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Reflectivity and Band Structure of Zn1-Xybxte Crystals

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□ ABSTRACT □

The reflectivity spectra of ZnTe and $Zn_{0.97}Yb_{0.03}Te$ single crystals were obtained in the 2 - 6eV photon energy range at room temperature. The introduction of Yb affects the band structure of ZnTe material. Its provides to the spectra revealed distinct structures at energies of E_1, E_1+□$_□$ and E_2 critical points and to the remarkable blurring of the maximum E_2, and to the disappearance of the maxima e_1 and $E_0^{'}$. The observed changes in the shapes of the spectra, caused by the presence of ytterbium Yb, have been compared with the calculated band structure of binary compound ZnTe available in the literature. The intra-atomic transitions, due to ytterbium introduced as an impurity to the ZnTe crystal, in the $Zn_{0.97}Yb_{0.03}Te$ material were also discussed.

Keywords: Reflectivity of $Zn_{1-X}Yb_XTe$, Molecular Beam Epitaxy growth of $Zn_{1-X}Yb_XTe$

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الانعكاسية والبنية القطاعية للبلورات $Zn_{1-x}Yb_xTe$

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□ الملخّص □

تم قياس أطياف الانعكاسية للبلورتين ZnTe و $Zn_{0.97}Yb_{0.03}Te$ في مجال الطاقة من 2 إلى 6eV في درجة حرارة الغرفة. إن إدخال الايتيربيوم Yb أثر على البنية القطاعية للمادة ZnTe. مما أدى إلى أن الأطياف أظهرت بنيات جلية عند طاقات النقط الحرجة E_1 و E_1+□□ كما أدى إلى تعرض القمة E_2 واختفاء القمتين e_1 و $E_0^{'}$. إن التغيرات الملاحظة في أشكال الأطياف، بسبب وجود الايتيربيوم Yb، تم مقارنتها مع البنية القطاعية المحسوبة للمركب الثنائي ZnTe المتوفرة في المراجع. نوقشت أيضاً الانتقالات الذرية الداخلية، نتيجة إدخال الايتيربيوم كإشابة إلى البلورة ZnTe، في المادة $Zn_{0.97}Yb_{0.03}Te$.

الكلمات المفتاحية: انعكاسية البلورات $Zn_{1-X}Yb_XTe$ ، تنمية البلورات $Zn_{1-X}Yb_XTe$ بطريقة الحزمة الجزيئية التراتبية.

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Introduction:

Zinc telluride is a promising semiconductor material of II–VI group for fabrication of high efficiency thin film solar cells and other optoelectronic devices due to its suitable intrinsic energy gap, 2.26 eV. Study on ZnTe also reveals that it can be used in optoelectronic detection of THz radiation. Photoluminescence study on ZnTe was also carried out in recent years [1].

In the last years, the examinations of rare earth (RE) interaction with semiconductor compounds were performed in many laboratories, because of their interesting optical properties and possible applications in semiconductor lasers and other optical devices [2]. On the other hand there are some problems with obtaining good quality crystals, and it limits routine applications of such materials. It concerns particularly II-VI semiconductors doped RE. Because of this our knowledge about optical properties of these materials is incomplete and based mainly on results of investigations of bulk samples having poor crystalline quality, a new way has been opened due to development of technique like molecular beam epitaxy (MBE) methods of thin film crystallization [3]. The samples under investigation were thin films of the ternary alloy semiconductors $Zn_{1-X}Yb_XTe$ (zinc blende). There are the solid solutions of YbTe crystallizing under normal conditions in rock salt structure and ZnTe crystallizing in zinc blende structure. The ternary alloy thin crystalline films possess the zinc blende structure [4].

Aim of study:

The investigation of the band structure of semiconductors explains one of the important problems of the solid state physics. The knowledge of energy structure presents both the scientific and the practical interest since it determines the most of physical processes, which occur in crystals. The study of the reflectivity and absorption spectra is the simplest experimental method. The study of absorption gives us the information about the band gap. The information about the band structure at energy $h\nu > Eg$ contains the reflectivity spectra in wide energy range (infrared, visible, near ultraviolet, vacuum ultraviolet).

The aim of the work is to present the spectral dependence of the reflectivity coefficient studies of a new kind of material MBE grown-$Zn_{1-X}Yb_XTe$ thin films. The room temperature reflectivity spectra were obtained for photon energies in the range 2-6eV for ZnTe and $Zn_{0.97}Yb_{0.03}Te$ crystals with the aim that some new data obtained allow us to construct band structure of the $Zn_{0.97}Yb_{0.03}Te$ material.

Experimental conditions:

The samples ZnTe and $Zn_{0.97}Yb_{0.03}Te$ were grown in the Institute of Physics, Polish Academy of Sciences, Warsaw- Poland. ZnYbTe thin films were grown by molecular beam epitaxy (MBE) system equipped with Zn, Te and Yb sources on ZnTe buffer layers crystallized on GaAs (100) substrates. At the chosen growth temperature (340°C), the maximum concentration of ytterbium was found to be 3% in ZnTe. X-ray investigations have shown that there was a small admixture of pure YbTe in the samples. From the optical measurements it follows that in ZnYbTe, Yb can be found both in $2^{[+]}$ (as in YbTe) and $3^{[+]}$ (as in Yb doped II-VI compounds) valence state [3, 4].

The measurements for photon energy range 2-4eV were carried out in the system equipped with quartz prism monochromator and a halogen lamp used as the light source.

At higher photon energies a vacuum monochromator based on a Seya-Namioka scheme was used. The radiation source was a hydrogen gas discharge lamp connected directly (without any window) with the monochromator. Other experimental details could be found in [5].

Results and discussion:

Figure 1 presents the reflectivity spectra of ZnTe and $Zn_{0.97}Yb_{0.03}Te$ from 2 to 6 eV at room temperature. We have indicated the main structures as E_0; e_1; E_1; $E_l + \Delta_l$; E'_0 and E_2. The band structure of ZnTe [6] is shown in Fig. 2. Several interband transitions related to the critical points (CPs) are indicated. The results presented in figure 1 are in the sequence, which allows us to compare the spectra obtained for $Zn_{0.97}Yb_{0.03}Te$ and ZnTe thin films. Such a comparison enabled us to reveal most of the changes occurred in the band structure caused by the presence of Yb ions.

The features seen in the reflectivity spectrum of ZnTe agree in both energy position and shape with the results published previously [7-9]. The fundamental energy gap E_0 is attributed to $\square_{\square v \square}\square\square_{\square c}$ transition. The E_1 and $E_l + \Delta_l$ transitions in the zinc-blende-type semiconductors may take place along the □ directions <111>, or at the L-point of the Brillouin zone (BZ). They represent transitions from the spin-orbit split valence bands to the lowest and second-lowest conduction bands, and have the same initial states. The E_2 $(X_{7v}–X_{6c})$ transition corresponds to a set of transitions poorly localized in k-space, which contain, or are close to, the lowest gap at the X-point.

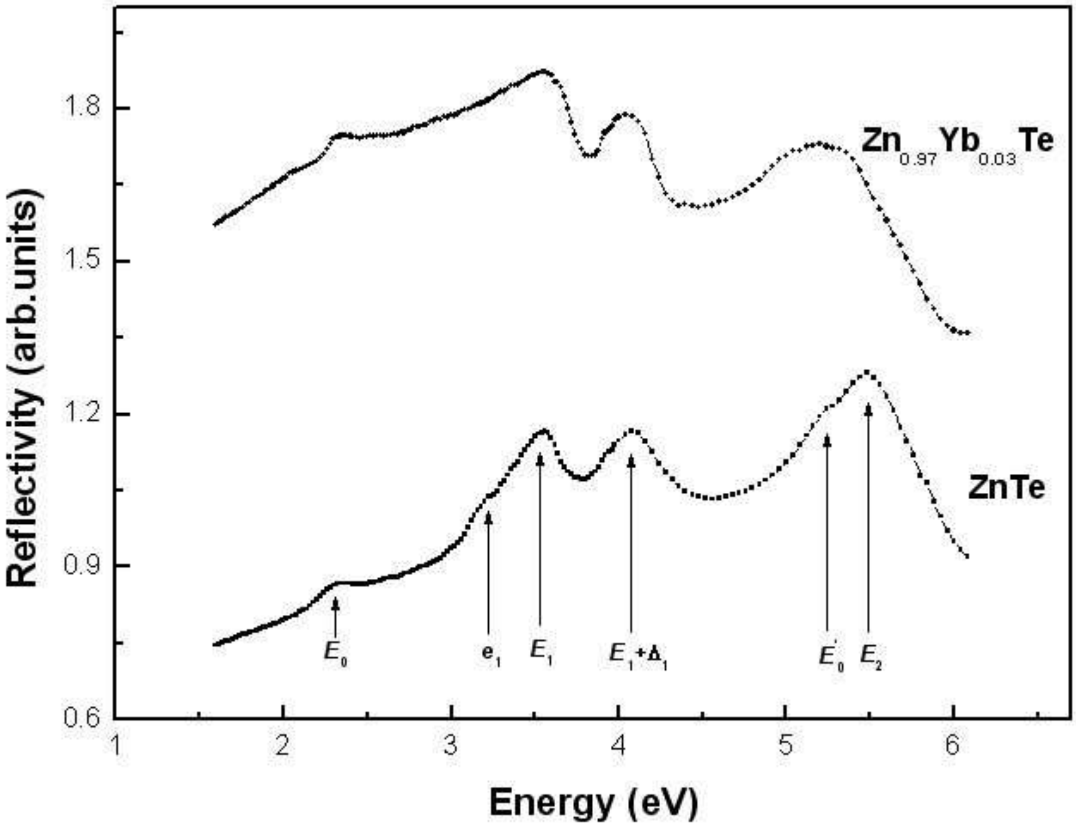

Figure 1. Reflectivity spectra obtained for ZnTe and $Zn_{0.97}Yb_{0.03}Te$ single crystals at room temperature. The notation used for the structures corresponding to ZnTe [7] and to YbTe [10].

Table 1. The energies of prominent features for ZnTe and $Zn_{0.97}Yb_{0.03}Te$ single crystals together with identification of the interband transitions [7-9].

Peaks	ZnTe	$Zn_{0.97}Yb_{0.03}Te$	Assignments
E_0	2,30	2,33	$\square_{8v\square}\square\square\square\square\square_{c}$
e_1	3,23	-	$L_{3v} - L_{1c}$
E_1	3,55	3,56	$\square_{3v}\square\square\square\square\square_{1c}$
$E_1+\square_{\square}$	4,08	4,06	$\square_{3v}\square\square\square\square\square_{1c}$
$E_0^{'}$	5,24	-	$\square_{\square v\square}\square\square\square_{\square c}$
E_2	5,48	5,20	$X_{7v} - X_{6c}$

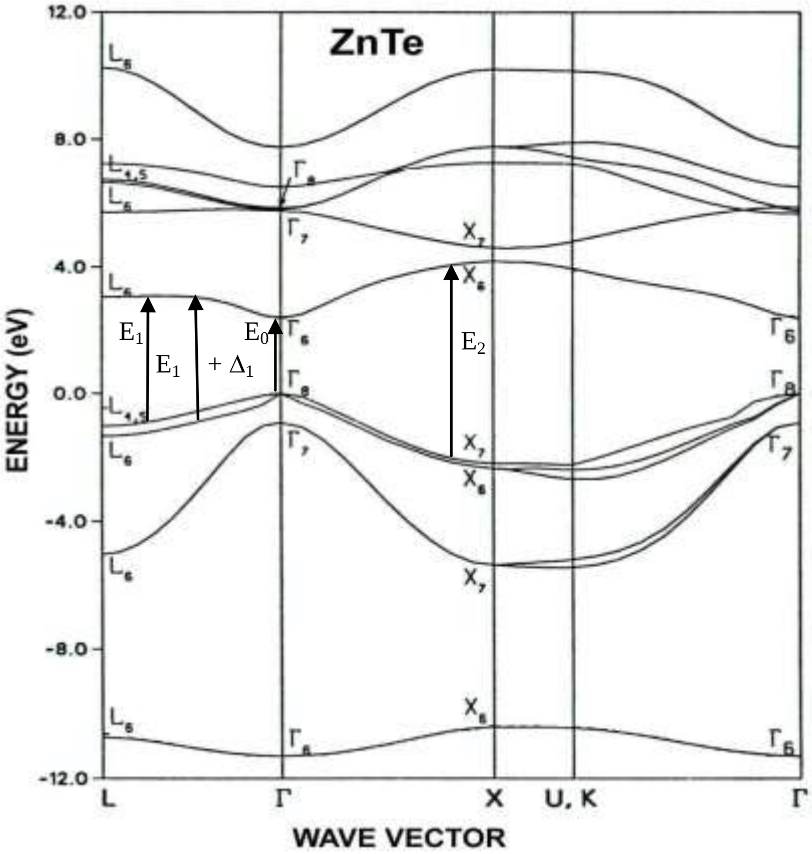

Figure 2. Energy band structure of ZnTe [6], and the interband transitions positions are indicated.

For ZnYbTe spectrum, the E_0 feature maximum occurs at 2,33 eV. The E_l and $E_l + \Delta_l$ maxima are very similar for those in ZnTe spectrum. For E_2 maximum at the energy position close to 5,20eV, very dramatic changes occur. This maximum strongly decrease and shifts to the lower energy.

The presence of Yb ions (see figure 1) gives

(i) almost no change in positions of some of the peaks (E_0, E_1, $E_1+ \Delta_1$) and, hence, it is easy to interpret them as due to interband transitions in pure ZnTe (see table I),

(ii) a remarkable broadening of the reflectivity peak E_2 obtained in the range of energy hν between 5 and 6eV,

(iii) a disappearance of a features labeled e_1 and $E_0^{'}$, observed in a ZnTe spectrum.

The analysis of the positions and shapes of the features observed for $Zn_{0.97}Yb_{0.03}Te$ thin film allow us to find the influence of YbTe on its optical properties. The overall shape of the $Zn_{0.97}Yb_{0.03}Te$ spectrum is very similar to that obtained for ZnTe, however we observe a disappearance of a features labeled e_1 and $E_0^{'}$ at 3,23 and 5,24eV, respectively. In the $Zn_{0.97}Yb_{0.03}Te$ crystal curve the YbTe precipitates were found. Note that the absorption edge in YbTe occurs at about 1,8 eV [10,11]. From the point of view of photoemission [12], the considerable f electrons in the upper valence band region (at □) has also been confirmed by resonant photoemission studies. They showed that the Yb f^{14} states were observed close to the edge of the valence band while the Yb f^{13} states were revealed deep in the valence band. Also, these workers arrive at the conclusion that the ytterbium levels are located close to the Fermi energy, and the structure of the valence band of ZnYbTe at the binding energy equal to 5eV is similar to this structure in ZnTe. They found also that ytterbium in ZnYbTe exists in two charge states Yb^{+2} and Yb^{+3}. The state Yb^{+2} is characteristic of ytterbium deposited on the surface. The maximum of this structure in ZnYbTe is observed at 1.25 eV. This feature occurring near the top of the valence band maximum (at □) supports our suggestion that there exists an interaction of the electrons in the valence band close to □ point of the BZ with the electrons of Yb.

We do not observe marked changes of E_l (at 3.57eV) caused by YbTe. The slight decrease in the $E_1+ \Delta_1$ peak height with respect to the E_1 peak, testify to the introduction of Yb states to the band structure of ZnTe. In this region, strong disorder due to the presence of the Yb states manifests itself. However, this peak does not shift in the presence of ytterbium but becomes rapidly broadened and it probably caused by the appearance of intra-atomic transition in this region.

The strongest maximum E_2 in ZnTe is likely to be strongly affected by the presence of the Yb ions. It is height decrease noticeably and shifts to lower energy. This effect suggests that the final states are located about ~ 4eV above the valence band maximum. This is consistent with results of a resonant photoemission study showed that ytterbium introduced as an impurity to the ZnTe crystal occurs as Yb^{+3} ions in the $Zn_{0.97}Yb_{0.03}Te$ material [12]. The structure of ZnTe valence band located at lower binding energy (~2.4 eV) is covered by the originated form Yb (4f) state.

Summary:

In this paper, we presented results of a study of the reflectivity of $Zn_{0.97}Yb_{0.03}Te$ and ZnTe single crystals. It follows from our results that there exits discernible change in the shape of the valence and conduction bands caused by the disorder occurring in the lattice by introducing of the ytterbium. In spite of that, the band structure of the $Zn_{0.97}Yb_{0.03}Te$ crystal resembles closely that of the ZnTe material.

An analysis of the reflectivity spectra of $Zn_{0.97}Yb_{0.03}Te$ and ZnTe enable us to state that the differences between corresponding spectra, leads to following conclusions:

1) A disappearance of a new maximum labeled e_1 and $E_0^{'}$, it is ascribed to contribution of the Yb states to L and □ states.

2) The maximum E_l (optical transition Λ_3-Λ_l), corresponding to the direction [111] in the Brillouin zone, is broadening by Yb contribution in the solid solution investigated. This effect is connected with the shape of the crystal potential, resulting from the absence of long range order in the crystal.

3) The optical transition contributing to the E_2 maximum, caused by the transition at X point of the BZ, is markedly modified in the solid solutions containing Yb. This peak is affected strongly by ytterbium.

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