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Low frequency noise (1/f) in the “intrinsic oxide-p-InSe” heterostructures

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The character of noise in photosensitive intrinsic oxide – *p*-InSe heterostructures is investigated for those obtained by thermal oxidation of the base semiconductor at T = 400°C for 15-120 min. It is established that the determinative noise in such structures is $1/f$ noise. It is shown that the observed dependences of noise spectral density on reverse bias differ from the Hooge’s relationship $S(f) \sim const \cdot V^n$, which is correct for majority of conventional semiconductors. It is shown that in such structures the signal-to-noise ratio can be related to structural peculiarities of rectifying barrier formation and changes of its parameters during the growth of the oxide film on the base semiconductor surface.

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1. Introduction

Indium selenide InSe belongs to the wide group of layered III-VI compounds having high anisotropy of electrical properties and heightened radiation resistance and it is a promising material for applications as solar energy cells. For instance, the solar efficiency of In_2O_3:Sn-*p*-InSe-Au cascade solar cells is of about 11 % [1]. This circumstance stimulates the creation and investigation of various diode structures based on InSe (Schottky barriers, MIS-, SIS-structures, heterojunctions). Oxidation of a semiconductor substrate is one of the simplest ways to prepare heterostructures (HSs). The results on the chemical composition of intrinsic oxide formed on an InSe surface (X-ray studies, Raman spectra, etc) are presented, for instance, in [2-4]. Electrical and photoelectrical properties of intrinsic oxide – p-InSe HSs prepared at different time-temperature oxidation conditions of the base InSe are presented in [5-7]. As operating photoelectric devices is essentially affected by noise characteristics, preferably of $1/f$ type, investigation of noise level and behaviour in intrinsic oxide – p-InSe HSs contributes to better understanding the processes occurring at preparation of such the structures. These investigations open a possibility to optimize photoelectrical parameters and receive maximum threshold characteristics.

2. Experimental procedure

Indium selenide single crystals *p*-InSe:Cd were grown by the Bridgman method from a non-stoichiometric melt. They were electrically homogeneous with a free carrier density $p \approx 10^{14}$ cm^{-3} and a Hall mobility of about 50 cm^2/(V·s) at T=300 K. Substrates of about 0.5 mm thick were cleaved from the ingot along the (100) plane and oxidized at T = 400°C during 15 to 120 min. The reasons for the selection of such oxidation conditions at preparation of intrinsic oxide – *p*-InSe HSs are as follows. First, according to [3], the heterostructures obtained by oxidation of InSe in the temperature range T = 350 - 450°C have the highest absolute photosensitivity. Second, according to [6, 7], during oxidation of an InSe surface one should expect the appearance of an In_2O_3 layer. According to [8], industry manufactured films of In_2O_3:Sn (ITO films) are prepared at 400 - 450°C. Third, heating p-InSe samples to T > 500-520°C, according to [9], leads to irreversible inversion of the conductivity type and, as a result, intrinsic oxide – *p*-InSe structures (if the oxide layer consists of In_2O_3) will not possess diodic properties due to the difference between the work functions of the substrate and the oxide film [9]. It is also worth to note that, according to [5], the oxide layer on a surface of indium monoselenide is not homogeneous but consists of some phases different in chemical composition. It was confirmed by X-ray studies as well as Raman and cathode luminescence spectra [2-4]. The properties of high-resistive transition layer between the semiconductor substrate and frontal oxide part have essential influence on electrical and photoelectric properties of intrinsic oxide – *p*-InSe HS. Since silver is the most appropriate for preparation of ohmic contacts to *p*-InSe [10], it was used as the contact material. A control of the presence or absence of the contact noise was carried out according to the method described in [11]. It indicates that the noise of the prepared contacts is negligible in comparison to that of the investigated matters.

As indium selenide can be used in photosensitive devices for near-IR spectral range [1], and majority of such devices operate at low (< 1000Hz) frequencies, noise characteristics of intrinsic oxide – *p*-InSe HSs were measured at frequencies below 1200 Hz by using a K 54.410 device.

3. Results and discussion

It is known that at low frequencies a noise with $1/f$ spectrum is dominant in both semiconductor samples and based on them devices. In this case the dependence of noise spectral density S(f) on bias V is described by the empirical Hooge's relationship [13]

$$S(f) = \text{const} \cdot V^n / f^{\gamma}, \qquad (1)$$

where $n \cong 2$ and $\gamma = 0.8 \div 1.5$. As follows from the experimental data, the dependence of $S(f)$ on reverse bias in the range $|V|$ = 0 -10 V for the intrinsic oxide – p-InSe HS obtained at different oxidation time of the base semiconductor is also described by relation (1). However, on contrary to conventional semiconductors where typically $n \cong 2$, this dependence has two well pronounced parts – with high values of n in the bias range $|V| = 0 \div 4$ V and smaller n values in the range $|V| = 4 \div 10$ V (Fig. 1).

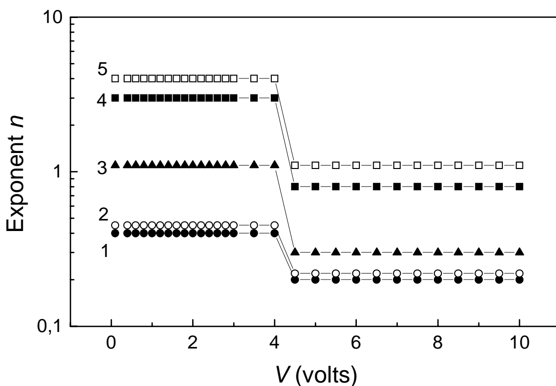

Fig. 1. Dependence of exponent n in relationship (1) on reverse bias V for heterostructures the intrinsic oxide – InSe obtained after oxidation of the base semiconductor at T = 400^{0}C during 1-15, 2-30, 3-60, 4-90, 5-120 min.

We have found the increase of n in the both parts with increasing oxidation time. In the first part the increase of n is more abrupt – it changes from 0.4 to more than 3 with increasing oxidation time from 15 to 120 min whereas for the second part the value of n increases from 0.2 to 1.1. The change of n for indium monoselenide through the annealing stages is to be connected with the growth of oxide film on surface of the base semiconductor, i.e. the formation of a barrier in the intrinsic oxide – p-InSe HS and changes of the barrier parameters with increasing time of thermal treatment. For instance, after an oxidation for 15 min the behaviour of the HS noise corresponds, in fact, to the photoresistive noise level for InSe [14]. It indicates on the absence of a barrier in such structures and is confirmed by the current – voltage characteristics (Fig. 2) as well as by the analysis of capacitance – voltage characteristics [5]. For intrinsic oxide – p-InSe HSs with not shaped rectifying barrier as well as for non-annealed samples of InSe the resistance fluctuations causing $1/f$ noise most likely have two-dimensional character [14]. As the layers of InSe are bound with Van der Waals forces, an increase of external electrical field applied to the structures in the direction across the layers much less affects the increase of S. It is caused by the fact that development of the resistance fluctuations appeared in some layers is complicated in three dimensions. So their contribution to the noise spectral density is less than in conventional semiconductors. Further increase of oxidation time to 30 min does not also lead to appearance of a barrier in intrinsic oxide – p-InSe HS – low values of noise voltage at forward and reverse biases (Fig. 3a, curve 1) are typical for structures with weak potential relief, which practically does not effect on carrier distribution. The intrinsic noise of such layers is of generation-recombination type and caused by the fluctuations of generation, recombination and trapping of carriers in bulk or on surface of InSe [15]. During further oxidation of the base semiconductor (60 min and more) drift and recombination potential barriers become shaped. It results in the appearance of current noise sources – fluctuations of the current (i_1) due to the barrier field separation of the pairs generated in the range of recombination barriers and fluctuations of the "forward" current i_2 caused by a decrease of the barrier height at the separation of carrier pairs, which equilibrates the current i_1 [16]. Oxidation of p-InSe for 100 min and more results in the change of the InSe conductivity type, increasing its resistance and, as a result, an increase of noise as $V_n \approx \text{const} \cdot i R_T \sqrt{\frac{\Delta f}{f}}$, where R_T is the dark resistance. The carried out measurements of the InSe resistivity, inverted by temperature influence, testified its essential decrease (by 1.5 to 2 orders of magnitude). In this case a direct current in the "inverted InSe – intrinsic oxide" HS should be also decreased. However, as one can see from Fig.2, there is a slight increase of the current density in comparison to the p-type material and that oxidized for t = 60 и 90 min. The reasons for it are the essential decrease of the built-in-potential in the intrinsic oxide – InSe HS from 0.7 eV (for the initial material) to 0.25 eV (for the inverted InSe) as well as a decrease of the thickness of the transition layer between the base material and the upper layer of the oxide [5]. The essential increase of the reverse current in the "inverted InSe – intrinsic oxide" HS (Fig.2, curve 5) in comparison to the structures obtained at oxidation of p-InSe for 60 min (Fig.2, curve 7) is a result of a disturbance of the consistency of the oxide film because of the appearance of small defects, cracks, etc. Fig. 3b shows dependences of signal-to-noise ratio (V_s/V_n) on reverse bias for the structures obtained at different times of oxidation of InSe. The maximum V_s/V_n value takes place for the HSs obtained after oxidation for 90 min (Fig. 3b, curve 3). In this case the buffer layer between the oxide surface and the base semiconductor is the most homogeneous with respect to its chemical composition. As a result, the trap density for it decreases in comparison to the structures obtained at shorter oxidation time [5]. The decrease of V_s/V_n for the structures obtained at a 120 min oxidation of the base semiconductor (Fig. 3b, curve 4) is a result of both the conductivity type inversion and a disturbance of oxide film consistency. As

in the case of photoresistive effect [14], the maximum V_s/V_n values are obtained at small reverse biases (~ 1 V) (Fig. 3b). At an increase of the bias $|V| > 1$ V the value of V_s/V_n decreases because of more essential increasing the noise level V_n in comparison to the signal V_s (Fig. 4, curves 5-7).

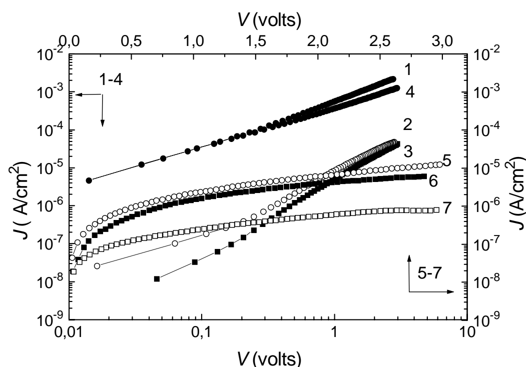

Fig. 2. Forward (1-3) and reverse (4-7) branches of dark current – voltage characteristics for intrinsic oxide – InSe heterostructures obtained at different oxidation time: 1 and 4 – 15-30, 3 and 6 – 60, 3 and 7 – 90, 2 and 5 – 120 min. T = 288 K.

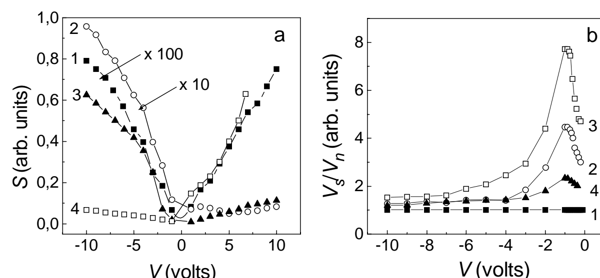

Fig. 3. Dependence of noise spectral density S on applied voltage (a) as well as signal-to-noise ratio (V_s/V_n) as a function of reverse bias (b) for intrinsic oxide – InSe HSs obtained by oxidation of p-InSe at $T = 400^0C$ for 1-15÷30, 2-60, 3-90, and 4-120 min. "+" of an external power source was applied to the base semiconductor. The measurements were carried out at a frequency $f = 400$ Hz. $\Delta f = 160$ Hz.

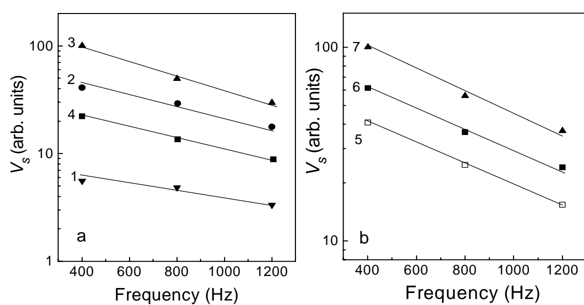

Fig. 4. Dependence of wanted signal V_s on frequency f (a) for intrinsic oxide – InSe heterostructures obtained at different oxidation time: 1-15÷30, 2-60, 3-90, and 4-120 min as well as dependence of V_s on reverse bias: 5-1, 6-5, 7 –10 V for the structure obtained by oxidation of the base semiconductor for 90 min measured at different frequencies.

The presented results can be explained by changes in the structure of the "oxide – layered crystal" interface during oxidation. It is necessary to consider this process as evolutional which in Se-In-In-Se layers occurs in the following way: i) breaking covalent bonds between atoms of the metal and chalcogen and formation of metal clusters, ii) formation of crystalline In_2O_3, iii) recrystallization of In_2O_3 during subsequent annealing. The atomic force microscopy (AFM) investigations of InSe oxidized surface have shown that after a 15 min oxidization some of randomly distributed nanoparticles (lateral dimensions < 1 nm) on the semiconductor surface with its effective thickness of about 10 nm. Layered InSe crystals are characterized by high anisotropy of elastic properties (elastic constant ratio $C_{11}/C_{33} \sim 3$) that increases with temperature [17]. It results in an increase of the plasticity of the crystal and decrease of the interaction between the layers ($C_{11}/C_{44} > 10$). Therefore, at a short-time oxidation (15 to 30 min) deformation of InSe crystal includes only several (~ 6) lattice periods in the vertical directions (for InSe the lattice parameter $c = 16.9$ Å [18]). In this case an oxide layer remain as unordered islands on the semiconductor surface. For such the samples the character and noise level are similar to those in the case of photoresistive effect in InSe [14]. Further oxidation of the semiconductor substrate leads to coalescence of the nanocrystallites, increasing the thickness of the oxide film and its recrystallization. As it is known, this process is more intensive in plastically deformed materials and is accompanied by formation of more large-scaled crystallites. As a result, the size and orientation of the grains change and the oxide film goes into a more stable thermodynamic state. It is established that after oxidation of indium selenide for 90 min In_2O_3 crystallites take cubic symmetry with a linear dimension of some nm with the (111) orientation in the (0001) plane of InSe. In this case deformation changes in the InSe substrate are observed along the C axis on a distance of about 48 nm. Such essential increase of the deformation range in InSe can be explained by the difference between the coefficients of thermal expansion α for In_2O_3 and InSe. For isotropic crystal In_2O_3 with a cubic lattice (the lattice parameter a =10.11 Å at room temperature) $\alpha = 7.2 \times 10^{-6}$ K^{-1} [19]. For hexagonal crystal InSe ($a = 4.048$ Å and $c = 16.904$ Å) $\alpha_a = (9.5 \pm 1)\times10^{-6}$ K^{-1} and $\alpha_c = (16.79 \pm 1.5)\times10^{-6}$ K^{-1} [18]. At increasing the oxide film thickness deformations at the oxide – InSe interface become redistributed between the film and substrate depending on the thickness ratio of the film d_1 and the substrate d_2 and their elastic constants. As indium selenide is more soft material in comparison to In_2O_3, relaxation of strains in the heterostructure will lead to a plastic deformation of the semiconductor at a small oxide layer thickness (< 50 nm) and the cracks are observed on the In_2O_3 surface. Cracking of the oxide layer

on the surface of the samples obtained at the long-term annealing of the semiconductor is one of the reasons of essential increasing the noise level.

4. Conclusion

Low-frequency noise in the intrinsic oxide – InSe heterostructures obtained by oxidation of the base semiconductor in open-air conditions at a temperature T=400 °C for 15 ÷120 min is investigated. At a short-term oxidation (<30 min) the noise level is practically the same as for indium selenide single crystals [14] that is an evidence of the absence of rectifying barrier in such samples. This conclusion is supported by the measurements of current – voltage and capacitance – voltage characteristics [5] as well as the investigations of the surface morphology of the oxidized samples.

The maximum values of signal-to-noise ratio were obtained at oxidation of the base semiconductor during 90 min. Further increase of oxidation time leads to the inversion of the InSe conductivity type and destruction of the integrity of the oxide film. As a result, we have found an abrupt decrease of the ratio as the noise spectral density increases more quickly than wanted signal.

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