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 CuGaSe2 and CuInSe2 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–VI2 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 structure1 and greatly reduced defect formation.4 On the contrary, when growing the cubic structure1 and greatly reduced defect formation important consequences: a tetragonal distortion of the original cubic structure1 and greatly reduced defect formation.

The integral composition was determined by energy dispersive x-ray emission spectroscopy (EDX) within the SEM for the CuGaSe2 films and by x-ray fluorescence (XRF) for the CuInSe2 films.

In Figs. 1 and 2 we show a typical series of SEM micrographs of CuGaSe2 and CuInSe2 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) 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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accordance with the conclusion that the facets are \{112\}_lat. \{112\}_lat facets could form along the [110] direction or the [110] direction. But the trenches always form along the [110] direction. It has been shown that the (001)_lat surface is Se terminated. 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 CuGaSe₂ and CuInSe₂. This indicates that the stability of the (001)_lat surface compared to the \{112\}_lat surface decreases with decreasing Cu content. Thus the relative stability of the \{112\}_lat surface should be due to the formation

FIG. 1. SEM micrographs of the cross section of epitaxial CuGaSe₂ 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.

FIG. 2. SEM micrographs of the cross section of epitaxial CuInSe₂ 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 $\{112\}_{\text{tet}}$ surfaces of CuInSe$_2$ are stabilized by Cu vacancies in the Cu poor case and by Cu$_{\text{In}}$ 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 $V_{\text{Cu}}$ is somewhat stronger than the stabilization by Cu$_{\text{In}}$, i.e., the $\{112\}_{\text{tet}}$ 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, we believe that the theory is applicable to these surfaces. The general trend is the same for both materials. The faceting 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 $\{112\}_{\text{tet}}$ surface of CuGaSe$_2$, compared to CuInSe$_2$.\textsuperscript{17}

Another difference is that the trenches in CuGaSe$_2$ are almost exclusively along the $[110]$ direction, i.e., the facets are the $(\overline{1}1\overline{2})_{\text{tet}}$ and the $(\bar{1}1\bar{2})_{\text{tet}}$ surfaces. In contrast on the CuInSe$_2$ surfaces also $(11\bar{2})_{\text{tet}}$ and $(\bar{1}\bar{1}2)_{\text{tet}}$ 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$_2$ $\{001\}_{\text{tet}}$ 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$_2$ $\{001\}_{\text{tet}}$ surfaces has been analyzed. Both surfaces show an increased faceting into $\{112\}_{\text{tet}}$ surfaces with decreasing Cu content. This indicates that the surface energy of the $\{001\}_{\text{tet}}$ surface is lower than the energy of the $\{112\}_{\text{tet}}$ surface in the Cu-rich regime, but the $\{001\}_{\text{tet}}$ surface is higher in energy than the $\{112\}_{\text{tet}}$ surface in the Cu-poor regime. This is in accordance with the calculation that predicts the strongest stabilization of the $\{112\}_{\text{tet}}$ surface by the formation of Cu vacancies.

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3. T. Kampschulte, A. Bauknecht, U. Blieske, M. Saad, S. Chichibu, and M. C. Lux-Steiner, Proceedings of the 26th IEEE Photovoltaic Specialist Conference, Anaheim, 1997 (unpublished), in this paper the direction of the trenches was erroneously given as [100].