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# Electrophysical properties of photosensors based on radiation-resistant $\text{Hg}_2\text{MnInTe}_6$ crystals

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## ABSTRACT

Electro-physical properties of  $\text{Cr}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  photosensors with a surface nanostructure (SNS) created by a special surface treatment were measured in this work. With this treatment, the surface lost its mirror-like shine and was perceived as matte. For comparison, the fabrication of a  $\text{Au}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  structure on a mirror surface was also performed.  $\text{Hg}_2\text{MnInTe}_6$  single crystals were grown by modified zone melting and have an electronic type of conductivity with a band gap equal to  $E_g=1.21$  eV and a high resistivity  $\rho \approx 2 \cdot 10^7 \Omega \cdot \text{cm}$  (at 293 K), which was determined from the linear section of the I-V curves. The initial section of the I-V curve for  $\text{Cr}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  at reverse bias (0.1 – 10 V) could be described within the framework of the Sah-Noys-Shockley model. At voltages greater than 10 V, a linear dependence of the I-V curve was observed, and at voltages greater than 200 V, currents limited by space charge (CLSC) were observed.  $\text{Cr}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  photosensors with SNS (matte surface) had significantly better electro-physical parameters than  $\text{Au}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  photosensors (mirror surface): smaller dark currents, higher rectification coefficient, and higher current monochromatic sensitivity. For example, at 1 V, the dark current for  $\text{Au}/\text{MMIT}/\text{In}$  is equal to  $I=29$  nA, and for  $\text{Cr}/\text{MMIT}/\text{In}$ , the dark current is  $I=2$  nA. At a voltage of  $U=10$  V, the dark currents are 150 nA and 7 nA, respectively. The rectification coefficient for  $\text{Cr}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  at 10 V was  $K \approx 40$ , and for  $\text{Au}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  it was  $K \approx 7$ . Due to the surface treatment before depositing rectifying contacts, the current monochromatic sensitivity  $S_\lambda$  for structures of  $\text{Cr}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  reached a maximum at a wavelength of  $\lambda \approx 1.15 \mu\text{m}$  and was equal to  $S_\lambda \approx 3$  A/W, and for  $\text{Au}/\text{Hg}_2\text{MnInTe}_6/\text{In}$  the sensitivity  $S_\lambda \approx 0.8$  A/W.

Keywords: Photosensors, radiation-resistant single crystals, AFM, contacts, CLSC, surface nanostructure, manufacturing

## 1. INTRODUCTION

An important feature of single crystals of  $\text{Hg}_2\text{MnInTe}_6$  (MMIT) is the high resistance to hard ionizing radiation [1-3]. A wide use of such semiconductors is hindered by the high concentration of stoichiometric vacancies, which also make these materials resistive to radiation. On the other hand, the existing stoichiometric vacancies significantly ensure semiconductor doping and formation of p-n junctions. As an alternative to the p-n junction, a contact metal-semiconductor of the Schottky type is used as a potential barrier [4-6]. We have already reported the study of a structure with a potential barrier based on MMIT [7]. By optimizing both the technology of growing single crystals and the technology of creating a potential barrier, we managed to significantly improve the parameters of the structure based on MMIT.

## 2. EXPERIMENTAL

MMIT crystals were prepared from 6N-purity elemental components in quartz ampoules, covered with a layer of graphite. First, the synthesis was carried out, and then crystal growths at a speed of  $\sim 1.2$  mm/hr., followed by slow cooling. An important difference in the technology for creating a rectifying contact, compared to what we did in [6], is the chemical treatment of the MMIT surface in a  $\text{KNO}_3$  solution for 20 minutes at the boiling temperature. Before such processing, high-quality polished crystals of MMIT with a size of  $4 \times 4$  mm<sup>2</sup> and a thickness of 0.8 mm were cleaned in a 1% solution of bromine in methanol and then washed in pure methanol. After that, the surface under the rectifying contact was protected with a chemically resistant varnish and again cleaned in a 1% solution of

bromine in methanol. Next, the varnish layer was removed, and indium was applied by thermal vacuum spraying over the entire surface for the ohmic contact. After the structures were heated in a vacuum for several seconds at  $T \approx 445$  K, Schottky-type rectifying contacts were deposited onto the MMIT by applying a thin ( $d \approx 20$  nm) translucent layer of chromium. Before applying chromium, the surface was treated in an argon plasma at a voltage of 400-500 V and a current of 25-30 mA for 15-20 minutes. The area of the ohmic contact was equal to  $S \approx 4$  mm<sup>2</sup>, and the rectifier one was  $S \approx 3.5$  mm<sup>2</sup>. A molybdenum mask was used to apply the rectifying contact. The substrate temperature during the thermal application of metals was equal to  $T = 100$ -150 °C.

### 3. RESULTS AND DISCUSSION

In this way Cr/n-MMIT/In structures were obtained. They had pronounced current-voltage (I-V) curves (see Figs. 1-2). The initial section of the I-V curves during reverse bias was well described within the framework of the Sah-Noys-Shockley theory. At higher voltages, there is a section of the I-V curves formed by CLSC (Fig. 2).

For comparison, we also fabricated Au/n-MMIT/In structures using a technique described in [7]. Gold was applied by thermal sputtering or chemical deposition. It should be noted that the most critical factor is the surface treatment. Thus, for direct results for comparisons, we changed the type of metal for the rectifying contact.

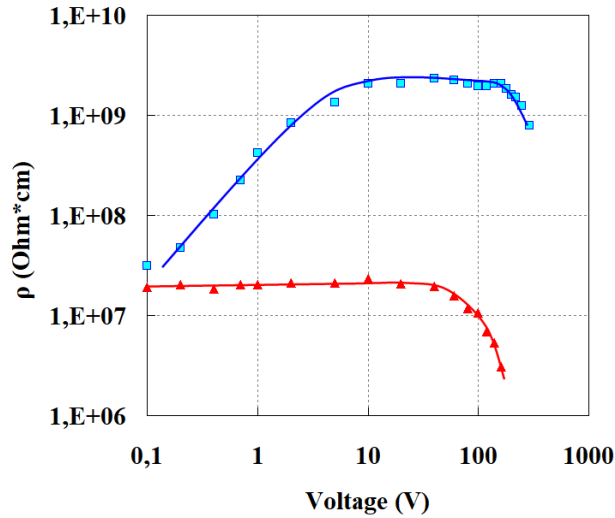


Fig. 1. Dependence of differential resistance vs. bias for Cr/n-MMIT/In. Direct voltage – squares; reverse bias – triangles (293 K).

Figure 2 shows the I-V curves of the structures with different methods of surface treatment for the rectifying contact (Cr/MMIT/In and Au/MMIT/In).

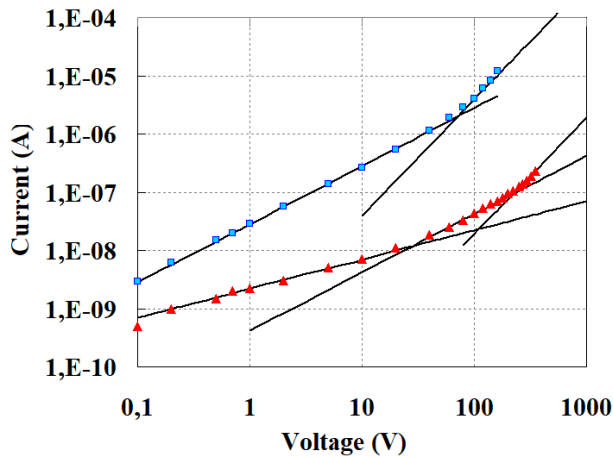


Fig. 2. Comparative I-V curves at reverse bias for the Cr/n-MMIT/In structure – triangles and Au/n-MMIT/In structure – squares. Solid lines are the theoretical dependences of  $I \sim U^{1/2}$ ,  $I \sim U$ ,  $I \sim U^2$ , respectively (300 K).

The initial section of the I-V curve for Cr/n-MMIT/In at reverse bias (0.1 – 10 V), for which  $I \sim U^{1/2}$ , is well described within the framework of the Sah-Noys-Shockley model. At voltages greater than 10 V, a linear dependence of the current on the voltage ( $I \sim U$ ) is observed, and at voltages greater than 200 V,  $I \sim U^2$  as expected for currents limited by space charge (SCLC).

As can be seen from Fig. 2, Cr/MMIT/In structures had a significantly higher rectification coefficient and significantly lower dark current. At  $U=1$  V, the dark current for Au/MMIT/In is equal to  $I=29$  nA and for Cr/MMIT/In  $I=2$  nA. At  $U=10$  V, the dark currents for the two structures were 150 nA and 7 nA, respectively. The rectification coefficient for Au/MMIT/In at  $U=10$  V is  $K \approx 7$ , and for Cr/MMIT/In -  $K \approx 40$ . In addition, the Cr/MMIT/In structures could work at reverse voltages of  $U \approx 300$  V, which confirms the high quality of such structures. We attribute this significant improvement in the electro-physical parameters of the Cr/MMIT/In structures to the surface treatment for the rectifying contact. The surface also differed upon visual inspection; it was not perceived as mirror-like, but as matte. We conducted a study of the surface on which the rectifying contact was created for the two types of structures with the help of an atomic force microscope (AFM). The corresponding AFM topographs are shown in Figs. 3a, b.

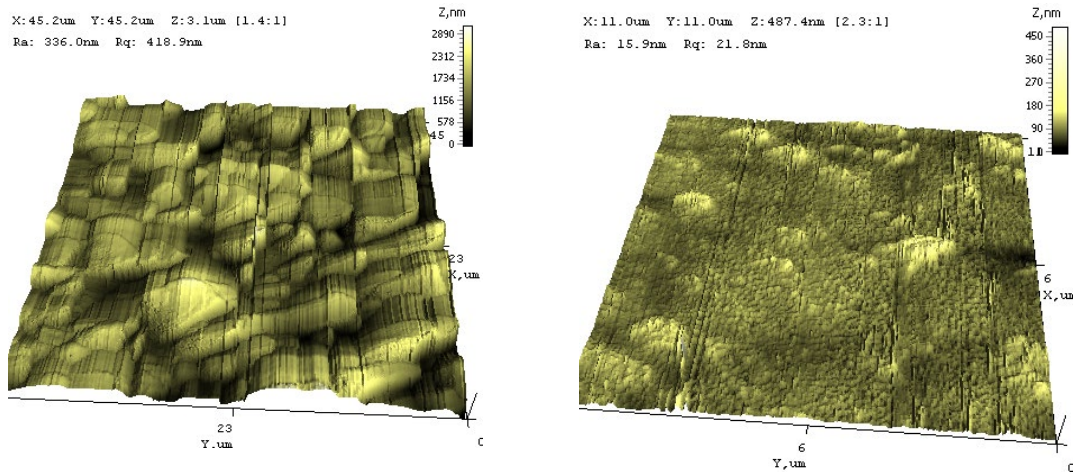


Fig. 3a. AFM surface topographs of the Au/n-MMIT/In structure (left) and Cr/n-MMIT/In structure (right).

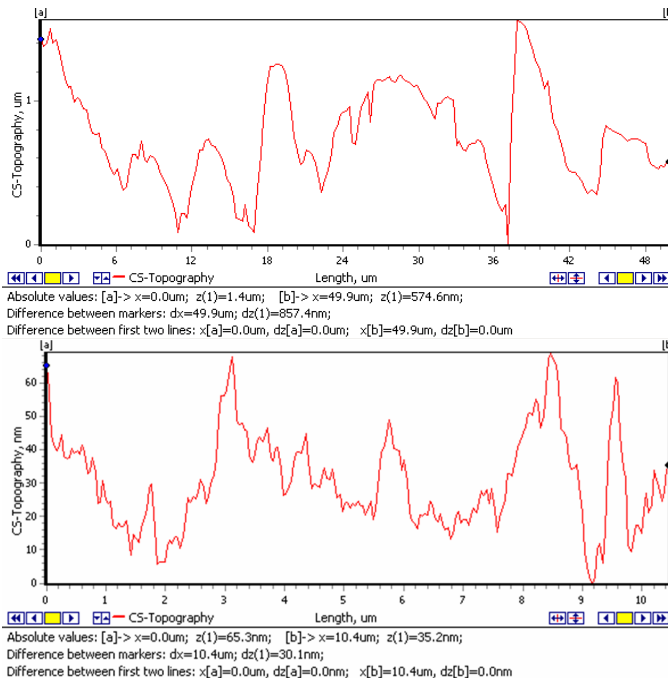


Fig. 3b. The surface **profiles** of the Au/n-MMIT/In structure (top) and the Cr/n-MMIT/In structure (bottom).

Using an atomic force microscope, we show that the surface of Cr/MMIT/In structures, which was visually perceived as matte, consists of small (10-50 nm) nanograins in the shape of pyramids, which can combine into larger ones (100-300 nm). Nanograins of small sizes are responsible for the formation of a high-energy radiation spectrum with  $h\nu > E_g$ . The band gap  $E_g=1.21$  eV was determined from measurements of the optical transmission spectra according to the method described in [8, 9]. Nanograins of large sizes participate in the processes of multiple reflection of the radiation falling on the surface, thus causing an increase in the probability of photon absorption, especially low-energy ones with  $h\nu < E_g$ . This leads to an increase in the monochromatic sensitivity in the region of the maximum  $S_\lambda$ . Measurements of the photosensitivity spectrum generally support this assumption. In Fig. 4 the spectral dependence of the current monochromatic sensitivity  $S_\lambda$  in absolute units is shown.

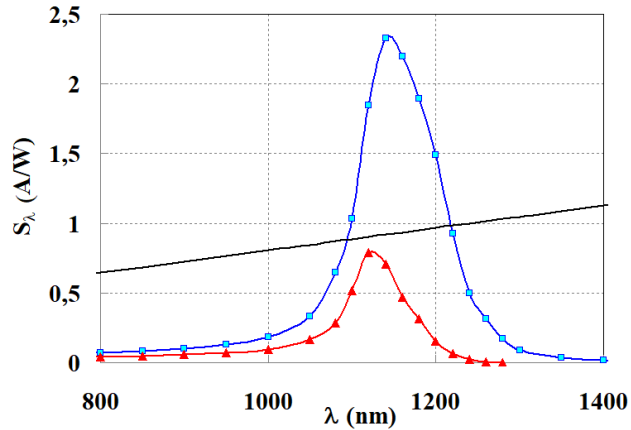


Fig. 4. Spectral dependence of the current monochromatic sensitivity at reverse voltage  $U=3$  V for Au/n-MMIT/In (mirror-like surface) – triangles, for Cr/n-MMIT/In (matte surface with SNS – squares. The solid line shows the theoretical dependence according to (1).

For the wavelength  $\lambda_{\max}=1.14$   $\mu\text{m}$  ( $h\nu\approx 1.09$  eV), the value of  $S_\lambda$  reaches a peak and is equal to  $S_\lambda\approx 2.3$  A/W, which is more than the maximum predicted value. We obtained similar results in [10-12]. It is possible to calculate the maximum theoretical value of  $S_\lambda$  using the well-known formula:

$$S_\lambda=0.806\eta\lambda T_\lambda S, \quad (1)$$

where  $\eta$  is the internal quantum yield, and  $T_\lambda$  is the transmittance of the material used for the front electrode. Accordingly, for  $\lambda_{\max}=1.14$   $\mu\text{m}$ , if we assume that  $\eta=1$  and  $T_\lambda = 100\%$ , then  $S_\lambda\approx 0.92$  A/W, which is less than observed experimentally. It should be noted that for Au/MMIT/In with a mirror-like surface  $S_\lambda\approx 0.8$  A/W. If the absorption and reflection losses by the Au-frontal contact are considered, then  $S_\lambda\approx 0.8$  A/W, which is a typical value for the current monochromatic sensitivity.

#### 4. CONCLUSIONS

Single crystals of n-type conductivity MMIT were grown by the method of modified zone melting. Cr/MMIT/In photodiodes with a surface nanostructure, which is sensitive to optical radiation in the range of 0.37-1.8  $\mu\text{m}$ , were produced.

Atomic force microscopy measurements confirmed the presence of small (10-50 nm) pyramid-shaped nanograins in the surface layer of the semiconductor, which can combine into larger ones (100-300 nm). Comparative experimental studies of two types of photodiodes, Cr/MMIT/In with SNS (matte surface) and Au/MMIT/In (mirror surface), showed a significant advantage for photodiodes with SNS. Such photodiodes had significantly smaller dark currents, a higher rectification coefficient, and a higher current monochromatic sensitivity at its maximum. The band gap of single crystals, which was determined from optical measurements, was equal to  $E_g = 1.21$  eV, which is close to the band gap of silicon, but MMIT single crystals have much higher radiation resistance, so photosensitive sensors and other devices based on this material can be of great practical importance.

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