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GROWTH AND STRUCTURAL CHARACTERISATION OF $CuGa_xSe_y$ LAYERS

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ABSTRACT: Heteroepitaxial layers of $CuGa_xSe_y$ were grown on (001) and (111) oriented Si substrates with molecular beam epitaxy despite high lattice and thermal mismatch. Growth kinetics were studied with *in-situ* reflection high energy diffraction. Rutherford backscattering ion channeling was used to characterize the crystal quality, channeling yields of 12% have been obtained for 800 nm thick (112) oriented layers on Si(111). Measurements of lattice vibrational properties with infrared absorption and Raman scattering show that the vibration modes are dependent on the stoichiomety of the layer. Photoluminescence measurements of Ga rich $CuGa_xSe_y$ showed a donor acceptor related emission at 1.57 eV.

Keywords: Chalcopyrite - 1: $CuGaSe_2$ - 2: Epitaxy - 3

1. INTRODUCTION

$CuGaSe_2$ (CGS) is an interesting material for photovoltaic devices, efficiencies of 9.3 % have been obtained for thin film solar cells [1]. In quarternary $Cu(In,Ga)Se_2$ devices Ga raises the bandgap and conversion efficiencies of up to 17.7 % have been obtained [2]. Because of its high bandgap of 1.7 eV $CuGaSe_2$ is also a promising candidate for advanced photovoltaic devices like tandem solar cells.

In order to improve the understanding of the basic material properties many researchers have studied heteroepitaxial layers of $CuGa_xSe_y$ on GaAs substrates grown by molecular beam epitaxy (MBE) and metallorganic chemical vapour deposition (MOCVD) [3,4,5 and references therein].

The choice of substrate material for heteroepitaxy is critical because differences in lattice and thermal expansion coefficients can give rise to structural defects. Reactions at the interface and diffusion can influence electronic properties. The lattice mismatch between CGS and GaAs is 0.6% and 3.3% between CGS and Si, respectively. Thermal expansion coefficients are $13.1 \cdot 10^{-6}$/K for CGS, $6.9 \cdot 10^{-6}$/K for GaAs and $3.0 \cdot 10^{-6}$/K for Si. These values suggest GaAs as appropriate substrate material for CGS epitaxy. However, the preferred growth direction of polycristalline $CuGa_xSe_y$ is (112) which can be obtained on (111) oriented substrates. GaAs substrates of this orientation are expensive, therefore it would be desirable to grow on silicon.

We have developed a process for the growth of epitaxial layers of $CuGa_xSe_y$ on (001) and (111) oriented Si substrates despite 4% lattice mismatch. Properties of the layers have been studied with electron channeling (EC), Rutherford backscattering (RBS), X-ray diffraction (XRD), photoluminescence (PL) and transmission electron microscopy (TEM).

2. GROWTH OF EPITAXIAL LAYERS

The layers were grown in a MBE system from elemental sources at a background pressure in the range of 10^{-7} mbar. Silicon substrates of (001) and (111) orientations were cleaned with a Shiraki method. The MBE system can be loaded with 3” wafers and is equipped with reflection high energy electron diffraction (RHEED) for *in-situ* study of growth kinetics. Growth of CGS starts with the formation of islands (3D growth) due to lattice mismatch between layer and substrate.

Growth temperatures in the range of 460 to 550°C were studied. Depending on substrate temperature twinning in the initial phase of growth is observed. Growth at higher substrate temperatures or a rapid thermal annealing step help to reduce the twinning.

The layers were cooled down in Se ambient at a rate of 5 °C per minute. Layers grown above 550 °C cracked after cooling to room temperature.

Growth kinetics and adhesion of the layers to the substrate depend critically on the substrate temperature, evaporation fluxes of Cu and Ga and the Se overpressure. Only Ga rich layers showed good adhesion to the Si substrate and could be grown reproducibly, while we were unable to grow Cu-rich *epitaxial* layers.

Fig. 1 shows a diffraction pattern of a (112) oriented layer in the $[11\bar{2}]$ azimuth of the Si(111) substrate. The pattern is characteristic for the chalcopyrite structure, the spots indicate 3D epitaxial growth due to lattice mismatch. Twinning can be observed after rotation of the sample to the $[1\bar{1}0]$ azimuth, where additional spots are visible in the initial stage of the growth.

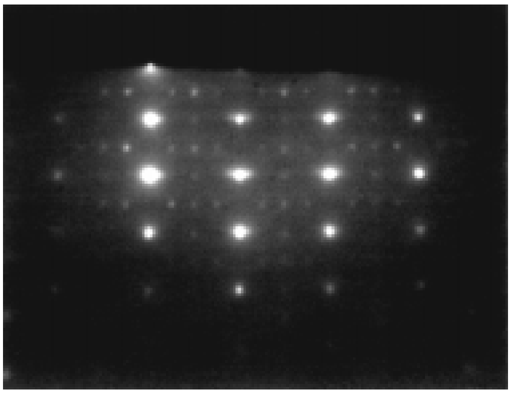

Figure 1: RHEED pattern of CGS/Si(111) in the $[11\bar{2}]$ azimuth of Si. The weak spots are typical for the chalcopyrite structure.

3. CHARACTERIZATION OF CRYSTAL PROPERTIES

Electron channeling (EC) in the scanning electron microscope (SEM) showed sharp and well resolved patterns indicating good crystal quality. On Si(001) 4-fold symmetry of (001) growth is observed, on Si(111) 3-fold symmetry ensures untwinned (112) growth.

In XRD only peaks related to Si and $CuGa_xSe_y$ were observed. Peaks due to segregations of binary phases like Cu_2Se or Ga_2Se_3 could not be found. X-ray linewidths of about 430 arcs have been measured in a θ–2θ setup for the 336 reflection of 800 nm thick layers.

Ion channeling was performed with a 2 MeV $^4He^+$ beam in order to determine the crystal quality. The channeling yield, χ_{min}, is defined as the ratio of backscattered intensities in aligned and random direction. Fig. 2 shows RBS channeling spectra of CGS/Si(111) with χ_{min} of 15%, layer thickness is 900 nm. For different epitaxial layers grown at temperatures between 530 and 550°C yields in the range of 12 to 15% were obtained. Samples grown at lower temperatures showed values of about 20 %. Similar values have been reported for $CuInSe_2$ on Si(111) [6]. Channeling yields for bulk single crystals are between 3 and 5%.

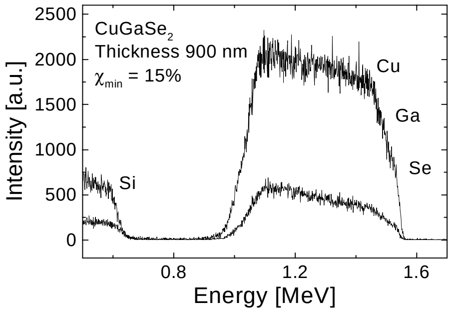

Figure 2: 2 MeV $^4He^+$ RBS channeling. Minimum yields of 10 to 15% are obtained.

Thickness and absolute composition of the layers can also be determined, if the peak shape is fitted with the RUMP simulation program. Values of layer thicknesses were found to be consistent with profilometer measurements. The composition is difficult to determine with 2 MeV RBS because the signals corresponding to Cu, Ga and Se are not well resolved due to small differences in mass number, as can be seen in Fig. 2. However, with 3 MeV RBS the compositions are evaluated with higher accuracy. They are consistent with values determined from energy dispersive X-ray analysis (EDX).

4. LATTICE VIBRATIONAL PROPERTIES

RBS measurements are not sufficient to decide whether the layers consist of single phase material. The backscattered ions could be collected from different domains or segregations, thus the resulting compositions could be averaged values. In XRD low intensity reflections of segregations of similar crystal structure could be hidden in the dominant peaks.

The study of lattice vibrational properties offers the possibility to detect segregations because of their different vibration modes. Raman measurements of $CuGa_xSe_y$ layers were performed in backscattering geometry with an Ar^+ laser emitting at 514 nm. The resolution was better than 2.5 cm^{-1}. The dominant feature is a peak at 185 cm^{-1} which is attributed to the vibration of Se against the cation lattice (A_1 vibrational mode) in the chalcopyrite structure. Two peaks at 247 and 273 cm^{-1} are attributed to TO and LO phonon modes, respectively, and correspond to E^1 and

B_2^2 vibrations. The peak positions of the measurements are consistent within 3 cm^{-1} to published values [7].

We were also able to investigate vibrational properties with IR transmission because the Si substrate is transparent in this range of wavelengths.

The lower spectrum in Fig. 3 shows IR absorptions of $CuGaSe_2$ with a small dip at 154 cm^{-1} and distinct dips at 187 and 248 cm^{-1}. These E and B modes are related to vibrations of the Ga-Se bonds.

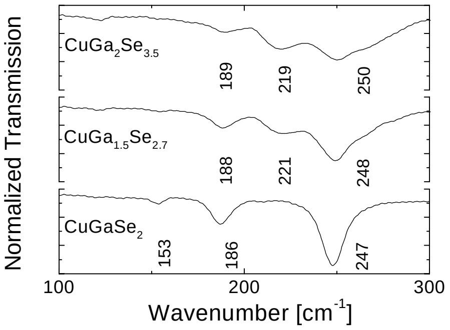

Figure 3: IR absorption is used to investigate the vibrations due to Ga-Se bonds (B and E modes). An absorption at 220 cm^{-1} is found on Ga rich samples.

The upper two spectra in Fig. 3 were recorded from Ga rich compositions. The absorption peaks are wider and small shifts are observed in all peaks, also a new absorption at 220 cm^{-1} is observed which could be due to disorder in the lattice or to a different structure. It was also found in $CuInSe_2$/Si for In rich samples [8].

5. PHOTOLUMINESCENCE PROPERTIES

Fig. 4 shows PL spectra of a (112) oriented Ga-rich layer. The excitation power was varied between 0.02 and 20 mW using a laser diode emitting at 672 nm.

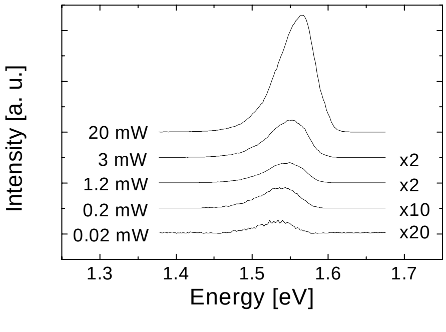

Figure 4: Power dependent PL spectra of $CuGa_{1.3}Se_{2.6}$ on Si(111). The blue shift with higher excitation power is typical for D-A transitions

The spectra are dominated by a broad emission peak located at 1.57 eV. The peak energy of this emission shifts to higher energies with increasing excition power. Position and shape are similar to reported peaks at 1.58 eV which are attributed to a V_{Se} to V_{Cu} donor-acceptor (D-A) transition [9,10]. This transition shows no significant change in shape or position for different Ga rich compositions. Furthermore, we did not observe any of the excitonic or deep level related transitions.

6. MICROSTRUCTURAL ANALYSIS

Microstructural properties of the $CuGa_xSe_y$ layers were studied with TEM. Samples were thinned mechanically and by ion milling with a standard procedure. Twins and stacking faults on $\{112\}$ planes are found at the interface to Si. Strain due to thermal and lattice mismatch between layer and substrate is partly relaxed by these faults.

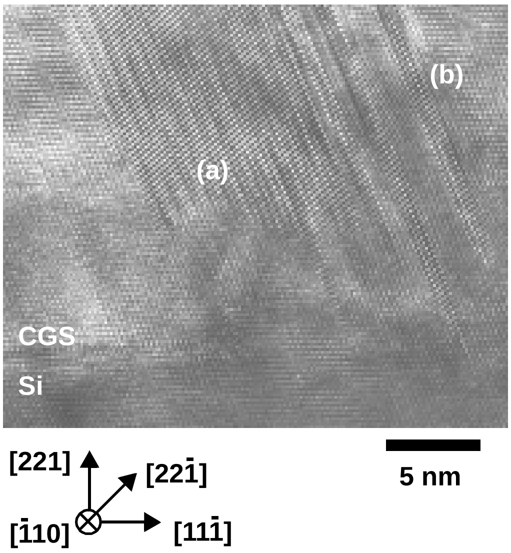

Figure 5: High Resolution TEM image of the interface between the CGS layer and the Si substrate. Twins (a) and dislocations help to relax stress due to thermal and lattice mismatch. Stacking faults extend into the layer (b).

Fig. 5 shows a high resolution image of the interface region between CGS on Si(111). At the interface some dislocations due to lattice mismatch are visible. If they relax, $CuGa_xSe_y$ can grow undisturbed (left side). In the middle (a) a nanotwin on a $(11\bar{2})$ plane, starting about 5 nm above the interface, can be seen. Such twins were mostly observed on $(11\bar{2})$ but not on (112) growth planes as it is the case for $CuInSe_2$ on Si(111) [11]. The boundary of the twin with the (112) growth planes is not coherent.

On the right side two extrinsic stacking faults on $(11\bar{2})$ planes extend from the interface into the layer.

It was observed that the number of nanotwins and stacking faults decreases with the thickness of the layer which explains the better crystal quality of thicker layers.

7. CONCLUSIONS

We have grown epitaxial $CuGa_xSe_y$ layers of different compositions on (001) and (111) orientated Si substrates. A process for growth of crack free epitaxial layers with thicknesses in the range of 800 to 1000 nm was developed. Due to the lattice mismatch of 3.3 % we observed twinned 3D epitaxial growth, the twinning can be reduced by a thermal annealing step.

The reproducibility of the growth has not yet reached to a satisfactory level, especially the annealing step and the Se overpressure have to be optimized. Furthermore, we have been unable to grow epitaxial layers with Cu rich compositions.

In XRD measurements linewidths of about 430 arcs were measured for the 336 reflection in θ–2θ setup. RBS ion channeling yields in the range of 12 to 15% have been obtained.

Photoluminescence studies on Ga rich samples revealed a broad emission peak at 1.57 eV due to a V_{Se} - V_{Cu} (D-A) transition.

IR transmission revealed a significant dependence on different stoichiometries. A new absorption at 220 cm^{-1} was found for Ga rich layers.

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