THE FERMI LEVEL TUNING BY ANNEALING IN SELENIUM VAPOR AND ARGON PLASMA ETCHING OF Bi_2Se_3 SURFACES

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In the near-surface area of Bi_2Se_3 crystals, in order to reduce concentration of charge carriers and Se vacancies, which are electronic donors, annealing in selenium vapor was used. It has been established that the most optimal mode is annealing at a temperature of 100-150 °C for 70 hours. Effective impact on the surface condition with an identical purpose is exerted by processing the sample in a glow discharge in an argon medium. It was determined that treatment with an ions dose of ~$1{,}1\cdot10^{17}$ ion/cm^{-2}, both after and without preliminary treatments in the form of annealing or chemical etching, leads to a significant decrease in concentration of carriers in crystals near-surface area.

Keywords: concentration of carriers, Se vacancies, annealing, selenium vapor, discharge, argon medium, treatment, ions dose, chemical etching.
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INTRODUCTION

Bi_2Se_3 crystals of $A^V{}_2B^{VI}{}_3$ type semiconductors are topological insulators (TI) –materials, with previously predicted and recently detected condensed state of matter [1-4], which allows unhindered movement of electrons in surface layers due to strong spin-orbit interaction and formation spin splitted surface states, which topologically protected from scattering by defects by symmetry with respect to time reversal. A continuous spectrum of these surface states forms a Dirac cone around point Γ of the Brillouin zone, where the direction of the spin moment is orthogonal to the wave vector. These materials surfaces study is a scientific and practical interest in the creation of high-speed devices and the miniaturization of their working elements.

The crystal structure of the Bi_2Se_3 compound belongs to the space group $D^5{}_{3d}$ and has a layered structure, represents a set of layers - quintets, perpendicular to the third-order symmetry axis C_3. Each quintet (*QL*) consists of five layers that alternate in the sequence $Se^{(1)}$–*Bi*–$Se^{(2)}$–*Bi*–$Se^{(1)}$. Chemical bonds in compound Bi_2Se_3 inside quintets are ion-covalent type, the connection between quintets carried by van der Waals forces.

These materials are doped to remove defects in the bulk of the material, which creating energy levels in the band gap and fixing the position of the Fermi level [5], becouse of control Fermi level relative to the Dirac node is a necessary condition for the practical use of topological insulators.The position of Fermi level is closely related to morphology and composition of surface, which affect the surface states in TI. In [6], it was noted that the real cleaved surface of these compounds consists of terraces with a step height, mostly a multiple of *QL*, against which terraces (islands) ending in semimetal atoms are observed.The presence of an additional surface charge on these islands shifts the E_F position to the region of higher energies. Although it is known that topological surface states (*TSS*) are resistant to non-magnetic surface disturbances, their dispersion of zones and spatial distribution are yet sensitive to surface defects.In particular, *Se* vacancies significantly modify the band structure of the Bi_2Se_3 surface. Enrichment with bismuth is usually observed with the growth of a crystal of stoichiometric composition due to the relative easyvolatility of the chalcogen. There are differences in the energy of the formation of *Se* vacancies, which are the main donor defects, in two nonequivalent layers of the chalcogen $Se^{(1)}$and $Se^{(2)}$, and the vacancies in the position $Se^{(1)}$ have the lowest formation energy of all intrinsic defects.This leads to the formation of *n*-type defects without significant compensation by *p*-type defects to a level of at least 0.1 eV above the bottom of the conduction band. In the presence of *Se* vacancies on the surface, several dangling bonds appear that interact with *TSS*, three dangling *Bi* bonds form under one Se vacancy, and, accordingly, three new states near the *K*point of Brillouin zone of the surface.The state at 0.4 eV is mainly associated with the *p*-orbitals of three *Bi* atoms, which have dangling bonds. The states below E_F are formed mainly by these three *Bi* atoms and partially by the *p*-states of $Se^{(2)}$ atoms [7].The vacancies of *Se* and antisite defects of Se_{Bi}, as the effect of electron doping, shift the Fermi energy upward to the conduction band; with increasing their density, the band structure becomes more complicated. A small number of *Se* vacancies on the surface do not destroy *TSS*, and with an increase in their number that violates the spin- orbit interaction, topological surface states can down from the first to the second quintet layer and separate from vacancies [7].

Annealing in selenium vapor leads to decrease in vacancies and number of charge carriers [8]. In [9, 10], it was shown that along with terraces ending chalcogen, terraces ending in bismuth can be observed, in [7] to study the band structure and charge density of surface states with a large number of *Se*-vacancies and layers ending *Se* or *Bi*, first-principle calculations were used. The substitutional defects of $Se^{(1)}$ edge atoms in

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quintets should not cross the critical threshold, since a change in the *p*-state symmetry will affect the probability of inversion of states in the Γ point vicinity of Brillouin zone. In some works, the issue of surface stability and stability during exposure in air was related to the dependence on the surface imperfection, such as vacancies, substitution defects, dangling bonds [11, 12].The formation of oxides up to 1 nm thick was observed, which could lead to a deterioration of topological surface states [13].Oxidation of bismuth atoms is possible with selenium vacancies or substitution of upper layers selenium by bismuth, in this case, dangling bismuth bonds that exist on the surface can interact with oxygen, and surface oxidation begins primarily with them. $Bi_2Se_3(0001)$ surface properties stability, and for most layered crystals, is related to the degree of surface perfection, since the $Se^{(1)}$ atoms of ideal *(0001)* surface have closed electron shells with bonds directed inside the quintets and have no unsaturated bonds [12].An ideal Bi_2Se_3 surface ending in a $Se^{(1)}$ layer has topological surface states (*TSS*) described by a single Dirac cone inside the bulk gap [7], which is consistent with calculations [2] and experiment [3].

Argon plasma etching is used in combination with lithographic methods for the manufacture of devices based on a topological insulator. Surface treatment with argon plasma [14] was used to reduce imperfection and to understand the effect of argon etching on topological insulators.

The purpose of this work is to study the surface properties of $(0001)Bi_2Se_3$ and establish the relationship between structural excellence and electronic properties during annealing in selenium vapor and treatment with argon plasma.

EXPERIMENT AND RESULTS

The morphology and electronic properties of the *(0001)* surface were studied, and the effect of annealing in selenium vapor and treatment with argon plasma on the surface properties of Bi_2Se_3 crystal was studied. We studied *n*-type samples of Bi_2Se_3 crystals obtained by the Bridgman method with a carrier concentration of $n = 1.1x10^{19}$ cm^{-3} and a thermopower $\alpha = -52$ μV /deg. The crystal surfaces obtained by cleavage along the chipped plane *(0001)* were studied.The surface composition of single crystals was studied on aX'Pert Pro XRD X-ray diffractometer of Panalytical B.V. (radiation at 45 kV and 40 mA in CuKα, scanning at 0.01 2θ ° steps and 1.2 s time).Surface images were obtained on an NC-AFM brand AFM at room temperature. The electronic properties were investigated by modulation spectroscopy of a weak-field electric reflection (ER) of light, using a 1-molar solution of *KCl* in water.The surface field was varied by applying an external potential difference to the electrostatic capacitor, one of the electrodes of which was a semiconductor, at a modulation frequency of the surface potential of the semiconductor of 512 Hz. The electric field of the surface space charge was regulated by applying a constant potential, bias. The effect of surface treatment on optical transitions near the critical points of the band structure made it possible to judge the state of the surface by a changing the broadening parameter, height and peak shift of the ER spectrum.A type of electro-optical effect, in which the position of Fermi level on the surface of a semiconductor changes under the influence of an external field or a charge of surface states, is usually called the zone filling effect (ZFE). In the ER spectra, the effect can manifest itself not only at the edge of the fundamental absorption of the material, but also at all allowed interband transitions, including unoccupied states near the Fermi level. When the electric bias is applied, the Fermi level remains unchanged in the bulk of the crystal, however, near the surface the filling of zones changes along the direction from the depth of the volume to the surface. In the method of electroreflection, light penetrating to a certain depth probes levels with different filling levels. Moreover, the mechanism of electroreflection is not just a transition associated with a critical point in the Brillouin zone. For the regime of accumulation on the surface, the modulation of band filling becomes the dominant ER mechanism.With strong doping of narrow-gap semiconductors, the Fermi level is advanced far into the conduction band. Under these conditions, the Franz-Keldysh effect in electroreflection is suppressed and practically does not appear.If the Fermi level is near the bottom of the conduction band, then both effects contribute to the ER mechanisms: the ZFE, which in the general case gives a broadened monopolar structure with an energy shift that grows with an applied field, and Franz-Keldysh, which appears as a bipolar line corresponding to a certain critical point [15,16].When the electric field creates a depleting bending of the zones, the Franz-Keldysh effect can become the predominant contribution to ER.

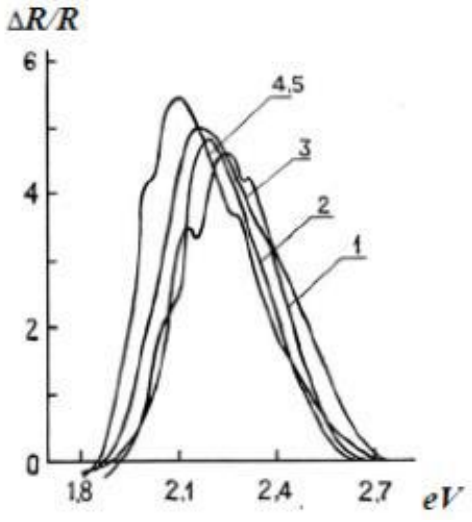


Fig. 1. ER spectra of Bi_2Se_3 crystals annealed in Se vapor for 70 hours at various temperatures:1-initial surface, 2-5 at 100, 150, 250, 300 ^{0}C, at bias voltages -0.3V, modulation 0.4V.

The ER spectra of Bi_2Se_3 samples annealed in selenium vapor at various temperatures and durations were measured in unpolarized light at constant bias and modulation voltages in the spectral range of 1.8 - 2.7

eV, shown in Fig. 1, were studied $T_3$and $T_{4.3}$(notation according to [17]) structures of spectra.

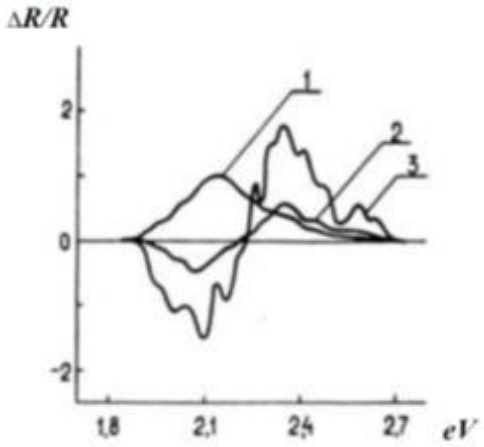


Fig. 2. ER spectra of Bi_2Se_3 crystals annealed in Se vapor at 300 ^{0}C for 70 hours, at bias and modulation voltages, 1-3: +0.3 and 0.5; +0.5 and 0.5; +0.8 and 0.5 V, respectively.

In the ER spectra of Bi_2Se_3 samples annealed in selenium vapor on Fig. 1, curve 2 shows a decrease in half-width of the integral spectral line and a shift of maximum to the longer wavelength region compared with the spectrum from the initial surface on curve 1. Changes in the spectrum indicate a decrease in the concentration of free electrons with a simultaneous decrease in scattering on surface defects, which can be explained by the filling of selenium vacancies upon annealing.This is confirmed by the disappearance of bismuth atoms peaks in X-ray diffraction patterns from the surface annealed in selenium vapor, see Fig. 3, b), compared with the initial surface containing bismuth peaks, see Fig. 3, a). For Bi_2Se_3 intrinsic defects in selenium enriched compositions, the energy of the formation of Se vacancies increases, and the formation energy of the acceptor-type bismuth vacancies decreases.Based on this a lower n-type conductivity can be expected when the Fermi level moves into the band gap in the volume, trying to cross the energy of formation of selenium and bismuth vacancies. Reduction of n-type defects - selenium vacancies also contributes to a decrease in electron concentration.

The shape of curve 3 in Fig. 1 shows that a further increase in the amplitude and shear with an increase in the annealing temperature is accompanied by an increase in the integral half-width of the spectral line in comparison with the initial surface. The intensification of light scattering that is already manifesting can be associated with the diffusion of excess *Se* atoms into the crystal lattice as defect centers, as well as with the aggregation of unevenly distributed surface nanoformations - vapor deposition products, see Fig. 4.In this case, the probability of occurrence of anti-structural defects of Se_{Bi}, is high, the formation energy of which becomes the lowest in the band gap [7], and for all growth variants they are donors, even if the Fermi level is at the bottom of the conduction band or is slightly higher.

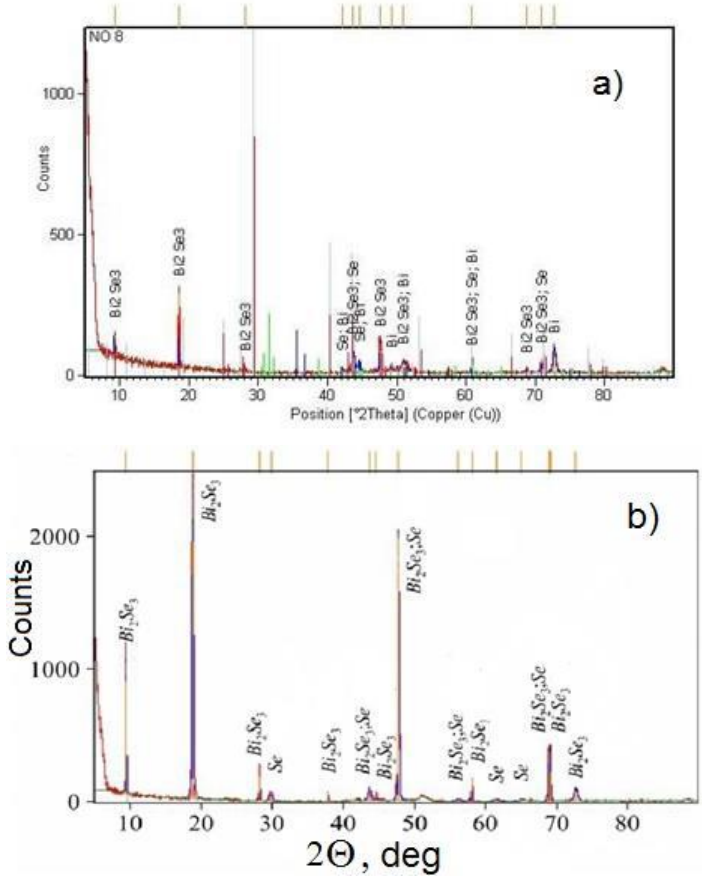
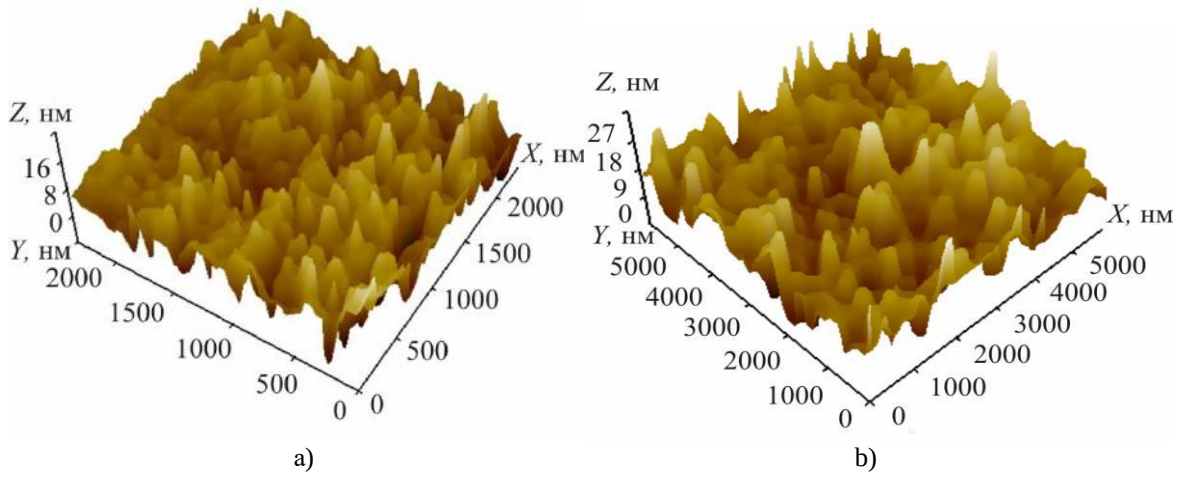


Fig.3. X-ray diffraction pattern from the initial surface of Bi_2Se_3 - a); and from the surface of Bi_2Se_3 annealed in selenium vapor for 70 hours at 200^{0}C - b).



a) b)

Fig. 4. 3D AFM images at room temperature of Bi_2Se_3 (0001) surface annealed in Se vapor for 70 hours, at 150^0C - a) and at 300^0C - b).

This trend persists until the annealing temperature of 250-300^{0}C, as can be seen in Fig. 4 a) and b), an increase in the annealing temperature leads to nanoislands enlargement on the surface. A further increase in the temperature of *Se* vapors up to 350^{0}C does not lead to any significant changes in the ER spectrum.

As noted above, in the electroreflection of crystals with a high carrier concentration ($n \approx 10^{18}$-10^{20} см$^{-3}$), the modulation of band filling prevails, the dominant role of which increases when enrichment bias is applied.The ER spectrum main features corresponding to the band filling modulation mechanism is its monopolarityand independence from light polarization. Under certain conditions, in degenerate Bi_2Se_3 crystals, it is possible to partially suppress the ZFE mechanism and activate Franz-Keldysh effect in the formation of the ER spectrum. This possibility was realized by transferring the bias into the depletion mode, as well as by treating the surface of the sample with argon plasma while maintaining a negative enrichment bias. Corresponding measurements were carried out on *n*-type Bi_2Se_3 crystals with n=1,1x10^{19} cm^{-3}.

The polarization anisotropy coefficient for monopolar spectra measured in the region of even weak surface enrichment turned out to be 1.3. When measuring the ER in the region of depletion bending zones, a monopolar line was transformed into a structure of two opposite in sign lines with approximately equal amplitudes, and the polarization anisotropy coefficient increased to 2.2.

To observe the polarization-dependent dipolar spectrum in the samples annealed in selenium vapor at 300°C for 70 hours, a larger depletion bias was required, causing the zones to bend upward (Fig. 2). This indicates an increase in the concentration of charge carriers with increasing annealing temperature, which is associated with the diffusion of excess Se atoms into the crystal lattice as defective donor centers.A similar transformation of the monopolar polarization-isotropic spectrum from the initial surface of the sample into a dipolar anisotropic occurred after the sample was treated in a glow discharge in argon, and the effect occurred while maintaining a negative bias on the sample.

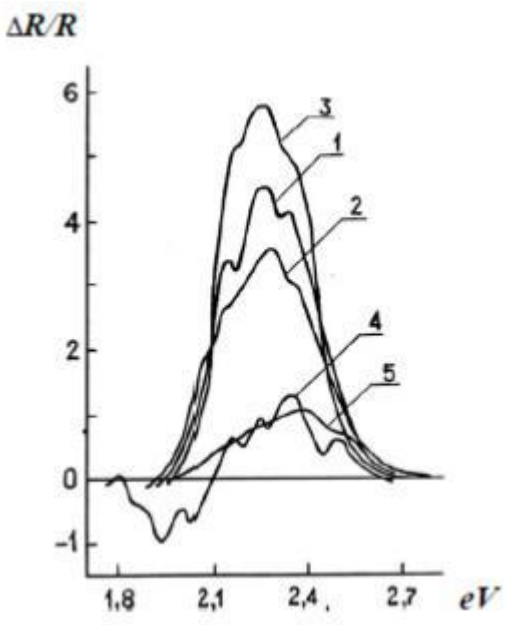


Fig. 5. ER spectra of Ar-plasma treated Bi_2Se_3 crystals: 1-initial surface, 2-5– treatment in the discharge by ion doses, respectively, D≈ 3,6·10^{15}; 1,1·10^{16}; 1,1·10^{17}; 4,3·10^{17}, at bias voltages -0.3V, modulation 0.4V.

Studied crystals exposed to glow discharge in argon medium with ions doses $D \approx$ 3,6·10^{15}; 1,1·10^{16}; 1,1·10^{17}; 4,3·10^{17} ion /cm^{-2}, the discharge current density was 0.2 A /m^2 at a voltage of 1.0-1.2 kV, the treatment time varied from 30s to 60min.Figure 2 shows the light ER spectra from the surfaces of Bi_2Se_3 crystals before and after treatment in Ar-plasma. Processing of fresh cleavage for 30s led to a weakening and broadening of the spectrum (curve 2) in comparison with the spectrum from initial surface (curve 1).Note that in the case of Bi2Se3, a broadened structure of the spectrum is observed and the phenomenological broadening parameter $\Gamma = \hbar / \tau$ determined by the scattering processes by impurities,

phonons, and other imperfections in the crystal structure is only an integral part of the general broadening of spectrum.A significant part of the half-width of the spectrum is associated with field broadening, which is sufficiently large at high levels of bias and modulation on the crystal.Leaving the bias and modulation on the samples unchanged by changes in the overall broadening of the spectra at various stages of plasma treatment, one can judge the changes in the imperfection of crystal near-surface layer.From these positions, the shape of curve 2 of spectrum indicates the appearance of a defective layer on crystal surface, probably due to the deposition of argon ions and their partial incorporation with the formation of radiation defects in near-surface region.With an increase in plasma treatment time to 1.5 min, the amplitude of the spectrum grows (curve 3) and reaches a value greater than that for the initial surface (curve 1), while the broadening of the spectrum decreases. Consequently, during the treatment of 1.5 min, corresponding to the dose of argon ions incident on the surface, $D \approx 1{,}1 \cdot 10^{16}$ ion / см$^{-2}$, prevails process of plasma etching the surface.Further processing with argon plasma up to 15 min. with an ion dose of ~ $1{,}1 \cdot 10^{17}$ ion/cm^{-2}, the amplitude decreased and the monopolar spectrum was transformed into two split peaks of opposite sign (curve 4). Apparently, after plasma cleansing of the surface, selenium atoms are knocked out, followed by adsorption on broken bonds of oxygen atoms of the air, which have a high electron affinity.As a result, a layer of positive space charge can form in the near-surface region due to localization of surface electrons on oxygen atoms and receiving of a near-surface electron-depleted layer.Although in this case, judging by the results of studies [14], where the action of argon plasma causes the broadening of characteristic Raman peaks without a significant change in the position of the peak, we can only assume structural transformation of the surface, and not its oxidation.Taking into account the high concentration of free charge carriers and the degeneracy of the samples, we note that the spectra are 1, 2, 3, in Fig. 5 correspond to the effect of band filling, and the dipolar shape of spectrum 4 and the long-wavelength shift of its energy position indicate that the surface of the semiconductor has turned into a non-degenerate state. Processing in Ar-plasma for 1 hour leads the surface to almost complete structural disorder (curve 5).

CONCLUSION

The results of these studies show that, for layered Bi_2Se_3 crystals, along with the deposition of NO_2 [18], HfO_2 [19] and other surface hole donors, by which it was possible to achieve the alignment of the Dirac cone site with EF, annealing in selenium vapor can be used to reduce vacancies *Se*, which are electronic donors: it has been established that the most optimal mode is annealing at a temperature of 100-150^{0}C for 70 hours.Effective impact on the surface condition with an identical purpose is exerted by processing the sample in a glow discharge in an argon medium. It was determined that treatment with an ion dose of ~$1{,}1 \cdot 10^{17}$ ion/cm^{-2}, both after and without preliminary treatments in the form of annealing or chemical etching, leads to a significant decrease in concentration of carriers in crystals near-surface area.

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