Features of the induced photopleochroism oscillations in a photosensitive structures based on CuInSe$_2$

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Abstract. The work is devoted to study of the phenomenon of oscillations induced photopleochroism depending on the different technologies for the creation of photosensitive structures CuInSe$_2$. Induced photopleochroism was observed, and peculiarities of this phenomenon are discussed. A conclusion is made such structures beneficial to apply as sensors of polarization light for fiber optic.

1. Introduction

Improvement of technologies for producing CuInSe$_2$ has allowed to increase the energy conversion efficiency of up to 18-20 %. The heat treatments have been found to be one important process step for improving the efficiency of solar cells on CIS. This contribution presents the first research of polarization photosensitivity of two different types structures which were obtained by vacuum and air het treatment of the CIS as grown bulk crystals.

However, these materials with sufficiently advanced technology can find its application as sensors linearly-polarized radiation in optical communication systems. The successful implementation of this direction depends on the polarization study of photosensitivity in these materials. It requires thorough research of photopleochroism induced in the different structures based on these materials.

2. The method

CuInSe$_2$ belongs to the group of ternary chalcopyrite compounds which derives from the group IV class of tetrahedral bonded semiconductors according to the Grimm-Sommerfeld rule, i.e. there must be an average of 4 valence atoms per atomic site. In these structures each atom has four neighbors arranged at the corners of a regular tetrahedron bonded by sp$^3$ bonds. The tetrahedral structure of the chalcopyrites can be considered as a superlattice structure of the sphalerite or zincblende structure which has a diamond like structure (such as Si) consisting of two inter-penetrating face centered cubic lattices, separated by a translation vector of (1/4, 1/4, 1/4). One sublattice is occupied by cations and the other by anions (II-VI and III-V compounds). In a ternary chalcopyrite compounds the cations are furthermore...
replaced by a one cation of higher valency and one cation of lower valency which occupy the cation sublattice in an ordered manner as shown in Figure 1. In that sense CuInS$\text{e}_2$ can be envisioned as the ternary analogue of the binary ZnS. The reduced symmetry, due to the two kinds of cations, leads to a primitive cell of eight atoms in the chalcopyrite structure compared to a primitive cell of two atoms in the zincblende structure. The Bravais lattice of the chalcopyrite is body centered tetragonal. Compared to the face centered cubic Bravais-cell of the zincblende the unit cell is doubled along the crystal c axis. If the different cations are distributed at random, the ternary compound has a sphalerite structure.

The electronic band structure of a chalcopyrite compound can in principle be derived from its II-VI analogue since in both structures (zincblende and chalcopyrite) the chemical binding is realized via hybrid sp3-orbitals. The resulting band structure at the $\Gamma$-point is determined by a s-type conduction band and a p-type valence band [1].

![Figure 1. Crystal structure of chalcopyrite lattice.](image)

However, it was shown that the uppermost valence bands of a I-III-VI$_2$ compound are largely influenced by the d-levels of the group I metal in the valence band [1]. As a consequence the valence band is split into three single bands due to spin-orbit interaction and due to the crystalld in the tetragonal structure (Figure 2). The interaction between the $\Gamma_{15}$ levels in figure 2 will raise the uppermost $\Gamma_{15}$ to higher energies, so that the direct band gap at the $\Gamma$-point of a chalcopyrite is in general 1 eV lower than the value of the respective II-VI compound. Theoretical calculations by Jaffe and Zunger revealed that the reduced band gap in chalcopyrites can be explained by two effects – a chemical effect $\Delta E_{\text{chem}}$ which is due to the p-d hybrids and a structural $\Delta E_{\text{struc}}$ which is related to the anion displacement in the chalcopyrite lattice.

The CIS polycrystalline ingots were prepared by directional crystallization. As grown n- and p-type conductivity crystals were electrically homogeneous and had the free carrier concentrations about $10^{18}$ cm$^{-3}$ at room temperatures. The CIS wafers were exposed to heat treatment at temperature 500 C in vacuum quartz ampoules (HV) at the constant volume and directly in the dry air (HA).

The HV is usually accompanied by conversion of conductivity of a p-type crystals. At heat treatment times about 1 min we prepare n-p-homotransitions (HT). With increase of time up to 10 min the conversion becomes bulky and from these wafers it is possible to make only the isotopic n’-n –HT.
It is important to emphasize, that the surface of plates after such a treatment does not visually differ from an initial state, and the conversion of the conductivity type is caused by formation of the $V_{ae}$ donors.

3. Results and discussion

At the illumination of such homotransitions the created films always charged negatively, that corresponds to a pass direction of these HTs. The photosensitivity of such HTs dominates at illumination on the formed films side and looks like narrow band spectrum with full width at half-height $\delta_{1/2}$ about 40 meV. The energy maximum $h\nu_{m}$ in the photoconversion efficiency spectrum is always located slightly below the CIS energy gap $E_{G} = 1.02$ eV. Typical sharp short wavelength fall down of the photosensitivity for such HTs in conditions of illumination from the side of obtained HW films is caused by the increase of influence of the optical absorption as approaching $E_{G}$.

The films where formed on the surface of wafers by the air treatment of CIS. The coloring of these films changed with the time of treatment and the conductivity type of initial wafers remained the same. The HA methods allow to prepare rectifying HT, the forward direction of which always corresponds to positive polarity of the external voltage displacement on a film. Under the illumination of the isotypic $p'$-$p$ and $n'$-$n$ HTs obtained by HA of the CIS crystals, the films always charged positively and corresponded to forward direction of such HTs. The photosensitivity maximum was achieved in $n'$-$n$-HTs, prepared by HA method at $t = 5$ min. The sign of photovoltaic effect was independent of location light probe and of photon energy and, hence, the CIS air treatment could be connected to active area formation in these structures.

Both types of obtained homojunctions for linearly-polarized light irradiation along a normal to the illumination plane (angle of incidence $\Theta = 0^\circ$) did not show and dependence on spatial orientation of the electrical field vector of light wave [1]. The main laws for the polarization photosensitivity investigations of different two types of CuInSe$_2$ homotransitions consists in following. All this different types of vacuum treatments of HTs demonstrates the angular dependencies of short circuit

![Figure 2. Splitting of energy bands for CIS.](image)
photocurrent $i^p$ (where the vector of electrical field parallel to the irradiation plane of incidence) and $i^s$ (when the vector of electrical field perpendicular to the irradiation plane of incidence) are consistent with the analysis based on Fresnel relations for passage process of light wave to the air/CuInSe$_2$.

![Induced Photopleochroism Spectra](image1)

**Figure. 3.** Induced photopleochroism spectra for CuInSe$_2$ for both type treatment (1- in vacuum; 2- on air).

![Induced Photopleochroism Spectra](image2)

**Figure. 4.** Induced photopleochroism spectra for ZnO:Al/p-GaAs:Mn structures at $\Theta = 85^\circ$ (1- experiment; 2- calculation without interferention).

In the case of heterojunctions obtained at the air, photocurrent is, as well as for $i^p$, at $\Theta > 0^\circ$ in the certain region of incidence angle shows an increase. This behavior may be connected with the decrease reflection losses also in the case of a $s$-wave [2]. This peculiarity can be explained [3] by interference of linearly polarized light in the entrance film of such structures. Which leads to oscillations in the spectral dependence of such homojunctions (Fig. 3).

The same dependences was obtained for example for ZnO:Al/p-GaAs:Mn structures (Fig. 4). The oscillatory character of the induced photopleochroism, which attributed to the interference of incident linearly polarized light [4] in the entrance window of such photosensitive structures, is clearly seen. Turning to the spectral dependences of the quantum efficiency of $p$- and $s$- wave phototransducers...
it is evident that the oscillations of the induced photocurrents $i_p$ and $i_s$ oscillate in antiphase [5]. For example, a minimum of $i_s$ corresponds to a maximum of $i_p$.

4. Conclusions

Presented here results show that structures based on CIS and thin films of different natures could find an application as narrow band photovoltaic devices for unpolarized and linearly polarized light. The main result of this research can be considered concluded that such structures advantageously be used as selective sensors of polarized light for optical fiber.

References

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