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Stability of surfaces in the chalcopyrite system

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The stable surfaces in chalcopyrites are the polar {112} surfaces. We present an electron microscopy study of epitaxial films of different compositions. It is shown that for both $CuGaSe_2$ and $CuInSe_2$ the {001} surfaces form {112} facets. With increasing Cu excess the faceting is suppressed. This indicates a lower surface energy of the {001} surface than the energy of the {112} surface in the Cu-rich regime, but the {001} surface is higher in energy than the {112} surface in the Cu-poor regime. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2192638]

The chalcopyrite structure of the I–III–VI_2 compound semiconductors can be considered as a double zinc blende structure. The availability of two different cation species has important consequences: a tetragonal distortion of the original cubic structure[1] and greatly reduced defect formation energies.[2] Another difference has only recently been discovered; while in the zinc blende structure of either III–V or II–VI compounds the most stable surfaces are the nonpolar {110} surfaces, in the chalcopyrite structure the stable surfaces are the polar $\{112\}_{tet}$ surfaces ($\{111\}_{cub}$). By the subscript "cub" we denote indices corresponding to the (cubic) zinc blende, while "tet" structures correspond to the (tetragonal) chalcopyrite structure. First it was observed that the cleavage planes in $CuInSe_2$ are the $\{112\}_{tet}$ and the $\{101\}_{tet}$ ($\{111\}_{cub}$ and $\{201\}_{cub}$),[3] unlike in zinc blende compounds where the cleavage planes are the $\{110\}_{cub}$ planes. When growing zinc blende compounds epitaxially on the stable {110} GaAs surface, the surface of the growing film can be obtained ideally flat.[4] On the contrary, when growing $Cu(In,Ga)Se_2$ epitaxially on {110} GaAs no flat $(220)_{tet}$ or $(204)_{tet}$ surface is obtained, but it breaks up completely into $\{112\}_{tet}$ facets.[5] These results are rather unexpected. In the zinc blende materials the nonpolar $\{110\}_{cub}$ surfaces are more stable than the polar $\{111\}_{cub}$ or $\{100\}_{cub}$ surfaces, since at the polar surfaces massive surface reconstructions are necessary to create an areal charge that prevents the catastrophic increase in electrostatic energy (e.g., Ref. 6). These surface reconstructions increase the surface energy considerably.[7] But it was shown that due to the low defect formation energies in chalcopyrite the massively reconstructed $\{112\}_{tet}(\{111\}_{cub})$ surfaces are stabilized compared to the $\{110\}_{tet}$ surfaces.[8,9] Depending on the composition of the crystal the cation terminated $\{112\}_{tet}$ surface is stabilized mostly by the formation of Cu vacancies V_{Cu} in the Cu-poor case or by Cu_{In} antisites on the Cu-rich side.

This letter has investigated the stability of the $\{220\}_{tet}$ surface compared to the $\{112\}_{tet}$ surface. It has been argued that the $\{112\}_{tet}$ surface should be the most stable one in the chalcopyrite system. In the current letter we investigate the stability of the $\{001\}_{tet}$ surface. It has been described previously that the $\{001\}_{tet}$ surfaces of $CuInSe_2$ (Ref. 10) or $CuGaSe_2$ (Ref. 11) show small trenches along the [110] direction of the substrate, which have been interpreted as $\{112\}_{tet}$ faceting.[10] In contrast to the $\{220\}_{tet}$ surface there exist almost atomically flat $\{001\}_{tet}$ areas in between the trenches.[11,12] Those flat areas could be prepared well enough to investigate the reconstruction of the $\{001\}_{tet}$ surfaces.[13] The $\{001\}_{cub}$ surface is more polar than the $\{111\}_{cub}$ surface, i.e., the areal charge density needed to prevent the "electrostatic catastrophe" is higher for the $\{001\}_{cub}$ surface than for the $\{111\}_{cub}$ surface. The same is true for the $\{001\}_{tet}$ surface compared to the $\{112\}_{tet}$ surface. No theoretical calculation is available for the $\{001\}_{tet}$ surface. It can be expected though that it is stabilized by defect formation as in the case of $\{112\}_{tet}$.

Epitaxial films of $CuGaSe_2$ and $CuInSe_2$ are grown by metal organic vapor phase epitaxy (MOVPE) onto GaAs(001) surfaces. The main advantage of MOVPE over other preparation methods is a very reliable composition control. Details of the deposition process can be found elsewhere.[14] The films grow with the *c* axis of the chalcopyrite structure perpendicular to the substrate.

The surface morphology of the films is investigated by a scanning electron microscope (SEM) with a field emission source (LEO1530 Gemini). The micrographs are taken of a cleaved face, rotated by an angle of 20°, to show the surface as well as the cross section. The samples cleave along the $\{110\}_{cub}$ planes of the substrate. This implies $\{110\}_{tet}$ planes as the cleavage planes of the film. These have been observed in crystals as well.[3]

The integral composition was determined by energy dispersive x-ray emission spectroscopy (EDX) within the SEM for the $CuGaSe_2$ films and by x-ray fluorescence (XRF) for the $CuInSe_2$ films.

In Figs. 1 and 2 we show a typical series of SEM micrographs of $CuGaSe_2$ and $CuInSe_2$ epitaxial films with different [Cu]/[III] ratios. All micrographs are on the same scale. The range of compositions is chosen to show the typical range of surface morphologies for each material. The more Cu-rich films show the same type of morphology as the top most films each in Figs. 1 and 2. The more Cu-poor films show similar surface morphologies as the bottom films in Figs. 1 and 2, unless they become so Cu poor that epitaxy is not possible anymore. The micrographs show the cross section together with the surface. In most cases the Kirkendall voids are visible at the interface which are due to the growth process and the loss of Ga from the substrate.[15]

All films have trenches, disturbing a flat $(001)_{tet}$ surface. The trenches extend along the [110] direction of the substrate. The angles between the facets and the surface are in

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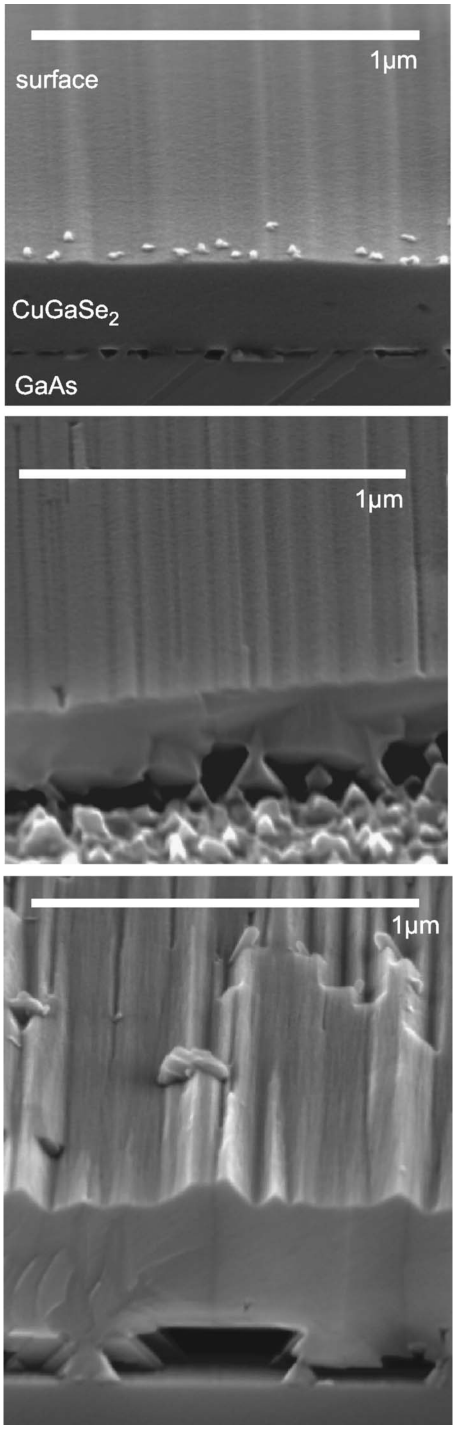

FIG. 1. SEM micrographs of the cross section of epitaxial $CuGaSe_2$ films with [Cu]/[Ga] ratio measured by EDX: (a) [Cu]/[Ga]=1.3, (b) [Cu]/[Ga]=1.1, and (c) [Cu]/[Ga]=0.8. All micrographs are on the same scale, the white bar indicates 1 μm. The increasing faceting with decreasing [Cu]/[Ga] ratio is clearly seen. For the Cu-rich films a section without copper selenide crystals was chosen.

accordance with the conclusion that the facets are $\{112\}_{\text{tet}}$. $\{112\}_{\text{tet}}$ facets could form along the $[110]$ direction or the $[1\bar{1}0]$ direction. But the trenches always form along the $[110]$ direction. It has been shown that the $(001)_{\text{tet}}$ surface is Se terminated.[13] The faceting occurs along the closely packed direction of the first and second layers, making their edges more stable.

Comparing the surfaces with different [Cu]/[III] ratios shown in Figs. 1 and 2 it becomes clear that the density and the depth of the trenches increase with decreasing [Cu]/[III] ratio for both $CuGaSe_2$ and $CuInSe_2$. This indicates that the stability of the $\{001\}_{\text{tet}}$ surface compared to the $\{112\}_{\text{tet}}$ surface decreases with decreasing Cu content. Thus the relative stability of the $\{112\}_{\text{tet}}$ surface should be due to the formation

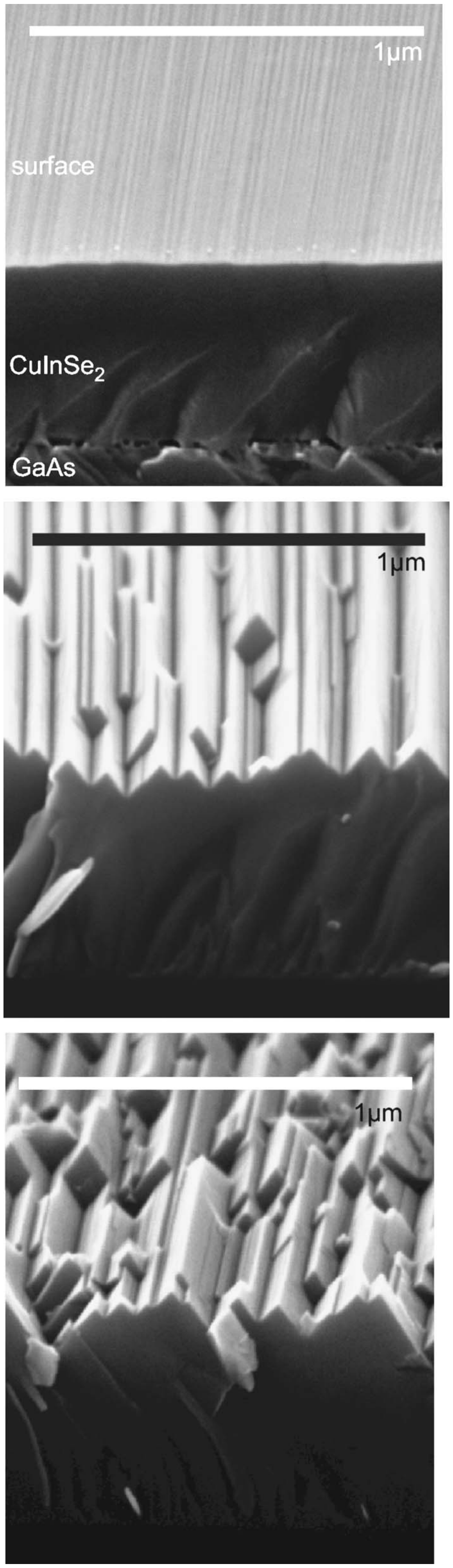

FIG. 2. SEM micrographs of the cross section of epitaxial $CuInSe_2$ films with [Cu]/[In] ratio measured by XRF: (a) [Cu]/[In]=1.1, (b) [Cu]/[In] =0.9, and (c) [Cu]/[Ga]=0.6. All micrographs are on the same scale, the white bar and the black bar indicate 1 μm. The increasing faceting with decreasing [Cu]/[In] ratio is clearly seen. For the Cu-rich films a section without copper selenide crystals was chosen.

of Cu vacancies. In Ref. 8 it is shown that the $\{112\}_{\mathrm{tet}}$ surfaces of $CuInSe_2$ are stabilized by Cu vacancies in the Cu poor case and by Cu_{In} antisites in the Cu-rich case. These calculations have been performed for the whole range of chemical potentials. In Ref. 9 the surface energies are calculated along the edges of the existence range of $CuInSe_2$. It is shown that the surface energy on the Cu-poor side is slightly lower than the energy on the Cu-rich side, indicating that the stabilization by V_{Cu} is somewhat stronger than the stabilization by Cu_{In}, i.e., the $\{112\}_{\mathrm{tet}}$ surfaces are most stable in the Cu-poor regime, in accordance with the observed surface morphology. The direct application of these calculations to our surface structures might be problematic, since our films grown by MOVPE could be terminated by H or hydrocarbons and the calculations are done for the clean surface. But since similar surface morphologies have been observed in films grown by completely different methods,[10,16] we believe that the theory is applicable to these surfaces. The $\{001\}_{\mathrm{tet}}$ surface is also a polar surface, which needs a strong reconstruction to provide surface charges. It can be expected that it is also stabilized by the formation of defects. From the increasing faceting with decreasing Cu content it is concluded that the surface energy of the $\{001\}_{\mathrm{tet}}$ surface is lower than the $\{112\}_{\mathrm{tet}}$ surface in the Cu-rich regime, but is higher in the Cu-poor regime. This could imply that the energy of the stabilized $\{001\}_{\mathrm{tet}}$ surface is between the energy of the $\{112\}_{\mathrm{tet}}$ surface stabilized by V_{Cu} and the energy of the $\{112\}_{\mathrm{tet}}$ surface stabilized by Cu_{In}. It could also imply that the energy of the $\{001\}_{\mathrm{tet}}$ surface is more strongly reduced by Cu_{In} than by V_{Cu}. This can only be answered by further calculations.

Comparing the surface morphologies for $CuGaSe_2$ and for $CuInSe_2$ we can draw a first conclusion that the general trend is the same for both materials. The faceting is stronger on the $CuInSe_2$ $\{001\}_{\mathrm{tet}}$ than on $CuGaSe_2$ $\{001\}_{\mathrm{tet}}$, implying that the stabilization of the $\{001\}_{\mathrm{tet}}$ with respect to the $\{112\}_{\mathrm{tet}}$ is stronger in $CuGaSe_2$ than in $CuInSe_2$. A recent calculation of the energetics of $CuGaSe_2$ grain boundaries versus $CuInSe_2$ grain boundaries also shows a much stronger influence of the reconstruction at the $\{112\}_{\mathrm{tet}}$ surface of $CuGaSe_2$, compared to $CuInSe_2$.[17]

Another difference is that the trenches in $CuGaSe_2$ are almost exclusively along the $[110]$ direction, i.e., the facets are the $(\bar{1}12)_{\mathrm{tet}}$ and the $(1\bar{1}2)_{\mathrm{tet}}$ surfaces. In contrast on the $CuInSe_2$ surfaces also $(112)_{\mathrm{tet}}$ and $(\bar{1}\bar{1}2)_{\mathrm{tet}}$ surfaces appear, more so with decreasing Cu content. This indicates that the stabilization of the trenches by the closely packed zigzag rows in the $[110]$ direction is stronger for $CuGaSe_2$ than for $CuInSe_2$. This is confirmed by the observation of rectangular pits on the $CuInSe_2$ $\{001\}_{\mathrm{tet}}$ surfaces (as in Ref. 10) which still have their long axis in the $[110]$ direction but are not long trenches as on the $CuGaSe_2$ surfaces.

The surface morphology of $CuGaSe_2$ and $CuInSe_2$ $\{001\}_{\mathrm{tet}}$ surfaces has been analyzed. Both surfaces show an increased faceting into $\{112\}_{\mathrm{tet}}$ surfaces with decreasing Cu content. This indicates that the surface energy of the $\{001\}_{\mathrm{tet}}$ surface is lower than the energy of the $\{112\}_{\mathrm{tet}}$ surface in the Cu-rich regime, but the $\{001\}_{\mathrm{tet}}$ surface is higher in energy than the $\{112\}_{\mathrm{tet}}$ surface in the Cu-poor regime. This is in accordance with the calculation that predicts the strongest stabilization of the $\{112\}_{\mathrm{tet}}$ surface by the formation of Cu vacancies.

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