The determination of the x value in doped $Hg_{1-x}Cd_xTe$ by transmission spectra*

Yue Fang-Yu(越方禹)[a)†], Chen Lu(陈 璐)[b)], Li Ya-Wei(李亚巍)[a)], Sun Lin(孙 琳)[a)], Yang Ping-Xiong(杨平雄)[a)], and Chu Jun-Hao(褚君浩)[a)c)]

[a)] *Key Laboratory of Polar Materials and Devices, Ministry of Education, East China Normal University, Shanghai* 200241, *China*

[b)] *Research Center for Advanced Materials and Devices, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai* 200083, *China*

[c)] *National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai* 200083, *China*

(Received 4 May 2011; revised manuscript received 20 May 2011)

Variable-temperature transmission/absorption spectra are measured on As-doped $Hg_{1-x}Cd_xTe$ grown by molecular beam epitaxy. The nonlinear temperature-dependent shift of the absorption edge is also observed, which is similar to our previous report on V_{Hg} (unintentionally)-doped HgCdTe. By referring to the empirical formulas of $E_g(x,T)$, the x value of the epilayer is calculated and its inconsistency between the extreme temperatures (e.g. 10 and 300 K) is discussed. The results confirm the assumption of the effect of shallow levels on the shift of the absorption edge, and suggest that the x value (or E_g) in intrinsic/extrinsic-doped HgCdTe should be determined by referring to as low a temperature as possible (e.g. 10 K), and not the commonly used temperatures of 77 or 300 K, when the transmission spectrum should be employed. This can give brief guidelines for fabricating HgCdTe-related devices.

Keywords: intrinsic/extrinsic-doped HgCdTe, bandedge parameters, transmission spectra

PACS: 78.30.Fs, 78.66.Hf, 78.20.Ci **DOI:** 10.1088/1674-1056/21/1/017804

1. Introduction

Mercury cadmium telluride (HgCdTe) as a narrow-gap semiconductor has been found to have wide applications in infrared detection. For fabricating high-performance HgCdTe-related devices, p-type doping has been widely investigated by intrinsic cation vacancy (V_{Hg})-doping during the past few decades. Nowadays, more attention is being paid to the extrinsic doping of arsenic (As) for its vital advantages in realizing extrinsic p-type conduction.[1,2]

To obtain the key parameters of HgCdTe materials and devices, intrinsic absorption spectra, normally at a temperature of 77 K (liquid nitrogen temperature) or 300 K (room temperature), have been frequently employed to analyse the bandgap (E_g) or cut-off wavelength, and accordingly the composition (x value) can be deduced by referring to empirical formulas, e.g. CXT by Chu *et al.*[3] or HSC by Hansen *et al.*,[4]

$$\begin{aligned} E_g(\mathrm{CXT}) &= -0.295 + 1.87x - 0.28x^2 \\ &\quad + (6 - 14x + 3x^2)(10^{-4})T + 0.35x^4, \quad (1) \\ E_g(\mathrm{HSC}) &= -0.302 + 1.93x + (1 - 2x)5.35(10^{-4})T \\ &\quad - 0.81x^2 + 0.832x^3. \quad (2) \end{aligned}$$

From the equations we can see that, for a given sample, its bandgap (E_g) should change linearly with temperature. However, the issue of how to determine the composition (x value) in intrinsic/extrinsic-doped HgCdTe remains to be addressed when the abnormal shift of the absorption edge with temperature has been reported in unintentionally (V_{Hg})-doped HgCdTe, as in our previous work.[5,6]

In this paper, the x value of As-doped (and V_{Hg}-doped) HgCdTe is discussed by measuring transmission/absorption spectra at different temperatures.

*Project supported by the National Basic Research Program of China (Grant No. 2007CB924901), the Shanghai Leading Academic Discipline Project, China (Grant No. B411), the National Natural Science Foundation of China (Grant Nos. 60906043, 60990312, and 61076060), the Shanghai Municipal Commission of Science and Technology Project, China (Grant Nos. 09ZR1409200, 10ZR1409800, and 10JC1404600), the Specialized Research Fund for the Doctoral Program of Higher Education, China (Grant No. 20090076120010), and the Fundamental Research Funds for the Central Universities, China (Grant No. 09ECNU).

†Corresponding author. E-mail: fyyue@ee.ecnu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

Instead of studying the reported nonlinearity of absorption-edge versus temperature, we discuss the observed difference in determined composition between typical temperatures (e.g. 10 and 300 K). The results suggest that: 1) the shallow acceptors in HgCdTe influence the linear shift of absorption edge with temperature, and the degree of the nonlinear shift depends on the density and the ionization energy of shallow levels; and 2) the transmission spectrum should be measured at an extreme low temperature (e.g. 10 K) to accurately determine the E_g (or x value) in doped HgCdTe, since those from the frequently used temperature of 77 or 300 K are diminished to some extent for the existence of the shallow levels.

2. Experimental details

The molecular beam epitaxy (MBE) samples were grown on undoped semi-insulating GaAs (211)B substrates at a normal growth temperature with a CdTe buffer layer over 3 μm, based on which the As doping was performed. For p-type conduction, the epilayers were followed by different annealing conditions (e.g. the two-stage annealing process).[7,8] As a result, the p-type epilayers at 77 K were due to the high density of either As_{Te} (As occupying Te lattice sites) or V_{Hg} (residual) or their compounds.[9,10] For comparison, the unintentionally (V_{Hg})-doped HgCdTe epilayers grown by MBE and liquid phase epitaxy (LPE, on the substrate of CdZnTe) were also prepared.[11]

The absorption spectra were measured by an evacuated Fourier transform infrared spectrometer, which was equipped with a beamsplitter of KBr and a liquid-nitrogen-cooled HgCdTe detector. The spectral resolution was set at 2 cm^{-1}. Before the experiment, the samples were treated with a quick etch to avoid the influence of surface smear, and then mounted on the cold finger of an Oxford recycling cryostat, of which the temperature could be continuously adjusted from 10 to 300 K.

3. Results and discussion

As reported in our previous work,[5,6] a non-monotonic shift of the absorption edge with increasing temperature has been observed in unintentionally (V_{Hg})-doped HgCdTe epilayers grown by LPE and MBE, where the abnormal (S-shape like) shift was tentatively ascribed to the existence of the intrinsic impurity of V_{Hg}, and the ionization energy of it was then roughly deduced to be ∼15 meV by calculating the energy difference of the abnormal shift of the absorption edge.

Following the traditional measurement, here we systematically performed variable-temperature transmission spectra on As-doped HgCdTe epilayers grown by MBE with p-type by annealing under different activation conditions. To obtain the evolutive mechanism of the absorption edge accurately, a temperature step of 5 K was used from 10 to 100 K during the measurement of the transmission spectra. Figure 1 gives the transmission spectra of a p-type As-doped HgCdTe at typical temperatures, where the doped As has been fully activated as As_{Te} by a two-stage annealing condition so that almost no other impurity level but As_{Te} exists in the epilayer, as described elsewhere.[9] From Fig. 1 we can see that the absorption edge shows a similar S-shape-like shift as temperature increases from 10 to 100 K (marked by the arrow curve). For clarity, we calculate the corresponding absorption coefficient spectra at different temperatures, and the results are shown in the inset of Fig. 1. It is obvious that the shift of the absorption edge energy (the so-called bandgap or E_g) is nonlinear with the change of temperature, in contrast to the well-known empirical formulas (e.g. CXT in the figure) that should represent a super-linear relationship of bandgap versus temperature ($E_g \sim T$). The abnormal shift energy of the absorption edge can be deduced to be about 10.2 meV by extrapolating the fitting line of the higher temperature part over 77 K (dashed) to 0 K, which may be attributed to the existence of extrinsic impurity levels (e.g. As_{Te} or related) if we take into account the foregoing assumption of V_{Hg} in unintentionally-doped epilayers. Correspondingly, the value of ∼ 10.2 meV can be ascribed to the ionization energy of As_{Te}, which is close to the results from other optical techniques and electrical measurements.[12−14]

It should be pointed out that a similar phenomenon of the absorption edge has also been observed in other As-doped epilayers with p-type conduction, regardless of As-activation, which means that the p-type may originate from the activated As_{Te} or the residual V_{Hg}, or the compound effect of these acceptors and the donor of As_{Hg} (unactivated As by occupying Hg lattice sites). Among these samples, the typical differences are the critical temperature point (generally from 30 to 100 K, covering the work tem-

perature of 77 K of HgCdTe) where the S-shape-like shift occurs, and the degree of the nonlinear shift energy. In this case, it is evident that the existence of the extrinsic impurity level of, for example, As_{Te} has the same effect on the shift of the absorption edge with increasing temperature as the intrinsic impurity level of V_{Hg}, and the ionization energy of the impurity levels in extrinsic/intrinsic-doped HgCdTe can be roughly evaluated from the variable-temperature transmission spectra.

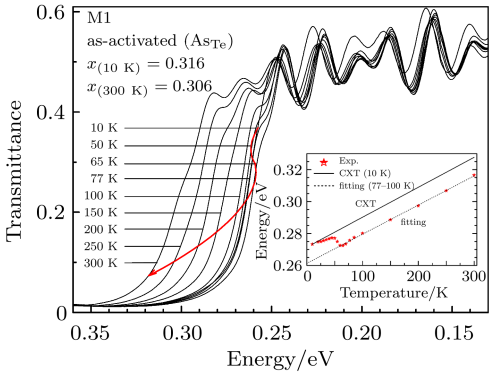


Fig. 1. (colour online) The transmission spectra of a p-type MBE-grown HgCdTe (As-activated) at different temperatures. The inset shows the result of calculated absorption coefficient spectra at different temperatures. The x value is evaluated by the transmission spectrum of 10 K, and its evolutive trend of E_g with temperature has been shown by CXT.

It is widely received that the x value in $Hg_{1-x}Cd_xTe$ can be accurately calculated from the absorption edge energy (by calculating the absorption coefficient spectrum at a certain temperature) by referring to the $E_g \sim x$ relationships (e.g. CXT or HSC in Eqs. (1) and (2), respectively). However, the linearity of $E_g \sim T$ represented by the equations is inconsistent with the nonlinear relationship of absorption edge energy versus temperature in the foregoing samples. Therefore, a key issue of how to determine the x value (or E_g) in doped HgCdTe should be addressed, that is, which temperature point (e.g. 10, 77, 300 K or any other temperature) should be referenced to when the transmission spectrum is used to determine the actual E_g, and to further evaluate the x value in doped-HgCdTe.

According to the absorption edge energy of the absorption coefficient spectrum (e.g. as shown in the inset in Fig. 1), we calculated the x values of all the samples at the two extreme temperatures of 10 and 300 K, separately, and the results are listed in Table 1, together with the values of their difference (Δx). For comparison, the calculated results of unintentionally (V_{Hg})-doped LPE samples are also shown in this table. Note that the sample MBE4 in Table 1 is As-unactivated, meaning that the doped As mostly acts as the donor of As_{Hg}. Thus, the p-type at 77 K in MBE4 suggests that acceptors like V_{Hg} (residual) and As_{Te} (potential) prevail over the donors of As_{Hg} or related.[15–17] From Table 1 we can see that the calculated x value of every sample at the lowest temperature of 10 K is not in accordance with that at the highest temperature of 300 K. In fact, the former is evidently smaller than the latter with a non-neglectable separation of about 0.009–0.021. However, a prepared sample should have a fixed composition, even if the post-growth annealing process has been imposed. Therefore, we should predict which x value in the table is the actual one for the corresponding sample.

By combining the interpretation of the abnormal shift of the absorption edge in V_{Hg}-doped HgCdTe[5] and the results of As-doped epilayers in this work, we can schematically depict the transition process of carriers related to impurity levels in the measurement of transmission spectra. Figure 2 shows the temperature dependence of the transition of carriers in p-type HgCdTe with three typical temperature ranges based

Table 1. Sample parameters including the major impurity, the carrier density (N_c) and its mobility (M_c) at 77 K, the calculated x values at 10 and 300 K, and their difference values (Δx).

	Major impurity	$N_c/10^{15}$ cm^{-3}	M_c/cm$^2 \cdot$V$^{-1} \cdot$s^{-1}	x_{10K}	x_{300K}	Δx
MBE1	As_{Te} (As-activated)	36.0	290	0.316	0.306	0.010
MBE2	As_{Te} (As-activated)	32.7	295	0.300	0.284	0.016
MBE3	V_{Hg} (undoped)	10.1	261	0.293	0.304	0.011
MBE4	As-unactivated[a)]	12.3	259	0.298	0.285	0.013
LPE1	V_{Hg} (undoped)	5.78	455	0.315	0.306	0.009
LPE2	V_{Hg} (undoped)	5.89	525	0.346	0.331	0.015
LPE3	V_{Hg} (undoped)	5.48	667	0.250	0.229	0.021

[a)] Including the predominant As_{Hg}, the potential As_{Te} and the residual V_{Hg}.

on the nonlinear shift. As shown in the figure, the carriers located in E_a (e.g. As_{Te} or V_{Hg}) are inactivated (A^0, known as the frozen-out effect of carriers) at the extreme low temperature down to 0 K (see Fig. 2(a)) and can be slowly activated (A^-) to join the transition of carriers as the temperature increases (see Fig. 2(b)), which leads to the occurrence of the S-shape-like shift of the absorption edge.[6] That is to say, the contribution of the absorption edge is almost due to the valence band (VB)–conduction band (CB) transition of carriers at an extreme low temperature (10 K), but at an extreme high temperature (300 K) the transition of the absorption edge is then absolutely determined by both the VB–CB and A^-–CB transitions. At this moment, the transmission spectra cannot distinguish the two transitions, so that the absorption edge energy determined at high temperature (e.g. 300 K) does not indicate the actual E_g transition of the sample, while that at the lowest temperature (10 K) can. As a result, the x value at the highest temperature (300 K) has been diminished (or "red-shifted") for the existence of the shallow acceptors in p-type HgCdTe (e.g. by As_{Te} or V_{Hg} or the compound effect), but that at the lowest temperature (e.g. 10 K) approaches the actual composition. It is not difficult to understand that the abnormal shift of the absorption edge will disappear and the data of the absorption (coefficient) spectra can track the CXT results (see the inset in Fig. 1), providing that the shallow acceptor does not exist or does exist but without enough density. Theoretically, an effective way to judge the transition possibility of carriers in impurity levels (or the S-shape-like shift) is to calculate the Fermi levels in doped HgCdTe at different temperatures.

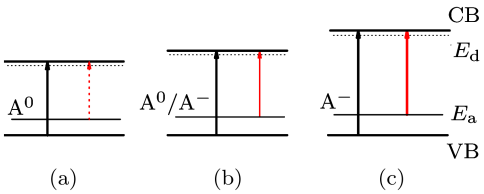


Fig. 2. (colour online) The absorption transitions of carriers in p-type HgCdTe at different temperatures. The E_a is only shown as a representative of the acceptors (e.g. V_{Hg}, As_{Te} or related). The thickness of the arrow line related to E_a simply denotes the possibility of the transition of carriers. (a) $T < 30$ K, (b) 30 K $< T <$ 100 K and (c) $T > 100$ K.

It should be mentioned that the energy of the absorption edge over 77 K up to 300 K varies linearly with the increase in temperature, and can almost match up with the CXT results of 300 K, as shown in the inset in Fig. 1, which hints that the calculated x value from the absorption coefficient spectrum at 77 K is close to that of 300 K. Thus, Table 1 only gives the x value of 300 K, but without showing that of 77 K. Here, we can see that the x value determined by the temperature of 77 or 300 K, which was frequently used to accurately determine the composition by measuring the transmission spectrum, cannot represent the actual x value and should be less than that of 10 K (or a lower temperature) if there exists a shallow acceptor like As_{Te} or V_{Hg} or their compounds in a high enough density. Of course the determined x values will be close to each other between the lowest and highest temperatures if the ionization energy of the shallow levels is not as big as the abnormal shift of the absorption edge appears. This is also the reason why we cannot observe the obvious S-shape-like shift of the absorption edge in intrinsic n-type HgCdTe, where the ionization energy of the intrinsic donor has been reported to be very small ($\sim$ 3 meV, also see the schematic position of E_d in Fig. 2).[18,19]

4. Conclusion

We investigated the determination of the x value (equivalently, E_g) in p-type HgCdTe (As/V_{Hg}-doped) by transmission spectra. The results further confirm the effect of shallow acceptors on the abnormal temperature-dependent shift of the absorption edge in doped-HgCdTe, and as a result a preliminary conclusion is drawn that the x value (or E_g) in doped-HgCdTe should be determined by transmission spectra at the lowest temperature (e.g. 10 K), since the frequently used temperatures of 77 or 300 K can make the determined x value decrease a little with the existence of shallow levels. The discussion also implies that a variable-temperature transmission spectrum can be used as a potential choice to roughly evaluate the ionization energy of the shallow level in narrow-gap HgCdTe semiconductors, as is done in other optical/electrical measurements.

Acknowledgments

We thank Prof. J. Shao for fruitful discussion.

References

[1] Sivananthan S, Wijewarnasuriya P S, Aqariden F, Vydyanath H R, Zandian M, Edwall D D and Arias J M 1997 *J. Electron. Mater.* **26** 621

[2] Edwall D, Piquette E, Ellsworth J, Arias J, Swartz C H, Bai L, Tompkins R P, Giles N C, Myers T H and Berding M 2004 *J. Electron. Mater.* **33** 752

[3] Chu J H, Xu S C and Tang D Y 1983 *Appl. Phys. Lett.* **43** 1064

[4] Hansen G L, Schmit J L and Casselman T N 1982 *J. Appl. Phys.* **53** 7099

[5] Yue F Y, Shao J, Lü X, Huang W, Chu J H, Wu J, Lin X C and He L 2006 *Appl. Phys. Lett.* **89** 021912

[6] Yue F Y, Shao J, Wei Y F, Lv X, Huang W, Yang J R and Chu J H 2007 *Acta Phys. Sin.* **56** 2878 (in Chinese)

[7] He L, Wang S L, Yang J R, Yu M F, Wu Y, Chen X Q, Fang W Z, Qiao Y M, Gui Y S and Chu J H 1999 *J. Cryst. Growth* **201/202** 524

[8] Wu J, Xu F, Wu Y, Chen L, Wang Y, Yu M and He L 2005 *SPIE* **5640** 637

[9] Yue F Y, Chu J H, Wu J, Hu Z G, Li Y W and Yang P X 2008 *Appl. Phys. Lett.* **92** 121916

[10] Yue F Y, Wu J and Chu J H 2008 *Appl. Phys. Lett.* **93** 131909

[11] Wang Q X, Yang J R and Wei Y F 2005 *Acta Phys. Sin.* **54** 5814 (in Chinese)

[12] Kenworthy I, Capper P, Jones C L, Gosney J J G and Coates W G 1990 *Semicond. Sci. Technol.* **5** 854

[13] Selamet Y, Grein C H, Lee T S and Sivananthan S 2001 *J. Vac. Sci. Technol.* B **19** 1488

[14] Shi X H, Rujirawat S, Ashokan R, Grein C H and Sivananthan S 1998 *Appl. Phys. Lett.* **73** 638

[15] Berding M A, Sher A, Schilfgaarde M V, Chen A C and Arias J 1998 *J. Electron. Mater.* **27** 605

[16] Sun L Z, Chen X S, Zhao J J, Wang J B, Zhou Y C and Lu W 2007 *Phys. Rev.* B **76** 045219

[17] Duan H, Chen X S, Huang Y and Lu W 2007 *Solid State Commun.* **143** 471

[18] Sun L Z, Chen X S, Sun Y L, Zhou X H, Quan Z J, Duan H and Lu W 2005 *Phys. Rev.* B **71** 193203

[19] Chang Y, Chu J H, Tang W G, Shen W Z, Tang D Y, Guo S P and Yuan S X 1995 *Acta Phys. Sin.* **4** 606 (Overseas Edition)