NONDESTRUCTIVE BAND-GAP PROFILE DETERMINATION OF HgCdTe LPE GROWN LAYERS

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Abstract Infrared transmission and photoconductivity spectra of mercury-cadmium telluride (MCT) epitaxial layers, grown by liquid phase epitaxy (LPE) on CdTe and CdZnTe wide band-gap substrates, were investigated both theoretically and experimentally at temperatures $T = 82$ K and $T = 300$ K in the infrared (IR) wavelength region 3-15 μm. The photoresponse position of the diodes was determined at cryogenic temperatures from the transmission spectra of room temperature. Theoretical calculations of optical density $D(\hbar\omega)$, needed for analysis of experimental optical transmission data, were performed in the framework of WKB approximation.

Key words mercury-cadmium telluride, graded band-gap, epitaxial layers.

Introduction

Most of modern $Hg_{1-x}Cd_xTe$ ternary compound IR photodetectors are manufactured from LPE films grown on CdTe and CdZnTe substrates[1~4]. Compositional depth nonuniformity seems to be an inherent feature of these films[5,6]. It causes the variations of band-gap with the depth, thus affects the IR device performance. In-plane composition nonuniformity also influences the physical properties of LPE-grown layers as well as the performance of IR devices on their substrates.

Despite the fact that the effect of composition grading on the optical, photoelectrical and electrical properties of $Hg_{1-x}Cd_xTe$ LPE-grown films has been investigated in several papers[7~13], some problems are still to be studied, especially in the case of noticeable and nonlinear compositional (and thus, band-gap) gradient, which is observed in some LPE-grown layers.

In LPE films with graded band-gap, the optical absorption differs from that in homogeneous layers due to the depth variation of band-gap $E_g(z)$. If the spatial variation of $E_g(z)$ on the scale of the light wavelength is weak enough, the WKB approximation can be used for theoretical calculations. Then the spectral dependence of the optical density $D(\hbar\omega)$ can be described by the following expression[14~16]

$$D(\hbar\omega) = \int_0^d \alpha(\hbar\omega, z)\,dz = \int_{E_{g\min}}^{E_{g\max}} \alpha(\hbar\omega, E_g)\frac{\partial z}{\partial E_g}dE_g, \qquad (1)$$

where d is the thickness of a film, $\alpha(\hbar\omega, z)$ is the local absorption coefficient, $E_{g\min}$ and $E_{g\max}$ are minimum and maximum energy gap of the layer, respectively. Both of them are dependent on the film depth between $z = 0$ and $z = d$. These points are shown in Fig. 1(a), where the energy diagram of the layer with linear and exponential band-gap grading is schematically shown.

It follows from (1) that $E_g(z)$ can be established if the values of $E_{g\min}$, $E_{g\max}$ and $\alpha(\hbar\omega, E_g)$ are known. With $\alpha(\hbar\omega, E_g)$, it is possible to calculate the dependence of $D(\hbar\omega)$ as well as $T(\hbar\omega)$ (optical transmission spectra) on the gradient composition of the layers by using a gradient $\Delta E_g/\Delta z$ as a fitting parameter.

In application to LPE $Hg_{1-x}Cd_xTe$ films, a simular problem of determining the dependence of $E_g(z)$ on the depth of film was investigated in several papers[8~13,17]. In [9] the value of $E_{g\min}$ and

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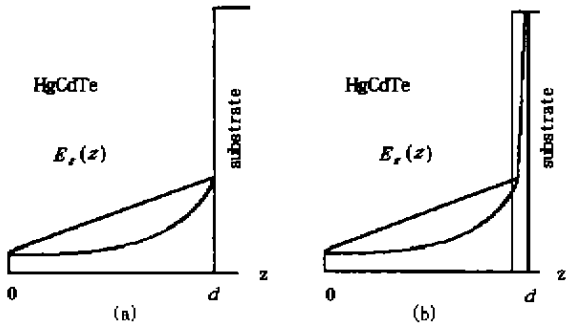

Fig. 1 Schematic energy diagram showing linear and exponential band gap grading in LPE $Hg_{1-x}Cd_xTe$ films without (a) and with (b) transition region at the interface

the thickness of the film are considered to be known, and $\triangle E_g/\triangle z$ is assumed to be constant. In [8] the determination of these parameters from the transmission spectra $T(\hbar\omega)$ of gradient films was attempted. The compositional profile $x(z)$ was represented by an expression with three fitting parameters. However, these parameters seem to be not independent. As was shown in [10], one can find several groups of parameters to fit experimental data rather well. In order to eliminate uncertainties in calculations, the total number of fitting parameters should be decreased.

The aim of this paper is to use the IR transmission measurements, both for the nondestructive determination of band-gap variation with the depth of MCT LPE-grown films, and for predicting their photosensitivity spectral position at cryogenic temperatures from the room temperature transmission spectra measurements.

1 Experimental results and analysis

The films investigated were grown by LPE method on (111) CdTe and $Cd_{1-y}Zn_yTe$ ($y=0.03-0.04$) substrates. Their thickness d was ranged from 15 μm to 35μm . The films were of p-type conductivity with a hole concentration $P_{77}=(6-20)\cdot 10^{15}$ cm^{-3}. IR transmission spectra were measured by using a grating spectrometer. Prior to the measurements, the films were etched in HBr + Br_2 solution for a short time to refresh the surfaces of the films. After etching, the films with mirror-like surfaces were investigated.

The calculated and measured $T(\hbar\omega)$ curves are shown in Fig. 2 and Fig. 3. The calculations were carried out in accordance with a technique developed for graded band-gap GaAlAs films[16]. The spectral region was divided into three parts: $\hbar\omega\leqslant E_{g\min}$, $E_{g\min}\leqslant\hbar\omega\leqslant E_{g\max}$, and $\hbar\omega\geqslant E_{g\max}$.

At photon energies $\hbar\omega<E_g$, the absorption coefficient in $Hg_{1-x}Cd_xTe$ crystals well obeys the Urbach rule[18]:

$$\alpha=\alpha_0\exp\left(\frac{\hbar\omega-E_0}{\Delta}\right), \tag{2}$$

where α_0, E_0 and Δ are determined experimentally from the study of the spectra of the fundamental absorption edge. Here, the parameter E_0 is close to the band-gap value.

In the present work, E_0 was taken to be equal to $E_g(z)$, i.e., the band-gap at a depth z. The parameter Δ was determined from the slope of the measured

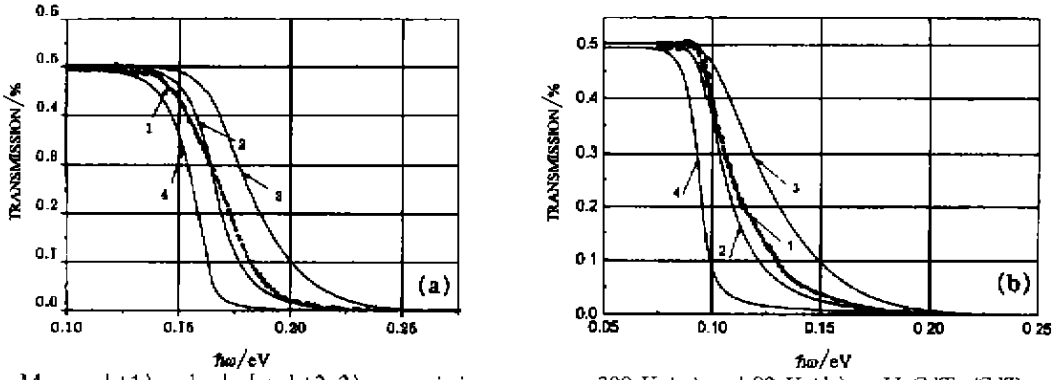

Fig. 2 Measured (1) and calculated (2,3) transmission spectra at 300 K (a) and 82 K (b) in HgCdTe/CdTe epitaxial film. Curves 2 and 3 are calculated for exponential and linear band gap gradient, respectively, whit parameters $E_{g\min}=0.162$ eV, $E_{g\max}=0.268$ eV ($T=300$K) and $E_{g\min}=0.097$ eV, $E_{g\max}=0.218$ eV ($T=82$K). Curves 4 are calculated for bulk crystal with $E_g=0.162$ eV and 0.097 eV at 300 K and 82 K, respectively. The thickness of the film is 15μm

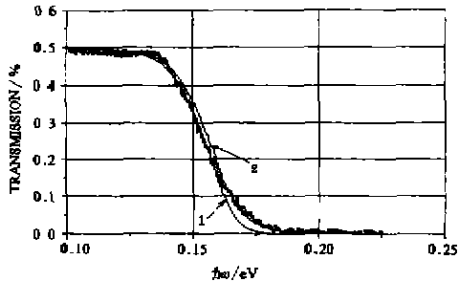

Fig. 3 Optical transmission spectra in HgCdTe/CdZnTe epitaxial film at 300 K. Theoretical curves are calculated for linear (1) and exponential (2) band gap gradient for $E_{g\min}=0.155$ eV, $E_{g\max}=0.190$eV. The thickness of the film is 35μm

$T(\hbar\omega)$ curves at $\hbar\omega<E_{g\min}$. The value of α_0 was derived from the fitting procedure for each sample separately. The best fit was obtained for α_0 ranging from 800 to 1500 cm^{-1}.

In the second spectral region, direct optical transitions for photons with energies $\hbar\omega>E_g$ are added to optical transitions within the Urbach's tail region. In the third region, absorption occurs only due to the direct optical transitions from the valence bands (light and heavy hole) to the conduction band. For calculations, the appropriate expressions of local absorption coefficient obtained in [19] were used. Also, calculations were carried out for absorption coefficient used by [9].

Two types of $E_g(z)$, the linear and the exponential ones, were chosen for calculations and fitting procedure. The exponential dependence $E_g(z)$ was approximated by:

$$E_g(z)=E_0+a\exp(z/b), \tag{3}$$

where constants E_0, a and b were determined for $z=0$ and $z=d$, provided that $E_{g\min}$ and $E_{g\max}$ are known. It is seen from Fig. 3 that in the samples with low band gap gradient the data calculated are not very sensitive to the choice of $E_g(z)$ dependence. However, this seems not to be the case for the sample with rather high gradient (see Fig. 2).

Following approach was used to estimate $E_{g\min}$ and $E_{g\max}$ values. In accordance with the theory developed in [15], the second derivative, $\partial^2 D(\hbar\omega)/\partial(\hbar\omega)^2$, should have extremas at energies where density of states has singularities. At least two singularities are to be observed if $E_g(z)$ is represented by smooth curve (see Fig. 1). Obviously, the first one is located at $z=0$. Without a transition region at the interface (see Fig. 1(a)), the second one is located at $z=d$, where density of states is significantly changed due to the abrupt band-gap variation. In the films with the transition region (see Fig. 1(b)) the exact form of $E_g(z)$ at the interface is unknown and its location can be defined within the accuracy of the thickness of this region. Typical spectra dependencies of the second derivatives of the optical density are shown in Fig. 4 and Fig. 5 for samples with different values of the band gap gradient. It is seen that two extremas are observed for experimental curves. Their energies were identified with minimum $E_{g\min}$ and maximum $E_{g\max}$ band gaps in the film. It should be pointed out that $E_{g\min}$ and $E_{g\max}$ can be defined unam-

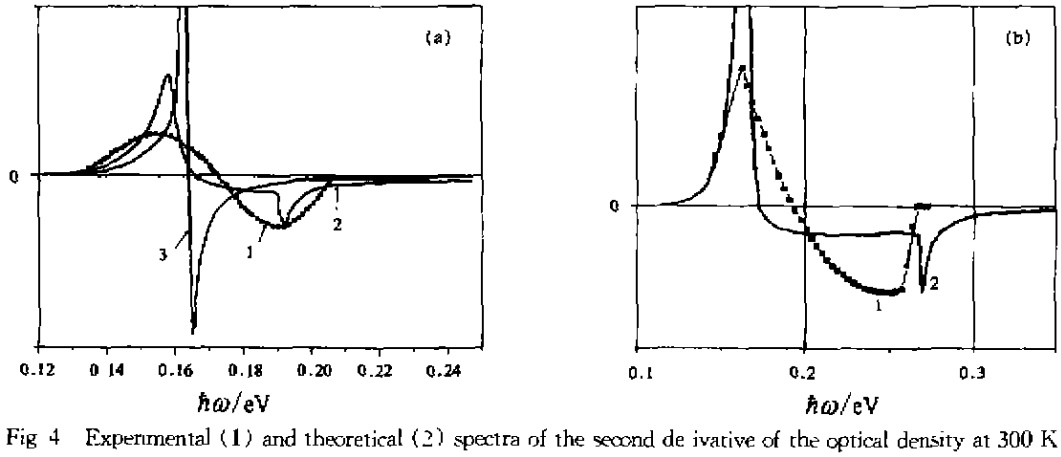

Fig 4 Experimental (1) and theoretical (2) spectra of the second derivative of the optical density at 300 K. Experimental data shown in (a) and (b) were derived from the optical transmission data shown in Fig. 3 and Fig. 2(a), respectively. The theoretical curve (3) is for bulk crystal.

biguously for LPE films without a transition region at the interface. In the opposite case, when the transition region is present, $E_{g\max}$ means an effective band gap at the interface between the epitaxial layer and the substrate.

If the band gap gradient is essential, the applicability of WKB approach becomes less obvious. In LPE grown films especially, the condition of applicability of WKB approach can be violated at the interface. However, the theory in [15] predicts that the behavior of the second derivative is still preserved, except that its amplitude decreases. In order to analyze this situation, computer simulation for different gradients was performed (see Fig. 5). If one compares the data shown in Fig. 4(a) and Fig. 4(b), it is seen that, in the samples with rather low band gap gradient, the experimental and calculated curves coincide well enough.

Increasing the band-gap gradient gives rise to the disagreement between experimental and calculated data. For instance, the best fit between the experimental and calculated curves $T(\hbar\omega)$ shown in Fig. 2(a) was achieved at $E_{g\max}=0.268$ eV that exceeds $E_{g\max}=0.250$ eV obtained from the experiments (Fig. 4(b)). The second derivatives of experimental transmission spectra curves have higher half-width values in comparison with the calculated ones. Similar results were obtained previously[15] for LPE films with linear band gap gradient.

The disagreement between experimental and calculated spectra can arise due to several reasons. The divergence in transmission data may cause large fluctuations in the second derivatives. Some smoothing is thus required before making differentiation. This may shift the position of the derivative peaks[15] as well as their half-width. The interface transition region may also affect both the amplitude and position of the derivative peak at energies close to $E_{g\max}$. In theoretical calculation, this region has not been taken into account.

By using the data obtained at $T=300$ K and the following expression[20] for band-gap as a function of composition and temperature

$$E_g(x,T)=-0.302+1.93x-0.81x^2+0.832x^3+5.32\cdot10^{-4}\cdot(1-2x)\left[\frac{-1822+T^3}{255.2+T^2}\right] \quad (4)$$

$x(z)$ can be calculated (Fig. 6). Chemical composition was also determined independently in cleaved samples by using the local X-ray microanalysis data. Within the experimental errors, the composition data measured agree well with those obtained from the analysis of the $T(\hbar\omega)$ spectra.

Gap profile was measured by photoconductive spectra combined with sequential removal of layers by chemical etching in Hbr + Br_2 solution. The gap was determined from the peak wavelength λ_p corresponding to the maximum of the normalized photoconductivity spectrum (see Fig. 7). The data obtained from the photoconductivity and optical trans-

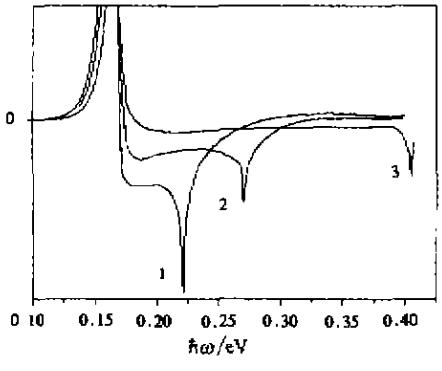

Fig. 5 Calculated spectra of the second derivative of optical density at $T=300$ K for the epitaxial film with thickness $d=15\mu$m and different gradient values: $\triangle E_g/\triangle V_z=38$ eV/cm (curve 1), $\triangle E_g/\triangle_Z=70$ eV/cm (curve 2) and $\triangle E_g/\triangle_z=160$ eV/cm (curve 3)

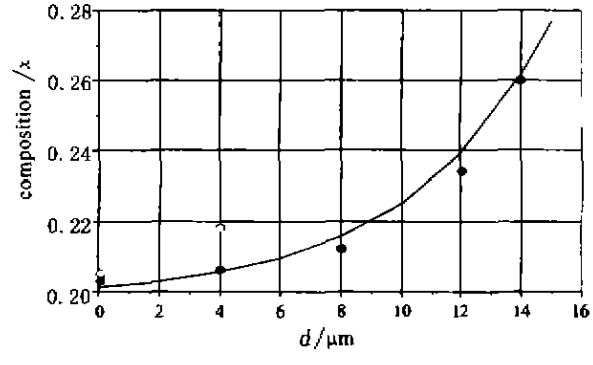

Fig. 6 Composition profile obtained from the optical transmission (solid line), X-ray microanalysis data (close dots) and photoconductivity (open dots). The composition obtained from X-ray microanalysis is determined within experimental errors $\Delta x=0.005$

mission spectra for the films with compositional gradient are not well correlated in contrast to the case for the bulk crystals without a band gap grading[21]. The disagreement is extremely pronounced for the thin film at approximately 3～4 μm. For this film the influence of the transition region is more pronounced. Obviously, the transmission spectrum of a rather thick film is less sensitive to the presence of the transition region.

The composition $x(z)$ found at room temperatures was used for the calculation of $T(\hbar\omega)$ spectra at $T = 82$ K, as shown in Fig. 2(b). One can see that the calculated and experimental curves agree well.

According to the procedure described above, the layers with rather low composition gradient (the built-in electric field $E_0 = dE_g/dz$ was estimated to be less than 30 V/cm) were investigated too. In this case, both composition and energy gap can be well approximated by the linear dependence on the depth z.

The linear dependence of the gap on the depth results in the constant electric field E_0 throughtout the film. The continuity equation [22,23] is

$$\frac{d^2\Delta n}{dz^2} - \frac{\mu_n E_0 \tau_n}{L_n^2}\frac{d\Delta n}{dz} - \frac{\Delta n}{L_n^2} = -\frac{G(z,\hbar\omega)}{D_n}, \quad (5)$$

where Δn is the concentration of the photogenerated carriers and $G(z,\hbar\omega)$ is optical generation rate. In equation (5) the diffusion coefficient D_n and diffusion length L_n are assumed to be independent on the composition. The boundary conditions are

$$J_{(ph)}(z=0) = -qD_p\left[\frac{\partial\Delta n}{\partial z}\Big|_{z=0} - 2m\Delta n(z=0)\right] = -qS_n\Delta n(z=0),$$

$$J_{(ph)}(z=d) = -qD_p\left[\frac{\partial\Delta n}{\partial z}\Big|_{z=d} - 2m\Delta n(z=d)\right] = -qS_n\Delta n(z=d), \quad (6)$$

where $m = qE_0/2kT$. Here S_n is the surface recombination velocity, and W_p is the width of the depletion layer.

The solutions of equation (5) were used for the calculations of photoconductivity spectra. Experimental and calculated spectra for p-$Hg_{1-x}Cd_xTe$ film with different band gap gradient are shown in Fig. 8. Figure 8 shows that in compositionally graded film the calculated spectra are shifted towards short wavelength region and this shift is large enough. And the calculations for the known composition gradient (curve 2) reasonably well coincide with the experimental data.

Hence, by analyzing $T(\hbar\omega)$ at room temperature, it is possible to predict photosensitivity spectra at 77K of $Hg_{1-x}Cd_xTe$ films with varying band-gap gradient.

2 Conclusions

The measured and calculated spectra of optical transmission in the graded-band-gap HgCdTd epitaxial layers ($E_g \leqslant 0.25$ eV) grown by LPE on the wide

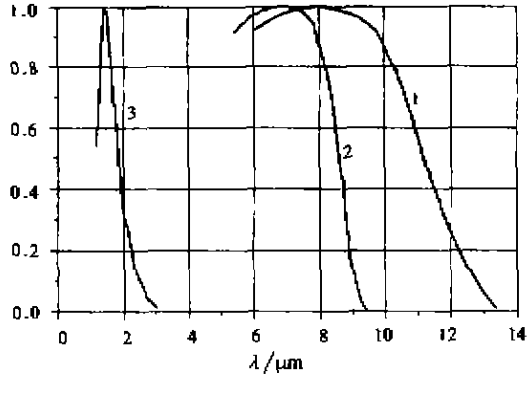

Fig. 7　Photoconductivity spectra at 82 K measured for as-grown film (1) and that sequentially etched in HBr + Br_2 solution for one minute (2) and three minutes (3). The thickness of as-grown film is 15μm

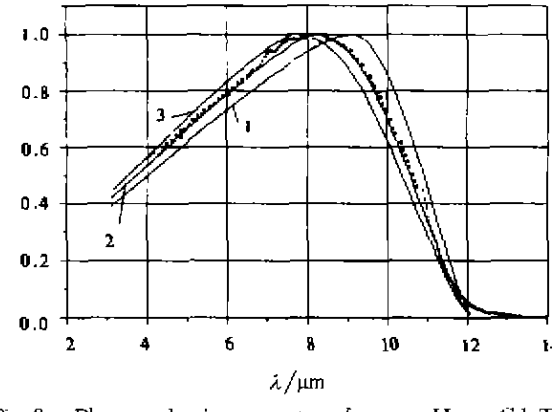

Fig. 8　Photoconductivity spectra of p-type $Hg_{1-x}Cd_xTe$ epitaxial layer with different composition gradient at $T = 77$ K. Dots are experimental data, and curves 1,2,3, are calculated data for gradients 30, 47 and 60 eV/cm, respectively. $E_{g\min} = 0.102$ eV, and film thickness $d = 10\mu$m are the same for all these curves

gap CdTe and CdZnTe substrates gave the possibility to establish nonlinear character of band gap (and compositional variation) with the depth of HgCdTe thin layers. From the above investigation, one can conclude that the optical transmission $T(\hbar\omega)$ spectra in $Hg_{1-x}Cd_xTe$ LPE grown films with graded band-gap are sensitive to the absolute value of the band gap gradient as well as to the form of the $E_g(z)$ which may be exponential or linear.

Our result shows it is possibile to define the photoresponse spectra of these layers at $T=77$ K and the operation temperature of photodetectors by using the measurements of optical transmission of HgCdTe graded-gap layers at $T=300$ K.

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