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Structural Characterization of MBE Grown $CuInSe_2$ Epitaxial Layers

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The structure of $CuInSe_2$ layers grown by molecular beam epitaxy on (001) GaAs substrates with the Cu/In ratio (γ) ranging from 0.62 to 1.53 has been characterized by a precise X-ray diffraction technique. It was found that these layers are highly oriented single crystals, and that the best chalcopyrite phase exists in a narrow composition range near γ = 0.98. The ratio of c-spacing to a-spacing (c/a ratio) reverses at γ = 0.98, indicating a stress cross over. The Cu_2Se phase was found in Cu-rich specimens.

1. Introduction

Chalcopyrite $CuInSe_2$ (CIS) is a promising material for making highly efficient solar cells.[1] It is important to relate optical properties to the microscopic structure in order to achieve high efficiency. The band gap energy is not only a function of the atomic composition but also depends on the degree of cation order.[2]

In the (Cu, In)Se_2 system, the ratio of Cu to In content (Cu/In ratio; γ) is expected to influence the crystal structure, because Cu/In ratio directly affects the charge balance in the crystal.

In the present study, we have characterized the structure of CIS epitaxial layers grown by molecular beam epitaxy (MBE) with the Cu/In ratio ranging from 0.62 to 1.53 using a precise x-ray diffraction technique. The precise lattice parameters along the a- and the c-axis were measured by Bond's method. The degree of cation order with various Cu/In ratios was estimated from the integrated intensities of X-ray reflection lines unique to the chalcopyrite phase.

2. Experimental

The CIS samples with the Cu/In ratio ranging from γ = 0.62 to 1.53 were prepared by MBE on a GaAs (001) substrate.[3] The Cu/In ratio was determined by electron probe micro analysis (EPMA). The samples are typically 1 mm thick. Bond's method[4] was used to determine the precise lattice parameters. The measurements were carried out using $CuK\alpha_1$ radiation (λ = 0.15405981 nm[5]) collimated with a pair of 0.2 mm slits spaced 320 mm apart in order to obtain a parallel beam. The x-ray diffractometer is capable of determining the ω angle to an accuracy of 1 arc-sec.

The integrated intensities of the chalcopyrite x-ray lines were measured for evaluating the degree of disorder of the cation. The integrated intensities of ω scans were measured using a detector with parallel-plate diffracted beam collimator and flat graphite monochromator. The adjustable aperture crossed-slit incident beam collimator with high power x-ray source (45kV, 400mA) gives an incident beam resolution / divergence of about 0.25 degrees.

3. Results and Discussion

Along the normal of the epitaxial layer surface and near the (004) GaAs substrate peak only the (008) peak from the CIS layer was observed by conventional $\omega/2\theta$ scans and not the (400) peak, as shown in Fig. 1. These results demonstrate that the layer is c-axis oriented. Furthermore, the fact that the (408) peak of CIS appears at the same tilt angle as the (404) substrate peak shows that the a-axis of CIS is aligned parallel with the a-axis of the GaAs substrate. It is concluded that this epitaxial layer is a highly oriented single crystal.

For measurements of the a-inter planar spacing of CIS, the (11.10) reflection was used, and for the c-spacing, the (008) reflection, respectively. In spite of a lattice mismatch along the a-axis of the substrate estimated to be approximately 2.3%, the a-spacing of CIS nearly agreed with that of the JCPDS diffraction data.[6] Thus, these specimens are almost totally relaxed probably through the generation of misfit dislocations at the interface.

The degree of disorder in specimens with different Cu/In ratios was evaluated by comparing the integrated intensities of the (103), (211) and (11.10) chalcopyrite reflections. The (103) and (211) do not appear in the spharelite structure (in which Cu and In atoms randomly occupy the cation sites), but (11.10) is seen in both structures. For each reflection the x-ray integrated intensity was given by the product of peak intensity and FWHM (full width at half maximum).

The integrated intensities scaled to the strongest of each type, are shown in Fig. 2. It is found that the specimen with γ = 0.98 is the most perfect chalcopyrite single crystal among these samples, having the strongest diffracted intensities and the smallest FWHM (0.25 degree) of (11.10), (103) and (211) reflections. In the rest of this paper we call this sample the standard specimen. For each sample, the difference between the integrated intensities of the (103) or (211) reflections, and that of the (11.10) reflection gives an estimate of the degree of disorder of the chalcopyrite phase. We also found that the best chalcopyrite phase exists in an apparently narrow composition range. This result is consistent with EXAFS studies of Yamaguchi et al.[8]

The lattice parameters of the

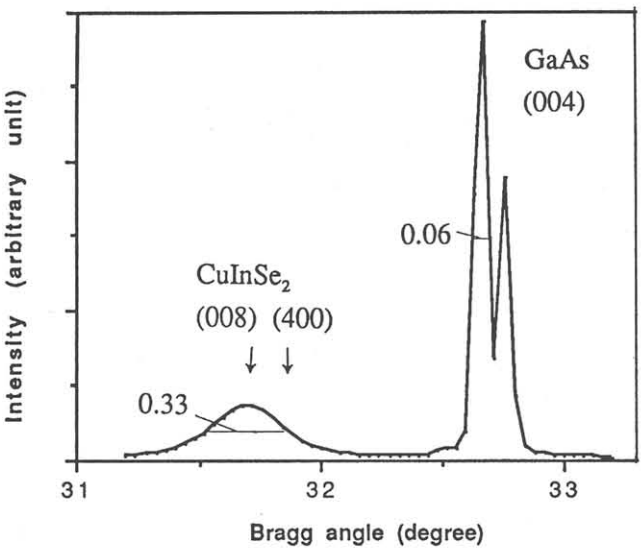

Fig.1 The (008) peak from the CIS crystal and the (004) peak from the GaAs substrate measured by a conventional $\omega/2\theta$ scan along the normal of the epitaxial layer surface.

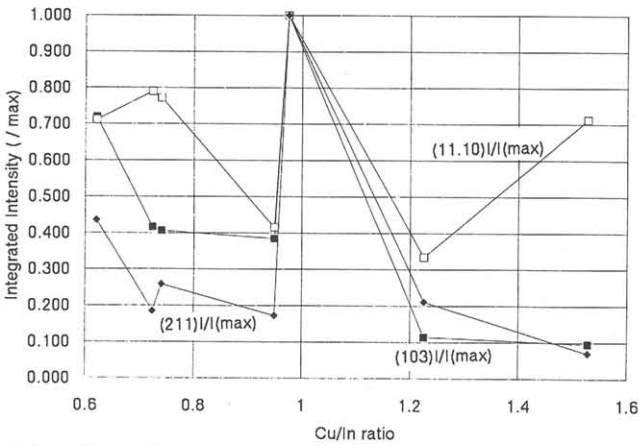

Fig.2 The integrated intensities scaled to the strongest of the (103), (211) and (11.10) chalcopyrite reflections for the specimens with various Cu/In ratios. The (103) and (211) do not appear in the spharelite structure, but (11.10) is seen in both structures.

standard specimen were determined to be c = 1.159201±0.000001 nm, a = 0.580172±0.000002 nm, and the ratio of c-spacing to a-spacing (c/a ratio) is 1.99803. The a-spacing of this specimen is a little larger than that of the JCPDS diffraction data (a = 0.57821 nm) and the c/a ratio is slightly smaller than that (c/a = 2.0095), which is due to the fact that the thermal expansion coefficient of the a-axis of CIS[7] is about twice that of GaAs.

The lattice parameters of specimens with different Cu/In ratios normalized to those of the standard specimen are shown in Fig. 3. The c/a ratio reverses at γ = 0.98, indicating a stress cross over. We think that both sides of this point have quite different mechanisms for relieving stress. The a-spacings in the In-rich specimens are smaller than that in the standard specimen, while the c-spacings are larger. Since the FWHM of the (11.10), (103) and (211) reflections in the In-rich specimens are large (more than 3 times that of the standard specimen), and the intensities are weak, it seems that polycrystals and/or large scale defects exist. Also the In-rich specimen has a small residual stress.

On the other hand, the a- and c-spacings in Cu-rich specimens are both smaller than in the standard materials. Furthermore, the difference between the integrated intensities of the (103) or (211) reflections, and that of the (11.10) reflection is large, so it seems that the degree of disorder in the chalcopyrite phase is large, approaching the spharelite structure. Also in a Cu-rich specimens a (060) reflection peak of Cu_2Se crystal was found, tilted by about 16 degrees from the c-plane. Since the Cu-rich specimens were expected to be Se-poor[3], it is likely that Se vacancies increase in number. We speculate that Cu-rich specimens contain an appreciable amount of point defects in the spharelite phase and the Cu_2Se phase.

In summary, it is found that MBE

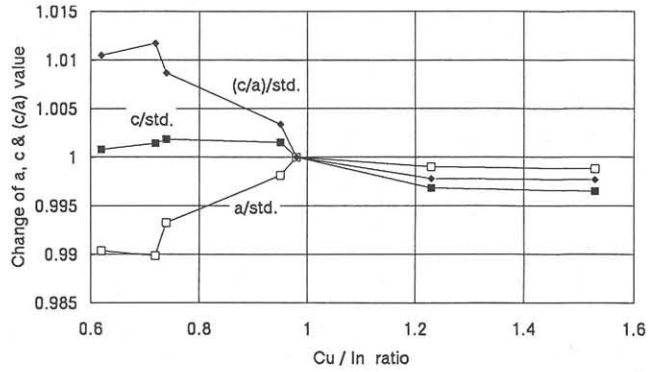

Fig.3 The lattice parameters of specimens with different Cu/In ratios normalized to those of the standard specimen. The lattice parameters of the standard specimen with γ = 0.98, are c = 1.159201±0.000001 nm, a = 0.580172±0.000002 nm, and c/a = 1.99803.

CIS epitaxially grown on the (001) GaAs substrates form highly oriented single crystals. The best chalcopyrite phase was found in a specimen with γ = 0.98 and exists in a narrow composition range. The a-spacings in In-rich specimens are smaller than the γ = 0.98 sample, while the c-spacings are larger. On the other hand, the a- and c-spacings in Cu-rich specimens are both smaller than that of the γ = 0.98 material. Furthermore Cu_2Se phase was found in the Cu-rich specimens.

Reference

1) S.Wagner, J.L.Shay, P.Migliorato and H.M.Kasper: Appl.Phys.Lett. 25 (1974) 434.

2) J.E.Jaffe and A.Zunger: Phys.Rev.B 29 (1984) 1882.

3) S.Niki, Y.Makita, A.Yamada, A.Obara, S.Misawa, K.Aoki, and N.Kutsuwada: Jpn.J.Appl.Phys. 32 (1993) Suppl. 32-3, 161.

4) W.L.Bond:Acta Crystallogr.:13(1960) 814.

5) R.D.Deslattes and A.Henins: Phys.Rev. Lett., 31 (1973) 972.

6) JCPDS diffraction data,file No.40-1487; D.K.Suri and K.C.Nagpal: J.Appl.Cryst. 22(1989) 578.

7) I.V.Bondar' and N.S.Orlova: Trans. Journal;Inorganic Materials, 21 (1986), 967.

8) H.Yamaguchi, Y.Kuwahara, H.Oyanagi, H. Nakanishi and T.Irie: Jpn.J.Appl.Phys. 32 (1993) Suppl. 32-3, 567.