CHIN. PHYS. LETT. Vol. 26, No. 4 (2009) 047804

Impurity Activation in MBE-Grown As-Doped HgCdTe by Modulated Photoluminescence Spectra *

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(Received 1 September 2008)

Modulated photoluminescence spectra have been performed to investigate the impurity activation in MBE-grown As-doped $Hg_{1-x}Cd_xTe$ ($x \approx 0.3$). The results show that the doped As mainly acting as donors in the as-grown samples can be fully activated as As_{Te} by two-stage anneals of 285°C/16 h + 240°C/48 h, of which the ionization energy has been determined to be about 10.5 meV, slightly smaller than that of intrinsic V_{Hg} (about 14.5 meV). However, the higher activation temperature (e.g. 400°C) at the first-stage can produce large numbers of excessive V_{Hg} and seriously deteriorate the quality of epilayers. This could give a brief guideline for preparing extrinsic p-type HgCdTe materials or devices.

PACS: 78.66.−w, 71.55.Gs, 78.55.−m, 71.55.−i

HgCdTe as a narrow-gap semiconductor has found wide applications in infrared detection. To realize large-scale high-performance infrared detector focal plane arrays, p-type in-situ doping is crucial, for which the element arsenic (As) is the favourite dopant for stability and low diffusivity.[1] However, As is amphoteric in HgCdTe grown by molecular beam epitaxy (MBE) so that it can be incorporated as a donor (As_{Hg}) or acceptor (As_{Te}) under Te-rich or Hg-rich growth conditions, respectively. Numerous investigations from electrical techniques and theoretic calculations[2−4] have been employed to identify the As activation and its ionization energy, and a postgrowth anneal (particularly two-stage anneals) is proposed for preparing extrinsic p-type conductivity by transferring As occupying Hg-sublattices to Te-sublattices at low activation temperatures. To our knowledge, some issues are still to be addressed about the As-related ionization energy, optimized activation conditions and the physical mechanism of lower activation temperature, as well as the potential impurity levels under different annealing conditions.[5−8]

In this Letter, the modulated photoluminescence (PL) spectra based on the step-scan of Fourier transform infrared (FTIR) spectroscopy have been performed on MBE-grown As-doped $Hg_{1-x}Cd_xTe$ ($x \approx 0.3$) to investigate the impurity activation. The impurity levels and their corresponding ionization energies under different annealing conditions are discussed and determined by combining with the theoretical calculation reports, electrical measurements and our previous works.

HgCdTe epilayers were grown in a Riber 32P MBE system on undoped semi-insulating GaAs (211)B substrates at a normal growth temperature of 185°C. A CdTe buffer layer of about 3 μm thick was grown prior to the HgCdTe nucleation.[9] The doping level was about $3.35 \times 10^{16}\,cm^{-3}$ from As_4 source. The composition and thickness (typically ∼6.0 μm) were evaluated by FTIR transmission spectra at low temperature.[10,11] The as-grown epilayer (M21) was cleaved into several pieces (M03, M16) and then annealed under different annealing conditions, as described in detail elsewhere[12] and simply shown in Table 1. The As concentration was quantitatively analysed by the second ion mass spectrometer (SIMS) measurements, which illustrated that the As in M03 and M16 were fully activated as acceptors. It should be pointed out that the p-type M21 was converted to n-type after n-type anneals (240°C/48 h under Hg-saturated pressure to eliminate V_{Hg}). For comparison, an undoped sample (M11) was annealed under vacuum without the participation of Hg to control the density of V_{Hg}.

The modulated PL measurements were performed with a step-scan-based FTIR spectrometer (Bruker IFS 66 v/S).[13] The focused 514.5 nm line mechanically-chopped at 1.8-kHz from an Ar^+ laser

*Supported by the National Basic Research Program of China under Grant 2007CB924901, Shanghai Leading Academic Discipline Project (B411), the National Natural Science Foundation of China under Grant No 60677022, and Shanghai Municipal Commission of Science and Technology Project under Grant Nos 07DZ22943 and 08JC1409000.

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was used to irradiate samples with a diameter of about 0.5 mm. The spectral resolution was set at 8 cm^{-1} (~1.0 meV). The samples were treated with a quick etch in a 1% Br_2/methanol solution to avoid the influence of surface smear, and then mounted on a cold finger of an Oxford cycling-cryostat CCCF1104 (or pulse tube-OptistatAC-V), of which the temperature could be continuously adjusted from 10 K (or 4 K) to 300 K.

Table 1. Sample composition x, doping, carrier density N_c and mobility M_c at 77 K, annealing and main impurity.

		Doping	$N_c(cm^{-3})$	$M_c(cm^2/Vs)$	Annealing(°C/h)	Impurity
M21	0.298	As-doped	1.2×10^{16}	259	as-grown	V_{Hg}, As_{Hg}, V_{Hg}-As_{Hg}, Te_{Hg}
M11	0.303	V_{Hg}-doped	1.0×10^{16}	261	360/16(vacuum)	V_{Hg}
M03	0.300	As-doped	3.3×10^{16}	295	285/16+240/48	As_{Te}
M16	0.305	As-doped	3.6×10^{16}	292	400/0.5+240/48	As_{Te}, (V_{Hg})

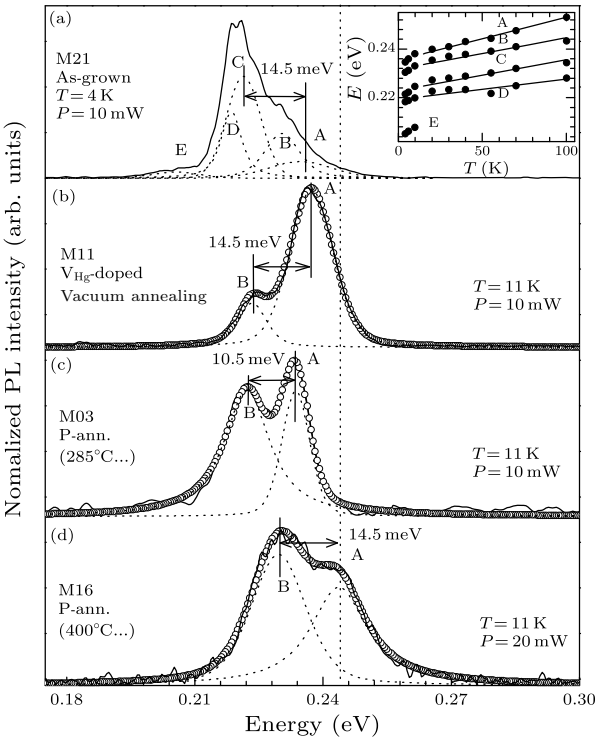


Fig. 1. Modulated PL spectra of M21 (a), M11 (b), M03 (c) and M16 (d), respectively, at 11 K (4 K for M21) under 10 mW (20 mW for M16). The dotted lines give the curve-fitting results. Inset: temperature dependence of peak energy.

Figure 1 typically shows the modulated PL spectra of all samples at low temperature T and low excitation power P. In order to reliably determine the peak position, curve-fitting procedures and second-order derivative operations have been performed on the spectra, respectively.[14] The scattering of less than ±0.5 meV between them represents that both of them are reliable to determine the peak position. It is noteworthy that no mathematical smoothing has been performed on the experimental data during the operations. For convenience, the curve-fitting results have been shown in the figure together with the peaks temporarily marked by A–E, respectively.

From Fig. 1(a) we can see that the as-grown M21 shows complicated PL spectra with about five evident peaks A–E. As mentioned above, from Hall measurements, M21 shows compensated p-type conductivity and can be converted to n-type by n-type anneals, which implies that the doped As largely occupy metallic sites and act as donors (As_{Hg} or related) in the as-grown samples, as reported by abinitio calculations.[15] Here the p-type of M21 represents that the density of V_{Hg} possibly created in the growth process was dominant. Thus, the carriers in M21 should mainly represent a sum over V_{Hg}, As_{Hg} (or related), Te_{Hg} (Te antisite) and the formed V_{Hg}–As_{Hg} complex by combining with the growth process and the theoretical calculation results.[16] The PL spectra at different temperatures can further disclose the transition mechanism of the above peaks. The evident temperature-dependence of peak energy is shown in the inset of Fig. 1(a), from which peaks A–E can be attributed to the transitions of band-to-band, As_{Hg}-to-band, band-to-V_{Hg}, Te_{Hg}-to-band and band-to-complex, respectively, as described in detail in our previous works,[12,17,18] where their corresponding ionization energies have also been determined to be about 8.5 meV (As_{Hg}), 14.5 meV (V_{Hg}), 20.0 meV (Te_{Hg}) and 33.5 meV (complex), respectively.

For the undoped M11 in Fig. 1(b), annealed under vacuum to control the density of V_{Hg}, it can be easily accepted that the p-type conductivity in M11 by Hall measurements is absolutely due to the intrinsic V_{Hg}, and peaks A and B can be safely ascribed to the transitions of band-to-band and band-to-V_{Hg}, respectively.[19] Thus, the ionization energy of V_{Hg} can be determined to be about 14.5 meV from the peak energy separation in Fig. 1(b), which is also well consistent with the above-mentioned result (between peaks A and C) in Fig. 1(a).

Figure 1(c) shows the PL spectrum of M03 at 11 K under 10 mW. From the p-type conductivity of Hall measurement at 77 K and the density of carriers in M03, which is almost equal to that of the doped As from SIMS results, it can be inferred that the As in M03 has been fully activated as acceptor and the carriers in it should origin from the extrinsic As_{Te}. According to the interpretation of the line originating

in a band-to-band transition,[20,21] peak A can be ascribed to the band-to-band transition while peak B should be attributed to the impurity-related transition of band-to-As_{Te}. From the figure the ionization energy of As_{Te} can be obtained as about 10.5 meV, which is close to the result of electrical measurements (3.0 $\sim$ 10.0 meV).[4,22] It is obvious that the ionization energy of extrinsic As_{Te} is slightly smaller ($\sim$4.0 meV) than that of intrinsic V_{Hg}, of which the same phenomenon has also been observed in electrical measurements.[23]

Figure 1(d) gives the PL spectrum of M16 at 11 K under a doubled excitation power of 20 mW. It is necessary to point out that the spectral shape and peak separation in Fig. 1(d) are similar to those of the spectrum of 10 mW except for the much better signal-to-noise ratio (SNR). In view of the annealing condition and Hall/SIMS measurements, the doped As in M16 has also been definitely activated as As_{Te} under the higher activation temperature of 400°C.[24] Combining with the discussions in M03, peak B in Fig. 1(d) seems to be related to the transition of As_{Te}. For clarity, Fig. 2 shows the T and P dependences of the integrated intensity ($\mathbb{I}$) and the peak energy, respectively. It is worth mentioning that the spectral SNR becomes worse quickly as temperature increases up to 100 K, and that the T- and P-dependent shapes of M16 are similar to those of M03 except for the different peak separation and values of $\mathbb{I}_B/\mathbb{I}_A$, as well as SNR of the original spectra.

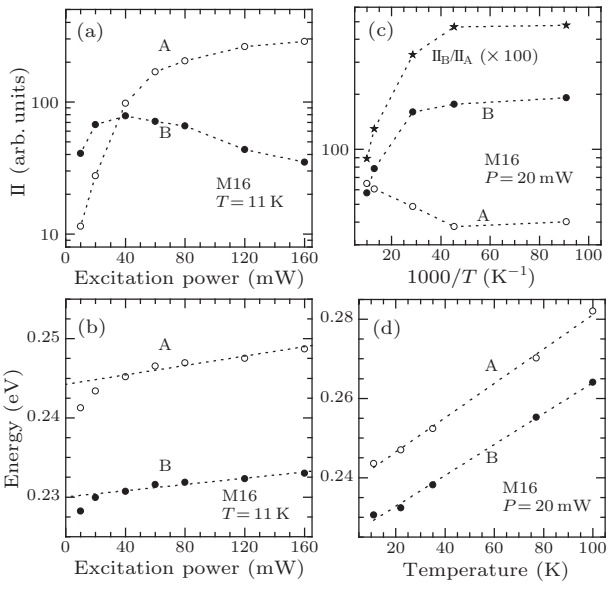


Fig. 2. P- and T dependence of the integrated intensity ($\mathbb{I}$) and the peak energy of M16. The values ($\mathbb{I}_B/\mathbb{I}_A$) with stars in (c) represent the integrated intensity ratio of peak B to peak A.

From Figs. 2(a) and 2(c) we can see that peaks A and B have the characteristics of band-related transition and impurity-related transition, respectively. As for the slight blue-shift of peak energy with the increase of excitation power in Fig. 2(b), it can be explained as the band-filling effect or the localized energy at low temperature.[25,26] From Fig. 2(d) the peak separation can be determined to be about 14.5 meV by extrapolation. However, it should be emphasized that this value is slightly larger than that of As_{Te} ($\sim$10.5 meV, in Fig. 1(c)) while almost close to that of V_{Hg} in Fig. 1(b), which may suggest that the origin of peak B in M16 is different from that of M03 in spite of their tiny separation (about 4.0 meV). Note the higher values ($\mathbb{I}_B/\mathbb{I}_A$) of M16 in Fig. 2(c) than that of M03 (see Fig. 1(c)), implying that the impurity levels in M16 have a higher transitional probability or higher concentration ratio.

To understand the discrepancy between M16 and M03, an existence of V_{Hg} has to be assumed with significant density in M16. That is to say, the high activation temperature (400°C) in the first stage has produced more additional V_{Hg} than the low activation temperature of 285°C. As we know, the introduction of excessive V_{Hg} would badly influence the quality of epilayers, which is also exhibited by the worse spectral SNR of M16 in Fig. 1(d) than that of M03 even under a doubled excitation power of 20 mW. Thus, the carriers in M16 should be composed of the dominant intrinsic V_{Hg} and the minor extrinsic As_{Te}, meaning that peak B in M16 is contributed by the transitions of main V_{Hg} and minor As_{Te}, which cannot be separated from each other in curve-fitting operations due to their tiny ionization energy difference ($\sim$4.0 meV).

It is also interesting to mention that in Fig. 1 an evident blue-shift of peak A (E_A, roughly corresponding to E_g) of M16 can be observed as compared to M03 at the same temperature, namely, $E_{A(M16)} > E_{A(M03)}$, which approximately represents the relationship of composition x with $x_{M16} > x_{M03}$. As can be seen from Table 1, this relationship is in accordance with the result from FTIR transmission spectra. It should be pointed out that M16 and M03 were cut from the same piece but with a different post-growth activation temperature, and that an appreciably larger blue-shift has also been observed when annealing under a higher activation temperature (e.g. 440°C).

Thus, by taking into account the facts above about M16, namely (i) the worse spectral SNR even under a doubled excitation power, (ii) the higher carrier density of impurity levels, (iii) the larger peak separation and closer to that of V_{Hg}, and (iv) particularly the bigger E_A (or E_g, x), a preliminary conclusion can be reached that the high activation temperature (e.g. 400°C or higher) at the first-stage could produce large numbers of excessive intrinsic V_{Hg} and deteriorate the quality of epilayers when activating the As as extrinsic acceptors As_{Te}, while the low temperature of 285°C is

more effective to activate the doped-As for preserving the intrinsic advantages of low growth temperature of MBE. Correspondingly, the larger x_{M16} (compared to x_{M03}) may be tentatively explained by the decrease of $(1-x)$ in $Hg_{1-x}Cd_xTe$ for additional V_{Hg} produced under higher annealing temperature, which needs further investigation.

In summary, we have discussed the impurity activation in As-doped MBE-grown MCT ($x \approx 0.3$) by using modulated PL measurements. The results show that As mainly acting as donors in the as-grown samples can be fully activated as extrinsic acceptors by two-stage anneals of 285°C/16 h+240°C/48 h, and the ionization energy has been determined to be about 10.5 meV, slightly smaller than that of intrinsic V_{Hg}. However, a higher temperature (e.g. 400°C or higher) at the first stage can produce excessive V_{Hg} and can seriously deteriorate the quality of epilayers.

We thank Dr J. Shao for help with the experiment.

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