Thermo-e.m.f. of hot current carriers in non-doped and doped crystals of a layered semiconductor n-InSe

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Abstract. Thermo-e.m.f. of hot current carriers is experimentally investigated in non-doped n-InSe crystals with a dark specific resistance of 2 \(10^5 \leq \rho_{dc} \leq 9 \times 10^7\) Ω cm at 77 K and doped with erbium with \(10^5 \leq N_{E_b} \leq 10^4\) at.%. It was found that its absolute value (|\(U_f|\)), in addition to \(E\) and \(T_0\), also depends on \(\rho_{dc}\) and \(N\). In the non-doped samples with \(\rho_{dc} \leq 1 \times 10^3\) Ω cm and doped with \(N_{E_b} \geq 10^2\) at.%, the dependence |\(U_f|\) consists of successive sections: |\(U_f| \sim E^2\), |\(U_f| \sim E\) and |\(U_f| \sim E^3\). In non-doped with \(\rho_{dc} \geq 5 \times 10^3\) Ω cm and alloyed with \(10^2 \leq N_{E_b} \leq 10^2\) at.%. samples at \(T_0 < 250\) K and low-heating \(E\) dependence |\(U_f|\) obeys the law |\(U_f| \sim E^\alpha\) with \(2 \leq \alpha \leq 5\). The value of \(k\) monotonously depends on \(N_{E_b}\) and reaches its maximum value at \(N_{E_b} = 5 \times 10^4\) at.%. At \(T_0 > 250\) K, in all the samples studied, as well as in non-doped low-resistance and doped with \(N_{E_b} \geq 10^5\) at.%. samples for all \(T_0\), the dependence |\(U_f|\) follows the theory of thermo-e.m.f. of hot current carriers in spatially homogeneous crystalline semiconductors. To explain the results in non-doped high-resistance and doped with \(10^5 \leq N_{E_b} \leq 10^2\) at.%. samples at \(T_0 < 250\) K, the influence of random macroscopic defects must also be taken into account. A qualitative explanation of the results is proposed.

1. Introduction

When a strong electric field acts on a semiconductor, depending on the material, external conditions, as well as the specifics and schemes used for experimental measurement of the method, various effects representing both scientific and practical interests can be observed [1-3]. The results obtained in the study of these effects, which often lead to the creation of fundamentally new functional elements for modern electronics, and in most cases turn out to be very effective methods for detecting the presence and nature of various types of defects (point, large-scale, specially created, uncontrolled and etc.), clarification of the mechanism of their influence on electronic phenomena in the studied semiconductor. One of the significant scientific and practical interest effects of a strong electric field in semiconductors is also "thermo-e.m.f." of hot current carriers [2, 4, 5], i.e. e.m.f. (potential gradient or voltaic effect) arising between the contacts of the test sample due to the heating of charge carriers in the transition region placed in the strong electric field of the non-rectifying metal-semiconductor contact. This phenomenon is directly caused by inhomogeneous heating (effective temperature gradient - \(T_c\) [2, 4, 5]) of free charge carriers in a semiconductor by a strong electric field and essentially differs radically from the Seebeck effect [6], which is associated with inhomogeneous
heating of the semiconductor itself. It is only conditionally called "thermo-e.m.f." and unlike the Seebeck effect, its value is determined by the gradient of the effective temperature of free carriers \( (T_i) \), and not by the temperature of the material itself \( (T_0) \). This allows for a constant value of \( T_0 \), i.e. without exposing the temperature values of the initial values of the crystal lattice parameters and local levels, as well as the picture of the electronic potential by changing \( T_i \) in a wide range (up to several thousand degrees), to reveal the features of the phenomena caused by the heating of free charge carriers by an electric field in semiconductors and the interaction of free carriers with various defects - both point and large-scale in the studied semiconductor. Earlier works \([2, 4, 5, 7–16]\) mainly reported the thermo-e.m.f. of hot current carriers in spatially uniform single crystals of semiconductors with a high mobility of free charge carriers, under conditions of different type of point defects (intrinsic, impurity, thermal, radiation). In spatially heterogeneous, i.e. possessing random large-scale (macroscopic) defects (LSD) \([17]\), samples of crystalline semiconductors thermo-e.m.f. of hot current carriers and the influence of LSD on the processes of heating and effects of hot carriers are currently poorly understood. An analysis of the corresponding theoretical and experimental studies shows that in a wide range of changes in external conditions, the influence of LSD on electronic processes in such semiconductors is dominant. Therefore, without changing the fluctuations of the electronic potential caused by these defects, by varying the value of \( T_i \) over a wide range, i.e. by heating free charge carriers with an electric field, one can obtain rich information about electronic processes and the role of chaotic large-scale defects in them in spatially inhomogeneous samples of crystalline semiconductors.

2. Materials and methods

Previous experimental studies \([18–20]\) show that one of the good examples of spatially inhomogeneous crystalline semiconductors can also be high-resistance indium selenide single crystals \( (\text{n-InSe}) \), the degree of spatial heterogeneity of which is expeditiously controlled by the content of the introduced impurity during weak doping with rare-earth elements \( (\text{REE}) \). This paper presents the results we obtained in the study of thermo-e.m.f. hot carriers in Bridgman-grown specially unalloyed and weakly \( (\text{when not creating solid solutions of n-InSe}) \) \( (\text{ErSe}) \) impurity content introduced \( \text{Er}=10^{-4} \text{ at.} \% \) erbium-doped bulk samples of n-InSe single crystals. Zeiss with an energy dispersive analyzer was installed with complex thermographic, radiographic and microscopic analyzes using modern equipment such as DSK-910, ADVENCE-8D, SINTECP 2, DRON-4-07 using CuK\( \alpha \) radiation at a step of 0.05 and an angle range of 8-135°, SEM firms Zeiss with an energy dispersive analyzer, it was found that the that the used ingots are chemically and structurally single-phase, do not have a substitution phase of selenides and Er oxides, have a high degree of single crystallinity \([22]\), relate to rhombohedral crystals with lattice parameters \( a=4.017 \text{ Å}, c=25.05 \text{ Å} \) \([23]\). In order to exclude the influence of effects caused by injection and elongation of charge carriers through current contacts; Joule and high-frequency pulsed heating of the test sample; by the inhomogeneous distribution of the free electric field charge carrier heating in the sample on the results obtained, the free current carrier heating process was carried out by exposing the studied sample to rarely repeated \( (\text{with a repetition rate of not more than 6-7 Hz}) \) electric field pulses with an ultrahigh frequency \( (\text{with a frequency of} \ 10^{10} \text{ Hz}) \) in samples with a thickness \( d \leq 2.5 \times 10^{-4} \text{ mm} \). The measurements were carried out in the ranges \( T=77+300 \text{K} \) and \( E=5 \times 10^{4}+4 \times 10^{5} \text{ V/cm} \) of the sample temperature and microwave electric field strength, respectively

3. Results and discussion

It was established that in the samples under study, regardless of the initial value of the specific dark resistance \( (\rho_{D0}) \) and the value of \( N_{Er} \) at microwave electric field strengths \( (E) \) greater than a certain critical value \( (E_{cr}) \), thermo-e.m.f. is observed hot current carriers. Its absolute value \( (|U_f|) \) depends on the microwave electric field strength \( (E) \) (Figure 1), the temperature of the sample \( (T_0) \) (Figure 2), as well as the value of the initial dark resistivity \( (\rho_{D0}) \) of the test sample and the percentage introduced impurities in specially non-doped and doped with erbium crystals, respectively (Figure 3).
doped low-resistance and doped Er with $N_{Er}>10^2$ at.% crystals, the dependence of $|U_T|$ on $\tilde{E}$ obeys the power laws $|U_T|\sim \tilde{E}^2$ and $|U_T|\sim \tilde{E}$ in the region of relatively weak and stronger heating electric fields, respectively. In undoped high-resistance ($\rho_{D0} \geq 5 \cdot 10^4 \Omega \cdot \text{cm}$ at 77 K) and doped Er with $10^{-5} \leq N_{Er} \leq 10^{-2}$ at.% samples in the low $T_0$ region and relatively weakly heating electric fields, the dependence $|U_T|(\tilde{E})$ obeys sharper power law $|U_T|\sim \tilde{E}^k$ (where $2 < k \leq 5$). At low temperatures ($T \leq 250$ K), with an increase in $N_{Er}$ from $10^5$ to $10^1$ at.$\%$, the value of $k$ varies non-monotonically and passes its maximum at $N_{Er}=5 \cdot 10^{-4}$ at.$\%$, and at higher $T_0$ for all of the studied samples, the dependence $|U_T|(\tilde{E})$ consists of the initial quadratic and subsequent linear sections.

![Figure 1](image-url)  

**Figure 1.** Dependence of the absolute value of the thermo-e.m.f. of hot current carriers ($|U_T|$) on the microwave electric field strength ($\tilde{E}$) in samples specially non-doped (curves 1 and 2) with different initial resistivity ($\rho_{D0}$) and doped with erbium (curves 3 and 4) with different percentage of the introduced impurity ($N_{Er}$) n-InSe crystals at 77 K.

$\rho_{D0}$, $\Omega$ cm: $1 - 2 \cdot 10^3$, $2 - 9 \cdot 10^6$; $N_{Er}$, at.$\%$: $3 - 5 \cdot 10^{-4}$; $4 - 10^{-1}$.

It was shown that the samples obtained at $T_0>250$ K in all studied, as well as in non-doped low-resistance and doped Er with $N_{Er}>10^2$ at.% samples in the low $T_0$ region, $|U_T|(\tilde{E})$ dependences obey the theory of thermo-e.m.f. of hot current carriers in spatially homogeneous crystalline semiconductors ($|U_T|\sim \tilde{E}^2$ and $|U_T|\sim \tilde{E}$ in the region of relatively weak and stronger heating electric fields, respectively [4, 5]). To explain the results obtained in non-doped high-resistance and doped Er with $10^5 \leq N_{Er} \leq 10^2$ at.% samples in the low $T_0$ range, it is also necessary to take into account the influence of large-scale chaotic defects.

The analysis, taking into account the early works [19, 20], devoted to the study of the influence of doping and the value of the initial dark resistivity on the magnitude and behavior of the mobility of free charge carriers ($\mu$) in n-InSe crystals, allows us to say that the experimental data obtained in this work the results for samples of pure low-resistance and doped with $N_{Er}>10^2$ at.% crystals are
satisfactorily explained on the basis of the theory of effects of hot charge carriers in spatially homogeneous crystalline semiconductors in the interaction of free charge carriers with phonons of various types [1, 2, 4, 5]. In non-doped high-resistance ($\rho_{D0} \geq 5 \cdot 10^4$ $\Omega \cdot cm$) and alloyed with $N_{Er} \leq 10^{-2}$ at.% samples, in order to explain the obtained experimental results, it is also necessary to take into account the significant effect on the mobility ($\mu$) and, accordingly, on the process of heating of free charge carriers the electric field of random macroscopic defects and fluctuations of the electronic potential caused by them [18, 24].

In all likelihood, the free charge carriers located in the main low-resistance matrix and having high mobility are heated by a strong electric field. Further, these hot current carriers transfer part of the excess energy acquired by them to free charge carriers with low mobility located in the LSD and cause them to overcome drift barriers. Detected "thermo-e.m.f." of hot charge carriers has a non-concentration nature (it is not caused by a change in the concentration of free charge carriers in the "hot" contact region as a result of electrical breakdown of impurity levels, an interband tunnel junction, or the capture of heated free charge carriers by some repulsive centers), and the drift nature is caused by a change their mobility when heated by an electric field. The dependences found in the experiment $|U_T|$, $|U_T(T_0)$, $|U_T(\rho_{D0})$, $|U_T(N_{Er})$ and the dependences of the curve $|U_T|\tilde{E}$ on $T_0$, $\rho_{D0}$ and $N_{Er}$ are satisfactorily explained with corresponding changes in the fluctuations of the electronic potential (spatial inhomogeneity of the sample [17, 24]) with a change in temperature, the percentage of introduced impurity, and the value of the initial specific dark resistance of the studied sample [24, 25].

Figure 2. Dependence of the absolute value of the thermo-e.m.f. of hot current carriers $|U_T|$ on the sample temperature ($T_0$) in samples specially non-doped (curves 1 and 2) with different initial resistivity ($\rho_{D0}$) and erbium-doped (curves 3 and 4) with different percentage of the introduced impurity ($N_{Er}$) n-InSe crystals at the microwave electric intensity fields $\tilde{E}=5 \cdot 10^3$ V·cm$^{-1}$.

$\rho_{D0}$, $\Omega$·cm: 1 - 2 $\cdot$ 10$^3$; 2 - 9 $\cdot$ 10$^6$; $N_{Er}$, at.%: 3 - 5 $\cdot$ 10$^{-4}$; 4 - 10$^{-1}$. 
Figure 3. The dependence of the absolute value of the thermo-e.m.f. of hot current carriers $|U_T|$ (curves 1 and 3) and the values of the exponent ($k$) of the $|U_T| (E)$ dependence (curves 2 and 4) on the initial value of the specific dark resistance ($\rho_{D0}$) and the percentage of the introduced impurity ($N_{Er}$) in specially non-doped samples (curves 1 and 2) and doped with erbium (curves 3 and 4) of n-InSe crystals at 77 K and a microwave electric field strength $\tilde{E}=5\cdot10^3$ V cm$^{-1}$.

4. Conclusion
In conclusion, it can be noted that:
- "thermo-e.m.f." of hot current carriers in specially non-doped and erbium-doped n-InSe crystals due to increased mobility of free main charge carriers (electrons) when they are heated by an electric field;
- specific features of thermo-e.m.f. found in the experiment hot current carriers in specially non-doped and Erbium-doped n-InSe crystals are associated with spatial heterogeneity of the samples under study;
- the influence of spatial heterogeneity of the test sample on free charge carriers with increasing degree of heating of the latter, gradually weakened.

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