

Deformation effects in fundamental reflectivity spectra of ZnTe thin films and single crystals

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The influence of structural defects and external stresses on the shape of ZnTe fundamental reflectivity spectra has been studied. The analysis of ZnTe monocrystalline and thin films reflectivity spectra shows the possibility of a quantitative estimation of these effects. Variation in the shape of a reflection spectrum and the appearance of enriched *fine structure* of spectra of materials subjected to stresses suggest an intermediate connection of these phenomena with the real structures of thin films and monocrystals.

1. Introduction

Investigation of the electronic structure of semiconducting materials by the analysis of their reflection spectra is, from the theoretical point of view, correct only for single crystals showing ideal lattice order. In practice, we are dealing quite often with substantially defected structure and consequently, with respectively deformed electronic structure in relation to theoretical computations.

As it has been proved by LILIENTAL [1], the ZnTe single crystals are contaminated by numerous structure defects, the quantity and kind of which depend on the method of crystal growth.

Crystals obtained from a liquid phase (from tellurium excess) contain large single crystalline grains with dislocation density (2×10^8 lines/cm²) lower than in crystals obtained from gaseous phase (dislocation density 5×10^9 lines/cm²). According to dislocation theory each defect of crystalline structure creates around itself a stress field, the value of which surpasses many times the macroscopic strength of the material.

The first successful trial of connecting together uniaxial stresses with the shape of reflection coefficient spectrum and positions of energy maxima within this spectrum has been carried out by GERHARDT [2], for Ge and Si single crystals. He noticed measurable displacements and extensions of the maxima as well as slope variations of spectrum as the function of the applied external pressure.

By analysing the reflection spectra of ZnTe thin films the authors of this work have proved [3, 4] that the structure defects introduced by technological conditions of preparation provoke measurable variations in their reflection spectra. The shifts of energy maxima, observed in reflection spectra of thin films in relation to positions of the corresponding maxima in reflection spectrum

of selected *ideal* single crystal, have been discussed in the papers mentioned above. It has been also suggested that those transpositions are caused by defects provoked by thermal shrinkage of the film and by its interaction with the substrate. It is likely to happen that apart from deformation effects connected with the interaction between the film and substrate, the non-neglected contribution to the shape of reflection spectrum is also due to random distributed stresses connected with failures of crystalline structures. A similar effect should be noticed also in single crystals. In the presented paper an attempt has been undertaken to determine for thin films and various quality ZnTe single crystals the influence of real structure on the shape of their fundamental reflection spectra in the energy range of 3–6 eV.

2. Analysis of reflection spectra shape of ZnTe thin films

An accurate quantitative analysis of the shape of light reflection spectra is at present not possible because the values of reflection coefficient depend also on the kind of reflecting surfaces, particularly, on their irregularity and heterogeneity [4, 5]. The dependence of the reflection spectrum shape on the deformation was proved by measuring the reflection spectrum of ZnTe thin film on mica substrate subject to compressive pressure and then to the extending one due to the bending of thin film on the substrate as a whole. Internal stress introduced in this way into the sample has been estimated as being equal to $(2-5) \times 10^7$ Pa. Figure 1, curve 1, represents the reflection spectrum of light before the deformation of 3.5 μm thick thin film. After the removal of force

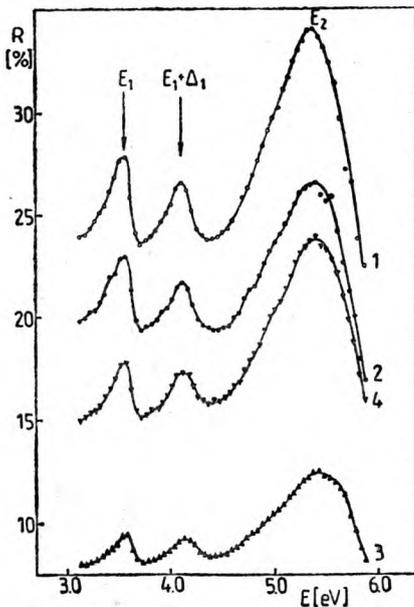


Fig. 1. Reflection spectrum shape of ZnTe thin films vs. deformation. Curve 1 — reflection spectrum before deformation, curve 2 — reflection spectrum after removal of force deforming the thin film, curves 3, 4 — reflection spectra of the deformed films (3 — compression, 4 — spreading)

deforming the thin film (curve 2) the shape of reflection spectrum is similar to that of spectrum non-stressed primarily; it is, however, necessary to ascertain that the heights of the corresponding maxima are slightly smaller. It may be supposed that in consequence of the deformation of thin films some irreversible strains, caused by low elasticity coefficient of the ZnTe film [12] and slide of the film lattice planes, have been introduced. This could bring about variation of stress distribution in the film after deforming and persistent disturbance of crystalline structure, and consequently, another shape of light reflection spectrum. Reflection spectra of the deformed film (curves 3 and 4) differ in essence from the spectra of non-deformed film. It seems that this effect can be described quantitatively by the ratios of the maxima intensities occurring in the examined reflection spectra determined as the ratios of absolute values of light reflection coefficient (including background) for given energy positions. The definite procedure was imposed by the inability of taking a correct account of light reflection, non related to interband transitions, in the determined points of band structure, e.g., E_1 , $E_1 + \Delta_1$, E_2 . Therefore, the intensity ratios quoted in Table 1 could not be related directly to the probabilities of optical transitions in the corresponding points. However, on the ground of these data one can come to conclusion about the trends in variations of spectrum shape. Similar tendency can be observed if in estimation, as a background the value of the reflection coefficient for 3 eV is taken.

Table 1 contains numerical values of the maxima of intensity ratios E_1/E_2 and $(E_1 + \Delta_1)/E_1$, calculated from the reflection spectra presented in Fig. 1.

Table 1

	E_1/E_2	$(E_1 + \Delta_1)/E_1$
Before deformation	0.82 ± 0.01	0.95 ± 0.01
Compression	0.76 ± 0.01	0.97 ± 0.01
Extension	0.75 ± 0.01	0.98 ± 0.01
After deformation	0.86 ± 0.01	0.94 ± 0.01

The differences in numerical values of the corresponding ratios of the maxima of intensities for the film before and after deformation are within error limits, these values differ considerably, however, from the values for compression and elongation or extension. This effect, as it seems, can be connected with the variation in the shape of bands due to deformation, which in turn causes the variation of density function of states and matrix interaction element. As it follows from the character of variation of the maxima intensities ratio in reflection spectrum of the deformed thin film, the total effect provoked by compressing uniaxial stress operating in (111)-plane is within error limits, the same as the effect caused by extending uniaxial stress in the same plane. Detailed analysis seems to be intricate, it would be premature to draw at present quantitative conclusions in view of the lack of advanced analysis of the shape of reflection spectra.

3. Analysis of reflection spectra shape of single crystals

Influence of uniaxial pressure on fundamental reflection spectrum of light for ZnTe single crystal has been noticed when the crystal was subject to stress in the (100)-direction. There is a distinct shape variation of the deformed crystal spectrum, if compared to reflection spectrum of the non-deformed crystal, that is manifested by the background slope and decrease of maximum E_2 height. The reflection spectrum shape of the crystal after deformation does not coincide with the initial reflection spectrum, hence it follows that in all the cases the applied extreme stresses were higher than the elasticity coefficient for ZnTe. In the analysis of the positions of maxima in thin-film reflection spectra as the reference we used the crystal, the reflection spectrum of which (after detailed analysis of additional examinations) has been accepted as a standard. Reflection

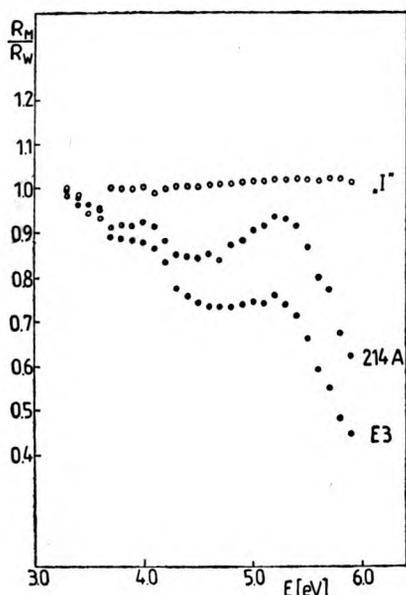


Fig. 2. Variation of reflection spectrum shape of monocystals ZnTe (I — crystal obtained from liquid phase, 214A — crystal from the group of weakly stretched single crystals, E3 — crystal with large internal stresses (birefringent))

spectra of single crystals have also been compared with the same *standard* crystal, dividing the examined spectrum by standard one by the *point to point* method. The curves obtained, normalized to the first point, are presented in Fig. 2. As fundamental reflection spectrum provides mainly information about electronic structure of the examined material, the ratio calculated in this way should contain information concerning the deviations of the electronic structure of the investigated single crystals from the structure of the standard crystal. In Figure 2 the straight line parallel to the energy axis refers to a single crystal I obtained by introducing a small number of crystal defects (growth from liquid phase). Thus it may be seen that the order in crystal I is the same as in the standard crystal. This fact has been also confirmed by X-ray examinations.

It should be emphasized that the standard crystal and the examined crystal I were grown in two different laboratories. The first — in the M. J. Kalinin Higher Engineering Military College of Communications (Kiev, USSR), and the second one I — in the Institute of Materials Engineering of the Military Technical Academy in Warsaw (Poland). Within the range of higher energies the values of reflection coefficient depart from the unity, showing the variation of relative reflection coefficient of single crystal E3. There is a distinct difference in values observed at high energies and those occurring at the beginning of the range. This crystal is birefringent, providing the existence of large internal stresses. An intermediate position in the Fig. 2 is occupied by the curve corresponding to the single crystal 214A. Therefore, it may be classified among the group of weakly extended single crystals, which is also compatible with the evaluation of stresses on the ground of X-ray examinations.

4. Fine structure of reflection spectra of ZnTe thin films and single crystals

Within the examined energy range there exist three distinct maxima in the reflection spectrum of ZnTe thin films. For all the examined specimens of ZnTe, one sees numerous maxima of the intensity considerably lower than E_1 , $E_1 + \Delta_1$ and E_2 maxima (Fig. 3) if compared with the E_2 maximum. The positions of the maxima within this *fine structure* have been primarily evaluated exactly from the average spectrum for the selected ZnTe thin film prepared from a num-

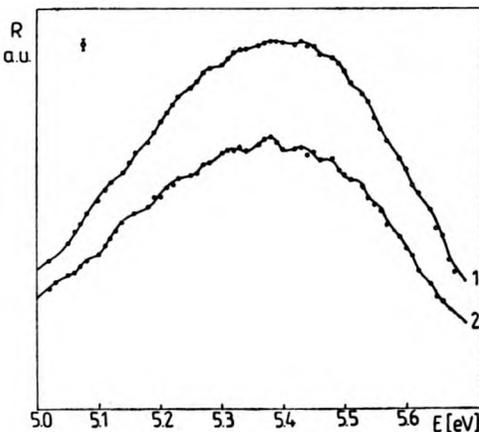


Fig. 3. Fine structure of ZnTe thin films. Curve 1 — reflection spectrum before deformation, curve 2 — reflection spectrum of the deformed film

ber of spectra for different areas of the film (altogether 21 spectra). The found positions of maxima and thresholds of the *fine structure* are presented in Table 2. For comparative reasons the positions of maxima found in reflection spectra of deformed thin film shown in Fig. 1 are also given. As it follows from this table, in consequence of deformation the number of observed maxima distinctly

Table 2

	E_1 [eV]				$E_1 + \Delta_1$ [eV]					
	Positions of maxima in reflectivity spectra for different areas of the film	3.23	3.58	3.75	3.91	4.13	4.40			
Before deformation		3.57	3.83		4.05	4.14	4.47	4.60		
Compression	3.23	3.33	3.55	3.83	3.89	4.15	4.49	4.63		
Spreading	3.23	3.50	3.54	3.81	3.90	4.14	4.25	4.47	4.57	4.65
After deformation		3.53	3.57		4.05	4.15	4.34	4.47	4.57	

Table 3

	E_1 [eV]			$E_1 + \Delta_1$ [eV]									
	I	3.22	3.50		3.83	3.99	4.13		4.70		5.09		
214A	3.23	3.53	3.77	3.84	4.00	4.11	4.34	4.53	4.70	4.85	4.98	5.15	
E3	3.196	3.54	3.77	3.85	3.96	4.11		4.48	4.56	4.64	4.85	4.98	5.12

grows. This fact seems to be linked with the suppression of degeneration of energy bands. Slight variations of band inclinations at different points of the Brillouin zone could also cause an increase of number of points at which Van Hove's conditions hold.

A similar *fine structure* has been noticed also in all spectra of light reflection from ZnTe single crystals (Table 3). In the reflection spectrum of a single crystal I the number of maxima was slightly smaller than in reflection spectra of the remaining two single crystals 214A and E3. Just the same as for thin films the existence of a rich *fine structure* of reflection spectra for single crystals can be linked with the suppression of degeneration of energy bands due to the existence of statistically distributed internal stresses connected with the real structure of crystals. These suppositions have been confirmed by X-ray examinations (the last column in Table 3). According to the results obtained a single crystal I does not show measurable internal stresses, whereas the existence of such stresses has been stated in two remaining single crystals 214A and E3.

The fine structure in light reflection spectra of several semiconductors has been observed by other authors [8, 9]. PHILIPS [9] interpreted this structure as transitions from metastable exciton levels. An exact explanation of the character of these transitions is, however, considered by him as an open problem.

E_2 [eV]												
			4.97	5.03			5.16		5.37		5.43	5.56
4.69				5.07		5.16	5.20	5.33	5.38			5.54
4.69	4.75	4.85	4.90	5.07	5.11	5.16	5.30	5.35	5.43	5.45	5.50	5.52
	4.73		4.99	5.12		5.20	5.26	5.36	5.44	5.48		5.53
	4.81						5.27	5.38	5.46			5.52

E_2 [eV]							
	5.40	5.52		5.76	5.86	without stresses	
5.25	5.34	5.38		5.65	5.78	5.86	low stresses
							large stresses
5.23	5.42	5.35	5.5	5.65	5.73	5.85	(crystal is birefringent)

Theoretical considerations of the band structure and the corresponding reflection spectra for $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ [10] confirm the possibility of the existence of maximum E_2 complex structure as an effect of a superposition of optical transitions from the areas of the Brillouin zone with lower symmetry. These results have been confirmed by Rodzik's experimental investigations concerning fine structure [11] as well as by shape variations of reflection spectra of HgTe and CdTe crystals subject to uniaxial compression.

5. Conclusions

From the results of the carried out investigations the following conclusions may be formulated:

1. Application of external uniaxial stresses to ZnTe thin films changes distinctly the energy positions of the maxima and the shape of spectra of fundamental light reflection, in the way similar to that occurring in presence of stresses provoked by the interaction of film and substrate contraction stresses and by defecting the crystalline structure in the course of technological treatment built in.

2. Introduction of external uniaxial stresses to ZnTe single crystals leads to similar results as for thin films.

A simple analysis of the intensity ratios carried out for reflection spectra in energy positions of the maxima enables a first quantitative description of stress influence on reflection spectrum shape and a comparative analysis of the quality of materials with respect to their real structures.

Variation of reflection spectrum shape and the appearance of enriched *fine structure* of spectra of materials subject to stresses, suggest an intermediate connection of internal stresses with real structure of thin films and monocrystals.

Acknowledgements — It is a pleasure to express acknowledgements to Prof. E. Igras from the Military Technical Academy in Warsaw, and Prof. I. V. Potykevich from the M. J. Kalinin Higher Engineering Military College of Communications in Kiev for providing monocrystals used in the experiments.

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Received November 2, 1983

Деформационные эффекты в основных отраженных спектрах пленок и монокристаллов ZnTe

Исследовано влияние структурных дефектов, а также внешних напряжений на вид основного отраженного спектра ZnTe. Анализ отраженных спектров монокристаллов, а также тонких пленок ZnTe позволяет оценить роль этих эффектов. Изменение вида спектров отражения, а также появление обогащенной „тонкой структуры” спектра в материалах, подвергаемых напряжениям, подсказывает непосредственную связь этих явлений с реальной структурой тонких пленок и монокристаллов.