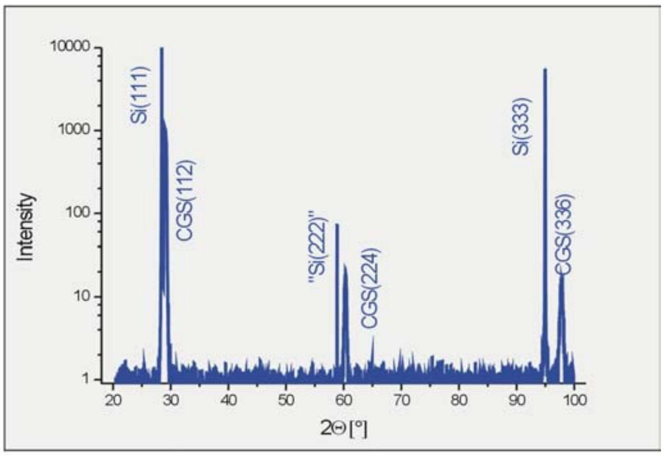


Fig. 3: Large area ω/2Θ-diffraction pattern of the CGS film grown on Si(111). Besides the n•(111)- reflections of the Si substrate, only higher orders of CGS(112)-reflections appear. Hence, there are no any polycrystalline phase. This suggests an epitaxial growth of CGS with predominant [112] growth direction. Note that $d_{(112)}$CGS < $d_{(111)}$Si.

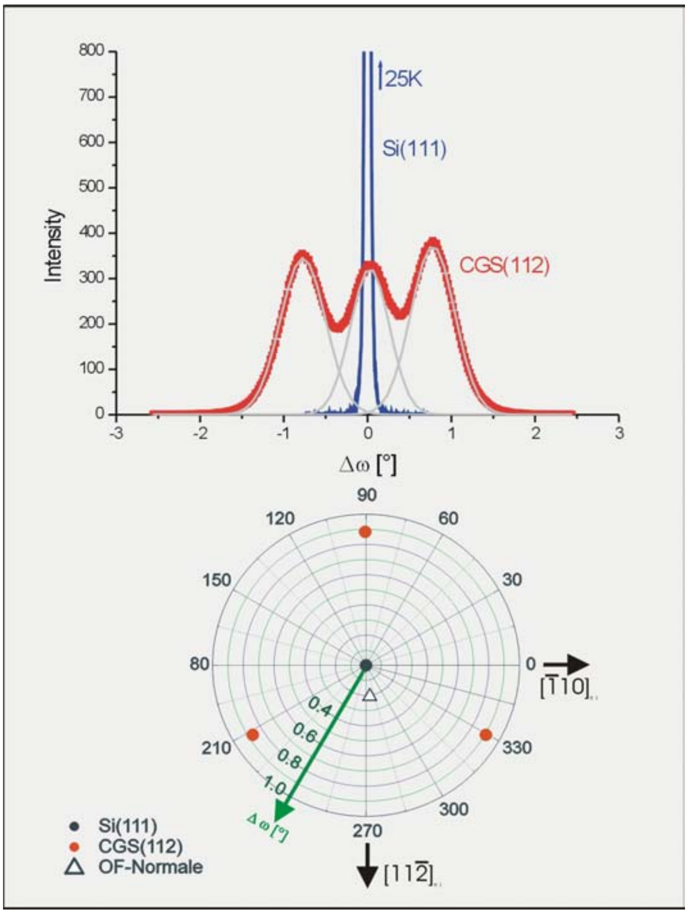
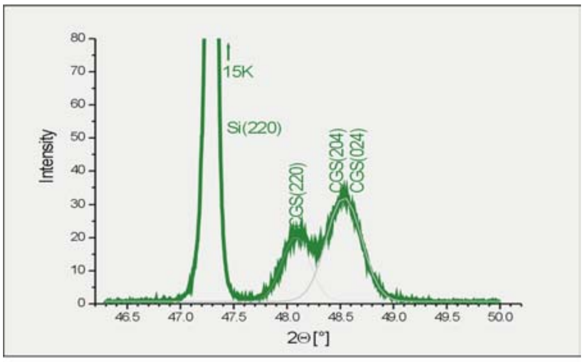


Fig. 4: Rocking curve (ω-scan) recorded with e thCGS(112)-reflection. The ´threefold necking´ of the CGS peak is caused by rotation twins of CGS domains,

which are preferred grown with small angle difference (0.8°) to the wafer normal, respectively to Si[111]-direction as shown in the stereographic projection. Threefold is their preferred lateral tilting, respectively orientated to the three inclined <001>-directions of the Si(111)-wafer.



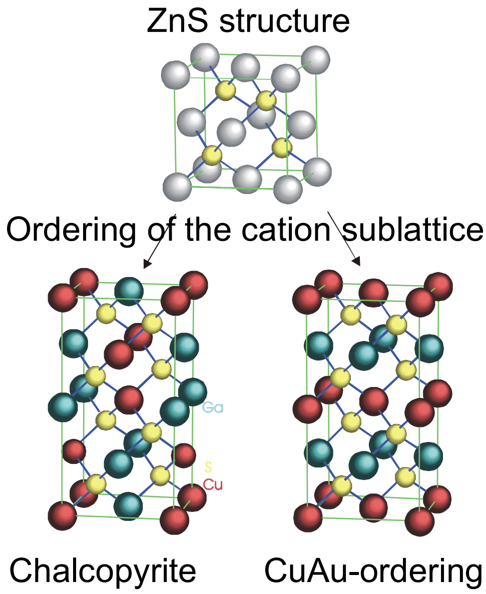
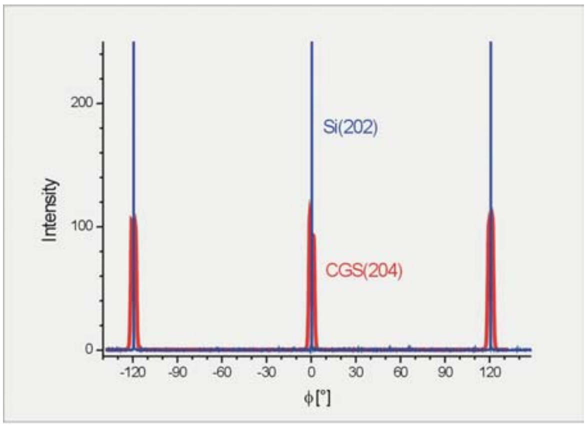


Fig. 5: ω/2Θ-diffraction pattern recorded with the asymmetric (204)/(024)- respectively (220)-reflections of CGS and the (220)Si-reflection for comparison only. The splitting of the (220)- and (204)/(024)-CGS reflections reveal the tetragonal chalcopyrite structure of the CGS thin film grown on Si(111).



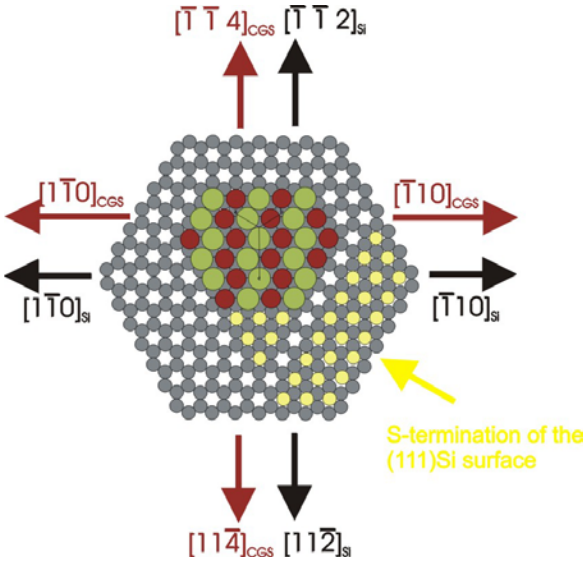


Fig. 6: Φ-scan recoded with the inclined (204)/(024)/(220)-reflections of CGS and {202}-reflection of Si for comparison. The Φ-rotation was accomplished around the surface-normal of the Si(111) substrate.

The diffractogram reveals the lateral orientation relation of the grown CGS thin film in respect to the Si(111) lattice. From this follows the lateral epitaxial relation as shown in the schema on the right. Lateral epitaxial relation of the CGS thin films grown on Si(111) substrates: $[001]_{CGS} \parallel \langle 001\rangle_{Si}$

Despite the usage of the 6°-off-axis (111)Si wafer as substrate it was found that the CGS thin films also epitaxially grew. The crystallographic relationship of CGS thin film and Si-substrate is given by the preferred alignment of the $[112]_{CGS}$-direction (growth direction) toward the $[111]_{Si}$-direction with an angle difference of ≈ 0.8° (normal relation) and the $[001]_{CGS}$-direction toward the inclined $\langle 001\rangle_{Si}$-axis. The CGS thin film is obviously composed of 120°-rotation twins due to three-fold symmetry of the Si(111) wafer surface.

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