Applied Surface Science 387 (2016) 477–482

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Stoichiometry dependence of the optical and minority-carrier lifetime behaviors of CdTe epitaxial films: A low-temperature and time-resolved photoluminescence study

Kai Tang, Xuanting Zhu, Liangqing Zhu, Wei Bai*, Jiawei Bai, Wenxia Dong, Jing Yang, Yuanyuan Zhang, Ye Chen, Xiaodong Tang*, Junhao Chu

Key Lab of Polar Materials and Devices, Ministry of Education, East China Normal University, Shanghai 200241, China

ARTICLE INFO

Article history:
Received 14 December 2015
Received in revised form 16 June 2016
Accepted 23 June 2016
Available online 25 June 2016

Keywords:
CdTe epitaxial films
MBE
Optical properties
Minority-carrier lifetime

ABSTRACT

Cadmium telluride (CdTe) epitaxial films (EFs) were grown on near-lattice-matched $Cd_{0.96}Zn_{0.04}Te$ (CZT) substrates by molecular beam epitaxy at different ambients to achieve Cd-rich samples with extra Cd molecular flux or Te-rich samples with extra Te molecular flux. The evolution of epitaxial growth was in situ monitored by reflection high-energy electron diffraction (RHEED). A two-dimensional growth mode was indicated by the streaky RHEED patterns. Crystal structures of the CdTe EFs were characterised by X-ray diffraction (XRD). XRD data suggested that the crystal quality of the CdTe EFs was improved by controlling the Cd and Te flux ratio. Low-temperature photoluminescence (PL) spectra were carried out in these CdTe EFs. The typical characteristic peak at ~1.552 eV denoted as the bound-to-free transition was only found in CdTe samples grown under an extra Cd flux, and Cd vacancy-related defects were absent in the Cd-rich EFs, confirming the Cd-rich or Te-rich states of the epitaxial CdTe films. Finally, minority-carrier lifetime was prolonged in Cd-rich CdTe EFs as supported by time-resolved photoluminescence (TRPL) measurement.

1. Introduction

CdTe is an important II–VI semiconductor material, which has been widely used as the substrate material for HgCdTe-based infrared array sensors, the absorber material for nuclear radiation detectors, and for thin film photovoltaic (PV) devices, and so on [1–5]. Recently, a breakthrough has been made in the conversion efficiency of CdTe thin film solar cell devices to up to 21.5%, gradually approaching the theoretically achievable efficiency of ~32% [6,7]. The efficiency of the PV cells is related to their open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), and fill factor (FF), which are lower than those expected in CdTe materials with a band gap of 1.5 eV [8,9]. The low V_{OC}, I_{sc}, and FF values are primarily correlated to the short minority-carrier lifetime because of the non-radiative recombination at grain boundaries and/or of point defects [10,11]. Therefore, finding the origin of defects and the relationship between recombination centres and minority-carrier lifetime are crucial for improving the performance of CdTe-based thin film solar cells.

Previous works indicated that the minority-carrier lifetime was reported to be prolonged in Te-rich CdTe samples because of the assumption that Te vacancies (V_{Te}) are the main deep-level defects [12–15]. However more recently, Ma et al. [2] have reported that theoretical results based on the Heyd-Scuseria-Ernzerhof hybrid functional of 2006 [16] evolved from the Kohn-Sham theory [17] and experimental data suggested that the V_{Te} is a shallow donor. It has been proposed that the Te antisite and Te interstitial are the main deep-level defect generators and that the minority-carrier lifetime of the Cd-rich samples is much superior to that of the Te-rich ones [2]. Consequently, the crystalline quality of the CdTe material is also improved significantly for samples grown with a Cd-rich ambient. For instance, the structural defects of CdTe polycrystalline film and bulk such as dislocations, twin boundaries, and grain boundaries were suppressed by $CdCl_2$ treatment or annealing in Cd overpressure [3,5,18–22]. Additionally, the complex defects of Cd vacancies of CdTe single crystals can be eliminated by Cd overpressure annealing processes [4].

---

* Corresponding author.
E-mail addresses: wbai@mail.sitp.ac.cn (W. Bai), xdtang@clpm.ecnu.edu.cn (X. Tang).

http://dx.doi.org/10.1016/j.apsusc.2016.06.142
0169-4332/© 2016 Elsevier B.V. All rights reserved.

Due to a lack of experimental data, at the current stage, it is still controversial whether the PV conversion efficiency of CdTe-based solar films can be promoted in either a Cd-rich or Te-rich ambient. On the other hand, there are a few reports on CdTe epitaxial single crystalline films grown by molecular beam epitaxy (MBE), which can provide tools to determine the stoichiometry of the materials being grown. Moreover, CdTe single crystalline films grown by MBE can rule out the defect states led by the grain boundaries occurring in polycrystalline samples, and thus more intrinsic physical properties can be optimised. In addition, MBE also provides greater control of variables, such as the Te and Cd flux ratio, and thus assists in minimising or eliminating Te- or Cd-related defect states. In this article, therefore, the MBE technique was used to grow CdTe epitaxial single crystalline films with different defect states. Low-temperature photoluminescence (PL) spectra was used to study the possible defect-related recombination mechanisms, and time-resolved PL (TRPL) was further employed to determine the minority-carrier lifetime of the CdTe EFs with various defect levels.

2. Experimental details

The EFs were grown by MBE technique from solid elemental sources in the Riber 32P system with a base pressure up to 1×10^{-10} torr. $Cd_{0.96}Zn_{0.04}Te$ (CZT) materials with (331) orientation were chosen as substrates showing a good lattice match with the grown CdTe films, and cleaned following well-established procedures [23], which consist of degreasing with organic solvents and etching in a weak (0.1%) solution of bromine in methanol, and then dipping briefly in concentrated HCl (50% in volume), and finally rinsing in de-ionised water, and drying and storing in an inert N_2 atmosphere before loading into the MBE system. The substrates were prebaked at 160 °C for one hour in the MBE high vacuum (10^{-10}–10^{-9} torr) preparation chamber to degas eventual traces of water and hydrocarbons left on the surfaces or incorporated during loading into MBE system [24].

Prior to deposition, CZT substrates were heated in the growth chamber at about 400 °C, which resulted in removal of the oxide overlayer as indicated by the appearance of streaky reflection high-energy electron diffraction (RHEED) patterns in Fig. 1(a). Three Knudsen-type cells were used for CdTe, Cd, and Te sources to grow CdTe EFs, respectively, and the extra Cd and Te effusion cells were used to control the stoichiometry of the CdTe EFs. The obtained CdTe EFs were denoted as nominal CdTe (NCT), Te-rich CdTe (TCT), and Cd-rich CdTe (CCT). Moreover, all these CdTe samples were grown under the same growth processes, namely the growth temperature was 260 °C and the growth rate was ~4 nm/min.

The growth processes were monitored in situ by RHEED with a voltage of 20 kV and a current of 1.6 A (STAIB Instruments NEK300R3-8), and XRD (Bruker D8) was used to characterise the crystal structures of the CdTe EFs. The PL spectra were measured with a step-scan Fourier transform infrared spectrometer-based modulated PL technique (Bruker IFS 80V/S) at 5 K maintained using a liquid helium cryostat. The spectrometer is a combination of a photovoltaic Si detector and a CaF_2 beamsplitter, and its spectral resolution is 12 cm^{-1}. The excitation source is a 514.5 nm Ar^+ laser, whose power density on the sample surface was set to 100 W/cm^2. The sub-picosecond (sub-ps) pulse of a Ti-sapphire amplifier (centred at 800 nm, 250 kHz repetition rate, and 100 fs pulse duration) was employed as the primary excitation source. The TRPL spectra were carried out with the excitation of a frequency-doubled sub-ps pulse at 400 nm at room temperature, and a time-correlated single-photon counting system (PicoHarp 300) with an Avalanche photodiode (APD) was used to collect the PL decay data.

Table 1
The PL line positions and assignments of the CCT, TCT, and NCT epitaxial films.

CCT (eV)	Assignment	TCT (eV)	Assignment	NCT (eV)	Assignment
1.562	A_1X-LO	1.571	D_1X-LO	1.574	D_1X-LO
1.552	(D^0, h)	1.562	A_1X-LO	1.565	A_1X-LO
1.541	A_1X-2LO	1.550	(e, A^0)	1.557	A_2X-LO
1.531	(D^0, h)-LO	1.540	DAP	1.547	(e, A^0)
1.510	(D^0, h)-2LO	1.529	(e, A^0)-LO	1.537	DAP
		1.519	DAP-LO	1.527	(e, A^0)-LO
				1.518	DAP-LO

3. Results and discussion

As a typical case, the RHEED patterns for the CdTe EFs under Cd-rich atmosphere at different growth stages, namely, 100 s, 10 min, and 250 min, are plotted in Fig. 1(b)–(d). And the RHEED patterns of the NCT and TCT EFs are also shown in Fig. 1(e) and (f), respectively. A two-dimensional growth mode is confirmed by the appearance of the streaky RHEED patterns. Some obvious features are noticed from these RHEED patterns. The applied CZT substrates through the above treatments show similar RHEED profiles, indicating that the treated CZT substrates show similar surface morphologies and that the effects of the substrate surface microstructures on the subsequent growth are possibly negligible. Compared to those of the NCT EFs, the RHEED streaks of the CCT and TCT EFs become more slender, and, in particular, the long and thread-like fringe RHEED patterns are demonstrated for the CCT EFs as shown in Fig. 1(d), implying the high crystal quality of the CdTe EFs in a Cd-rich ambient.

Fig. 2 shows the XRD patterns of the NCT, TCT, and CCT EFs. The full width at half maximum (FWHM) are calculated to be ~288 arcsec of the NCT films, ~256 arcsec of the TCT films, and ~205 arcsec of the CCT films, respectively. These values suggest that the supplement of excess Cd or Te sources can promote the crystal quality of the CdTe EFs, in line with the results confirmed by RHEED data. Note that the XRD peak position has a shift at different atmospheres as given in the inset of Fig. 2, *i.e.*, the peak of the TCT EFs shifts towards a lower degree while the peak of the CCT ones has a shift to a higher degree. This data implies that the cell volume of the TCT EFs increases while the cell volume of the CCT EFs drops, possibly resulting from the larger ionic radius of Te^{2-} (221 pm) than that of Cd^{2+} (95 pm) due to the inevitable existence of interstitial and antisite defects in II–VI materials [25]. These results also support the realisation of Cd-rich and Te-rich CdTe EFs by controlling Te and Cd flux ratios.

PL spectra of the NCT, CCT, and TCT EFs at 5 K are plotted in Fig. 3(a)–(c). Each transition at different energy regions can be assigned for similar transitions. Generally, the energy near 1.59 eV denoted as X-band is the free excitons (FX) and the excitons bound to neutral acceptors and donors (denoted as A_1X, A_2X, D_1X, and D_2X, respectively) [19,22,24,26,27]. The features around 1.55 eV are the free electrons to acceptors (e, A^0), donors to valence band (D^0, h), and the donor-acceptor pair (DAP) transitions [26–31]. A broad luminescence band around 1.45 eV is denoted as the Y-band and/or A-centre [4,19,27,32] along with its longitudinal-optical phonon (LO) replicas ($\hbar\omega_{LO} = 21.3$ meV) [1]. The peak at ~1.35 eV is labeled as Z-band [5,33]. Some different characteristic PL peaks are found in these CdTe EFs, *i.e.*, (1) the 1.552 eV (D^0, h) peak is only observed in CCT films, found in the Cd-rich CdTe samples where it is attributed to V_{Te} [2,3], further supporting that the CCT films are in a Cd-rich state; and, (2) the DAP can be suppressed in CCT EFs as further given in Table 1, implying the suppression of V_{Cd}-related defects in the Cd-rich state.

Exciton energy transitions at ~1.59 eV of the NCT, TCT, and CCT EFs are plotted in Fig. 3 (d)-(f). The corresponding exciton-related PL peaks for the NCT, CCT, and TCT EFs can be resolved by curve fit-