ELECTRONIC AND OPTICAL PROPERTIES =

Effect of Nonstoichiometry and Doping on the Photoconductivity Spectra of GeSe Layered Crystals

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Abstract—The polarization photoconductivity spectra of Bi-doped nonstoichiometric GeSe layered crystals grown by static sublimation were investigated. Two strongly polarized maxima at the photon energies $hv_{max} =$

1.35 eV ($\mathbf{E} \parallel \mathbf{a}$) and 1.44 eV ($\mathbf{E} \parallel \mathbf{b}$) due to the $V_1^v \longrightarrow V_1^c$ and $\Delta_2^v \longrightarrow \Delta_1^c$ optical transitions, respectively, were found in the spectra of nominally undoped GeSe crystals near the intrinsic absorption edge at 293 K. In the low-temperature region, an exciton photoconductivity band peaked at $hv_{max} = 1.32$ eV, which is due to exciton dissociation at the cation vacancies, was revealed. With an increase in excess Se in crystals, a sharp increase in the intensity of the exciton peak in the photoconductivity spectra was observed. It is shown that doping of GeSe crystals with donor Bi impurity is an effective tool of the control of their electrical and photoelectric properties. Although introduction of Bi into germanium monoselenide does not lead to the conductivity conversion from the *p* to *n* type, a sharp increase in the resistivity is observed, the crystals become photosensitive, and a strong impurity band peaked at 1.11 eV arises in the photoconductivity spectra.

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1. INTRODUCTION

Germanium monoselenide GeSe has two polymorphic modifications: the stable low-temperature α phase, with a distorted NaCl-type structure characterized by the orthorhombic-lattice parameters a = 4.387 Å, b =3.837 Å, and c = 10.83 Å and the space group D_{2h}^{16} -Pcmn. At a temperature of 924 K, the orthorhombic structure is transformed into the ideal NaCl-type structure with the lattice parameter of the cubic β phase a = 5.730 Å (at 929 K) [1, 2]. The β phase is stable up to the melting temperature $T_m = 943$ K. The mechanism of the $\alpha \longrightarrow \beta$ phase transition in germanium monochalcogenide was considered in detail in monograph [1]. Germanium monoselenide is a phase of variable composition with the homogeneity range deviated from stoichiometry to an excess of selenium. The peak in the melting curves corresponds to the solid solution containing \sim 50.7 at % Se [3]. This circumstance determines the specificity of the compound under consideration (high concentration of charged vacancies in the Ge sublattice and, accordingly, high hole concentration) and the mechanism of dopant dissolution. Despite the numerous investigations of the electrical [4–8] and optical [9–18] properties of GeSe crystals, there are only two studies [6, 7] devoted to the effect of nonstoichiometry on the electrical properties of GeSe, whereas the influence of impurities on the photoelectric properties has not been investigated. According to the data obtained by us, the photoconductivity spectra turned out to be a characteristic most sensitive to nonstoichiometry and doping of GeSe crystals.

In this paper, we report the results of studying the polarization photoconductivity spectra of Bi-doped nonstoichiometric layered GeSe crystals.

2. EXPERIMENTAL

Nominally undoped and Bi-doped GeSe single crystals were grown by static sublimation in sealed quartz cells with an inner diameter of 18–22 mm and a length of 180–200 mm, evacuated previously to a pressure of 133 Pa. As the starting material for crystal growth, we used stoichiometric GeSe and solid solutions within the homogeneity range of the $Ge_{1-x}Se$ phase with different vacancy concentrations: $Ge_{0.97}Se$ and $Ge_{0.93}Se$. Synthesis of the starting material was performed by direct alloying of the elemental components (Ge with a resistivity of 50 Ω cm and Se of V-5 high-purity grade) taken either in the stoichiometric ratio or with an excess of Se. To obtain doped crystals, metallic Bi in amounts of 0.5 and 1.0 at $\overline{\%}$ was added to the charge before the beginning of the synthesis, and the synthesis was performed in the presence of the Bi impurity. By the end of the synthesis, the cell was shaken to locate the grown polycrystalline ingot at one of the cell ends, which was



Fig. 1. Photoconductivity spectra of the GeSe crystal grown from a stoichiometric charge, measured at T = (a) 293 and (b) 100 K in the (1) **E** || **a** and (2) **E** || **b** polarizations.

placed then in a horizontal two-zone tube resistance furnace. The optimal growth conditions were, 900 K in the evaporation zone, and 800 K in the condensation zone.

The crystals grown were plane-parallel plates up to $8 \times 15 \times 0.1$ mm in size. The layered crystal structure accounts for the platelike habit of the crystals with the well-developed (001) faces. Coplanar contacts were formed on the (001) natural faces of the crystals by alloying In or depositing aquadag in such a way that an electric field was applied along the crystallographic axis **b**. It was ascertained by measuring the thermopower sign that both nominally undoped and Bi-doped GeSe crystals had *p*-type conductivity.

The photoconductivity spectra were measured in a dc electric field (which did not exceed 5 V/cm) modulating the intensity of light incident on a sample by a disk chopper. For a modulation frequency of 130 Hz used in the measurements, the light pulse duration greatly exceeded the generation and relaxation times of nonequilibrium charge carriers. A DMR-2 double monochromator was used as a spectrometer. The intensity of monochromatic light was always chosen so as to maintain the lux–ampere characteristic linear in the entire wavelength range under study. A modulated luminous flux from the monochromator passed through a polarizer (Glan prism) and was normally incident on the sample surface. Since the **a** and **b** crystallographic axes lie in the plane of the layered stack, it was possible to investigate the anisotropy of the photoconductivity spectra in the layer plane. Note that in most cases the anisotropy of physical properties of layered crystals is investigated only along and across the layers. The load resistance R_{l} , used to select the desired signal, was chosen according to the condition $R_l \ll R_0$ (R_0 is the sample resistance) to provide a linear relation between the measured signal and the value of photoconductivity. The desired signal, after amplification and synchronous detection, was measured by an ÉPP-0.9 M potentiometer. The photoresponse was normalized to the number of incident photons.

3. RESULTS

Nominally undoped GeSe crystals are characterized by low resistivity and photosensitivity. At the temperature T = 293 K, the specific dark conductivity measured in the layer plane is $\sigma_d = 20-100 \ \Omega^{-1} \ cm^{-1}$ and the hole Hall mobility $\mu_p = 80-100 \ cm^2/(V \ s)$. Investigation of the temperature dependence of the dark conductivity of undoped GeSe single crystals showed that it has a metallic character; i.e., in the temperature range 100– 400 K σ_d is almost independent of *T*.

Independent of the degree of nonstoichiometry, two peaks are observed in the photoconductivity spectra of the crystals under study at T = 293 K. One of these peaks is observed in the **E** || **a** polarization at a photon energy $hv_{max} = 1.35$ eV and the other is observed in the **E** || **b** polarization at the photon energy $hv_{max} = 1.44 \text{ eV}$ (Fig. 1a). Thus, for layered GeSe crystals, the positions of peaks in the photoconductivity spectra recorded on the cleavage plane depend strongly on the mutual orientation of the electric vector **E** of a light wave and the **a** and **b** crystallographic axes. The long-wavelength wing in the spectrum of the photoconductivity signal $I_{\rm ph}(hv)$ is controlled mainly by the behavior of the absorption coefficient. For the $\mathbf{E} \parallel \mathbf{a}$ polarization, at photon energies hv < 1.34 eV, we observe an exponential increase in steepness of 15-25 eV⁻¹ in the photoresponse with increasing hv. Such an increase is characteristic of direct optical transitions [11, 12]. With a decrease in temperature, both intrinsic peaks in the photoconductivity spectra shift to shorter wavelengths at rates $\partial h v_{\text{max}} / \partial T = 3 \times 10^{-4}$ (the peak at 1.35 eV) and $6.6 \times 10^{-4} \text{ eV/K}$ (the peak at 1.44 eV).

The character of transformation of the photoconductivity spectra, depending on the degree of nonstoichiometry, clearly manifests itself only in the low-temperature region. For example, in the photoconductivity spectra of the crystals grown from a stoichiometric charge at T = 100 K (Fig. 1b), two peaks are observed near the intrinsic absorption edge: a low-energy peak at $hv_{max} = 1.41$ eV in the **E** || **a** polarization and a high-



Fig. 2. Photoconductivity spectra of the GeSe crystal grown from a nonstoichiometric charge $Ge_{0.97}Se$, measured at T = 100 K in the (1) E || **a** and (2) E || **b** polarizations and (3) in unpolarized light.

energy peak at $hv_{max} = 1.47$ eV in the **E** || **b** polarization. In addition, in both polarizations, a weak feature in the form of a shoulder at a photon energy of ~1.34 eV manifests itself on the long-wavelength slope of the photoconductivity spectra.

An insignificant deliberate deviation of the initial polycrystalline charge from stoichiometry to excess of selenium affects the photoconductivity spectra of the crystals grown (Fig. 2). Figure 2 shows that at low temperatures (100 K) the energy position of the intrinsic peak in the **E** || **a** polarization remains the same as for the crystals grown from a stoichiometric charge: $hv_{max} =$ 1.41 eV. In the same polarization, two more features manifest themselves as inflections in the high-energy spectral region at photon energies of ~1.55 and ~1.75 eV. In the photoconductivity spectra recorded in the $\mathbf{E} \parallel \mathbf{b}$ polarization, the main peak is observed at the energy $hv_{max} = 1.575 \text{ eV}$; i.e., it is shifted by 0.1 eV in comparison with the crystals grown from a stoichiometric charge. In addition, three more features at 1.42, 1.75, and 2.25 eV are observed.

The photoconductivity spectra of the crystals grown from the charge with a chemical composition corresponding to the melting maximum in the liquidus curve exhibit radical changes (Fig. 3). For such crystals, the dominant peak for both polarizations is the lowestenergy peak at $hv_{max} = 1.32$ eV, which manifests itself in the spectra of the crystals of the first two types as a shoulder on the long-wavelength slope of the main band-to-band peak. Both intrinsic peaks are diffused, although they can be resolved in the **E** || **a** polarization using a high spectral resolution (Fig. 3, curve 1).

Doping of IV–VI semiconductor compounds is widely used as a directed synthesis method. In this case, it is possible not only to vary the composition and thus to change, in particular, the free carrier concentration, but also to produce materials with new properties.

SEMICONDUCTORS Vol. 40 No. 2 2006



Fig. 3. Photoconductivity spectra of the GeSe crystal grown from a nonstoichiometric charge $\text{Ge}_{0.93}$ Se, measured at T = 100 K in the (1) E || **a** and (2) E || **b** polarizations.

These considerations are valid for germanium monoselenide. For example, doping of layered GeSe crystals with bismuth leads to a sharp increase in the dark resistivity by more than four to five orders of magnitude and the occurrence of high total photosensitivity (the ratio for the change in the resistivity $\rho_d/\rho_l = 10^3$ at the illuminance $L = 10^4$ lx, where ρ_d is the dark resistivity and ρ_l is the light resistivity).

Figures 4 and 5 show the polarization photoconductivity spectra of the Bi-doped GeSe crystals (for two different doping levels), measured at T = 100 K. The photoconductivity spectra of the GeSe crystals grown from a charge with the maximum deviation from stoichiometry and containing 0.5 at % of Bi (Fig. 4) retain all features characteristic of nominally undoped crystals. The only differences are that the intensity of the exciton peak at $hv_{max} = 1.32$ eV decreases in both polar-



Fig. 4. Photoconductivity spectra of the Ge_{0.93}Se crystal doped with Bi (0.5 at %), measured at T = 100 K in the (1) **E** || **a** and (2) **E** || **b** polarizations.



Fig. 5. Photoconductivity spectra of the Ge_{0.93}Se crystal doped with Bi (1.0 at %), measured at T = 100 K in the (1) **E** || **a** and (2) **E** || **b** polarizations.

izations and the strong impurity band peaked at $hv_{max} = 1.11$ eV becomes dominant. An increase in the Bi content (to 1 at %) in the crystals is accompanied by a further increase in the intensity of the impurity peak and its weak red shift ($hv_{max} = 1.06$ eV). In this case, the intensities of the exciton and both intrinsic peaks decrease (compare Figs. 4 and 5).

4. DISCUSSION

To establish the nature of the peaks observed in the photoconductivity spectra of the layered GeSe crystals in the fundamental absorption region, we will use the data on the anisotropy of the intrinsic absorption edge of [9–14], the electroreflectance spectra, and the calculations of the band structure [15–18], taking into account the selection rules for optical dipole transitions. Single-crystal germanium monoselenide is a direct-gap semiconductor with the band gap $E_g = 1.29 \text{ eV}$ [15], which has a highly anisotropic intrinsic absorption edge [9–12]. The minimum direct gap in GeSe corresponds to the $V_1^v \longrightarrow V_1^c$ transition [16–18]. Taking into account the data on the energy band structure of germanium monoselenide, we can conclude the following:

(i) The pronounced peak at 1.35 eV in the photoconductivity spectra of the layered GeSe crystals is intrinsic and due to the direct interband $V_1^v \longrightarrow V_1^c$ transitions between covariant portions of the bands, which are allowed in the **E** || **a** polarization.

(ii) The peak at 1.44 eV is due to the indirect interband transitions from the top of the valence band to the bottom of the conduction band $(\Delta_2^v \longrightarrow \Delta_1^c$ transitions, allowed in the **E** || **b** polarization).

The high-energy features at 1.75 and 2.25 eV in the photoconductivity spectra of the GeSe crystals (Fig. 2)

correspond to deeper states, which manifest themselves in the reflectance spectra and electroreflectance spectra [15–17].

In studying the anisotropy of the absorption spectra of GeSe crystals at low temperatures [9, 10, 13, 14], an exciton peak was revealed, which is located at 1.35 eV at T = 100 K. Hence, it is natural to relate the observed photoelectric effect in the region of exciton absorption with exciton dissociation. There are several possible mechanisms of exciton dissociation leading to the occurrence of exciton photoconductivity in semiconductors. First, an exciton can dissociate into a free electron and hole through the interaction with phonons; in this case, the dissociated pair of free carriers can be responsible for the photoconductivity observed. According to this mechanism, a decrease in the crystal temperature should be accompanied by a sharp decrease in the exciton signal, because the number of lattice phonons decreases exponentially with decreasing temperature. For the GeSe crystals studied by us, the photoconductivity in the exciton band, in contrast, sharply increases with decreases in the sample temperature. In addition, with increasing nonstoichiometry of the GeSe crystals, the photoconductivity signal in the exciton band exceeds the signal related to the interband transitions. This phenomenon is possible only when the effective lifetime of the carriers, arising as a result of the exciton dissociation, exceeds the lifetimes of electron-hole pairs generated directly by photons. This fact should not occur in the case of the thermal dissociation of excitons.

There is another mechanism of exciton dissociation that can be used to explain the specific features of photoconductivity observed in GeSe crystals. An exciton generated by light near the point k = 0, where the kinetic energy is low, migrates through the crystal and can either annihilate, emitting a photon, or dissociate, interacting with impurity atoms (cation vacancies in the case under consideration). As a result, a free carrier arises in the crystal, whose lifetime may differ significantly from the lifetime of a free electron-hole pair. The relation between the numbers of annihilating and dissociating excitons is determined by the concentration of impurity atoms with which the exciton can interact and the exciton lifetime before the spontaneous annihilation. Taking into account the above considerations, the maximum observed at $hv_{max} = 1.32 \text{ eV}$ in the photoconductivity spectra can be attributed to the photodecomposition of excitons at cation vacancies in the GeSe lattice.

The long-wavelength wing of signal $I_{ph}(hv)$ in the **E** || **a** polarization is controlled mainly by the behavior of the absorption coefficient and may be distorted by local inhomogeneities caused by the presence of a large number of charged vacancies in the cation sublattice, stacking faults, and impurity atoms and the potential profile related to these defects. This distortion leads to the diffusion of the band edges.

With an increase in the nonstoichiometry of the crystals, an acceptor impurity band is formed due to the presence of intrinsic defects (cation vacancies) in high concentrations $(10^{17}-10^{18} \text{ cm}^{-3})$, which is convincingly evidenced by the metallic character of the temperature dependence of the conductivity of such crystals. The investigations of the temperature dependences of the resistivity and the Hall constant R_H of the GeSe crystals with hole concentrations from 7×10^{16} to $5 \times 10^{17} \text{ cm}^{-3}$ [5] showed that, at the critical carrier concentration $p_c \approx 4 \times 10^{17} \text{ cm}^{-3}$, a metal–semiconductor transition occurs and the band gap contains an impurity band due to the dominant defects. The conductivity at p_c is $20 \Omega^{-1} \text{ cm}^{-1}$, which is comparable with the minimum bulk metallic conductivity.

The presence of a large number of charged vacancies, as well as extended planar defects [8] and screw dislocations [19] is responsible for the occurrence of stresses in the GeSe lattice (vacancy induces tensile strains around it). The lattice disorder of some kind, arising in this case, removes the prohibition in the selection rules for optical transitions, which manifests itself in the intensity decrease of intrinsic peaks, their broadening, and the reduction of their polarization dependences. In addition, the exciton band peaked at 1.32 eV (Fig. 3), which is due to the dissociation of excitons upon their interaction with lattice defects, dominant becomes in the photoconductivity spectrum.

Doping of IV–VI compounds with Bi impurity leads to the occurrence of a number of additional effects related to the defect formation due to the deviation from stoichiometry. The introduction of a substitutional impurity in large amounts (comparable with the amount of intrinsic point defects) into the sublattice of a Group-IV element leads to an additional change in the concentration ratio of the main components in the crystal. When the sizes of the impurity atom introduced into the lattice and those of the substituted atom differ significantly, the doping may be accompanied by the generation of additional intrinsic point defects and the change in the form of their location in the crystal.

In IV–VI compounds, the type of an impurity (donor or acceptor) is generally determined by its valence. Atoms of Group-V elements (Bi, Sb) substitute cations, having one electron more in their external shell in comparison with substituted atoms, act as donors. However, the presence of a large number of Ge vacancies significantly affects the character of the incorporation of impurities into the lattice of germanium monochalcogenides. For example, in germanium and tin tellurides, two mechanisms of the dissolution of Bi atoms are implemented [20]. In the low-concentration range, impurity atoms occupy predominant vacancies and change the carrier concentration according to their valence. At the same time, the vacancy solubility of impurities depends on the vacancy concentration in the starting material. For example, the Bi solubility in GeTe increases from 0.4 to 1.5 at % with an increasing

SEMICONDUCTORS Vol. 40 No. 2 2006

number of vacancies [20]. It should be noted that the vacancy solubility of impurities is restricted, and the limiting concentration of dissolved impurity atoms is always lower than the vacancy concentration. In the presence of free vacancies, Bi impurity can be dissolved in large amounts by substituting germanium in lattice sites, as impurities are dissolved in lead chalcogenides. In this case, the change in the carrier concentration is determined by the valence ratio of Ge and Bi.

Taking these data into account, we can suggest that the main dissolution mechanism of the small amounts of Bi impurity in germanium monoselenide with a significant deviation from stoichiometry is also the filling of cation vacancies. Occupying vacancies, Bi atoms transfer their valence electrons to Se atoms, thus decreasing the total hole concentration and leading to the observed drop in the dark conductivity and the increase in the total photoconductivity. When impurity atoms occupy vacancies, along with a decrease in the vacancy concentration, we observe an increase in the concentration of point defects of a new type—impurity substitutional defects, responsible for the impurity photoconductivity band peaked at $hv_{max} = 1.11$ eV.

In the higher-concentration range, Bi impurity, being dissolved by substituting germanium, increases simultaneously the vacancy concentration in the starting material, due to which the conductivity conversion from the p- to n type in GeSe crystals is impossible. When the cation size exceeds the size of the Ge ion (the case of Bi impurity), compressive strains arise, partially compensating for the tensile strains near other vacancies.

It is likely that the actual process of defect formation in doped nonstoichiometric germanium monochalcogenides is more complex and includes the complex formations of intrinsic point defects and impurity atoms, and, maybe, new phases (binary or ternary) due to the chemical interaction of the impurity with one or two main components.

5. CONCLUSIONS

A significant deviation from stoichiometry and the existence of a wide one-sided homogeneity range in GeSe leads to the formation of a large number of cation vacancies in GeSe crystals $(10^{17}-10^{18} \text{ cm}^{-3})$. This process results in *p*-type conductivity, the formation of an acceptor impurity band, and, as a result, the metallic character of the temperature dependence of the conductivity and the blurring of fine effects in the photoconductivity spectra. Doping of GeSe crystals with donor Bi impurity is an effective tool for controlling their electrical and photoelectric properties. At the same time, the conductivity type of GeSe crystals cannot be converted by intentional doping with bismuth.

In the low-temperature region, exciton effects in layered GeSe crystals play an important role not only in the processes of optical absorption, but also in photoconduction.

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