Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 6147–6150
www.elsevier.com/locate/tsf

Epitaxial and polycrystalline $CuInS_2$ thin films: A comparison of opto-electronic properties

J. Eberhardt [a,*], K. Schulz [a], H. Metzner [a], J. Cieslak [a], Th. Hahn [a], U. Reislöhner [a], M. Gossla [a], F. Hudert [c], R. Goldhahn [b], W. Witthuhn [a]

[a] Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany
[b] Institut für Physik, Technische Universität Ilmenau, PF 100565, 98684 Ilmenau, Germany
[c] Fachbereich Physik, AG Dekorsy, Universität Konstanz, Fach M 700, 78457 Konstanz, Germany

Available online 18 January 2007

Abstract

Epitaxial and polycrystalline thin $CuInS_2$ (CIS) layers were grown by means of molecular beam epitaxy (MBE) on single crystalline silicon substrates of 4 inch diameter. Photoluminescence (PL) studies were performed to investigate the opto-electronic properties of these layers. For the epitaxial CIS, low-energy-hydrogen implantation leads to the passivation of deep defects and several donor–acceptor (DA) pair recombinations (from 1.034 eV to 1.439 eV) and two free-to-bound (FB) transitions (at 1.436 eV and 1.485 eV) become observable at low temperatures (5 to 100 K). Excitonic luminescence is completely absent for all investigated epitaxial CIS layers. This contrasts sharply with the PL of the polycrystalline films which is dominated by excitonic luminescence (1.527 eV). Also a donor-to-valence band transition at 1.465 eV (BF-1) and one donor–acceptor recombination at 1.435 eV (DA-1) were observed, while luminescence from deep levels is not present at all. Based on these data, a refined defect model for $CuInS_2$ with two donor and two acceptor states is presented. Under comparable growth conditions, the electronic quality of polycrystalline CIS is superior to epitaxially grown material.

Keywords: $CuInS_2$; MBE; Photoluminescence

1. Introduction

In order to achieve an optimum match with the solar spectrum, the ternary chalcopyrite semiconductor $CuInS_2$ (CIS) with its direct fundamental band gap of 1.5 eV and a high absorption coefficient in the visible spectrum is an alternative to the analogous Se-based material $CuInSe_2$. Due to the higher band gap, CIS promises potentially higher open circuit voltages and should be, in principle, more favourable for thin-film solar cells. However, the conversion efficiencies for $CuInS_2$ solar cells are presently below 13% [1] compared to 19,2% for Cu(In, Ga)Se_2 photovoltaic devices [2]. A deeper knowledge of defect-related band gap states is necessary to understand and control recombination, compensation and intrinsic doping effects which thus represent key issues for solar cell performance. To investigate the opto-electronic properties, power- and temperature dependent photoluminescence measurements were performed. In this work, results of molecular beam epitaxy (MBE) grown single crystalline and polycrystalline CIS layers on Si substrates are compared. Based on these data, we refine the previously proposed defect model for $CuInS_2$ [3] by introducing a second FB- and a new BF transition.

2. Experimental

Both epitaxial and polycrystalline thin $CuInS_2$ layers were deposited by means of MBE. The epitaxial CIS layers were directly grown on commercial Si(111) wafers of 100 mm diameter [4–7]. No ex situ chemical etching or rinsing was performed on these Si wafers; instead, they were cleaned and terminated in a high-temperature sulphurisation step [8,9]. Polycrystalline films were deposited on untreated Si(100) wafers covered with a sputtered polycrystalline Mo buffer layer of 200 nm thickness. Copper and indium (purity 99.9999%) were evaporated in standard hot-lip effusion sources (VTS CreaTec). The sulphur (purity 99.9995%) was provided by a three stage cracker source based on our own design [10].

* Corresponding author. Tel.: +49 3641 947 313; fax: +49 3641 947 302.
E-mail address: eberhardt@pinet.uni-jena.de (J. Eberhardt).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.12.039

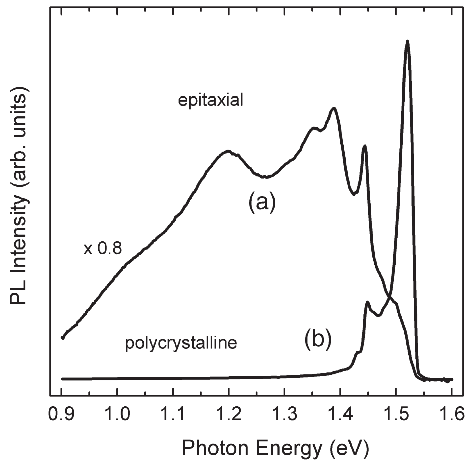

Fig. 1. Comparison of PL spectra of epitaxial CIS after H-treatment (a) and a KCN-etched polycrystalline thin $CuInS_2$ film (b). The spectra were measured at $T=5$ K and with 150 mW excitation power. The intensities are normalized as indicated.

During film growth, the substrates were rotated continuously. The substrate temperature was 820 K for epitaxial and 870 K for polycrystalline CIS, respectively. Rutherford backscattering spectroscopy (RBS) with an incident α-energy of 3.5 MeV was carried out to determine composition, thickness and surface roughness of the samples. The samples discussed in this paper were slightly copper rich. After a wet-chemical KCN-etching step, the Cu to In atomic ratio changed for the epitaxial layers from 1.2 for the as-grown state to 1.1 and for the polycrystalline films from 1.37 to nearly stoichiometric. Following the etching step, low-energy-hydrogen implantation into the epitaxial CIS layers was carried out at room temperature with a kinetic energy of 500 eV for the H_2^+ molecular ions (250 eV per atom) and a fluence of 1.0×10^{15} cm^{-2}. It was demonstrated in a previous publication [11] for other semiconductors that this type of soft hydrogen loading avoids lattice damage and is well suited to, for example, passivate acceptors under defined conditions. Photoluminescence was excited by the 514-nm line of a continuous wave Ar^+ laser. Power dependent measurements were performed by tuning the laser output power and employing neutral density filters. The emission was dispersed by a 2.0-m focal length single grating monochromator and analysed by means of lock-in technique with a LN_2-cooled Ge-detector or a Si-photodiode, respectively. All measured data were corrected for the spectral response of the system.

3. Results and discussion

Fig. 1 shows typical low-temperature PL spectra of low-energy-hydrogen implanted epitaxial CIS (curve a) and a KCN-etched polycrystalline layer (curve b) demonstrating strongly different recombination behaviour of both types of the material. The influence of the H-treatment of the as-grown state of epitaxial CIS layers was already discussed [3]. Epitaxial films show defect-related transitions and the PL spectra are dominated by broad luminescence of deep levels. A low-energy-hydrogen implantation leads to the passivation of deep defects and thus several donor–acceptor (DA) pair recombinations (from 1.034 to 1.439 eV) and two free-to-bound (FB) transitions (at 1.436 eV and 1.485 eV) become observable at low temperatures (5 to 100 K). Excitonic luminescence is completely absent for all investigated epitaxial CIS layers. A numerical evaluation with least squares fits and assuming seven transitions of Gaussian shape leads for $T=5$ K and 5 mW excitation power to the identification of the following transitions: one free-to-bound transition (FB-1) at 1.485(3) eV and six donor–acceptor transitions at 1.439(3) eV (DA-1), at 1.392(3) eV (DA-2), at 1.349(3) eV (DA-3), at 1.309(3) eV (DA-4), at 1.199(5) eV (DA-5) and at 1.034(5) eV (DA-6), respectively. In contrast to this, the PL of KCN-etched polycrystalline thin films (curve b in Fig. 1) is dominated by excitonic luminescence at 1.527 eV. Furthermore, a donor-to-valence band transition (BF) at 1.465 eV and a DA recombination (1.435 eV) were observed. For all investigated polycrystalline samples, luminescence of deep levels is not present at all.

In order to improve our defect model for $CuInS_2$ based on earlier data [3], additional investigations on hydrogen implanted epitaxial layers were performed, such as temperature dependent PL measurements. Fig. 2 shows PL spectra of epitaxial CIS after H-treatment over a temperature range from 5 to 100 K. From 5 to 65 K, the temperature step between two spectra amounts to 15 K. With rising temperature, the intensity of DA-1, DA-2, DA-3 and FB-1 decreases and for more than 80 K both DA-2 and DA-3 vanish almost completely. This behaviour is explained by the complete thermal ionization of the donors and acceptors at higher temperatures. In contrast to this, DA-1 apparently survives up to high temperatures.

As a result of least squares fits to the data, assuming seven transitions of Gaussian shape, Fig. 3 shows the quantitative temperature behaviour of the observed transitions. At low temperatures (from 5 to 65 K) DA-1 decreases in the same way as DA-2. At higher temperatures its behaviour is comparable to FB-1. This behaviour strongly suggests that there is a second FB transition (FB-2) at the energetic position of DA-1. Assuming the same energetic shift for FB-1 and FB-2 with

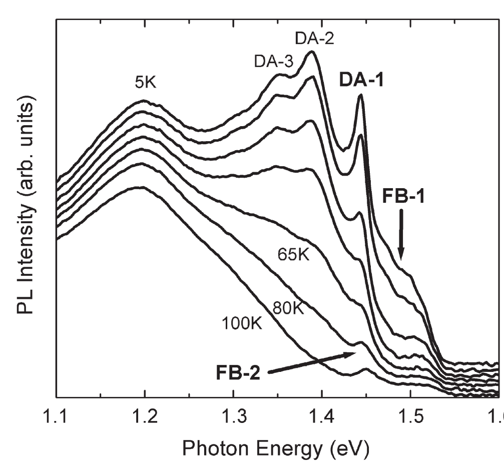

Fig. 2. Temperature dependence of epitaxial CIS after H-treatment. All spectra were measured with 150 mW excitation power.