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Strain relaxation of CdTe films growing on lattice-mismatched substrates

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Abstract We have deposited CdTe films by laser-assisted epitaxy approach and investigated the influence of substrate and film thickness on the film properties. Grown on Si(001), GaAs(001), and quartz substrates; the CdTe films exhibit preferential orientation along the cubic CdTe(111) direction. When the films are thin (<500 nm), a blueshift of the band gap and splitting of valence bands were observed. These results are attributed to the existence of residual strains induced by mismatch of the film lattice constant with that of the substrate, and by their difference in thermal expansion coefficients. The bulk band-gap energy of 1.5 eV was achieved on the surface of thick CdTe films grown on Si(001) substrate, indicating that strain was almost completely relaxed in this case. Our results demonstrate that by a proper selection of substrate and film thickness it is possible to grow film semiconductors with band gap approaching those of bulk crystals.

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1 Introduction

Much effort has been devoted to the development of room-temperature radiation detectors for defense applications [1–3]. Compound semiconductors based on materials, such

as cadmium telluride (CdTe), hold great promise for these applications. In order for a semiconductor to operate as radiation detectors at room temperature, they need to possess a number of features: (1) a large enough band gap and low enough carrier density to minimize current noises; (2) free from traps that act to reduce the useful signal; (3) higher carrier mobilities to produce pulses with fast rise time; (4) a high atomic number element for good stopping power of high energy radiation; and (5) a long carrier lifetime to allow efficient charge collection. So far high-quality bulk single crystals of CdTe-based semiconductors appear to have many of these properties. A wide variety of techniques [4] have been used to grow these bulk crystals, such as the Bridgman and Czochralski methods.

On the other hand, film semiconductors have the advantage that they can be grown much faster than bulk crystals. In particular, CdTe films can be grown by a number of techniques, including molecular beam epitaxial (MBE) [5, 6], metalorganic chemical vapor deposition (MOCVD) [7], and laser-assisted epitaxy or pulsed-laser deposition (PLD) [8–10]. In general, thin films grown epitaxially on a lattice-matched substrate have been found to have crystalline quality comparable or even better than of the bulk crystals. For example, AlGaAs thin films grown on lattice-matched GaAs substrates have higher quality than the corresponding bulk crystals. CdTe films have so far been grown primarily on lattice-mismatched substrates. These films are usually strained because of the difference in lattice constants and/or coefficients of thermal expansion between the epilayer and the substrate. As a result, these thin films often have poor electronic properties as compared to the corresponding bulk material. It is well known that extended defects, such as dislocations, can form in epilayers grown on lattice-mismatched substrates. However, it is possible to localize these defects at the interfacial region [11]. Thus, by

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increasing the film thickness, it may be possible to grow strain-relaxed epitaxial films with crystal quality approaching that of the bulk crystal [12]. We have used the laser-assisted epitaxy technique, which is a high-vacuum film deposition method, to grow CdTe films on a number of lattice-mismatched substrates. We demonstrate that micron-thick single crystalline CdTe films can be grown on Si(001) substrates with the band gap approaching that of the bulk single crystal.

2 Experimental details

The CdTe films were grown on Si(001), GaAs(001), and quartz substrates at various substrate temperatures (T_s) in a vacuum of $\sim 3 \times 10^{-7}$ torr using the laser-assisted epitaxy technique. The excitation source is a KrF excimer laser emitting 30 ns pulses and operating at a wavelength of 248 nm. The pulse energy of the laser beam is approximately 160 mJ and the repetition rate is 5 Hz. CdTe target with purity of 99.999% was mounted on a rotating target holder and ablated to produce the precursor vapor. The substrates were attached to a substrate holder and heated at 500°C for more than 10 min to thermally remove any contamination before cooling to the desired temperature for film deposition. The distance between the target and the substrates was about 5 cm.

The CdTe films were characterized by modulated photoreflectance (PR) spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). In the PR measurements, the samples were excited with a 325 nm pump beam chopped at 310 Hz. The probe beam came from a high-pressure tungsten lamp after being dispersed by a monochromator with a 600/mm grating. The reflected light was detected by a Si photodiode and a lock-in amplifier. XRD measurements were carried out using the Cu K_α radiation with a Siemens D5000 diffractometer.

3 Experimental results and discussion

Since the lattice constant of CdTe (6.480 Å) is much larger than that of GaAs (5.653 Å) and Si (5.431 Å), (111) oriented cubic CdTe films have been found to grow on these (001) oriented substrates [5–10] in order to minimize the surface free energy. We discuss the properties of CdTe films grown on these two substrates separately.

3.1 CdTe films of different thickness grown on Si(100)

Figure 1a shows the typical XRD patterns of CdTe films grown on Si(001) substrate at $T_s = 300^\circ\text{C}$ and with film thickness less than 1 μm . The dominant domain orientation

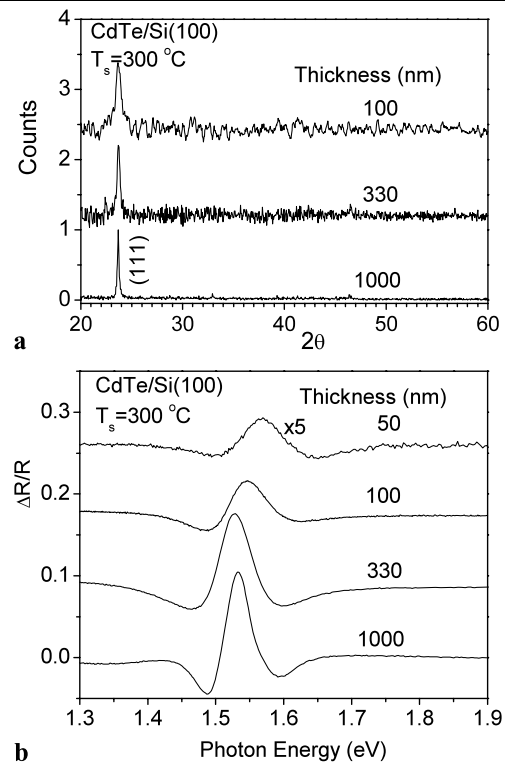


Fig. 1 (a) XRD patterns and (b) PR spectra of CdTe films with different thicknesses

of the CdTe film is found to be [111]. The width of the (111) diffraction peak is found to be broader for the thinner films indicating that there are either more defects or the crystallites are smaller in the thinner films. With increasing film thickness the lattice constant of CdTe as determined from the XRD become closer to that of the perfect bulk crystal showing that strain relaxation occurs as thickness increases.

The XRD results are consistent with the results derived from the PR spectra shown in Fig. 1b. The existence of strain in the CdTe film is manifested in the PR spectra by shifts in the band gap as the film thickness is increased. The band-gap energies can be obtained by fitting the measured PR curves using sums of Lorentzians [13], $\Delta R/R = \text{Re}[Ae^{i\Phi}(E - E_0 + i\Gamma)^{-m}]$, where A is the amplitude, Φ is the phase angle, E_0 is the onset energy of interband absorption (to be referred to as the “band-gap energy”), Γ is the broadening factor, and $m = 2.5$ for bulk semiconductors. We found that the curves in Fig. 1b could be fitted well by a sum of two Lorentzians, as illustrated in Fig. 2. This suggests that the band gap is split by strain into two transitions. The inset of Fig. 2 shows that, when the film thickness increases from 50 to 1000 nm, the split decreases in energy from 49 to 18 meV while the fundamental band gap decreases from 1.574 to 1.513 eV. We note that the last value approaches the bulk value of 1.50 eV [14, 15]. The decrease in both the splitting and the band-gap energy indicates that the strain is relaxed to some extent with increasing the film thickness.

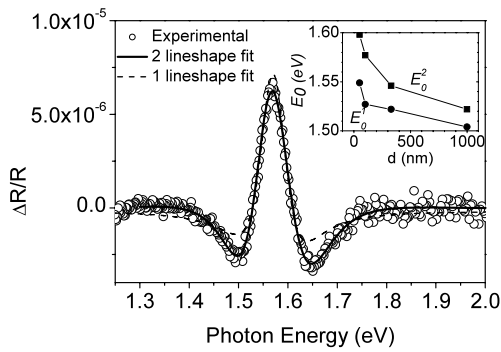


Fig. 2 PR spectrum of the CdTe/Si(100) with thickness of 50 nm. The inset is the fitting results of the band-gap split as function of film thickness

CdTe films grown on Si(001) typically have been shown to have two orthogonal crystalline domains [6]: CdTe[1–10]||Si[110] and CdTe[11–2]||Si[1–10], in which the lattice mismatch is reduced to 16 and 3% along the [1–10] and [11–2] directions, respectively. The domains are compressed in both directions [6, 16], which is different from the case of CdTe grown on GaAs(001) [17]. In addition to the strain introduced by the lattice-mismatch, a difference in the thermal-expansion coefficients of the epitaxial layer and the substrate can introduce thermal strains. For the CdTe/Si system, the CdTe layer can be biaxially strained because the thermal expansion coefficient of CdTe ($4.8 \times 10^{-6}/\text{K}$) is greater than that of Si ($2.6 \times 10^{-6}/\text{K}$). When the sample is cooled from the growth temperature to room temperature, the CdTe film undergoes a tensile strain. These two types of strains are primarily responsible for changing the band gap energies of the CdTe films from that of the bulk crystals.

In general, a strain can be decomposed to a hydrostatic and a shear component. The former leads to a change of the fundamental band-gap energy while the latter causes a splitting of the heavy- and light-hole bands. Even though the [111] orientation of the CdTe(111) domains is, in principle, parallel to the [001] orientation of the Si(001) substrate, the shear strain can still change from site to site due to the presence of several equivalent [110] axes within the Si(001) plane. Since XRD results show that there is practically no change in the lattice parameter of the CdTe films along [111] direction as a function of film thickness, the CdTe band-gap split cannot be attributed to a uniaxial strain along the [111] direction [18]. However, an increase in the fundamental band-gap energy in the thin CdTe film with respect to that of a bulk CdTe suggests that a compressive biaxial strain is present in the CdTe epilayers [19].

3.2 CdTe films grown on Si(100) at different substrate temperatures

A series of thick CdTe samples ($>3 \mu\text{m}$ thick) were grown at different temperatures T_s on Si(001) substrates in order

to study the evolutions of the crystal quality as well as the band-gap energy as a function of T_s . We found that the CdTe films grown at below 100°C are amorphous with band gap of about 1.6 eV at room temperature. As T_s is increased to 100°C and above, CdTe crystallites oriented preferentially along the [111] direction are formed as shown by the XRD results in Fig. 3a. It is clear that the CdTe (111) diffraction peak is located at lower angles when grown at 100 and 150°C as compared to the samples grown at higher T_s . This implies that the lattice constant perpendicular to the growth plane is increased at lower T_s . In the meantime the band-gap energy is increased at low T_s as shown by the PR spectra in Fig. 3b. Multiple transitions are observed for the samples grown at 250 and 300°C , indicating the residual strain becomes larger at higher growth temperatures. On the other hand, the transition energies may be related to the quantum confinement effect of the small crystallites. Figure 3(c) shows SEM images of CdTe films grown under different temperatures. The average diameter of CdTe crystallites increases from about 35 nm to 170 nm as T_s increases from 100 to 300°C . For a crystallite with 35 nm in diameter embedded in amorphous CdTe with 1.6 eV band-gap energy, the confinement energy is about 3 meV, much smaller than the observed increase at $T_s = 100^\circ\text{C}$. However, it is possible that smaller crystallites exist in films grown at lower temperatures, the resulting quantum confinement effect can therefore contribute to the observed high energy shift of the band-gap energy at 100 and 150°C . At higher growth temperatures ($>200^\circ\text{C}$), quantum confinement effects would be negligible.

The transition energies can be obtained by fitting the PR spectra with Lorentzians. The PR spectra can be fitted with two Lorentzians for the samples grown at 100 and 150°C , and three Lorentzians for the samples grown at $T_s \geq 200^\circ\text{C}$. The results obtained by fitting the experimental PR spectra are summarized in Fig. 4a. As T_s increases, the lowest transition energy (E_0) continuously decreases and reaches a constant value whereas the higher ones (E_{01} and E_{02}) continue to increase with T_s .

To understand the results in the thick CdTe films, we propose that these films actually consist of two layers: one is a thin layer (of thickness comparable to the critical layer thickness) adjacent to the interface which is highly strained but not dislocated, and the other is a thick top layer where the strain has mostly been relaxed by dislocations. The E_0 transition comes from the strain-relaxed top layer while the higher energy transitions (E_{01} and E_{02}) arise from the strained layer at the interface. At $T_s < 100^\circ\text{C}$ only amorphous CdTe forms and the band gap of the amorphous phase is usually larger than that of the crystalline phase. When $T_s > 100^\circ\text{C}$ crystallites start to form but their strain cannot be relaxed effectively by the low substrate temperature. With

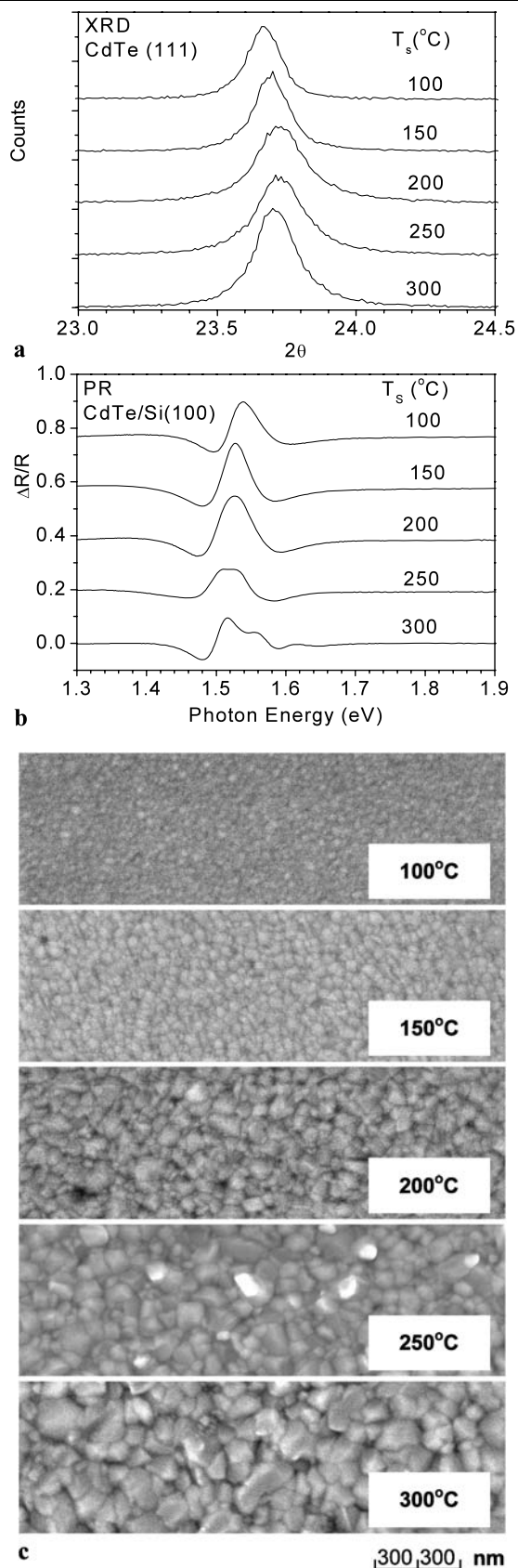


Fig. 3 (a) (111) XRD peaks, (b) PR spectra, and (c) SEM images of the thick CdTe/Si(100) films grown at different temperatures

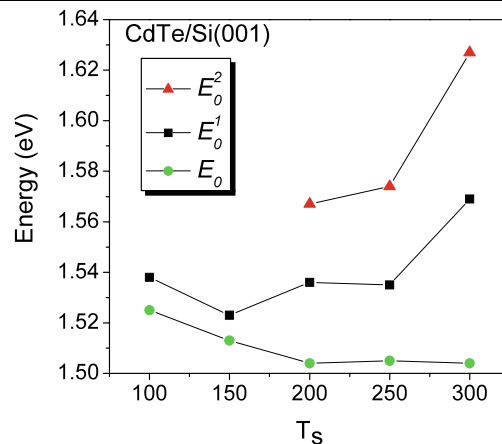


Fig. 4 The transition energies obtained by fitting the curves in Fig. 3b using Lorentzian lineshape

increasing T_s ($>200^\circ\text{C}$), the strained thin layer near the interface becomes more strained due to increase in the thermal stress resulting in an increased split between the heavy- and light- hole states as shown by E_{01} and E_{02} in Fig. 4a. Meanwhile, the dislocation starts to relax the strain of the crystallites far from the interface. As a result, the E_0 transition decreases in energy and reaches a constant value. This explanation is in agreement with the XRD results in Fig. 3a that shows an increase in the out-of-plane lattice constant at $T_s < 200^\circ\text{C}$ due to the residual strains existing in the films grown at low T_s .

We have considered the possibility that the increase of E_0 at low T_s ($<200^\circ\text{C}$) may partly be due to quantum confinement effects [20] because the size of the crystallites is usually smaller at low T_s . The quantum confinement effect of these smaller crystallites can contribute to the high-energy shift of the band gap as observed for the samples grown at 100 and 150°C . However, at higher growth temperatures ($>200^\circ\text{C}$), quantum confinement effects on band gap should be negligible because of the large crystallite sizes. Strain relaxation in the top layer of the films grown at higher temperature is inferred by comparing the inset of Fig. 2 with Fig. 4. For the films with thickness less than $1\ \mu\text{m}$ as in Fig. 2, the strain still exists throughout the film, thus only two transitions (E_0^1 and E_0^2) have been observed. With increasing film thickness ($>3\ \mu\text{m}$) the strain in the top layer has been relaxed resulting in the observation of three transitions (E_0 , E_0^1 and E_0^2), where E_0 transition comes from the strain-free top layer. In the inset of Fig. 2 this strain relaxation continues even as the film thickness is increased leading to continued decrease in the value of E_0 . In the case of Fig. 4, the film is already quite thick so the strain in the top layer is already partly relaxed. As the growth temperature is increased this strain is further relaxed. However, the strain relaxation saturates at T_s above 200°C as suggested by the value of E_0 .

The above results suggest that thick films grown at temperatures above 200°C will achieve the maximum amount

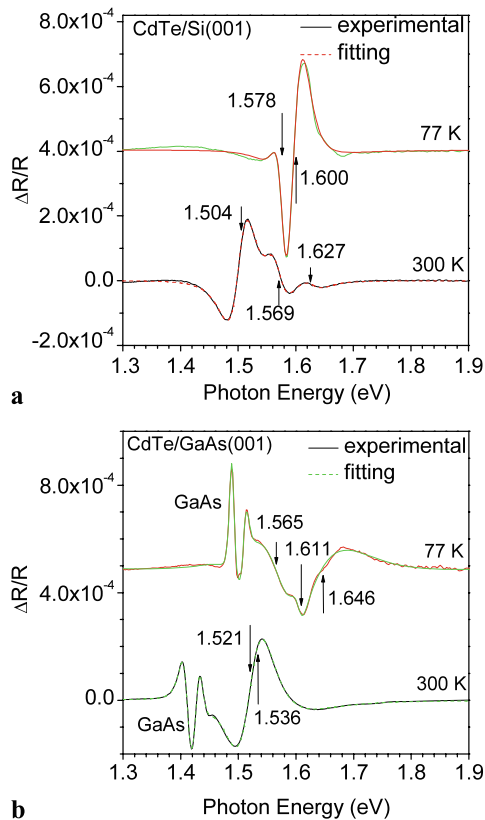


Fig. 5 PR spectra of (a) CdTe/Si(100) and (b) CdTe/GaAs(100) measured at 77 K and room temperature. The transition energies are obtained by fitting with the Lorentzian lineshape

of strain relaxation in their top layers. This conclusion is verified in Fig. 5a which shows the PR spectra of a 3 μm thick CdTe film grown at 300°C on Si(001), measured at two different temperatures. The strong feature at 1.504 and 1.600 eV at 300 and 77 K, respectively, are nearly equal to the band-gap energies of bulk CdTe at the corresponding temperatures (1.50 and 1.60 eV at 300 and 77 K, respectively). These results indicate that this CdTe film is indeed nearly strain free. The high energy features at 1.569 and 1.627 eV at 300 K are attributed to the splitting of heavy- and light-hole states due to the large shear strain in the thin layer at the interface as discussed earlier. At 77 K, however, the PR spectrum can be well fitted by only two Lorentzians, indicating that the shear strain is actually smaller at low temperature. More importantly, the fundamental band-gap energy of the strained interface layer shifts in opposite direction relative to the bulk band gap at 300 and 77 K. This difference is a manifestation of the opposite signs of the thermal-strain- and lattice-mismatch-induced strain. At 300 K, the CdTe lattice is compressed as a result of the larger lattice constant of CdTe than that of silicon, resulting in a blueshift. At 77 K, the CdTe lattice becomes tensilely strained since the thermal expansion coefficient of CdTe is

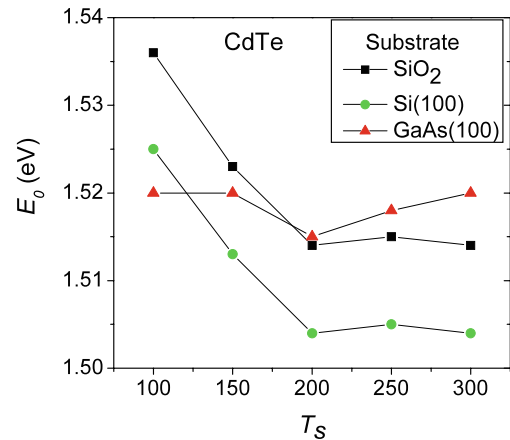


Fig. 6 Comparison of E_0 transition of thick CdTe films grown on Si(100), GaAs(100), and quartz substrates

1.8 times larger than that of silicon, producing a redshift of the band-gap energy.

3.3 CdTe films grown on GaAs(100) substrates

Unlike CdTe films grown on Si(100), the CdTe domains in the CdTe(111)||GaAs(001) films are compressed along the [1–10] direction while extended along the [110] direction [12]. Furthermore, CdTe's thermal expansion coefficient ($4.8 \times 10^{-6}/\text{K}$) is smaller than GaAs ($6.0 \times 10^{-6}/\text{K}$). Thus, the lattice-mismatch-induced strain and the thermal strain of CdTe film grown on GaAs have opposite effects on its band-gap energy. Competition between these two effects make it difficult to predict qualitatively the behavior of the band-gap energy and split in CdTe films grown on GaAs(001) substrates.

Figure 5b shows the PR spectra of a CdTe/GaAs(001) sample grown at 300°C. The dominant structures at 1.521 eV (300 K) and at 1.611 eV (77 K) are larger than those of the CdTe/Si(001) sample shown in Fig. 5a. The multiple transitions induced by strains are also more prominent at 77 K. The split states are located on the either side of the main feature at 1.566 and 1.646 eV (77 K). This indicates that the shear strain in the CdTe layer is larger at low temperature, which is different from that of the CdTe/Si(001) sample. The larger fundamental band gap of CdTe/GaAs(001) sample can be explained by the larger thermal expansion coefficient of CdTe than that of GaAs substrate leading to a compressive strain.

3.4 Comparison between properties of CdTe films grown on different substrates

We have also grown CdTe thin films on quartz substrates. Details of the results on these films will be presented elsewhere. We plotted in Fig. 6 the transition energy E_0 of CdTe

films grown on different substrates as a function of T so we can compare the substrate effect on the band-gap energy. It is interesting to note that, at low T_s , E_0 is almost independent of T_s for the CdTe/GaAs(001) sample while E_0 decreases with increasing T_s for the samples grown both on Si and quartz. At higher T_s , the larger E_0 values in the CdTe/GaAs(001) and CdTe/quartz films suggest that they both have larger strains than the CdTe/Si(001) film. The closeness of the E_0 values in the latter films to those of the bulk crystals indicates that strain is completely relaxed in them. It should be noted that this finding applies only to the top layer of thick CdTe films grown on Si(001) substrate since the thin bottom layer near the substrate remains highly strained.

4 Conclusions

Using laser-assisted epitaxy approach, CdTe films of varying thickness have been fabricated on Si(001), GaAs(001), and quartz substrates at different growth temperatures. All films, except for the almost amorphous ones grown at temperature below 100°C, show a preferential orientation with (111) axis of the CdTe zincblende along the growth direction. A blueshift of the fundamental band gap with respect to the bulk value is observed in photoreflectance spectra of the thinner films (<500 nm) as well as the films grown at low growth temperatures (<200°C) and attributed to residual compressive strain and/or quantum confinement effect of the small crystallites. Multiple transitions have been attributed to strained-induced splitting of heavy-hole and light-hole states of CdTe layer close to substrate. With increasing film thickness and growth temperature the strains in the top layers are largely relaxed; as a result, the band-gap is reduced. An important finding of the present work is that the strain in thick CdTe films grown on Si(001) substrate at temperatures above 200°C can be well relaxed so that their band gap approaches the value of bulk CdTe crystals. This makes it possible to substitute bulk crystals with crystalline CdTe films for the purpose of studying their applications, such as radiation detectors.

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