Strong Disorder in HgCdTe Studied with Optical Methods and X-Ray Diffraction

D A Andryushchenko¹, I N Trapeznikova², N L Bazhenov², M A Yagovkina², K D Mynbaev², V G Remesnik³ and V S Varavin³

¹ ITMO University, Saint-Petersburg 197101, Russia
² Ioffe Institute, Saint-Petersburg 194021, Russia
³ Rzhanov Institute of Semiconductor Physics, Novosibirsk 630090, Russia

dimitriy296@mail.ru

Abstract. Optical transmission, photoluminescence, and X-ray diffraction have been used for studying structural disorder in Hg₁₋ₓCdₓTe (x=0.3–0.4) films grown by Molecular-Beam Epitaxy on GaAs and Si substrates. According to all three methods, studied films immediately after the growth showed quite different scale of the disorder. After thermal annealing films showed similar optical properties, yet their structural properties remained different. It appears that the ability of Hg₁₋ₓCdₓTe to gain good optical quality under annealing for considerably disordered initial material is not directly structure-related.

1. Introduction
Hg₁₋ₓCdₓTe (MCT) solid solutions have been studied intensively for many years due to their importance as materials for infrared photodetectors [1]. One of the subjects of these studies was disordering, as the weak Hg-Te chemical bond leads to large-scale compositional fluctuations [2,3] and high density of structural and point defects [4,5]. For films grown by Molecular-Beam Epitaxy (MBE) on ‘alternative’ (in respect to traditional CdZnTe) (013)GaAs and (013)Si substrates, the presence of large-scale ‘technological’ compositional fluctuations, probably due to MBE being a non-equilibrium growth method, was reported on the basis of luminescence studies [6]. These fluctuations seemingly do not hinder fabricating material suitable for developing high-performance photodetectors [7], yet a question remains on what degree of disorder MCT allows for while still remaining a semiconducting solid solution. We studied a number of MCT films with similar chemical composition (CdTe molar fraction x), which after the growth showed ‘normal’ and ‘abnormal’ optical properties that could be attributed to the different degree of the disorder, and followed the effect of thermal annealing on this disorder.

2. Experimental details
The films were grown by MBE on (013)Si or (013)GaAs substrates with ZnTe and CdTe buffer layers as described elsewhere [8]. The ‘absorber’ layers of the films had uniform composition x=0.35–0.40 with thickness d ranging from 5 to 9 µm. The properties of the films were studied with optical transmission (OT), photoluminescence (PL) and X-ray diffraction (XRD). OT spectra were recorded at 300 K with the use of Shimadzu 8400 Fourier-Transform IR spectrometer. PL spectra were recorded in 4.2–300 K temperature range with the use of an MDR-23 grating monochromator. PL signal was
excited by a semiconductor laser with the wavelength 1.03 μm and registered with an InSb photodetector with the use of a lock–in amplifier. XRD studies were performed with the use of Bruker D2 Phaser diffractometer equipped with a non-monochromatic CuKα radiation source.

Immediately after the growth the films had n-type conductivity with electron concentration at $T=77$ K $n_{T}=1(1−10)×10^{14}$ cm$^{-3}$. Parts of the films were subjected to post-growth annealing (260–300 °C, 2–6 h) under low mercury vapour pressure (10$^{-5}$ atm) in helium atmosphere. This annealing converts n-type conductivity into p-type via generation of mercury vacancies, which are acceptors in MCT.

3. Experimental Results

After the growth, MCT films typically undergo routine check with OT measurements, which allows for double-checking the composition and estimating the spectral response of the prospective photodetector [9]. This procedure is repeated after annealing, and it is at this stage that sharp changes in the spectrum may indicate a disorder-related problem; this shows off as a drastic shift of the OT edge [10]. Figure 1 shows OT spectra of the studied films. The spectra are shown for as-grown films (curves 1, 2 and 3) and samples annealed into p-type conductivity (1', 2' and 3'). The spectra in figure 1(a) appear to be typical of MBE-grown MCT, with a remarkably sharp absorption edge and pronounced interference fringes at low wavenumbers [11]. In figure 1(a) one can see that after the annealing, the changes in OT are almost invisible for samples grown on both GaAs ($x=0.376$, curves 1 and $1'$) and Si ($x=0.385$, curves 2 and $2'$) substrates ($x$ was determined for the as-grown films).

Figure 1(b) shows OT spectra of another MCT film, which was grown on GaAs substrate. The spectra again are shown for the as-grown film (curve 3) and the film after annealing (curve 3'). In these spectra, one can see a substantial shift of the wavenumber corresponding to 50% OT after annealing. This shift, from 3080 to 3356 cm$^{-1}$, in terms of $x$ meant an increase in the composition from $x=0.362$ to $x=0.386$. To make sure there was no composition gradient along the thickness of the film, OT spectrum was also recorded for a sample with $~1.5$ μm-thick layer chemically removed from the surface immediately after the growth. This spectrum, which is shown by curve $3''$, was very similar to that represented by curve 3, which was indicative of the lack of the gradient.

Low-temperature ($T=4.2$ K) PL spectra (not shown) of the two films grown on GaAs substrate demonstrated a strong difference in the position of the maximum of the spectra of the as-grown films (which could be partly explained by the difference in their chemical composition), and in their full-width at half-maximum (FWHM) values. For the film with $x=0.376$, the FWHM of the single PL line (usually attributed to the luminescence of excitons localized at compositional fluctuations, LE [2,3,6]) was $~17$ meV, while for the film with $x=0.362$ it was two times larger, 34 meV. A typical FWHM of the LE line at 4.2 K for an MCT film grown by MBE on a GaAs substrate, according to Ref. [6], does not exceed 20 meV with record low value being $~9$ meV. At 300 K, the FWHM of the spectrum for the as-grown film with $x=0.376$ was 40 meV, for the as-grown film with $x=0.362$, 60 meV.

After the annealing, for the film with $x=0.376$ the FWHM of the LE line of the PL spectrum recorded at 4.2 K was reduced to $~10$ meV, for the film with $x=0.362$, to $~14$ meV. Thus, after the annealing the FWHMs of the LE lines of low-temperature PL spectra for these two films became similar. At 300 K the spectra of the two annealed films also had similar FWHMs of $~40$ meV.

Figure 2 shows temperature dependences of the position of the maxima of the LE lines $E_{PL}$ of the two films determined from to the experimental data, and temperature dependences of the bandgap energy $E_g(T)$ calculated according to empirical $E_g(x,T)$ relation from Ref. [12] for the given $x$ values. As can be seen, for the as-grown films (curves 1 and 3) at $T<100$ K there was a considerable gap between $E_{PL}(T)$ and $E_g(T)$. This was obviously due to the above-mentioned origin of the optical transitions, caused by recombination of LEs [2,3,6]. It is believed that in MCT at higher temperatures, inter–band transitions involving free carriers dominate [2,3], so the energy of the PL peak approaches that of $E_g$. One can see in figure 2 that for the as-grown films with $x=0.376$ and $x=0.362$ the difference between $E_{PL}$ and $E_g$ at low temperatures is different. Indeed, for the film with $x=0.376$ at 4.2 K it comprises 50 meV, while for the film with $x=0.362$, 62 meV. At 300 K, the energies of the PL peaks
in both cases corresponded to the calculated values of $E_g$. After the annealing the behavior of $E_{PL}(T)$ in respect to $E_g(T)$ for the two films became similar (curves 1’ and 3’).

Figure 1. Room-temperature OT spectra: (a), as-grown (curves 1 and 2) and annealed into p-type (1’ and 2’) films with $x=0.376$ (1, 1’, GaAs substrate) and $x=0.385$ (2, 2’, Si substrate); (b), spectra of a film with $x=0.362$ grown on GaAs substrate, shown for as-grown material (curve 3), annealed film (3’), and a sample with ~1.5 µm-thick layer removed immediately after the growth (3’’).

Figure 2. Temperature dependences of the position of the maxima of the LE bands $E_{PL}$ (symbols) and calculated bandgap energy $E_g$ (lines) for two films grown on GaAs substrates: as-grown (curves 1 and 3) and annealed (1’ and 3’) samples with $x=0.376$ (a) and $x=0.362$ (b), respectively. For the annealed samples, calculated $E_g(T)$ curves are shown for $x=0.383$ (a) and $x=0.386$ (b), respectively. Symbols 3’’ in image (b) show $E_{PL}(T)$ for the film with $x=0.362$, where immediately after the growth a ~1.5 µm-thick layer was removed from the surface.

Figure 3 shows XRD curves of the films before and after annealing. The curves are shown for film with $x=0.385$ (Si substrate, curves 1 and 1’) and film $x=0.376$ (GaAs substrate, curves 2 and 2’). The peaks at $2\theta=97.5^\circ$ originate from the substrates, and this explains the different positions of these peaks for the two samples. The peaks at $2\theta=97.7^\circ$ were the main diffraction peaks originating from the epitaxial films (the peaks at $2\theta=98.1^\circ$ were due to non-monochromatic character of the excitation radiation used). As can be seen, after the annealing the positions of the peaks from the films remained the same in both cases. The FWHMs of the peaks did not change after the annealing either, so some decrease in the intensity of XRD signal could be related to decrease in the sizes of coherent scattering regions due to the fact that diffusion of point defects in the course of annealing possibly resulted in their accumulation at extended defects. The XRD curves for the film with $x=0.362$ are not shown, as the diffraction signals both before and after the annealing were very weak. This obviously was indicative of low crystalline quality of this, which could not be improved by the annealing.
4. Discussion

The results of our study suggest that the studied films, though having similar chemical composition, had a different scale of disorder. For the film with \(x=0.385\) grown on Si substrate and for the film with \(x=0.376\) grown on GaAs substrate, the scale seemed to be typical of MBE-grown MCT, and the disorder could be related solely to compositional fluctuations [6]. For the film with \(x=0.362\) grown on GaAs substrate, the scale of the disorder was much larger. The nature and the exact type of this type of disorder remain unclear. The density of the so-called ‘V-shaped’ defects [8], which is the main large growth defect in this type of material, in this film was typical of MBE-grown MCT and equaled \(~2000\ \text{cm}^{-2}\). Thus, the observed disorder unlikely originated from ‘V-shaped’ defects. On the other hand, it is known that MBE-grown MCT has an ability to demonstrate spontaneous composition modulations with a period of hundreds of nanometers [10]. These modulations were observed directly with Transmission Electron Microscopy [13]. With the XRD setup used they could not be detected, yet the important result of our work is that it seems that optical properties of MBE-grown MCT films are not that strictly related to the structural quality of the material. Further studies are needed to find relation between these two kinds of properties. A relation of the studied anomalies to those in electrical properties of MCT [10] is also of considered interest.

5. Conclusion

In conclusion, using optical transmission, photoluminescence and X-ray diffraction experiments, we have studied disorder in \(\text{Hg}_1-x\text{Cd}_x\text{Te} (x=0.3–0.4)\) films grown with Molecular-Beam Epitaxy on GaAs and Si substrates. We have found that as-grown films with similar chemical composition may have a very different scale of disorder. After post-growth thermal annealing, all the studied films showed similar optical properties, but their structural properties remained different.

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