ISSN 1063-7826, Semiconductors, 2007, Vol. 41, No. 2, pp. 155–158. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © I.V. Bodnar', A.A. Vaĭpolin, V.Yu. Rud', Yu.V. Rud', E.I. Terukov, 2007, published in Fizika i Tekhnika Poluprovodnikov, 2007, Vol. 41, No. 2, pp. 160–163.

SEMICONDUCTOR STRUCTURES, INTERFACES, AND SURFACES

Fabrication and Photoelectric Properties of Oxide/$CuIn_5Se_8$ Heterojunctions

I. V. Bodnar'[a], A. A. Vaĭpolin[b], V. Yu. Rud'[c], Yu. V. Rud'[b]^, and E. I. Terukov[b]

[a]*Belarussian State University of Information Science and Radio Engineering, ul. Brovki 17, Minsk, 220072 Belarus*
[b]*Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia*
^e-mail: yuryrud@mail.ioffe.ru
[c]*St. Petersburg State Polytechnic University, ul. Politekhnicheskaya 29, St. Petersburg, 195251 Russia*

Submitted June 20, 2006; accepted for publication June 27, 2006

Abstract—Single crystals of the *n*-$CuIn_5Se_8$ compound of hexagonal modification have been grown by direct crystallization from melt. On the basis of the experimental study of its thermal interaction with air oxygen, a method for fabricating new oxide/*n*-$CuIn_5Se_8$ heterojunctions is proposed. Electrical and photoelectric properties of the structures obtained have been investigated. It is shown that the interaction of *n*-$CuIn_5Se_8$ of hexagonal modification with air oxygen makes it possible to obtain heterojunctions with high photosensitivity. The new technology can be used in the design of broadband optical radiation converters based on *n*-$CuIn_5Se_8$ crystals.

PACS numbers: 61.10.-i, 61.82.Fk

DOI: 10.1134/S1063782607020078

1. INTRODUCTION

The ternary compound $CuIn_5Se_8$ belongs to defect semiconductors of the $A^IB^{III}_{2n+1}C^{VI}_{3n+2}$ type and is formed in the quasibinary Cu_2Se–In_2Se_3 cut at $n = 2$ [1, 2]. Such semiconductors, as well as their simplest ternary analog $CuInSe_2$ ($n = 0$), are promising materials for designing high-efficiency thin-film solar cells with high radiation resistance. Currently, effective techniques for obtaining homogeneous crystals of these peculiar semiconductor phases and photoconversion structures on their basis are being actively sought [3, 4]. This study continues this important direction in semiconductor electronics and is devoted to the development of a new technique for fabricating heterojunctions based on the little-studied $CuIn_5Se_8$ compound.

2. EXPERIMENTAL

$CuIn_5Se_8$ single crystals were grown by direct crystallization from melt (vertical Bridgman method). The starting materials were copper, indium, and selenium with purity above 99.999%. Taken in the stoichiometric ratios, the elementary components, in the amount of ~25 g, were loaded into double quartz ampoules with a tapered bottom. After evacuation of the internal ampoule to a residual pressure of ~10^{-3} Pa, it was placed into the second quartz ampoule of larger diameter, which was also evacuated. This procedure prevents the synthesized material from oxidizing in air if the internal ampoule cracks during crystallization. A quartz rod (holder) was welded to the bottom of the external ampoule and attached to a vibrator.

Initially, the temperature in the furnace was increased at a rate of ~50 K/h to 1000–1020 K. At these temperatures, isothermal holding with vibrational stirring was performed for 2 h. Then, at the same rate, the temperature was increased to 1220–1230 K (without switching off the vibration) and held steady again for 2 h. Then vibration was switched off and direct crystallization from melt was performed with a decrease in the furnace temperature at a rate of ~2 K/h to complete solidification of the melt. To homogenize the ingots obtained, they were annealed at 1020 K for 150 h. The single crystals of the $CuIn_5Se_8$ ternary compound grown under such conditions had a diameter of ~12 mm and a length of ~40 mm.

The composition of the $CuIn_5Se_8$ single crystals grown was determined by electron-microprobe X-ray analysis on a Cameca-SXIOO system.

The homogeneity and structure of the single crystals grown were analyzed by X-ray diffraction. Diffraction patterns were recorded on an automatic computer-controlled DRON-3M X-ray diffractometer in CuK_α radiation with a graphite monochromator.

3. RESULTS AND DISCUSSION

The results of the electron-microprobe X-ray analysis showed that the elemental composition of the single crystals grown corresponds to the formula composition; i.e., the component ratio is Cu : In : Se = 1 : 5 : 8.

The diffraction patterns of samples cut from different portions of the single crystals grown showed that the compound under study is crystallized in a hexago-

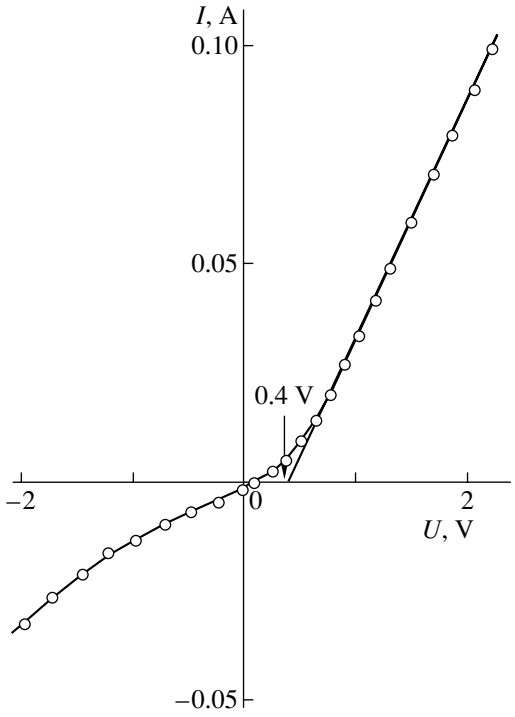

Fig. 1. Stationary *I–V* characteristic of the oxide/*n*-$CuIn_5Se_8$ heterostructure at $T = 300$ K. The forward direction corresponds to the negative polarity of the external bias on the oxide film.

nal structure. The unit-cell parameters calculated by the least-squares method using the reflections for which $2\theta > 60°$ are $a = (4.040 \pm 0.005)$ Å and $c = (32.75 \pm 0.01)$ Å. These values are in good agreement with the data of [5]. The $CuIn_5Se_8$ crystals grown had a pronounced cleavage in the (001) plane, which is indicative of a layered structure. The (001) odd-order reflections have low intensity; i.e., we can speak about a substructure with a doubly diminished unit cell ($c = 16.38$ Å). In the same series, the reflections of the 8th, 10th, 12th, 18th, and 20th orders have high intensity. Thus, the general character of the structure is roughly outlined: it is composed of five-layer packets with small differences in the structure of neighboring packets; these packets result in the doubled unit-cell parameter c.

It is noteworthy that the hexagonal structures of $CuIn_5Se_8$ and InSe crystals with the unit-cell parameters $a = (4.040 \pm 0.002)$ Å and $c = (16.02 \pm 0.005)$ Å are similar. Indeed, it turns out that the $CuIn_5Se_8$ structure is an ordered analog of the InSe structure, in which the positions of eight In atoms are substituted by 1Cu + 5In + 2 vacancies.

To fabricate the photosensitive structures, we used freshly cleaved mirror (0001) planes of $CuIn_5Se_8$ single crystals with a thickness of ~(0.1–0.2) mm. Since the cleaved single crystals had a mirror-smooth surface, they were not subjected by any additional treatment before the fabrication of heterojunctions. The proposed method for fabricating heterojunctions on the basis of $CuIn_5Se_8$ single crystals involves the thermal interaction of these crystals with air oxygen. As the experiments show, during the interaction of $CuIn_5Se_8$ wafers with air oxygen, homogeneous interference layers are formed on their surface; they have a light gray color in the integral light of an incandescent lamp. The thickness and, respectively, color of the $CuIn_5Se_8$ layers formed on substrates can be changed by varying the temperature and time of heat treatment. During heat treatment in evacuated ampoules, the appearance of the cleaved surface did not change. This fact indicates that the changes occurring on the surface of the $CuIn_5Se_8$ wafers are caused by their interaction with air oxygen.

As the first investigations showed, the layers formed in the thin surface region of *n*-$CuIn_5Se_8$ wafers also had *n*-type conductivity and their resistance was several orders of magnitude lower than that of the surface layers in the initial state. It should be noted that the resistance of layers almost does not change in the temperature range $T = 80$–400 K. We can suggest that heat treatment of the *n*-$CuIn_5Se_8$ wafers in air is accompanied by the formation of thin ($d \lesssim 1$ μm) layers of native oxide in their surface regions. Since there are three components taken in a certain relation ($n = 2$) in the initial state of the semiconductor wafers, and the environment has a fairly complex composition, it is necessary to continue study of the detailed mechanism of interaction of $CuIn_5Se_8$ with the environment. Undeniably, the main result obtained is that this interaction leads to the formation of interference oxide layers in the surface layer of the ternary compound wafers. We suggest that the obtained contact between $CuIn_5Se_8$ and the oxide layer may provide for the formation of new photosensitive structures.

Measurement of the stationary current–voltage (*I–V*) characteristics of the isotype oxide/*n*-$CuIn_5Se_8$ heterostructures obtained by us for the first time showed pronounced rectification. At bias voltages $|U| =$ 1–2 V, the rectification ratio in the best structures is small and reaches a value of ~5, which is characteristic of many isotype heterojunctions [6].

Figure 1 shows the *I–V* characteristic that is typical for the oxide/*n*-$CuIn_5Se_8$ heterojunctions obtained. The forward direction corresponds to the negative polarity of the external bias on the oxide layer. With an increase in the voltage $U > 0.6$ V in the forward direction, the dark current in all heterojunctions obtained follows the linear law:

$$I = \frac{U - U_0}{R_0}, \qquad (1)$$

where the cutoff voltage $U_0 \approx 0.4$ V, and the residual resistance $R_0 \approx 20$–25 Ω at $T = 300$ K. In the range of forward and reverse biases $|U| \lesssim 2.5$ V, the current through such heterojunctions follows the power law $I \propto U^\gamma$ with the exponent $\gamma = 1.0$–1.1. Such behavior can be determined by the tunneling of charge carriers or cur-

rents limited by the space charge in the mode of carrier velocity saturation [7, 8]. Apparently, the observed large values of reverse currents and their increase with bias (Fig. 1) are related to peripheral defects in the heterojunctions obtained, arising as a result of wafer splitting in the (0001) plane.

When an oxide/*n*-$CuIn_5Se_8$ heterojunction is exposed to unpolarized light, the photovoltaic effect arises and the oxide layer always has a negative charge. The photosensitivity of the heterojunctions obtained is higher when they are illuminated from the side of the oxide layer, and their maximum photovoltaic sensitivity S_U^m is more than two orders of magnitude higher than the corresponding value for the In/*n*-$CuIn_5Se_8$ structures obtained by us previously on the same starting crystals (see table). This circumstance characterizes the new proposed method for fabricating light converters on the basis of $CuIn_5Se_8$ single crystals as the most effective to date.

In Fig. 2, the spectral dependences of the relative quantum photoconversion efficiency $\eta(\hbar\omega)$ in the range of photon energies $\hbar\omega$ = 1.0–2.5 eV for the oxide/*n*-$CuIn_5Se_8$ heterojunctions obtained by oxidation (curve *1*) and surface-barrier In/*n*-$CuIn_5Se_8$ (curve *2*) structures are compared. The structures under comparison were formed on the same initial $CuIn_5Se_8$ crystal. This comparison shows that the photosensitivity spectra of such different types of structures are almost identical. Indeed, the spectral position of the region of maximum photosensitivity ($\Delta\hbar\omega^m$) and the bandwidth at half maximum $\delta_{1/2}$ in these structures almost coincide (table, Fig. 2). Analysis of the long-wavelength edge $\eta(\hbar\omega)$ within the theory of fundamental absorption (Fig. 3) [9, 10] shows that the interband absorption and the band gap values for indirect (E_G^{ind}) and direct (E_G^d) transitions in $CuIn_5Se_8$ crystals are insensitive to their thermal oxidation (table, Fig. 3).

Photoelectric properties of the structures based on $CuIn_5Se_8$ crystals at 300 K

Type of structure	S_U^m, V/W	$\Delta\hbar\omega^m$, eV	$\delta_{1/2}$, eV	E_G^{ind}, eV	E_G^d, eV
Oxide/*n*-$CuIn_5Se_8$	580	1.1–1.2	0.78	0.79	0.92
In/$CuIn_5Se_8$	1	1.1–1.25	0.78	0.79	0.93

Thus, a new method for fabricating photosensitive oxide/$CuIn_5Se_8$ heterojunctions has been developed and the first photosensitivity spectra of these heterojunctions has been obtained for the first time in a wide range of incident photon energies (0.8–2.5 eV). It is established that the complex thermal interaction of the ternary chalcogenide $CuIn_5Se_8$ with environment makes it possible to fabricate heterojunctions with the highest (for this semiconductor) photosensitivity, while the band gap value satisfies the condition of maximum efficiency of solar radiation conversion [11]. Therefore, the method proposed for fabricating heterojunctions

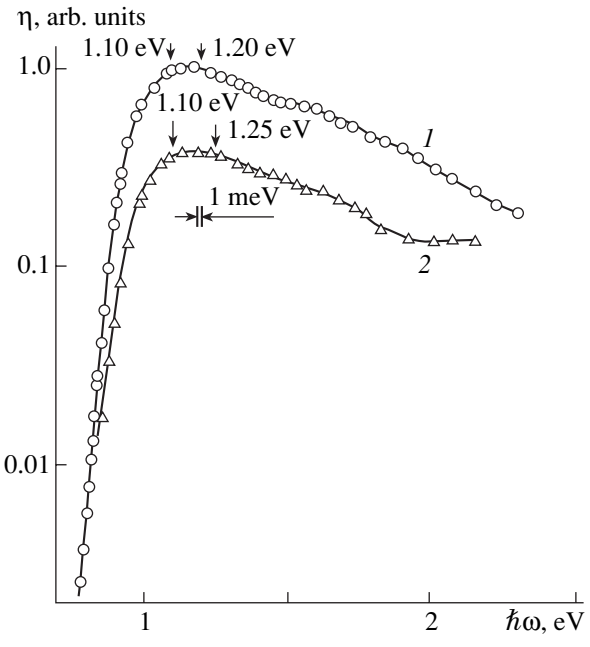

Fig. 2. Spectral dependences of the relative quantum photoconversion efficiency of the (*1*) oxide/*n*-$CuIn_5Se_8$ and (*2*) In/$CuIn_5Se_8$ structures at T = 300 K. To exclude overlap, spectra *1* and *2* are shifted along the ordinate axis.

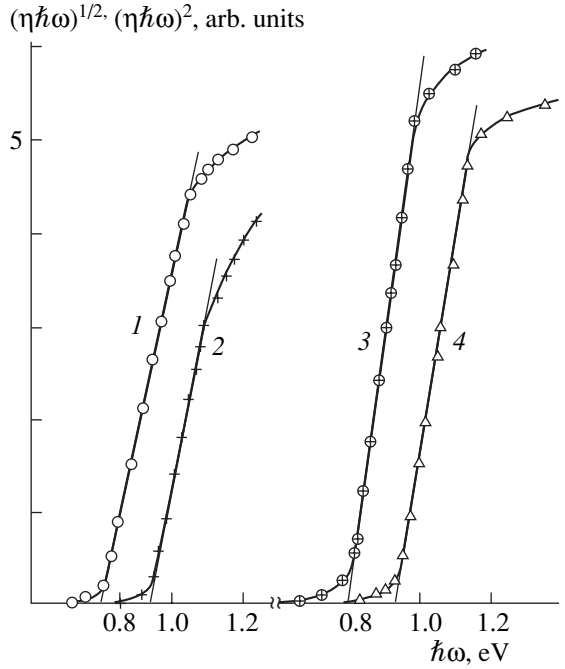

Fig. 3. Dependences (*1*, *3*) $(\eta\hbar\omega)^{1/2} = f(\hbar\omega)$ and (*2*, *4*) $(\eta\hbar\omega)^2 = f(\hbar\omega)$ for the (*1*, *2*) In/$CuIn_5Se_8$ and (*3*, *4*) oxide/*n*-$CuIn_5Se_8$ structures at T = 300 K.

based on the new ternary chalcogenide $CuIn_5Se_8$ can find application in broadband photoconverters.

ACKNOWLEDGMENTS

This study was supported by the program New Principles of Energy Conversion in Semiconductor Structures of the Division of Physical Sciences, Russian Academy of Sciences, and the INTAS project no. 03-6314.

REFERENCES

1. O. Lundberg, M. Edoff, and L. Stolt, in *Abstract Book of Solar World Congress, ISES-2003* (Göteborg, Sweden, 2003).
2. I. V. Bodnar', T. L. Kushner, V. Yu. Rud', et al., Zh. Prikl. Spektrosk. **69**, 520 (2002).
3. I. V. Bodnar', S. E. Nikitin, G. A. Il'chuk, et al., Fiz. Tekh. Poluprovodn. (St. Petersburg) **38**, 1228 (2004) [Semiconductors **38**, 1192 (2004)].
4. I. V. Bodnar', E. S. Dmitrieva, S. E. Nikitin, et al., Fiz. Tekh. Poluprovodn. (St. Petersburg) **39**, 426 (2005) [Semiconductors **39**, 402 (2005)].
5. U. C. Boehnke and G. Kuhn, J. Mater. Sci. **22**, 1635 (1987).
6. B. L. Sharma and R. K. Purohit, *Semiconductor Heterojunctions* (Pergamon, Oxford, 1974; Radio i Svyaz', Moscow, 1979).
7. M. A. Lampert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970; Mir, Moscow, 1973).
8. E. Hernandez, Cryst. Res. Technol. **33**, 285 (1988).
9. S. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981; Mir, Moscow, 1984).
10. Yu. A. Ukhanov, *Optical Properties of Semiconductors* (Nauka, Moscow, 1977) [in Russian].
11. A. G. Milns and J. J. Feucht, *Heterojunctions and Metal–Semiconductor Junctions* (Academic, New York, 1972; Mir, Moscow, 1975).

Translated by Yu. Sin'kov