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CuAu-type ordering in epitaxial CuInS₂ films

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Ordering of Cu and In atoms in near-stoichiometric CuInS₂ epitaxial films grown on Si (111) by molecular beam epitaxy was studied by transmission electron microscopy. Nonchalcopyrite ordering of the metal atoms in CuInS₂ is observed, which is identified as CuAu-type ordering. Sharp spots in electron diffraction patterns reveal the ordered Cu and In atom planes alternating along the [001] direction over a long range. High-resolution electron microscopy confirms this ordering. The CuAu-ordered structure coexists with the chalcopyrite ordered structure, in agreement with theoretical prediction. © 1998 American Institute of Physics. [S0003-6951(98)01132-2]

Ternary semiconductors such as CuInX₂ (X=S,Se) have attracted considerable interest due to their application in solar cells and their potential for other optoelectronic devices.¹ These applications impose certain requirements for the degree of structural perfection of the ternary solids. The density of stacking faults and point defects must be minimized by means of optimized growth techniques. Although profound knowledge about the governing defects is mandatory, transmission electron microscopy (TEM), the most powerful technique for the characterization of chalcopyrites, has been employed only to a small extent. In this letter an epitaxial film of CuInS₂ grown on Si substrate is investigated by means of TEM revealing a special structure.

Normally the A^IB^{III}X₂^{VI} (A=Cu, B=In, Ga, Al) compounds crystallize in the chalcopyrite structure which is derived from the zinc-blende structure. This derivation is accomplished by the ordered replacement of the group II atoms in accordance to the Grimm–Sommerfeld rule: The average number of valence electrons per atom must equal four.² In the case of CuInX₂, the A^I and B^{III} elements, Cu and In, are ordered alternately on the (201) planes of the metal sublattice. The X atom is centered in a tetrahedron with two A and two B atoms at the corners, forming A₂B₂ type tetrahedra. One conventional unit cell then consists of eight A₂B₂ tetrahedra. This ordering of the metal atoms introduces nearly a doubling of the unit cell dimensions in the [001] direction relative to the zinc-blende-like cubic unit cell. It governs the structure of the CuInX₂ compounds at room temperature which at transition temperature T_c (800–1300 K) transforms into a disordered zinc-blende-like structure. The Grimm–Sommerfeld rule for the metal atoms in an A^IB^{III}X₂^{VI} system, however, can also be fulfilled by a metal ordering different from the chalcopyrite. For instance, the so-called CuAu-ordering consists of alternating A and B (100) planes while the CuPt ordering consists of alternating A and B (111) planes in the metal sublattices. The tetrahedra in CuAu-

ordering are still A₂B₂ type while in CuPt-ordering they are A₃B and AB₃ type. Wei *et al.* studied theoretically the polymorphic order–disorder transition in CuInSe₂, the compound most closely related to CuInS₂. Among the six directly calculated structures at 1:1:2 stoichiometry, they found that the formation energy of CuAu ordering is only 8 meV/4 atoms higher than the energy of chalcopyrite ordering while for CuPt ordering the energy is 213 meV/4 atoms higher. The growth of A^IB^{III}X₂^{VI} films below T_c could result in “trapping” into a metastable mixture of chalcopyrite and CuAu-like modifications,³ but an experimental verification has not yet been reported.

CuInS₂ films investigated were grown by molecular beam epitaxy (MBE) on Si(111) substrates that were miscut toward [112] by 4°. The substrates were cleaned and hydrogen terminated by a wet-chemical treatment including a final etching in NH₄F solution. After preparation, the substrates were immediately transferred into vacuum and heated to the growth temperature of 520 °C. MBE growth occurred at a rate of 0.2–0.25 nm/s. The sulphur pressure was kept at 2 × 10⁻³ Pa which adjusts the equivalent pressure ratio of the sulphur to metal beams to approximately 20 to 1. For observation in the transmission electron microscope, cross-sectional and plan-view samples were carefully prepared by conventional methods.⁴ A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with an energy-dispersive x-ray spectroscopy (EDX) detector, was used.

The epitaxial growth was confirmed by x-ray diffraction⁵ and by the selected-area electron diffraction⁶ from regions containing both the silicon substrate and the film, taken from cross-sectional and plane-viewing samples. The chalcopyrite (112) plane grows parallel to the Si (111) plane. The formation of the chalcopyrite phase in the films was confirmed by checking the reflection condition of 101, 121, 123, and 213 in the electron diffraction patterns. Those reflections are not allowed for the disordered zinc-blende-like structure. As determined by integral EDX measurements, the film under investigation was slightly Cu poor, i.e., the atomic percentages established are Cu 24.3 ± 1.2 at. %, In 26.7 ± 1.6 at. %, and S

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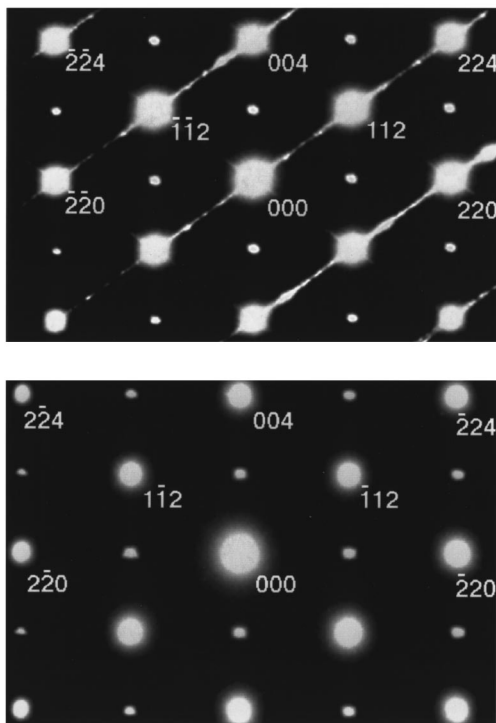


FIG. 1. Electron diffraction patterns, along the $[\bar{1}\bar{1}0]$ zone axis (upper) and the $[110]$ zone axis (lower).

49.0 ± 2.5 at. %. Two electron diffraction patterns are shown in Fig. 1. The $(\bar{1}\bar{1}0)$ electron diffraction pattern [Fig. 1(a)] was taken from a $[110]$ cross-sectional specimen. The specimen was tilted so that the incident electron beam is exactly parallel to the $[\bar{1}\bar{1}0]$ axis and perpendicular to the $[221]$ growth axis. The (110) pattern [Fig. 1(b)] was obtained from a plane-view specimen with an incident beam perpendicular to the $[110]$ zone axis and inclined by 35° to the $[221]$ growth axis. Besides the strong Bragg reflections at 004, 220, 112 which stem from the chalcopyrite structure, additional reflections appear at positions 002, 110, 222, and 114. In perfectly ordered and stoichiometric chalcopyrite CuInS_2 , the metal atoms at well-defined positions cannot give rise to any diffraction intensity at 002, 110, 222, and 114 positions. Therefore we regard the atypical spots as originating from regions in the epitaxial film where the location of the Cu and In atoms deviates from chalcopyrite. Moreover, on account of the sharpness of these spots, we conclude that the Cu and In atoms are arranged highly ordered. The extra reflections in Fig. 1 could also stem from some Cu-poor compounds such as $\text{Cu}_{0.75}\text{In}_{2.25}\text{X}_4$ (Ref. 7) or $\text{Cu}_3\text{In}_4\text{X}_8$ (Ref. 8) having a primitive tetragonal cell. While the integral composition of our sample is far from such Cu-poor compositions, we performed EDX measurements in the nonchalcopyrite-ordered regions in order to exclude the effect of local inhomogeneities. The EDX measurements from the nonchalcopyrite ordered region show no significant deviation from the stoichiometry of chalcopyrite-ordered region given above.

For the 1:1:2 stoichiometry, among the possible nonchalcopyrite orderings of Cu and In atoms,³ the CuAu-type ordering can give the reflections at position 002, 110, 222, and 114 in the (110) and $(\bar{1}\bar{1}0)$ diffraction pattern. For this type of ordering, the $0,0,0$ and $\frac{1}{2}, \frac{1}{2}, 0$ sites in a tetragonal unit cell are preferentially occupied with Cu atoms and the $\frac{1}{2}, 0, \frac{1}{4}$,

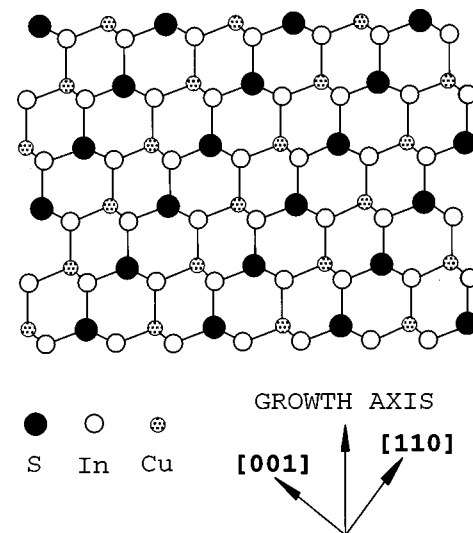


FIG. 2. $[\bar{1}\bar{1}0]$ projection of the perfectly CuAu-ordered structure in CuInS_2 .

and $0, \frac{1}{2}, \frac{1}{4}$ sites preferentially occupied with In atoms. A perfectly ordered structure of this type is schematically shown in Fig. 2. The structure consists of alternating Cu and In monolayers along the $[001]$ direction. Due to the difference in the scattering amplitudes of Cu and In atoms, the Cu and In monolayers are expected to produce lattice fringes with different brightness when viewed along the $[\bar{1}\bar{1}0]$ direction. This is indeed found in the nonchalcopyrite-ordered region of our sample by high-resolution electron microscopy (HREM), shown in Fig. 3. For comparison a high-resolution lattice image of a chalcopyrite ordered region is inserted. In chalcopyrite structure, the stacking sequence along $[\bar{1}\bar{1}0]$ direction is $(\text{Cu}-\text{In})-(\text{In}-\text{Cu})-(\text{Cu}-\text{In})$. The averaged atom scattering amplitude will not cause contrast variations in this projection. The difference in the real image of those two ordered structures is obvious. Image simulations calculated with a multislice image simulation program (CERIUS2) confirmed that the lattice fringes shown in Fig. 3 are not caused by thickness artefacts or defocus effects in electron microscope. An example of image simulations is given as inset in

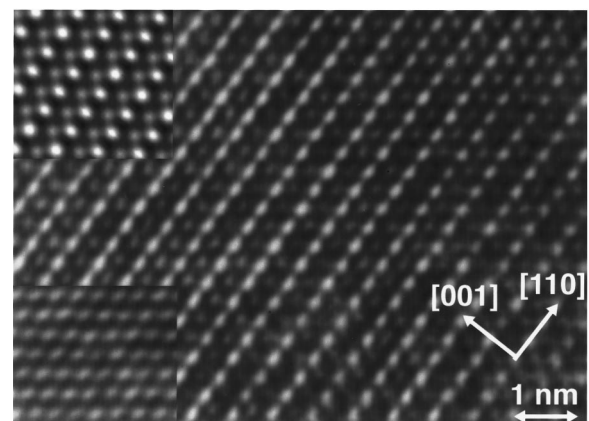


FIG. 3. Experimental high-resolution image of the CuAu-ordered structure in CuInS_2 , taken with the electron beam parallel to $[\bar{1}\bar{1}0]$ direction. Bottom left: an experimental high-resolution image of the chalcopyrite structure; top left: simulated high-resolution image of the CuAu-ordered CuInS_2 . Parameters for the simulation are spherical aberration of the objective lens $C_s = 1.35$ mm, thickness $t = 10.16$ nm, defocus $df = -40$ nm.

Fig. 3. From electron diffraction patterns, EDX measurements and real space imaging we identify the nonchalcopyrite ordered structure as the CuAu-type ordering of Cu and In atoms in the MBE prepared CuInS₂ film. The CuPt ordering which would give rise to additional reflections at (112)/2 and contrast differences on alternating (112) planes was not observed.

HREM reveals the CuAu ordering only in areas which also produce superlattice reflections. If these reflections were caused by double diffraction,⁹ they would also have to appear in the diffraction pattern from the regular structure. This, however, is not the case, hence we rule out double diffraction as an explanation for the origin of superlattice reflections. In order to assure that the observed CuAu ordering of metal atoms is not induced by ion milling during the specimen preparation for TEM investigation, we studied specimens that were thinned otherwise, either *only* by mechanical polishing or by *direct* removing the Si substrate with a sharp knife. The electron diffractions from those specimens give the same patterns as shown in Fig. 1; unfortunately they are unsuited for normal TEM and HREM investigations due to the difficulty in tilting and rotating. While the sample displayed in Figs. 1 and 3 was grown under slightly Cu-poor conditions, it should be emphasized that CuAu ordering of metal atoms was also observed for Cu-rich films grown on Si (111) substrates.

In Fig. 1(a), the strong Bragg reflections are streaked out along the [221] direction. This is due to the stacking faults formed in the (112) growth planes during MBE, as revealed by HREM and x-ray diffraction. The absence of any streaking in the superlattice reflections indicates that the CuAu-ordered region contain much fewer stacking faults than the chalcopyrite region or none. We also did not observe the antiphase boundaries in the CuAu-ordered region which may produce diffuse intensity on the superlattice reflections.

According to the theoretical study of the formation energy of different ordered CuInSe₂ structures,³ the coexistence of chalcopyrite and CuAu-ordered crystal phases appears well justified: For CuInSe₂, the total energy of the CuAu-ordered structure is only 8 meV/4 atoms higher than of the ground state chalcopyrite structure, comparable values are expected for CuInS₂.¹⁰ Considering the average thermal energy of $kT \sim 60$ meV at growth temperature, the formation of the metastable CuAu-type structure appears possible. Also, the absence of the CuPt-type ordered structure in the epitaxial films is explained by the ground state calculations: the electronically noncompensated A_3B and AB_3 tetrahedra lead to an increase in total energy of 213 meV/4 atoms which prevents the formation of the CuPt-like structure. On the other hand, the observation of CuPt-ordering has been reported for CuInSe₂ films grown by deposition of Cu, In, and Se on heated Si substrates¹¹ and on Mo-coated soda-lime glass.¹² However, it has been pointed out that the CuInSe₂ films used for these observations were prepared under heavily Cu-rich conditions. In a Cu-rich CuInSe₂ film, the impurity phase of Cu₂Se can be segregated, thus, the presence of β phase of Cu₂Se in a Cu-rich CuInSe₂ film could be an alternative explanation for the reported CuPt ordering.¹³

Ordering of the metal atoms has also been observed in many III–V semiconductor alloy thin films¹⁴ and in the II–

VI-based diluted magnetic alloy films of ZnFeSe₂.¹⁵ The ordered structure in these alloys is unusual because according to bulk thermodynamics, ordering is not energetically preferred. It was shown by Gomyo and co-workers¹⁶ and later by Zunger and co-workers¹⁷ that the ordering in epitaxial III–V films is induced by surface effects, where dimerization leads to the energetical stabilization of ordered structures. We found that the CuAu-ordered structure does not grow *directly* at the CuInS₂/Si(111) interface. Moreover, x-ray diffraction data of epitaxial CuInS₂ grown on Si(001) and Si(110) also indicate the existence of CuAu ordering for these substrate orientations,¹⁸ in contrast to the III–V compounds. These findings suggest that cause and driving force for the CuAu ordering in CuInS₂ are different from those for the CuAu or CuPt ordering in III–V semiconductor alloys. It is an open question, to what extent growth kinetics influences the formation of the metastable CuAu-type order. Further investigations are still needed.

In conclusion, we observed the nonchalcopyrite ordering of cations in a MBE prepared I–III–VI₂ semiconductor film. To the best of our knowledge, the newly discovered metastable phase was identified as CuAu-type ordered structure. The coexisting of the chalcopyrite ordered structure with CuAu- rather than the CuPt-ordered structure is in good agreement with the theoretical predictions of Wei *et al.*³ However, the CuAu ordering extends over a long range and cannot be explained as a mere local deviation from chalcopyrite order as the theoretical calculation predicts.³

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