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Wavelet analysis of composition microinhomogeneities of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals grown from melt

O.N. Chugai, S.L. Abashin, A.V. Gaidachuk, D.P. Zherebyatiev, I.V. Lunyov, A.A. Poluboiarov*, S.V. Sulima*

N.E. Zhukovsky Kharkiv National Aerospace University, Chkalova str., 17, Kharkiv, 61070, Ukraine

**Institute for Single Crystals of NAS of Ukraine, Lenin Ave., 60, Kharkiv, 61001, Ukraine*

chugai@xai.edu.ua

Linear dependencies of composition of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.03 - 0.15$) crystals grown from melt were measured along direction of its growth. Wavelet analysis shows that in these dependences for Zn mole fraction corresponding to different sections there are several harmonic components with spatial period about units – tens micrometers. Anisotropy of low-frequency dielectric properties on crystals where specified direction is physically marked out was revealed. Peculiarities of crystal composition and properties are explained with self-oscillating processes at their growth.

Keywords: A^{II}B^{VI} crystals, dielectric permittivity, semiconductors solid solutions, composition inhomogeneities, wavelet analysis.

Виміряні лінійні залежності складу вирощених з розплаву кристалів $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.03 - 0.15$) у напрямку їхнього росту. Вейвлет-аналіз показав, що в цих залежностях для мольної частки Zn, що відповідає різним ділянкам, є кілька гармонічних складових з просторовим періодом порядку одиниць – десятків мікрметрів. Виявлена анізотропія низькочастотних діелектричних властивостей кристалів, при якій фізично виділений є зазначений напрямок. Особливості складу і властивостей кристалів пояснені автоколевальними процесами при їх рості.

Ключові слова: кристали A^{II}B^{VI}, діелектрична проникність, тверді розчини напівпровідників, неоднорідності складу, вейвлет-аналіз.

Измерены линейные зависимости состава выращенных из расплава кристаллов $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.03 - 0.15$) в направлении их роста. Вейвлет-анализ показал, что в этих зависимостях для мольной доли Zn, соответствующих разным участкам, имеются несколько гармонических составляющих с пространственным периодом порядка единиц - десятков микрометров. Обнаружена анизотропия низкочастотных диэлектрических свойств кристаллов, при которой физически выделенным является указанное направление. Особенности состава и свойств кристаллов объяснены автоколебательными процессами при их росте.

Ключевые слова: кристаллы A^{II}B^{VI}, диэлектрическая проницаемость, твердые растворы полупроводников, неоднородность состава, вейвлет-анализ.

Introduction

It is well known that a characteristic feature of solid solution semiconductors is a heterogeneous composition that significantly affects their electrical and optical properties. Moreover, the heterogeneity of composition is determined not only by statistical distribution of atoms over the lattice sites, but also by the conditions of solutions growth. In recent decades interest in the study of the effect of growth conditions on the specified semiconductor solutions composition feature has sharply increased. This is due to the possibility of spontaneous modulation (see. Eg. [1-2]) or in other words the superlattice ordering [3] of their composition. Notice that solid solutions investigated in mentioned and other studies differ in composition one from another, but represent as thin layers with thickness of several μm . The particular role of the surface simplifies composition self-structuring in such layers in comparison

with the bulk solid solutions with the same components content [4]. In work [5] we first reported on the observation of self-organization of the composition in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ($x = 0.05 - 0.20$) bulk crystals grown from the melt. The aim of this work consists in a detailed study of these solutions heterogeneity. We notice that these solutions are one of the most promising materials for uncooled gamma-ray detectors [6]. That is why the vast majority of studies on their composition spatial distribution are closely linked to the achievement of physical properties which are important for this application. For example, in work [7] the composition distribution in $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystalline ingot has been investigated in connection with the uniformity of optical and electrical properties. In work [8] the correlation of Zn content with electrical resistivity of crystals doped with Se have studied. Also we should notice, solid solutions of cadmium – zinc telluride are still used as a substrates for

the $Hg_{1-x}Cd_xTe$ layers in optoelectronic devices [9].

Method of experiment

Investigated crystals were grown from melt under high pressure of argon. Crystal wafers oriented with its plane parallel to the axis of the ingot were cut from it. One of these wafers after surface mechanical lapping is shown in Fig. 1a. The numbers I, II and III mark the position of linear sections along which the crystals composition was measured by energy dispersive electron microscope PЭМ – 106. Sections were oriented parallel to the ingot axis (Z-axis in the Figure 1a inset). Their length was $50 \mu m$. Measurements were performed in the region of the spot $1 \mu m$ diameter with pitch of the same magnitude. Their relative error depends on the content of the solid solution components and in case of Zn is 20%. Before these measurements wafer surface had not only lapped but also was mechanically polished and chemically etched to remove affected surface layer. The same operations were used in production of rectangular samples from the wafers ($7 \times 6 \times 5 \text{ mm}$) for measuring real and imaginary parts of dielectric permittivity of crystals at low frequencies. Sample planes were oriented perpendicular to the axes X, Y and Z (see Figure 1a inset). Electrical contacts to planes were created by coating with conducting lacquer TLC. Condenser-type method with partial filling of the space between plane capacitor plates with samples was used for measuring ϵ' and ϵ'' .

In our studies of $Cd_{1-x}Zn_xTe$ crystal composition microinhomogeneities we paid special attention to changing in the mole fraction of Zn (i.e. x) along with the coordinate since this value determines crystal band gap. Fig. 2a shows the dependence of x coordinate for the section I (see. Fig. 1a), and Fig. 2b – the same dependence, but after the wavelet analysis. As is well known [10, 11], this analysis allows us to solve a wide range of experimental data processing tasks, including tasks of solid state physics (see. Eg. [12]). In our work, wavelet analysis was applied to filter mentioned dependence, i.e. $x(\ell)$, assimilated to “signal structure”. Pursued goal was not only in detecting frequency of signal, but also in ascertainment of other its features. It was taken into account that the studied data characterize transient process whose statistical properties are unknown. Therefore filtering operation which removes both fast (fluctuations) and slow (trend) components from the dependence $x(\ell)$ was applied. We should notice that these components can provide useful information, but to receive it indicated composition dependence had to be measured at other magnitudes of d .

Results and discussion

Wavelet analysis has carried out using application package MatLab [13]. Thereby for the initial coordinate

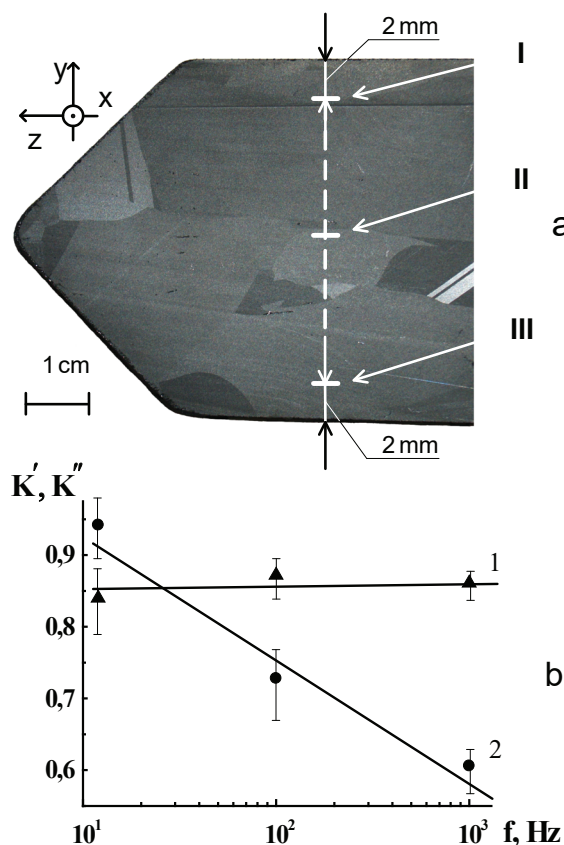


Fig. 1. Image of $Cd_{1-x}Zn_xTe$ wafer in reflected light (a) and anisotropy coefficients dependencies of dielectric permittivity by frequency. Data is averaged by all investigated samples (b).

dependence x represented as a sequence $x_n = x(nd)$, $n = 0, 1 \dots N-1$, ($N = 50$) direct discrete wavelet transform

$$W(k_i, \ell_j) = a_i^{-1/2} \sum_{n=0}^{N-1} x_n \psi^* \left(\frac{nd - \ell_j}{a_i} \right)$$

has been carried out, where $W(k_i, \ell_j)$ is a value of wavelet coefficient for the wave number $k_i = \lambda_i^{-1}$ (λ_i – spatial period) and coordinate ℓ_j , ψ is a basic function of the wavelet transform, * symbol corresponds to the complex conjugation, a_i is a parameter determined by the observation scale of investigated dependence in the k – space, but not directly related to k_i . We should notice that the selection of specified function is one of the main difficulties of the wavelet signal filtering, which characteristics are insufficiently known. As the result, the knowledge of these characteristics would allow optimizing selection of the basic function using one or another criteria. However, in our studies, as noticed above, it was only

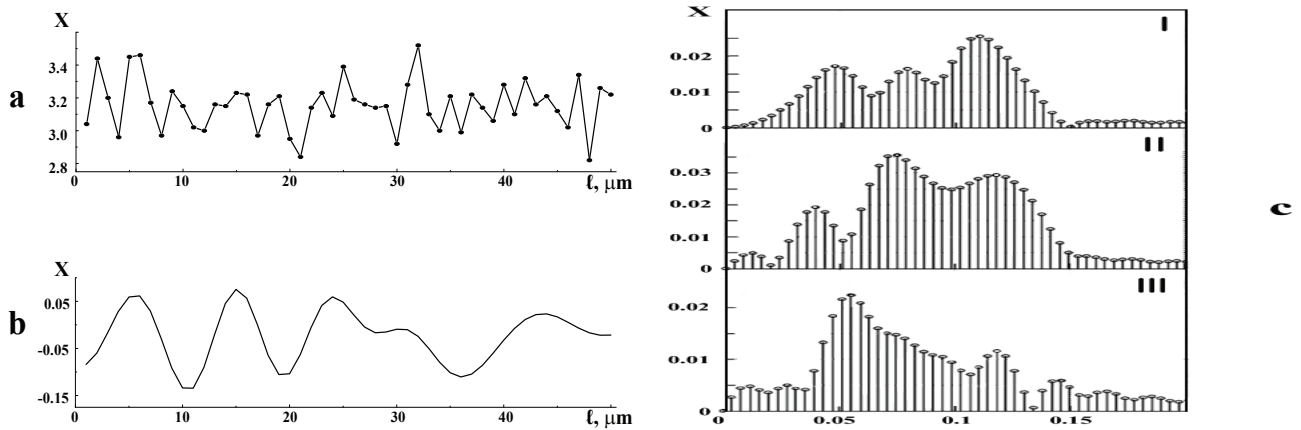


Fig. 2. Initial coordinate dependence of Zn mole fraction $x(\ell)$ in crystals (a) and result of its wavelet analysis (b); c – result of $x(\ell)$ dependence Fourier transform for wafer sections marked with Roman figures; numbers in parentheses are spatial periods expressed in μm corresponding to the selected maximums of transformed dependence.

known that the “composition signal” $x(\ell)$ of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ crystals is periodic. The initial selection of ψ function was determined by the presence of sharp peaks in this signal (see. Fig. 2a). So we used Daubechies and Symlet wavelet function (both biquadratic). Further analysis was based on reaching minimum of a quadratic loss function obtained after the inverse wavelet transform of the “composition signal” to the source signal. It is ascertained that almost in all cases the lowest values of this function provides Symlet wavelet. So further only results obtained with this wavelet are given.

At the beginning of the computational procedure source data vector has multiplied by a quadratic matrix of wavelet transform. Resulting wavelet coefficients were divided into approximate $app(K, j)$ and detail $det(K, j)$ components whose number was twice less than in the original data vector. K and j indexes determine the scale of the weight conversion function and its position on the axis lengths, respectively. For separating wavelet coefficients applied function «dwt» of MatLab environment, which realizes the algorithm discrete wavelet transform proposed by Mallat, was used [14]. Specified data vector multiplication and division operations have performed multiple components to achieve the maximum level of “composition signal” expanding m . As a result we received a set of wavelet coefficients that were used for the inverse wavelet transform with their additional weighting

$$x(\ell) = \sum_{j=0}^{N-1} \alpha(K) app(K, j) \varphi_K(\ell) + \sum_{K=0}^m \sum_{j=1}^{N-1} \beta(K) det(K, j) \Psi_{K,j}(\ell)$$

where $\Psi_{K,j}(\ell)$ is a basic function designated above ψ

and $\varphi_K(\ell)$ is the corresponding scaling function, $\alpha(K)$ and $\beta(K)$ are weight coefficients for corresponding expanding level K . Relation $x(\ell)$ obtained as a result of described procession for one of examined wafers surface sections, as mentioned above is shown in Fig. 2b.

Stated above assumption about the presence of periodic components in investigated dependence and the possibility of their extraction by using wavelet filtering confirm the data shown in Fig. 3. This figure contains two wavelet spectrograms [10], each of them represents coefficient $W(k_i, \ell_j)$ dependence of value ℓ and level of expanding K . Spectrograms have obtained for the primary and wavelet filtered dependence $x(\ell)$ for the section indicated I in Fig. 1a. Dark areas on spectrograms correspond to positive and light ones to negative values of $W(k_i, \ell_j)$. This coefficient limits are allocated with shades of gray. Comparing the figure parts one to another one can see that region for which $K = 1 - 7$ have become more homogeneous as a result of filtering. This region corresponds to a fluctuating change of “composition signal”. However, remaining part of the spectrogram has not experienced any change. It is important that at this part light and dark areas alternate in certain directions which could indicate the presence of periodic changes in solid solution composition.

With the purpose of determining periodic components in dependencies $x(\ell)$ for different sections filtered ones have been subjected to a Fast Fourier Transform (FFT). Results of this transform for three sections at one of investigated wafers (see. Fig. 1a) are shown in Fig. 2c. It can be seen that each of sections is characterized by own composition distribution (i.e., x) in the k -space.

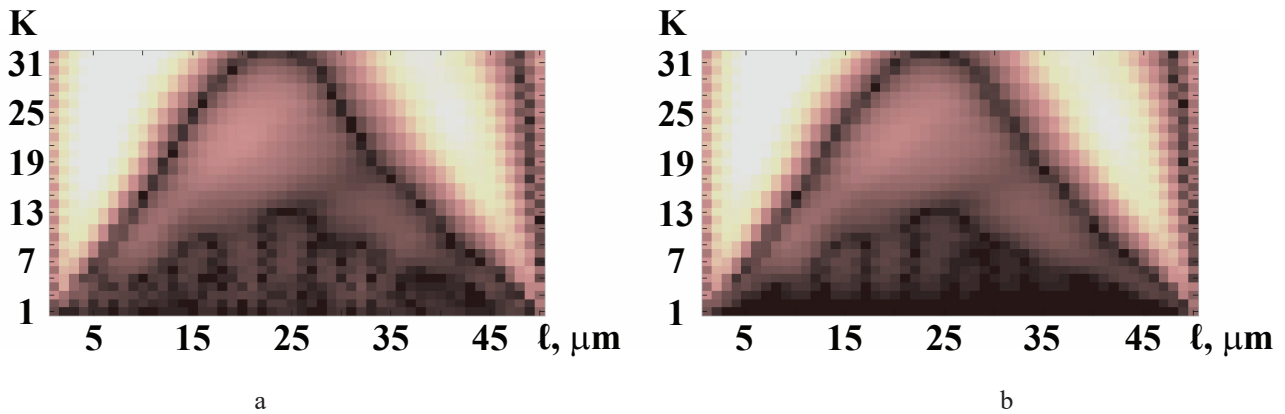


Fig. 3. $x(\ell)$ dependence wavelet spectrograms for one of crystal surface sections before (a) and after (b) wavelet filtration.

Moreover, such distributions have two or three dominant peaks (“composition harmonics”).

The fact that the amplitude of these harmonics is relatively small, taking into account Zn content measurement error given above is essentially important. It raises the question are whether detected periodic variations in the composition due to their smallness real. In our opinion, in favor of an affirmative answer to this question suggests not only described features of wavelet spectrograms (see. Fig. 3), but also the observation of “composition harmonics” on a number of sections oriented with its surface along growth direction on different samples. In view of it we should note that the analysis of other solid solution components content with method set above also showed the presence of harmonic components in changes of these magnitudes. And the greatest amplitudes of these harmonics for Cd and Te atoms were as a rule 2-3 times higher than for Zn atoms.

Among possible causes of observed self-organization composition in $Cd_{1-x}Zn_xTe$ crystals, obviously, should be excluded those are characteristic for the thin layers and are closely linked to their surface [4]. In addition, it is unlikely that mechanical stresses occurred due to heterogeneity play a key role in mentioned self-organization since the difference in lattice constants of ZnTe and CdTe crystals is about 6% [15]. Spinodal decomposition of the solid solution should also be excluded as another reason because according to [16], the critical temperature of such decomposition in $Cd_{1-x}Zn_xTe$ crystals with $x < 0.3$ is significantly below 300 K. Taking all this into account, we assume that the most likely cause of composition self-organization in investigated crystals are self-oscillating (auto-wave) processes in their growth. Similar processes were observed in growing crystals of different composition by various methods. Therefore it’s not surprising that different mechanisms of self-oscillations near the surface of the growing crystal are suggested. Although uncontrolled impurities can affect the growth of investigated crystals,

but in our opinion auto-wave processes during crystallization none the less have a different nature. We mean transient convection currents in the melt, which basic conditions of occurrence are non-uniform temperature field and the large size of the growing crystal [18]. This assumption consists not only with considerable dimensions of investigated crystals (see. Fig. 1a), but also with observation of several “harmonics composition” on them (see. Fig. 2c). Mentioned work ascertained that in unsteady convection mode energy spectrum of temperature fluctuations has a discrete character. Convection currents distinction near different crystal zones seems to be natural. It can explain peculiarities of $x(\ell)$ dependencies in k – space for different ingot zones. Of course study of convection currents in specific thermal growth conditions of $Cd_{1-x}Zn_xTe$ crystals in connection with their composition peculiarities lays as separate problem.

Observation of dielectric properties anisotropy in crystals matches expressed assumption about their growth peculiarities. Fig. 1b illustrates this peculiarity of properties. It shows the typical dependences of anisotropy coefficients

$$K' = \frac{\varepsilon'_y}{\varepsilon'_z} \text{ and } K'' = \frac{\varepsilon''_y}{\varepsilon''_z} \text{ for real and imaginary components}$$

ε^* dependencies measured in the direction indicated by the subscript (see. Fig. 1a). Coefficients values are averaged over all samples of the same plate to eliminate possible influence on the measurement results of two-dimensional structural defects on the measurement results cause they have a random orientation and are clearly visible on the polished wafer surface. We notice that such defects are characteristic for melt-grown $A^{II}B^{VI}$ crystals with cubic modification [19]. As we can see from Fig. 1b, the direction of their growth is physically marked at electric polarization of investigated crystals in low-frequency region.

Conclusion

1. That way the wavelet analysis allowed to reveal the spatial ordering of $Cd_{1-x}Zn_xTe$ crystals composition which has a significant influence on their dielectric properties.

2. Investigation of such composition feature is important both for complete study of its connection with electric and other crystal properties and to improve the technology of their growth.

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