

PHOTORESPONSE SPECTRA OF INTRINSIC OXIDE - p-InSe HETEROJUNCTIONS

V. M. Katerynychuk*, M. Z. Kovalyuk, M. V. Tovarnitsky

Chernivtsi Department of the Institute of Materials Science Problems of the National Academy of Sciences of Ukraine, 5, Iryna Vilde St., 58001 Chernivtsi, Ukraine

Intrinsic oxide - p-InSe photosensitive heterojunctions were created by thermal oxidation of the crystal substrates in open air. Long-term (for several days) oxidation of the substrates results in changes of both the photoresponse spectra and photoelectrical parameters of the heterojunction. This change is a consequence of the formation of additional oxide phases, which modify the photoresponse band and influence on potential barrier formation at the crystal substrate. For the best intrinsic oxide-p-InSe heterojunctions the open-circuit voltage and short-circuit current reach the values of 0.6 V and 30-35 mA/cm², respectively, at 100 mW/cm² power density of illumination.

(Received July 4, 2003; accepted August 21, 2003)

Keywords: InSe, Intrinsic oxide, Heterojunction, Photoelectrical properties

1. Introduction

InSe single crystals with the room temperature energy gap $E_g=1.2$ eV belong to semiconductors with layered crystalline structure. This structure allows cleaving the substrates of different thick with a mirror-like surface quality without any additional treatments. Their thermal oxidation in open air results in the creation on their surface of an oxide layer having conductive and transparent properties. The grown oxide film together with an InSe base create a photosensitive heterojunction [1]. At the same time the oxidation conditions can affect both the creation of the additional oxide phases [2,3] and photoelectrical parameters of corresponding *intrinsic oxide* - p-InSe heterojunctions [4].

In this paper the long-term oxidation of InSe substrates was investigated and we have found an essential improvement of photoelectric parameters for *intrinsic oxide* - p-InSe heterojunctions (HJ).

2. Experimental procedure

p-InSe single crystals were grown by the Bridgman method adding cadmium to the charge before synthesis. Depending on quantity of the added impurity the resistivity of p-InSe samples across the layers was in the range 10^3 - 10^4 ohm-cm. The cleaved plates with typical dimensions $12 \times 5 \times 0.4$ mm³ were oxidized in air in an electrical furnace at different time – temperature conditions: from 200 to 500 °C with the temperature step of 50 °C and the oxidation time from 5 to 60 minutes with the time step of 5 min. The long-term oxidation was carried out for 1 to 5 days with a one day step. On the basis of the testing and selection of the prepared HJ we have established that the best photoelectric parameters are typical for the samples obtained by oxidation at 450 °C. After oxidation the samples were cut off along the perimeter and only one cleaved surface with the oxide layer was kept. Indium of a high purity well wetting both the semiconductor and oxide surfaces was applied as a

* Corresponding author: chimsp@unicom.cv.ua

contact material. To eliminate undesirable non-ohmicity of the contacts to p-InSe its surface was mechanically damaged.

The HJ photoresponse spectra were investigated at room temperature using a MDR-3 monochromator with a 26 Å resolution. The illumination was directed onto the oxide film side. The HJ photoresponse was normalized with respect to the quantity of incident photons.

The capacitance-voltage characteristics of the investigated HJ at 300 K were measured by using a E8-2 capacitance meter with a relative error of capacitance of about 5×10^{-3} .

3. Results and discussion

3.1 Photovoltaic properties

The chemical nature of the oxide phases created during thermal oxidation of InSe was investigated by the cathodoluminescence method [2] and by analyzing the HJ photoresponse spectra [3]. But in [3] a long-term oxidation was not considered. The HJ samples preparation and investigation of their photoresponse spectra at room temperature is a simple investigation method of the structural oxide phases appeared on the InSe surface. The photoresponse spectra of the structures under investigations are shown in Fig. 1.

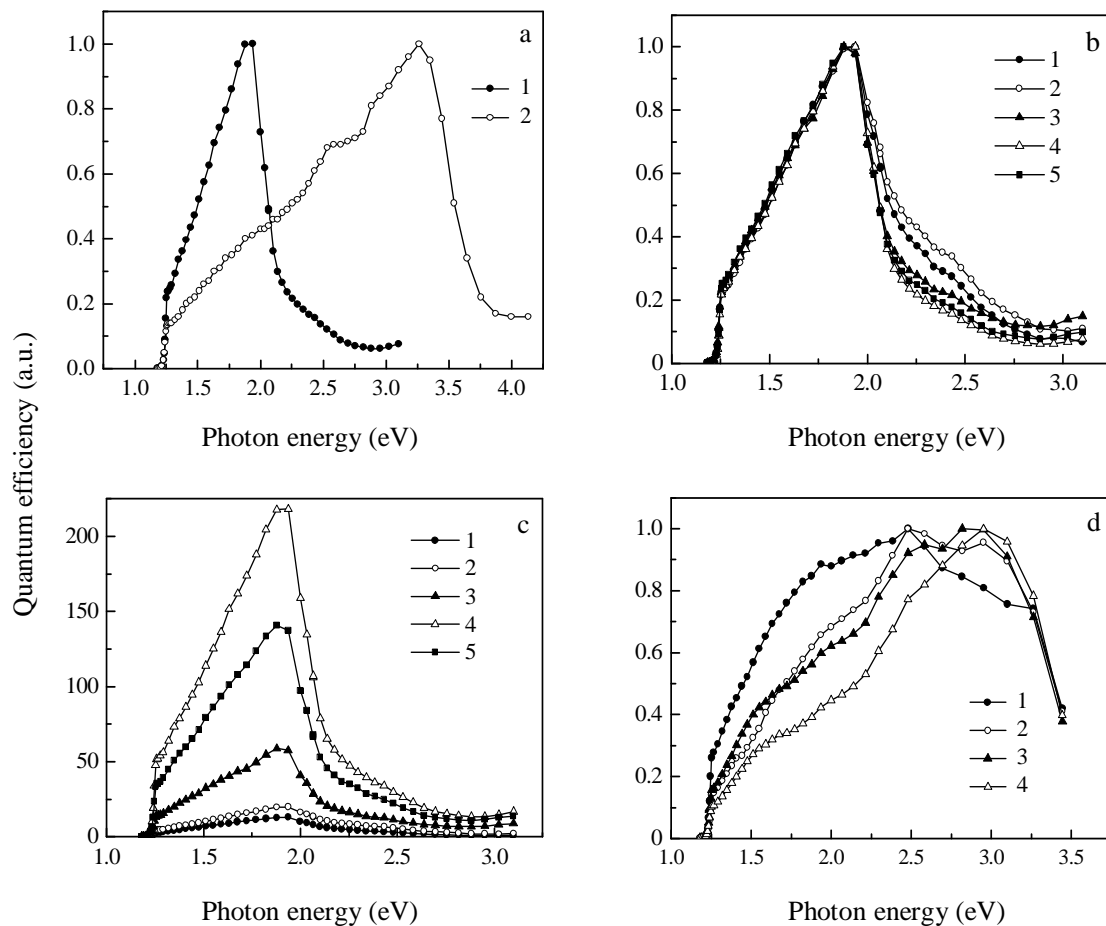


Fig. 1. Room temperature photocurrent quantum efficiency spectra for *intrinsic oxide* - p-InSe HJ formed by oxidation of InSe at 450°C with different oxidation times. a: 1 – 4 days and 2 – 15 min.; b: 1 – 1, 2 – 2, 3 – 3, 4 – 4, and 5 – 5 days; c: 1 – 1, 2 – 2, 3 – 3, 4 – 4, and 5 – 5 days with photoresponse in absolute values; d: 1 – 4 – 15 min with subsequent annealing in vacuum for 2 – 1, 3 – 2, and 4 – 3 days; 1 – non-annealed sample.

We have found that the form of the photoresponse spectra essentially depends on oxidation time of the p-InSe substrates. As one can see from Fig. 1(a), the photoresponse band is restricted from the both sides. The photoresponse energy edges are located at 1.2, 2.0, and 3.7 eV. The long-wave edge responds to the absorption of light in the base material whereas the short-wave edge - to the absorption of light in the oxide film. The corresponding energy positions of the photoresponse edges and their comparison to the literature data allow for the identification of the chemical composition of the oxide phases. As know from the literature, the In_2O_3 oxide film is formed at a short-term oxidation (5 to 15 min) [1], and the $\text{In}_2(\text{SeO}_4)_3$ oxide film – at a long-term oxidation [2,3,5]. These are intermediate layers between the p-InSe and In_2O_3 layers. Their thickness increase with increasing oxidation time, but still remains enough thin to prevent the short-wave absorption in the investigated HJ (Fig. 1(b)). As one can see from curves 4 and 5, their short-wave edges are more abrupt than those for curves 1-3 what is evidence of phase homogeneity and the fact that the formed layer becomes thicker.

To find out opportunities of formation of other phases, the structures prepared by oxidation in air at 450 °C for 15 min were then also annealed in vacuum at the same temperature. We have no found the formation of new chemical phases in the photoresponse spectra of the corresponding samples (Fig. 1(d)). Their photoresponse spectra do not essentially differ from those for non-annealed samples, and the characteristics of HJ samples annealed in vacuum are much worse than those for the structures only oxidized in air.

For comparison the spectra from Fig. 1(b) are shown in Fig. 1(c) in the absolute values of photocurrent. One can see from this figure that the photocurrent values essentially change depending on the oxidation time. For the samples under investigations the increase of the oxidation time results in increasing the absolute value of the short-circuit photocurrent. The photocurrents for curves 1 and 4 differ by a factor of 20.

Fig. 2 shows the dependences of the HJ open-circuit voltage (a) and short-circuit current (b) on oxidation time measured for two groups of the samples. Testing was carried out for two groups of the samples at their illumination with a 100 mW/cm^2 light power. As follows from this figure, a general tendency to the improvement of photoelectric parameters takes place for the both groups of samples. In addition, we have established that the optimum conditions of oxidation are a 4 day keeping of the samples at 450 °C.

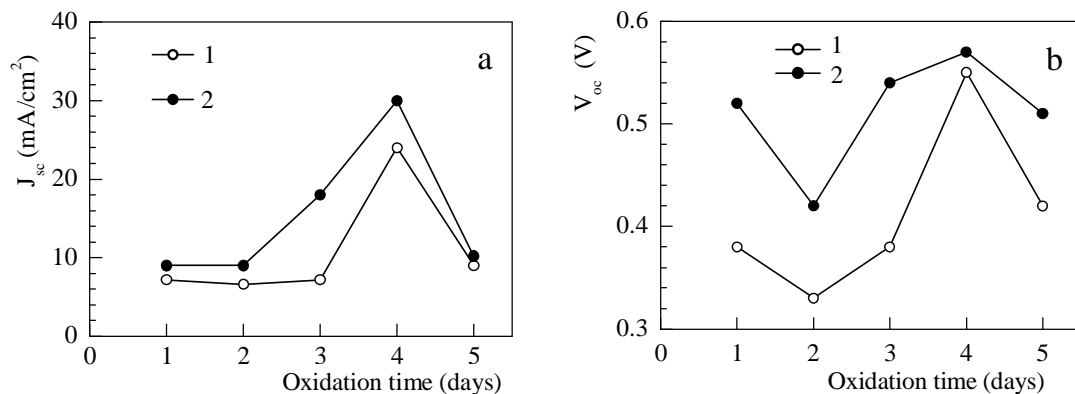


Fig. 2. Short-circuit current (a) and open-circuit voltage (b) of *intrinsic oxide*-p-InSe HJ vs oxidation time for two different group of the samples prepared at the same conditions. $T=295 \text{ K}$.

3.2 Capacitance-voltage and current-voltage characteristics

Due to the appearance of the additional oxide phase for the long-term oxidized HJ samples and an improvement of their photoelectrical parameters it is necessary to investigate the rectifying properties of the HJ. The samples oxidized at 450 °C for 4 days were selected for the investigation.

These samples had the best photoelectrical parameters. The HJ capacitance-voltage characteristics were measured for determination of the potential barrier height and are presented in Fig. 3. The HJ C-V characteristics were got at different testing signal frequencies. Their frequency dependence is related to the influence of a HJ series resistance on these characteristics [6]. At $1/C^2$ -V coordinates the C-V characteristics are linear that it is evidenced from the abrupt character of investigated p-n-junction. As follows from [6], to obtain the real value of the barrier height it is necessary to approximate the received cut-off voltage to the zero frequency according to the law $U_{\text{cut-off}} = f(\omega^2)$, where $\omega = 2\pi f$ and f is the linear frequency of the testing signal. The approximated values appeared to be too overestimated in comparison to the energy gap of InSe (see the insert in Fig. 3). The measurements of C – V characteristics for many samples showed that the barrier height determined from them lay in range 1 to 3 eV and is not reproducible. In our opinion this is a consequence of the fact that the apparent capacitance is the sum of two connected capacitances. One of them corresponds to the real barrier and another one is a result of nonohmicity of the current contact to the substrate. Both capacitances appear due to the formation of depletion layers on the frontal and back substrate sides. The latest of them is not constant and depends on a damaged surface quality. Therefore, the apparent $1/C^2$ -U characteristics, plotted in Fig. 3, are shifted to higher values of $1/C^2$ with respect to those caused by the barrier. This shift is reflected in the fact that the barrier height values differ from sample to sample. It means that only the concentration of a non-compensated acceptor impurity $N_A - N_D$ is the reliable parameter obtained from the C-V characteristic. From its slope we have determined for $N_A - N_D$ to be of the order of 10^{15} cm^{-3} . The same order of magnitude for the major carrier concentration in p-InSe doped with cadmium was obtained in [7].

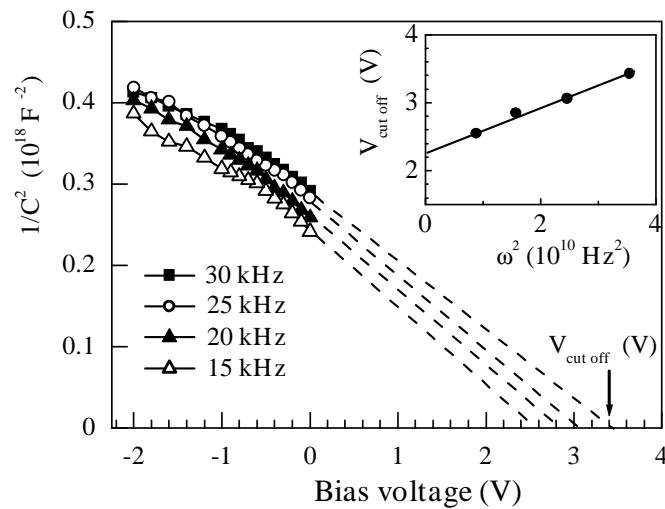


Fig. 3. Capacitance-voltage characteristics of *intrinsic oxide* – p-InSe HJ at different frequencies. In the inset –cut-off voltage vs frequency. T=295 K.

To investigate the current transfer mechanisms in the intrinsic oxide - p-InSe HJ there were measured its forward-biased current-voltage characteristics. They are shown in Fig. 4. In logarithmic coordinates all investigated HJ samples at different time oxidation exhibit two dependences: $I \sim U$ and $I \sim V^3$. The cubic $I - V$ dependence appears at higher forward biases and covers the current range by several orders of magnitude. Its appearance takes place due to the depletion layer in the back contact range. In spite of the fact that the total HJ voltage is forward-biased, the depletion layer is reverse-biased because of voltage redistribution. For this cubic $I - V$ dependence the charge transfer through the insulator layer is determined by space-charge limited currents [8].

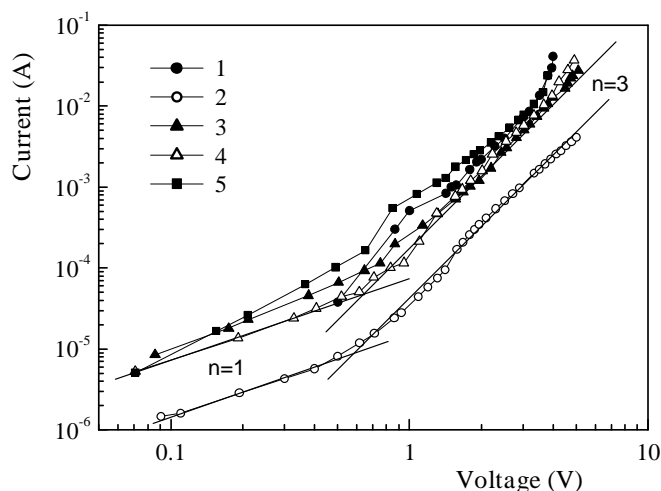


Fig. 4. Forward-biased current-voltage characteristics of *intrinsic oxide* - p-InSe HJ with different oxidation times. The number of the curves corresponds to oxidation time in days. Straight lines correspond to $n=1$ and $n=3$ exponential dependences.

Our measurements of both $C - V$ and $I - V$ characteristics indicate the existence of the additional depletion region at the collector contact range in *intrinsic oxide* - p-InSe HJ.

4. Conclusion

In the present work it is shown, that the choice of oxidation conditions of p-InSe<Cd> crystals allows to create a potential barrier in the system of the semiconductor - oxide and to change the photoelectric parameters of the prepared heterojunctions. The height of the barrier and, therefore, the open-circuit voltage can reach values of about 0.6 V corresponding to a half of the InSe energy gap, and the short-circuit photocurrent can approximately vary by a factor of 20 depending on oxidation time. In the photoresponse spectra we have detected the changes connected to the formation of In_2O_3 and $In_2(SeO_4)_3$ oxide phases. They essentially affect the shape of the photosensitivity bands. Electrical characteristics of the investigated heterojunctions indicate the influence of series resistance. It is established, that the main cause of its existence is non-ohmicity of the collector contact to p-InSe. Damaging of its surface is insufficient for the elimination of this non-ohmicity.

References

- [1] V. N. Katerinchuk, M. Z. Kovalyuk, *Tech. Phys. Lett.* **18**, 70 (1992).
- [2] O. A. Balitskii, R. V. Lutsiv, V. P. Savchyn, J. M. Stakhira, *Mater. Sci. Eng.* **B56**, 5 (1998).
- [3] V. P. Savchyn, V. B. Kutsay, *Thin Solid Films*, **361-362**, 123 (2000).
- [4] S. I. Drapak, V. B. Orletskii, Z. D. Kovalyuk, V. V. Netyaga, *Semiconductors* **37**, 187 (2003).
- [5] O. A. Balitskii, N. N. Berchenko, V. P. Savchyn, J. M. Stakhira, *Mater. Chem. Phys.* **65**, 30 (2000).
- [6] A. M. Goodman, *J. Appl. Phys.* **34**, 329 (1963).
- [7] J. Martinez-Pastor, A. Segura, J. L. Valdes, A. Chevy, *J. Appl. Phys.* **62**, 1477 (1987).
- [8] M. Lampert, P. Mark. *Current Injection in Solids*, Academic Press, New York and London, 1970.