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Epitaxial and polycrystalline CuInS₂ layers: Structural metastability and its influence on the photoluminescence

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ABSTRACT

Thin epitaxial and polycrystalline CuInS₂ (CIS) films were grown on single crystalline Si(111) and Mo-coated Si substrates, respectively, by means of molecular beam epitaxy from elemental sources. Photoluminescence (PL) measurements were performed to investigate the optical properties of both, epitaxial and polycrystalline CIS films. Epitaxial CIS samples show defect related transitions only and the PL spectra are dominated by broad luminescence peaks of deep levels, while excitonic transitions are completely absent. This contrasts sharply with the PL of the polycrystalline films, which is dominated by excitonic luminescence. Contributions due to shallow defects are observed with a small intensity only. However, luminescence peaks of defects with electronic levels deep in the band gap are not present at all. This includes the broad PL lines around 1.2 or 1.3 eV which are typical for polycrystalline CIS solar-cell material. X-ray diffraction and selected area electron diffraction measurements were employed in order to study the crystal structure. The epitaxial CIS films show a coexistence of the metastable CuAu-type (CA) ordering with the ground-state chalcopyrite (CH) structure, while the polycrystalline layers crystallize exclusively in the ground-state CH ordering. Hence, the coexistence of the metastable CA ordering and the ground-state CH structure in the epitaxial films is accompanied by a high density of electrically active intrinsic defects with levels deep in the band gap.

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1. Introduction

CuInS₂ (CIS) is a ternary chalcopyrite semiconductor with a direct fundamental band gap of 1.56 eV at 4.2 K [1] combined with a high absorption coefficient in the visible spectrum. Hence, CIS is frequently employed as an absorber material in thin-film solar cells. The crystal structure of the ground-state of CIS is the tetragonal chalcopyrite structure (CH). There is also a metastable tetragonal structure in which the metal atoms assume a CuAu-ordering (CA). Based on the higher band gap of CIS compared to the analogous Se-based material CuInSe₂, solar cells with CIS absorbers should achieve, in principle, higher open circuit voltages and higher efficiencies. Especially the possibility to grow lattice matched Cu(In,Ga)S₂ thin films epitaxially on Si substrates [2] bears the possibility for high-efficient CIS devices. However, the efficiencies for epitaxial CIS absorbers are hitherto limited to 3.2% [3], while polycrystalline CIS solar cells reached 11.4% [4]. Results of optical and structural investigations on single crystalline and polycrystalline CIS layers grown on Si substrates are discussed in this publication. When these data are combined, it is found that the occurrence of the metastable CA ordering in CIS layers is accompanied

by the absence of excitonic transitions and the appearance of a high density of electrically active intrinsic defects.

2. Experimental

Both, epitaxial and polycrystalline CIS layers were deposited in the same molecular beam epitaxy (MBE) vacuum system. The epitaxial layers were directly grown on 100 mm Si(111) wafers [5] which were cleaned and terminated in a high-temperature sulfurisation step at 1200 K [6]. Polycrystalline CIS films were grown on top of untreated Si(001) wafers with 100 mm diameter, which had been coated before with a polycrystalline Mo buffer layer of 200 nm thickness by means of radio frequency magnetron sputtering. During CIS deposition, copper and indium with purity 99.9999% were evaporated in standard hot-lip effusion sources (VTS CreaTec), whereas sulfur (purity 99.9995%) was provided by a three-stage cracker source based on our own design. The substrate temperature during film growth was kept at temperatures of 820 K for epitaxial and 825 K for polycrystalline CIS, respectively. Rutherford backscattering spectroscopy with an incident particle energy of 3.5 MeV of the He⁺ ions was used to determine the composition of the CIS layers. All investigated samples were grown slightly copper rich. After a wet chemical KCN-etching step, the Cu to In atomic ratio changed for the epitaxial layers from 1.2 for the as-

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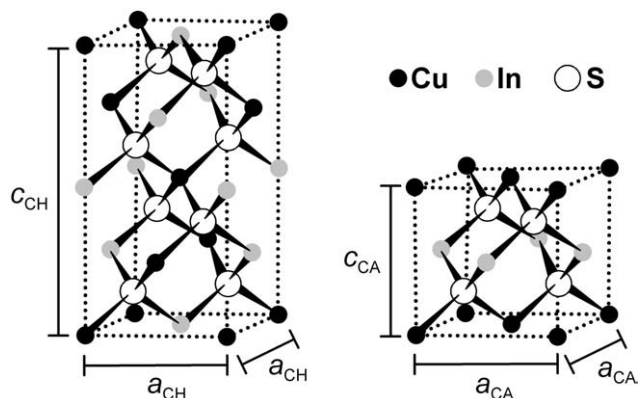


Fig. 1. Sketch of the relevant tetragonal lattice structures of CuInS_2 : ground-state chalcopyrite (CH) structure (left) and metastable CuAu-type (CA) structure (right).

grown state to 1.1 and for the polycrystalline films from 1.37 to nearly stoichiometric. Photoluminescence (PL) was excited by the 514-nm line of a continuous wave Ar^+ laser. The emission was dispersed by a 2.0 m focal length single grating monochromator and analyzed with a silicon photodiode by means of lock-in technique. All measured data were corrected for the spectral response of the system. X-ray diffraction (XRD) measurements were performed in order to study the crystal structure. The epitaxial samples were measured in reflection geometry (Bragg-Brentano) at the Rossendorf beamline ROBL of the European Synchrotron Radiation Facility in Grenoble (France) [7]. The wavelength of the X-rays was chosen to be 0.1001 nm. For the polycrystalline CIS layers, the XRD measurements were carried out in a Bragg-Brentano geometry and $\text{Cu K}\alpha$ radiation was used. In case of the epitaxial CIS layers, selected area electron diffraction (SAED) investigations were performed using a JEM-3010 (JEOL) transmission electron microscope (TEM) operating at 300 kV.

3. Results and discussion

Fig. 1 shows the relevant crystal structures of CuInS_2 . The tetragonal CH structure (left) is the ground-state structure, whereas the CA-type ordering (right) represents a metastable structure, which is also tetragonal. For CIS, the formation energy of the CA structure is only 2 meV/atom above the one of the CH structure [8]. Hence, the reported coexistence of CH and CA structure in epitaxial CIS layers [9–11] is explained by thermodynamic reasons [9].

In Fig. 2 typical low-temperature PL spectra of epitaxial and polycrystalline CIS layers are depicted. Both types of materials show strongly different recombination mechanisms. Epitaxial films in the as-grown state show defect related luminescence only and the PL spectra are dominated by transitions between deep band-gap levels. In accordance to our data published earlier [12], four distinct PL lines are found in the as-grown epitaxial CIS samples: 1.48 eV (#2), 1.44 eV (#4), 1.2 eV (#5) and 1.0 eV (#6). Based on detailed power dependent PL measurements, these observed transitions have already been identified as follows: one free-to-bound transition FB-1 (#2) and three donor-acceptor transitions DA-1 (#4), DA-4 (#5), and DA-5 (#6). Excitonic luminescence is completely absent for all investigated epitaxial CIS layers. The deep levels in the epitaxial samples reveal a high density of electrically active intrinsic defects. This contrasts sharply with the observed PL spectra of polycrystalline CIS samples, where an excitonic line at 1.53 eV (#1) dominates the luminescence. Additionally, a donor-to-valence band transition at 1.46 eV (#3) and the already known donor-acceptor recombination DA-1 at 1.44 eV (#4) are found [13]. As shown in Fig. 2, luminescence of deep levels is not present at all in polycrystalline CIS layers. This holds for all investigated polycrystalline samples. Also, the broad PL lines around 1.2 or 1.3 eV, which are typical for polycrystalline CIS solar-cell

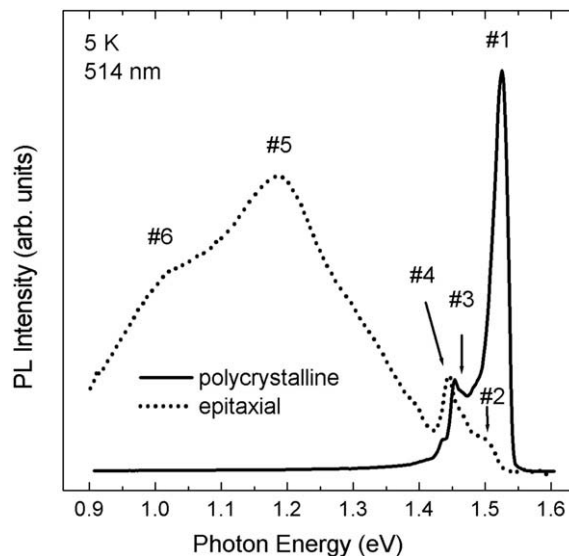


Fig. 2. Comparison of typical PL spectra of epitaxial and polycrystalline CIS layers on Si substrates. Both spectra were recorded at $T=5$ K, with an excitation power of 150 mW and a laser-spot size of approx. 0.8 mm^2 . The PL lines #1 to #6 have already been identified in our previous work [12,13].

material [14], were not observed. The outlined PL results reveal the optoelectronic quality of polycrystalline CIS to be superior to that of epitaxially grown CIS. This is a remarkable difference particularly with regard to the nearly identical growth conditions and suggests a structural origin rather than an impurity induced effect.

In order to further elucidate this striking contrast, investigations of the crystal structure of both types of material were performed. Fig. 3 shows a X-ray-diffraction pattern of an epitaxial CIS film on Si(111). Here, both types of ordering, the CH and CA-type, can be detected [15]. These structures can easily be distinguished in XRD if the proper reflections are chosen. The selection rules for the CH structure are $h+k+l=2n$ and if $h=k$, then $2h+l=4n$, while $h+k=2n$, l arbitrary holds for the CA structure [11]. The inset shows the (110) reflection, which is exclusively due to the CA structure. This clearly proves the existence of the latter, while the two reflections showing up between 18.0° and 18.1° are a clear manifestation of the coexistence of both ordering schemes. Since the form factors

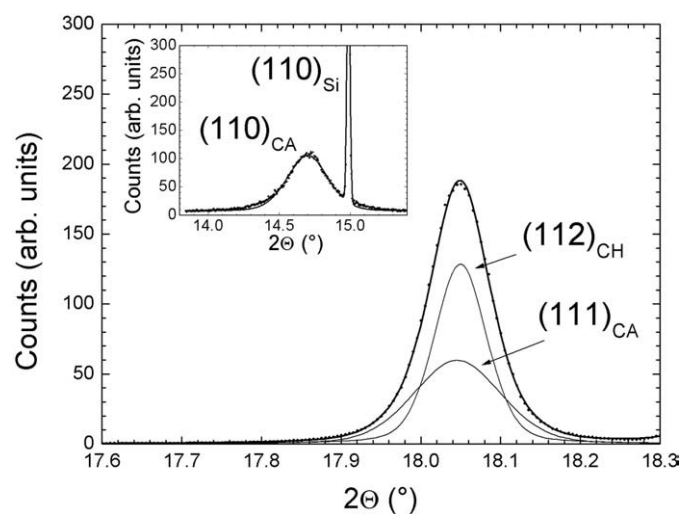


Fig. 3. X-ray-diffraction pattern of an epitaxial CIS film on Si(111). The film shows two reflections, which correspond to the chalcopyrite phase, i.e. $(112)_{\text{CH}}$, and the CuAu-phase, i.e. $(111)_{\text{CA}}$. The volume fractions are $79 \pm 6\%$ for the CH-phase and $21 \pm 6\%$ for the CA-phase. The inset shows the $(110)_{\text{CA}}$ reflection together with the forbidden $(110)_{\text{Si}}$ reflection which appears due to multiple scattering processes.

for elastic scattering are practically identical for both types of ordering the intensities for the $(111)_{\text{CA}}$ and $(112)_{\text{CH}}$ reflections give a direct impression of their volume fractions within the sample. Thus, the volume fractions of the CH and CA-type phase were calculated by evaluating all detected reflections, which are due to both types of ordering. The thin solid lines in Fig. 3 represent least-squares fits to the data (dots), assuming two reflections of pseudo-Voigt shape corresponding either to the CH or the CA ordering. The resulting volume fractions amount to $79 \pm 6\%$ for the CH phase and $21 \pm 6\%$ for the CA phase. The analysis of the integral intensity of the (110) reflection confirms these volume fractions.

The SAED pattern of the $[111]_{\text{CH}}$ -zone axis of an epitaxial CIS sample on Si(111) is shown in Fig. 4. Selected reflections are denoted by the respective Miller indices. The CIS reflections (303) and (213) are exclusively assigned to the CH structure, whereas (022) and $(1\ 10)$ are caused by the CA ordering exclusively. All other denoted reflections cannot be assigned exclusively to one of the both structure types. The SAED pattern in Fig. 4 confirms the coexistence of the ground-state CH and metastable CA ordering in epitaxial CIS.

Also, polycrystalline CIS layers were structurally investigated by means of XRD. Typical $\omega/2\theta$ overview scans of polycrystalline CIS samples grown on Mo-covered Si(001) (not shown here) show chalcopyrite reflections of CIS only [16]. The analysis of the integral intensity of all CIS reflections and the comparison to a simulated XRD pattern of polycrystalline CIS revealed a slightly stronger occurrence of the grains oriented in (112) , (004) , and (200) directions as compared to the random case. Nevertheless, a noticeable texture was not observed in all investigated polycrystalline CIS samples. However, the chalcopyrite splitting of reflections such as $(220)_{\text{CH}}$ and $(204)_{\text{CH}}$ can easily be detected in all polycrystalline samples, underlining their high structural quality. Fig. 5 depicts a high resolution scan of the strongest CIS reflection, i.e. (112) . Here, and in contrast to the already discussed XRD measurements on epitaxial CIS (ref. Fig. 3), the polycrystalline CIS film shows only one $(112)_{\text{CH}}$ reflection, corresponding to the CH phase. Furthermore, the thin solid lines in Fig. 5, representing least-squares fits to the data (dots) and assuming two reflections of pseudo-Voigt shape, are due to the Cu- $K\alpha_1$ and $-K\alpha_2$ radiation. In analogy to the illustration of Fig. 3, the inset of Fig. 5 depicts the position of the (110) CA reflection, where no signal was detectable. Hence, polycrystalline CIS layers grown on Mo-coated Si(001) crystallize exclusively in the CH ordering. A contribution caused by the CA ordering could not be detected.

For the following discussion, it is important to note that the epitaxial CIS layers are monocrystalline indeed and thus do not contain grain boundaries. In previous investigations, using XRD [5] and TEM [6], we showed the epitaxial CIS layers to contain stacking

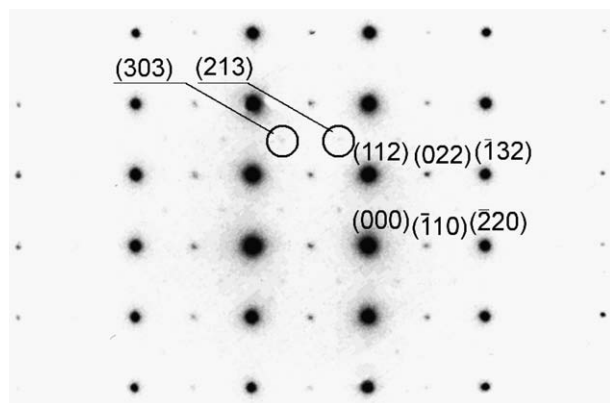


Fig. 4. The SAED pattern of the $[111]_{\text{CH}}$ -zone axis of an epitaxial CIS layer grown on Si(111) shows reflections of both chalcopyrite and CuAu ordering. The circles are used in order to highlight the (303) and (213) chalcopyrite reflections.

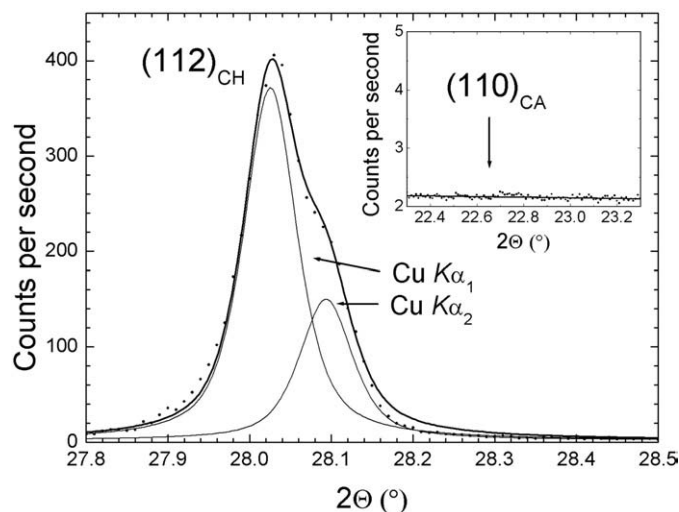


Fig. 5. X-ray-diffraction pattern of a polycrystalline CIS layer, grown on a Mo-coated Si substrate. The film shows reflections corresponding to the chalcopyrite phase only. The double peak structure in the $(112)_{\text{CH}}$ reflection is caused by Cu- $K\alpha_1$ and $-K\alpha_2$ radiation. The inset shows the calculated position of the (110) reflection of the CuAu-phase, which is indicated by the arrow.

faults, twin boundaries, and misfit dislocations as planar defects, but the films did not reveal any sign of polycrystallinity.

Our results show the coexistence of the CH and CA phases in epitaxial layers always to be accompanied by a high density of deep defects, which cause the defect-related transitions in the PL together with the absence of excitonic emissions. Due to the very similar growth temperatures, the survival of the CA phase in epitaxial layers is certainly not a pure temperature effect. Rather, as we assume, the grain boundaries in the polycrystalline CIS films support the surface segregation of excess Cu and S as an CuS_x phase, whereas such easy diffusion paths do not exist in epitaxial CIS and so the nonstoichiometry is kind of frozen in. Then, it is this deviation from the 1-1-2 CH stoichiometry (detected by means of RBS), which promotes the formation of defects and of the metastable CA phase. Rudigier et al. [17] reported that during the annealing process of CuIn precursors in S atmosphere the formation of CIS starts with the metastable CA ordering. The transformation into the preferred CH structure strongly depends on precursor composition. While Cu-rich films crystallized finally in the CH structure exclusively, no such phase transformation was observed for Cu-poor samples. In perfect agreement with our results on polycrystalline samples, these findings of Rudigier et al. suggest the copper (and sulfur) excess to be important for a development of a high crystal quality of CIS. However, it appears to be essential as well that these agents finally leave a stoichiometric CIS crystal behind and segregate as surface phase. Otherwise, as seen in our epitaxial layers, also Cu-rich CIS films have a high defect density and the CA phase can survive. Hence, in contrast to common expectations, the absence of grain boundaries in epitaxial CIS layers is responsible for their poor crystal quality.

4. Conclusions

Both, epitaxial and polycrystalline CIS layers were grown on Si substrates in the same MBE vacuum chamber under comparable growth conditions. The presented PL data show these materials to exhibit strongly different recombination mechanisms. Epitaxial CIS samples show defect related transitions only. Excitonic transitions are completely absent. This contrasts sharply with the observed PL spectra of polycrystalline CIS layers, where the luminescence is dominated by

an excitonic peak. Moreover, luminescence of deep defect levels is not present at all in polycrystalline CIS samples.

XRD measurements revealed a coexistence of the metastable CA ordering with the ground-state CH structure in epitaxial CIS films. The resulting volume fractions amounted to $79 \pm 6\%$ for the CH phase and $21 \pm 6\%$ for the CA phase. SAED measurements confirmed the coexistence of the CH and CA ordering in epitaxial CIS on Si(111). Polycrystalline CIS layers were also structurally investigated by means of XRD. The data show polycrystalline CIS layers to crystallize exclusively in the ground-state CH structure.

When compared to polycrystalline CIS, the inferior structural and optoelectronic quality of slightly Cu-rich epitaxial CIS is explained by the absence of grain boundaries.

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