ELECTROCHEMICAL NANOSTRUCTURING OF $CuInSe_2$ BULK CRYSTALS

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Abstract

We show that chalcopyrite $CuInSe_2$ crystals can be nanostructured by electrochemical treatment in an aqueous HCl solution. To make the crystals suitable for electrochemical nanostructuring, they are subjected to thermal treatment either in vacuum or in Zn vapors. The morphology of the produced material and the diameter of pores are found to be a function of the resistivity of the samples attained after thermal treatment. The pore diameter can vary in a range of 100 nm to 1 μm. The influence of thermal treatment and electrochemical etching on the photoluminescence spectra is analyzed.

1. Introduction

Solar cell technologies using I-III-VI_2 direct band-gap chalcopyrite semiconductors as the absorber layer have attracted great interest [1]. $CuInSe_2$-based solar cells are currently demonstrating the leading performance amongst thin-film technologies: 20% conversion efficiency [2] and excellent stability. $CuInSe_2$ is a semiconductor with the direct band gap near 1.05 eV and an absorption coefficient exceeding 10^5 cm^{-1} [3]. In spite of the high value, the reached conversion efficiency of 20% is still far from the theoretical limit for a one-junction solar cell [4]. This is indicative of the importance of further technological improvements.

One way of boosting the performance of solar cells consists in coating them with a textured layer. The idea is to trap more light so that it bounces around inside the cell instead of reflecting back out, since reflection means the loss of the light, which is absorbed to solar cell and generates electric power. Light trapping regimes were implemented in thin-film silicon solar cells with a photonic pattern [5], in textured multicrystalline silicon [6], in GaAs solar cells textured with dielectric 1D and 2D nanopatterns [7], etc. Nanopatterning of solar cells was produced by nano-imprint lithography [8, 9], by surface etching processes [10], or by the formation of a porous silicon layer on a textured silicon wafer [11]. A porous layer can be produced by anodization [11]. Electrochemical treatment proved to be a powerful tool for the preparation of a variety of porous morphologies also in III-V [12] and II-VI [13, 14] materials.

The goal of this paper is to demonstrate that electrochemical treatment can be also applied for the nanostructuring of $CuInSe_2$ crystals, particularly for patterning the surface of the samples to reduce the reflection at the surface in the case of their implementation in solar cells.

2. Sample preparation and experimental results

$CuInSe_2$ single crystals were grown by chemical vapor transport (CVT) in a closed system

using iodine as a transport agent. The polycrystalline material preliminary synthesized in iodine atmosphere at a temperature of about 800°C from a stoichiometric mixture of the elemental constituents was used as the raw charge in the CVT. The iodine concentration was approximately 5 mg cm^{-3}. The source temperature and the growth temperature were about 820 and 770°C, respectively. The system was cooled down slowly at a rate of 10°C/h to avoid straining of the crystals after crystal growth.

Electrochemical treatment for nanostructuring was performed in an electrochemical cell as described elsewhere [15]. A fourPt electrode configuration was used: a reference electrodein the electrolyte, a reference electrode on the sample, acounter electrode and a working electrode. The area of the sample exposed to the electrolyte solution was 0.1 cm^2. The anodic etching was carried out in a 5% HCl:H_2O electrolyte in the potentiostatic regime at room temperature.The resulting morphology of the etched samples was studiedusing a TESCAN scanning electron microscope (SEM). The photoluminescence (PL) wasexcited by a LD Pumped all-solid state MLL-III-532 laser andanalyzed through a double spectrometer. The resolution wasbetter than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

3. Results and discussions

The as-grown $CuInSe_2$ crystals are n-type with resistivity in the order of 10^5-10^6 Ω·cm. In is known that low resistivity crystals are required for nanostructuring by electrochemical treatment. For decreasing the resistivity of the as-grown $CuInSe_2$ crystals, several types of thermal treatment have been applied. Crystals with the resistivity down to 0.2 Ω·cm were produced by annealing of crystals in vacuum. For a further decrease in resistivity, the samples were subjected to annealing in Zn vapors. The samples were subjected to annealing during 30 h. The parameters of samples as a function of the technological conditions are presented in the table.

Table. Electrical parameters of $CuInSe_2$ crystals subjected to different thermal treatment

Sample treatment conditions	As grown, #1	Annealed in vacuum at 500°C, #2	Annealed in vacuum at 600°C, #3	Annealed in vacuum at 700°C, #4	Annealed in Zn vapors at 600°C, #5	Annealed in Zn vapors at 700°C, #6
ρ (Ω · cm)	$10^5 \div 10^6$	12	0.6	0.2	0.06	0.03
n (cm^{-3})	-	$2\cdot10^{15}$	$5\cdot10^{16}$	$2.1\cdot10^{17}$	$1.1\cdot10^{18}$	$7\cdot10^{18}$
μ (cm^2/V·s)	-	250	210	140	90	30

The PL spectra of the samples #1 to #6 with parameters from the table are presented in Fig. 1. The spectrum of the as-grown sample consists of several near-band-edge lines and several deeper PL band at 0.99, 0.97, and 0.96 eV. Among the near-band-edge lines, two most intensive lines at 1.036 and 1.028 eV assigned previously as M2 amd M5 lines [3] are attributed to the recombination of bound excitons [16, 17], while the band at higher photon energies (1.042 eV) is due to the recombination of free excitons [3]. The bands at 0.99 and 0.97 eV have been previously attributed to donor-acceptor transitions involving shallow donor and different

acceptors [18], such as [Cu_{In}–Cu_i] complex and V_{Cu} center [19-21].

The annealing of crystals in vacuum at 500^{o}C leads to a decrease in the luminescence intensity by a factor of 10, to a broadening of the lines related to the recombination of bound excitons, and to the disappearance of the band associated with the recombination of free excitons. An increase in the annealing temperature to 600^{o}C leads to the quenching of the exciton lines and the emergence of a new broad and asymmetric PL band in the near-band-edge region (at 1.056 eV). The intensity of this band decreases with the increase in the annealing temperature to 700^{o}C, while it is broadened and its maximum shifts to higher energies. This PL band is attributed to the band-to-band transitions, since the shift of the maximum and its broadening correlates with the shift of the equilibrium Fermi level. A similar behavior was observed for the near-band-edge PL band in $CuInS_2$ crystals subjected to similar thermal treatment [22] and in ZnSe single crystals annealed in Zn melt containing Al impurity [23].

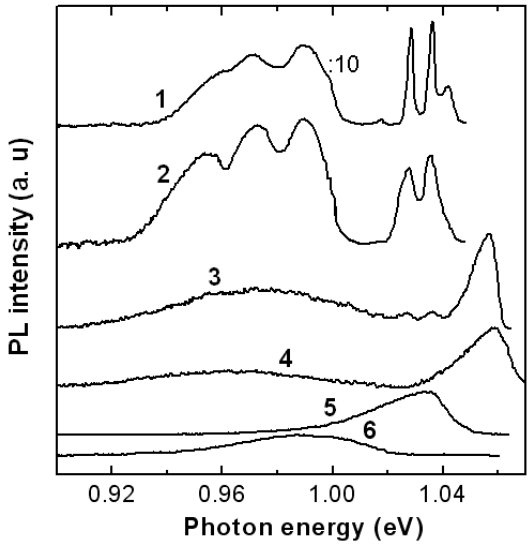

Fig. 1. PL spectra of $CuInSe_2$ crystals measured at T = 10 K. The numbers of curves correspond to the number of samples in the table.

The annealing of crystals in Zn vapors instead of vacuum leads to a further increase in the carrier concentration. At the same time, taking into account the decrease in carrier mobility, one can suggest that a partial compensation of conductivity occurs due to the formation of acceptor centers in addition to donors. As a result, the near-band-edge PL band is shifted to lower photon energies in the samples annealed in Zn vapors as compared to the samples annealed in vacuum (compare curves *4* and *5* in Fig. 1). This behavior is explained in terms of the theory of heavily doped semiconductors developed by Shklovskij, Efros, Levanyuk, and Osipov in the early 1970s [24, 25]. According to this theory, the asymmetric shape of PL bands is caused by the potential fluctuations in the material. These fluctuations are probably caused by high concentrations of charged defects. It should be mentioned that in ternaries compositional fluctuations can also give rise to disorder and cause very similar fluctuations of the bandgap energy.

In the case of heavy doping, the defects do not constitute a discrete distribution of defect levels inside the bandgap. Instead, the energy levels form a continuous distribution function. Consequently, the distribution function of shallow states overlaps the distribution function of conduction and valence band states. As a result, the so-called band tails are developed. Therefore, the PL band on curve *5* in Fig. 5 can be attributed to band-to-tail (BT) electronic transitions.

The increase in the annealing temperature in Zn vapors from 600 ^{o}C to 700 ^{o}C leads to a

further shift of the PL band to lower photon energy and its splitting into two bands (see curve *6* in Fig. 1). This splitting is explained by the fact that in heavily doped semiconductors the recombination between the conduction band and an impurity level can occur via two channels. The first so called tail-to-impurity (TI) recombination takes place between the electrons that are localized in the conduction band tails and the holes that are localized at the acceptor state (the PL band at 0.98 eV in curve *6* in Fig. 1). The second so-called band-to-impurity (BI) recombination takes place between the free electrons in the conduction band and the holes that are localized at the acceptor state (the PL band at 1.00 eV in curve *6* in Fig. 1). Similar electronic transitions have been observed in other heavily doped chalcopyrite materials [26-28].

The conductivity of samples directly influences the processes of electrochemical etching. The morphology of surface of samples #3, #4, and #5 from the table after electrochemical treatment under the applied voltage of 0.7 V in aqueous HCl electrolyte is shown in Fig. 2. One can realize the formation of porous layers with various diameters of pores, it being around 200 nm for sample #5, 300-400 nm for sample #4, and around 1 μm for sample #3. Therefore, the diameter of pores sharply decreases with increasing the conductivity of the material. One can see also from Fig. 2 that in sample #4 some pore merging occurs, while in sample #3 several pores merge into a larger unit. Apart from that, the pore formation in the sample with high resistivity (sample #3) is highly inhomogeneous, porosification was found to occur only in separate regions. Probably the resistivity is not uniform in this sample. In samples #1 and #2 no electrochemical reaction occurs under the voltage up to 1 V, while material decomposition occurs at a higher voltage.

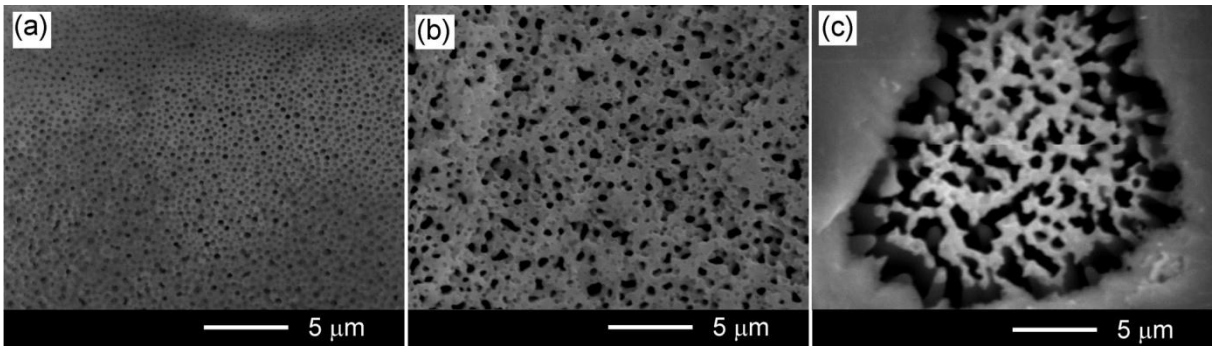

Fig. 2. SEM images of surfaces of $CuInSe_2$ crystals with numbers #5 (a) #4 (b) and #3 (c) in the table subjected to electrochemical treatment at 0.7 V in an aqueous HCl electrolyte.

In the sample #6 with lowest resistivity, a uniform porous structure is formed with a mean dimension of pores around 100 nm as shown in Fig. 3.

Figure 4 compares the PL spectra of $CuInSe_2$ samples before and after electrochemical treatment. One can see that electrochemical etching leads to the increase in the PL intensity. Apart form that, in sample #3 the electrochemical treatment leads to narrowing the band-to-band emission and the increase in the intensity of lines related to the recombination of bound excitons. This suggests a good passivation of the porous skeleton surface and the increase in the material quality as a result of treatment.

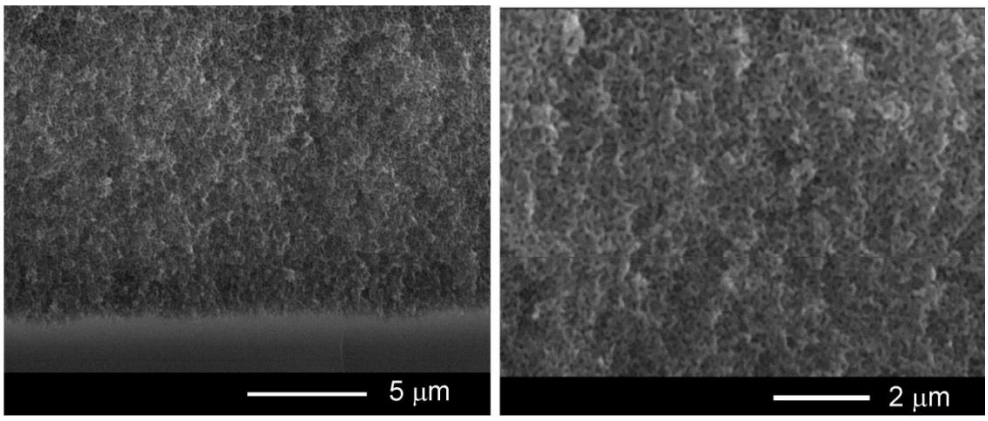

Fig. 3. SEM images in cross section of $CuInSe_2$ crystals with numbers #6 in the table subjected to electrochemical treatment at 0.7 V in an aqueous HCl electrolyte.

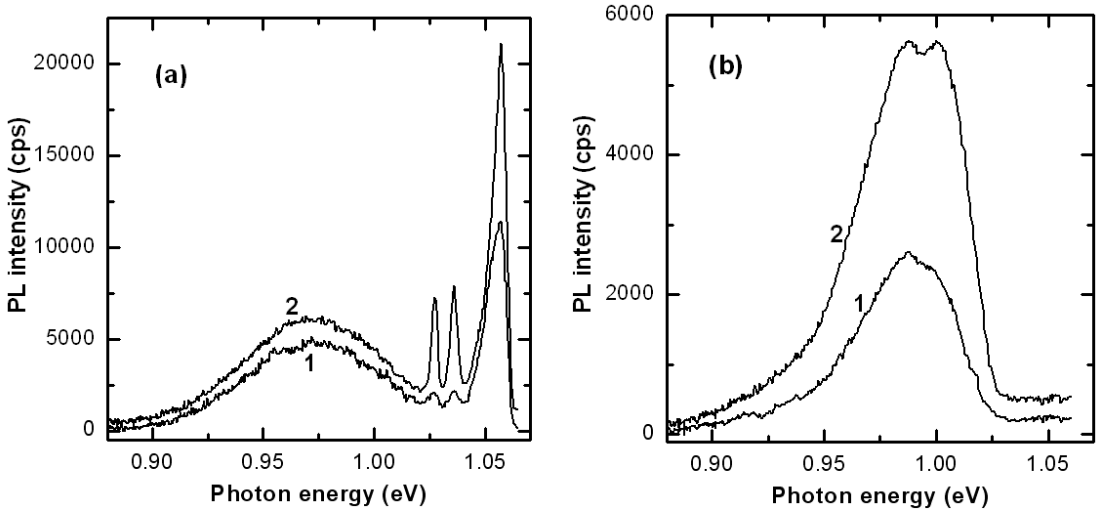

Fig. 4. PL spectra of #3 (a) and #6 (b) $CuInSe_2$ samples before (curve *1*) and after (curve *2*) electrochemical etching. The spectra are measured at T = 10 K.

4. Conclusions

The results of this study demonstrate possibilities of producing nanostructured layers and nanopatterned surfaces on $CuInSe_2$ crystals. In order to reduce the resistivity of the as-grown crystals and make them suitable for electrochemical etching, they should be subjected to annealing in vacuum or in Zn vapors. The analysis of PL spectra demonstrates that passivation of the porous skeleton surface and increase in the material quality occurs as a result of electrochemical treatment which is also important in the development of solar cells.

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