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RESONANCE TUNNELING AND SLOW ELECTRON REFLECTION SPECTRA IN LAYERED BiTeI AND BiTeBr SEMICONDUCTORS

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Based on the analysis of the transmission spectra and low-energy electron backscattering (LEEB) spectra in the monocrystalline BiTeI and BiTeBr samples the character of slow electron interaction with solids due both to the surface electron state excitation and the peculiarities of band energy structure in the solid bulk have been clarified. High transparency of layered BiTeI and BiTeBr semiconductors has been found for low-energy electrons. The resonance mechanism of this phenomenon has been suggested.

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1. Introduction

Most of the electron spectroscopy methods used in the study of solid surface are based on the detection of 5 ÷ 2000 eV energy electrons emitted by the surface or scattered by it. It is known [1], that the 10 ÷ 10^3 eV energy electrons possess the lowest free path length ($l \leq 10$Å), therefore, the electron spectra in this energy range are extremely sensitive to the state of the surface of samples under study. Within the 1 ÷ 10 eV range, l increases with energy decrease and at ~1 eV electron energy it reaches the value of $l \sim 10^3$Å. Hence, the low-energy electron spectroscopy should provide information not only on the surface electron states but also on the energy structure of the bulk solids. This assumption may be checked by comparing the low-energy electron transmission and scattering spectra. Such experiment can be realized for layered narrow-band BiTeI and BiTeBr single crystals.

The first experiment on slow-electron transmission through BiTeI and BiTeBr has been carried out in 1975 [2]. The authors made an attempt to interpret the peculiarities of the low-energy electron transmission spectra for these crystals by using the spectral function $(\hbar\omega)^2 \varepsilon_2(\hbar\omega)$ and $Im\ \varepsilon^{-1}(\hbar\omega)$ $(\varepsilon = \varepsilon_1 + i\varepsilon_2)$ derived from the Kramers-Kronig relation. However, the lack of calculations on the energy band structure and integral state density in valence band and high-energy free bands has not allowed to interpret unambiguously the obtained results.

2. Experimental

A new type of electron spectrometer - the trochoidal electron spectrometer (TES) - has been developed providing the 30 ÷ 50 meV incident electron energy spread and the 40 ÷ 80 meV energy resolution within the 0 ÷ 20 eV energy range. The spectrometer design and operation were described elsewhere [3]. This TES allows the following experiments to be performed: (i) the studies of the energy dependence of elastically backscattered (180°) electron intensity; (ii) the study of the constant

residual energy spectra, including almost zero energy; (iii) the detection of the energy dependence of electron current having passed the sample.

The experiments were carried out by means of a high-vacuum apparatus ($P \sim 5 \times 10^{-7}$ Pa pressure) at the samples with fresh surfaces obtained by cleavage.

When studying the reflection spectra the electron beam was directed normally onto the sample surface, and only the backscattered (180°) electrons were detected. When investigating the transmission spectra the incident electron beam also was directed normally onto the sample surface, and the electron current transmitted through the sample was measured. The incident electron energy was varied from 0 to 20 eV with a 0.02 eV step.

BiTeI and BiTeBr semiconductors have attracted our attention mainly due to the fact that such crystals grow in the form of thin plates with specular surfaces. Thus, no technological difficulties occurred when producing monocrystalline samples with natural faces of the 4 ÷ 14 μm thickness.The samples under study were produced by direct synthesis of initial components in stoichiometric composition in evacuated (to 10^{-2} Torr) quartz ampoules. When growing crystals by gas-transport reaction method, the hot end of the ampoule was kept at 763 K, while the cold one at 723 K. Within a week, the cold area produced single crystals in the form of plates with specific metal gloss. Bismuth telluride halides are crystallized into the hexagonal lattice with the D_{3d}^3 spatial group [2].

We have found when studying the Hall's effect and the specific heat that BiTeI and BiTeBr compounds are n-type semiconductors with large free charge carriers concentrations. In particular, for BiTeI, $n \sim 4 \times 10^{19}$ cm^{-3}, while the electron mobility is 210 ÷ 450 cm^2/V·s. The thermal width of the energy gap is ~ 0.4 eV. Fermi level is located by 0.20 ÷ 0.27 eV above the bottom of the conduction band depending on the electron concentration.

3. Results

The optical properties and energy structure of BiTeI and BiTeBr in the intermediate IR region of the spectrum have been substantially studied in [4,5]. According to these works, the optical width of the energy gap at $T = 300$ K is 0.35 eV for BiTeI and 0.42 eV for BiTeBr single crystals.

The results of the studies of the electron transmission spectra for BiTeI and BiTeBr thin plates are shown in Figs. 1,2.

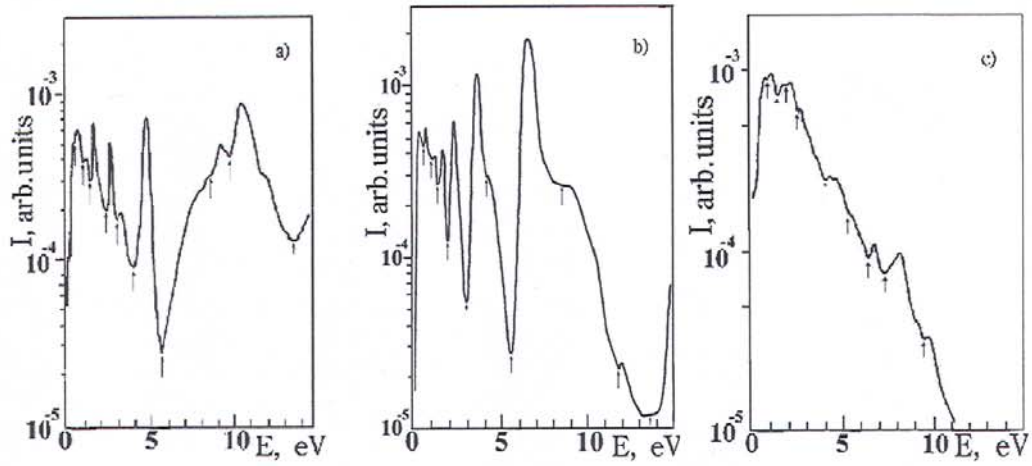

Fig. 1. Low-energy electron transmission spectra for the monocrystalline BiTeI samples of different thickness taken from different technological batches: a) d = 4 μm; b) d = 6 μm; c) d = 10 μm. Electron current through the samples was normalized to the incident electron current).

As is seen from the comparison of curves in Fig. 1, with the increasing sample thickness the fine structure features are smoothed and the electron transmission coefficient is essentially reduced. We did not succeed in the production of BiTeBr single crystals with the thickness less than 12 μm, therefore, the spectra in Fig. 2 reveal the fine structure much less pronounced than for the thicker BiTeI samples.

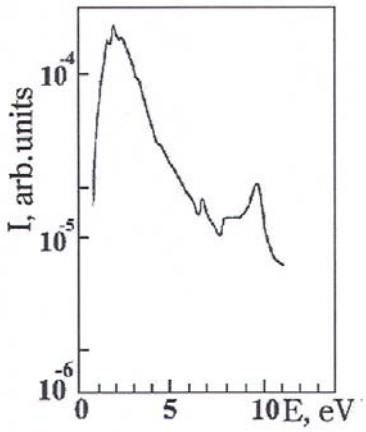

Fig. 2. Low-energy electron transmission spectra for the monocrystalline BiTeBr (d = 12 μm) samples.

The transmission spectra for different technological batches slightly differ in shape, but the energy positions of the most pronounced features are almost similar. This can be clearly evidenced from the Table 1, where the energies of the corresponding minima in electron transmission for the samples under study were taken from Fig. 1.

Table 1. Energy positions (in eV) of twelve minima in the electron transmission spectra for three BiTeI samples.

Sample No.	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}	E_{11}	E_{12}
1	0.65	1.05	1.45	1.85	3.00	4.60	5.70			8.70	11.90	13.60
2	0.60	1.10	1.50	2.00	3.10	4.10	5.65			8.70	10.90	13.70
3		1.00	1.50	1.90	2.80	4.10	5.70	6.50	7.30		9.50	

4. Discussion

Contrary to the total current spectroscopy, in which electron enter the solid from vacuum and the collector is a metal contact deposited directly onto the rear plane of the sample, in our case the incident electrons fell onto the sample from vacuum, while the electrons, which have passed the sample, also entered vacuum, and were detected by a Faraday cup. Therefore, in our experiments, the value by which electron had increased its energy in the subsurface space charge region when entering the crystal, was equal to the value of electron energy loss at the exit from the opposite crystal face, since the state of both sample surfaces was the same prior to the measurements.

One may expect from the data reported in [1] that the transparency of samples will increase with decreasing incident electron energy E_0, since the mean free path increases. But the fact that 5 ÷ 15 μm thick samples "transmit" electrons with the 0 ÷ 10 eV energy, though reducing considerably their intensity, appeared to be surprising.

In our opinion, the most probable reason for the appearance of the fine structure of non-diffraction origin in the transmission spectra at low E_0 is the resonance elastic scattering of slow electrons close to the inelastic thresholds [6]. This elastic scattering mechanism results from the production of relatively long-lived complexes in solids comprising the decelerated electron and the quasiparticles: plasmon+electron → "plasmonium", exciton + electron → " excitonium", etc. At the incident (or, probably, secondary) electron energies E_0 close to the inelastic threshold, an abrupt change of the elastic scattering effective cross section occurs, and the forward scattering, i.e. the scattering at low angles with respect to the incident electron direction, prevails. This process can be modelled as follows [7,8]. If the energy E_0 of the incident electron is close to the energy level of the electron in the potential well E, such electron can be trapped into this well and stay inside the well for a sufficiently long time. The time of electron stay T in the well can be defined from the condition of barrier transparency:

$$\frac{1}{\tau} = W \cong exp\left\{-\frac{2}{\hbar}\int_{x_1(E_0)}^{x_2(E_0)}\sqrt{2m[U(x)-E_0]}dx\right\}, \quad (1)$$

where $x_1(E_0)$, $x_2(E_0)$ are the coordinates of the points, which correspond on the left and on the right to the condition $U(x)=E_0(x_2-x_1)$ that determines the potential well width at the E_0 height.

The total probability of electron transmission through the potential barrier can be presented as $W=W_1+W_2$, where W_1 and W_2 are the probabilities of entering the well and exit from the well per unit time. The probability of the resonance trapping of electron to the level E in the potential well is proportional to the factor:

$$\frac{W_1}{\left(\frac{E_0-E}{\hbar}\right)^2+\left(\frac{W_1+W_2}{2}\right)^2}. \quad (2)$$

The probability of electron transmission through the potential well from the left side to the level $E(W_1)$ and that of electron exit from the level E through the barrier from the right side (W_2) is determined from:

$$P \sim \frac{W_1 \cdot W_2}{\left(\frac{E_0-E}{\hbar}\right)^2+\left(\frac{W_1+W_2}{2}\right)^2}. \quad (3)$$

If the energy difference E_0 - E is large (non-resonant case), then the first addend in the denominator in (3) is larger than the second one, $P \sim W_1W_2$, i.e. the electron tunneling probability is low.

In the case, when $E_0 = E$ and $W_1 = W_2$:

$$P \sim \frac{4W_1 \cdot W_2}{(W_1+W_2)^2} \approx 1. \quad (4)$$

It follows from (4) that the tunneling probability at $E_0 = E$ does not depend neither on the barrier height nor on its width. This means that, at given scattering mechanism, electrons incident normally to the sample surface may penetrate in substantial depth and determine the main quantity of electrons passed through the sample. In this case one may identify the extrema in the current spectra of electrons having passed through the target - they should be related to the elastic scattering.

We have carried out additional studies of electron transmission spectra for BiTeI by using another monochromator for incident electrons with 0 ÷ 100 eV energies. These spectra reveal two broad maxima close to 10 eV and 20 eV being separated by a minimum at 15 eV. At $E_0 > 25$ eV the transmission is sharply reduced, and at $E_0 > 50$ eV no transmission was noticed.

Since it is quite difficult to produce very thin samples with non-damaged surfaces for a number of materials, only the scattered (reflected) spectra can be studied in this case. In order to justify the assignment of the features in these spectra to the interband transitions into the sample volume, we have studied the energy dependences of the intensities (EDI) of elastic LEEB and constant residual energy spectra (Figs. 3, 4).

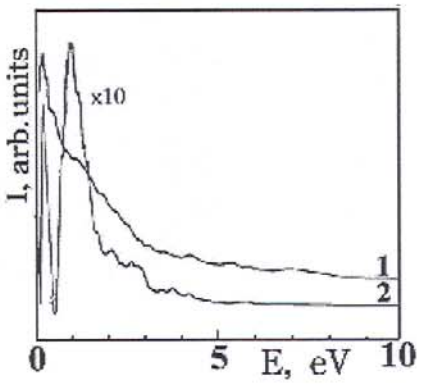

Fig. 3. LEEB spectra for BiTeI single crystal. 1 - elastic scattering EDI;
2 - constant residual-energy spectra ($E_r \sim 0$ eV).

As is seen from Fig. 3, the fine structure in the constant residual energy spectra is revealed much clearly than for the elastic LEEB EDI, though in the elastic scattering EDI for the perfect surfaces this structure may also be revealed quite distinctly (Fig. 4). For each of BiTeI and BiTeBr samples the energy positions of the features in the transmission spectra and constant residual energy spectra agree well. This means that the low-energy electron scattering spectra provide information not only on the energy structure of surface states but also on the interband transitions in the crystalline solid volume.

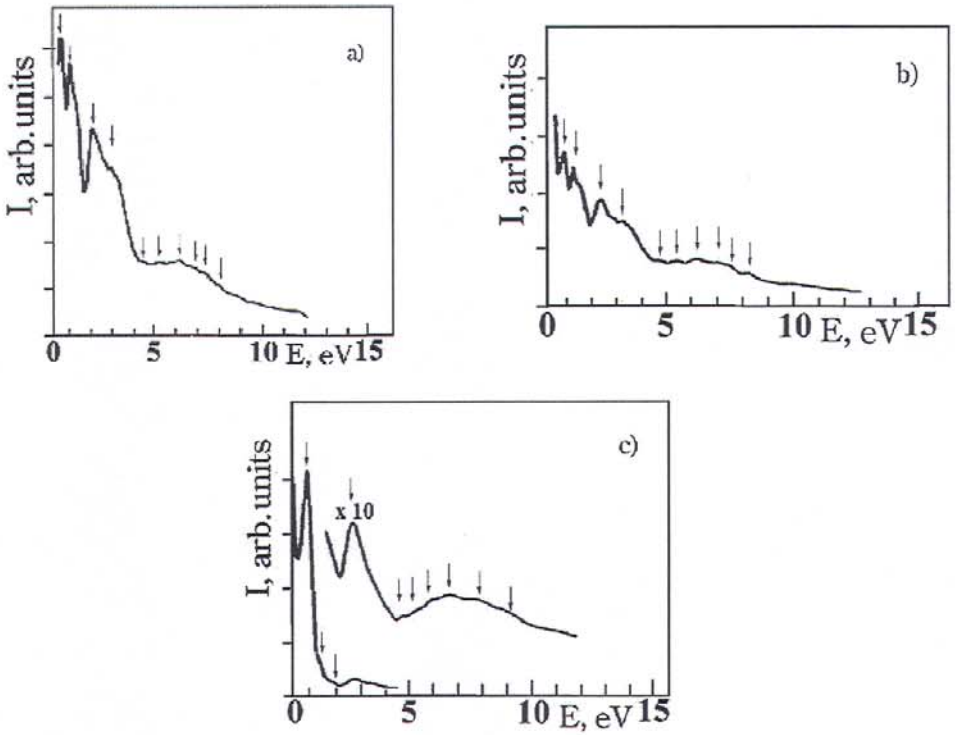

Fig. 4. Elastic LEEB spectra EDI for BiTeBr single crystals taken from different technological batches.

For both types of spectra at the $E_0 = 0 \div 10$ eV energies for BiTeI and BiTeBr single crystals the fine structure is clearly observed. Since in order to reduce the charge at the sample surface due to the electron beam we have used strongly degenerated *n*-type semiconductors, the anomalies related to the transitions from the valence band top to the bottom of the conduction band are slightly shifted with respect to the optical data towards the higher energies: ~ 0.50 eV for BiTeI and ~0.60 eV for BiTeBr. It should be noted that such discrepancies may also result from the technological peculiarities of the production of the above compounds.

It is known that at the formation of single crystals during the technological cycle the free carrier concentration in the layered structures may vary from layer to layer. This results in the change of inner fields strengths. Possibly, just this fact explains the differences in the energy dependences for BiTeI and BiTeBr taken from different technological batches. The low-energy electron scattering pattern may also be complicated by other effect, e.g. monolayer thickness effect, the influence of peculiarities of the chemical interaction in monolayers and between the monolayers, the interactions of the charged electron beam with a space charge region.

5. Conclusions

The similarity in the energy positions of the features in the transmission spectra and inelastic low-energy electron scattering spectra for BiTeI and BiTeBr (at $E_0 > E_g$) allows one to state that the features in the LEEB spectra are due not only to the surface electron and vibrational states, but also to the peculiarities of the bulk energy structure. The features in these spectra also agree well with the optical data. However, the LEEB spectra are much more informative.

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