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Band-gap engineering of $Cd_{1-x}Zn_xTe$ films deposited by pulsed laser deposition

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ABSTRACT

We demonstrate enhanced band-gap tunability in $Cd_{1-x}Zn_xTe$ thin films ($x = 0$, 0.03, 0.06, 0.1, 0.2, or 1) fabricated directly from $Cd_{1-x}Zn_xTe$ targets using pulsed laser deposition (PLD). All the $Cd_{1-x}Zn_xTe$ films have uniform thicknesses of ~200 nm, crystalline sizes of ~20 nm, and are highly oriented in the [111] direction. The annealed $Cd_{1-x}Zn_xTe$ targets allow better compositional control of the $Cd_{1-x}Zn_xTe$ films than non-annealed targets. This new process using a single target with high compositional uniformity provides better tunability of the $Cd_{1-x}Zn_xTe$ film lattice parameter (6.49 to 6.09 Å) and band gap (1.48 to 2.22 eV) by increasing the Zn concentration (x) from 0 to 1.

1. Introduction

Single-crystal CdTe is a p-type II-VI semiconductor material that has attracted attention as an X-ray, gamma-ray, and neutron detector because of its low leakage current and high detection efficiency at room temperature [1,2]. Furthermore, CdTe compounds have great potential in opto-electronic devices because their direct band gap (~1.5 eV) is closely matched to that of the solar spectrum and they have high absorption coefficients [3]. In particular, $Cd_{1-x}Zn_xTe$ ternary compounds have been actively investigated because of their wide range of band gaps, which can be varied from 1.5 eV (for CdTe) to 2.3 eV (for ZnTe) simply by controlling the concentration of Zn [4,5]. Such a wide band-gap range provides flexibility in the type of devices that can be fabricated with this alloy. For photosensors, the increased band gap results in reduced leakage current by increasing the electrical resistivity of the device, and the strong bonding between Zn and Te provides high detection efficiencies when the material is employed in radiation detectors [6]. Several deposition methods have been used to deposit $Cd_{1-x}Zn_xTe$ films, including close-spaced sublimation [7], radio-frequency (RF) magnetron sputtering [8], chemical vapor deposition [9], and two-source vacuum evaporation [10]. Unlike these methods, pulsed laser deposition (PLD) can be used to deposit thin films with complex stoichiometry because all of the components in the target ablate at the same time owing to the intense laser beam, regardless of their binding energies [11]. While this is a clear advantage for PLD, it also demonstrates the need to carefully control the target composition to achieve the desired composition in films deposited by PLD. Another advantage of film deposition by PLD is that the films can be crystallized at relatively low temperatures because of the high energy and deposition rate of the ablated species [12]. Previous reports of $Cd_{1-x}Zn_xTe$ films deposited from multiple targets using PLD indicate that the resulting films are Zn-poor and Te-rich because of the low sticking coefficient and high volatility of Zn compared with those of Cd and Te [13]. Thus, it is difficult to precisely control the concentration of Zn (x) in $Cd_{1-x}Zn_xTe$ films deposited by PLD using multiple targets. Furthermore, Te-rich films may have Te inclusions that can act as charge traps, significantly reducing the overall energy resolution and efficiency of the resulting devices [14].

In this study, we demonstrate improved band-gap tunability of $Cd_{1-x}Zn_xTe$ thin films deposited by PLD directly from $Cd_{1-x}Zn_xTe$ single targets with high compositional uniformity. The effect of thermal annealing on the compositional uniformity of the targets and films is also investigated. The measured lattice parameters and band gaps of the $Cd_{1-x}Zn_xTe$ films ($x = 0$, 0.03, 0.06, 0.1, 0.2, or 1) are compared with the theoretical values.

2. Experimental details

$Cd_{1-x}Zn_xTe$ ($x = 0$, 0.03, 0.06, 0.1, 0.2, or 1) targets were fabricated by hot pressing a mixture of CdTe and ZnTe powders.

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The starting powders of CdTe (deposition grade, 250 μm, purity >99.99%, Sigma-Aldrich Korea) and ZnTe (deposition grade, ~100 mesh, purity >99.99%, Sigma-Aldrich Korea) were mixed using an SPEX mill (8000D Dual Mixer/Mill, SPEX Sample Prep, Inc.) for 1 h. The mixture was then placed in a stainless steel mold with a cylindrical cavity (25.4 mm in diameter) and hot pressed at 600 °C for 3 h under a pressure of ~350 MPa. The hot-pressed targets were annealed at 600 °C for 15 h in Ar to ensure better compositional uniformity. In this paper, the *as*-pressed and annealed samples are labeled $Cd_{1-x}Zn_xTe$_HP and $Cd_{1-x}Zn_xTe$_Heat, respectively.

The $Cd_{1-x}Zn_xTe$ films were deposited on SiO_2 or glass substrates by PLD (Pioneer 180 PLD, Neocera Inc.) from the corresponding $Cd_{1-x}Zn_xTe$ target. Prior to deposition, the glass and SiO_2 substrates were cleaned by ultrasonication in acetone, isopropanol, and deionized water and dried in a N_2 stream. After placing the target and substrate in a chamber, the chamber was evacuated to 1×10^{-6} Torr, and Ar gas was used to adjust the deposition pressure to 20 mTorr. A KrF excimer laser with a wavelength of 248 nm was used to ablate the target at a fluence of 0.75 J/cm^2 and a frequency of 10 Hz. Before deposition, the target was cleaned by a pre-ablation process using 5000 laser pulses with the substrate shutter covering the sample. The target was then ablated with 20,000 laser pulses to deposit a $Cd_{1-x}Zn_xTe$ film on the substrate. For comparison, $Cd_{1-x}Zn_xTe$ films ($x = 0.03$ or 0.06) were also deposited from separate CdTe and ZnTe targets. They were obtained by sequentially depositing nanometric layers of CdTe and ZnTe for 40 cycles. For $Cd_{0.97}Zn_{0.03}Te$ films, the number of laser shots per cycle was set to 486 and 14 for CdTe and ZnTe, respectively. For $Cd_{0.94}Zn_{0.06}Te$ films, the number of laser shots per cycle was set to 472 and 28 for CdTe and ZnTe, respectively. The substrates were maintained at room temperature during the depositions.

The crystal structures and phases of the targets and films were analyzed using X-ray diffraction (XRD; CN2301/Ultima III, Rigaku) with a Cu radiation source ($E_{K_\alpha} = 8$ keV). The composition of the targets was examined using energy-dispersive X-ray fluorescence (ED-XRF; SEA 1200VX, Rigaku). A rhodium anode X-ray tube with a typical input power of 50 kV and 1 mA was used for primary excitation. An energy resolution of 145 eV FWHM was measured at 1 μs peaking time for 50 s. The composition of the films was examined using X-ray photoelectron spectroscopy (XPS; PHI 5800, ULVAC-PHI) with an Al radiation source ($E_{K_\alpha} = 1.49$ keV). The spectra of each region were obtained at a constant pass energy of 20 eV and a step size of 0.1 eV. The morphology and the thickness of the films were evaluated by scanning electron microscopy (SEM; Zeiss Supra, Zeiss). The films were coated with Pt to improve the image quality during SEM analysis. From the SEM images, the crystal sizes were calculated using the linear intercept method. The band gap of the films was determined from the absorption and transmittance spectra measured in the wavelength range 199–995 nm using ultraviolet–visible spectroscopy (UV–vis spectroscopy; Agilent 845, Agilent Technologies).

3. Results and discussion

Fig. 1 shows the XRD patterns of the targets and films with various compositions. The targets have randomly oriented crystals showing three dominant peaks corresponding to the (111), (220), and (311) planes. The films are highly oriented in the [111] direction. The hot-

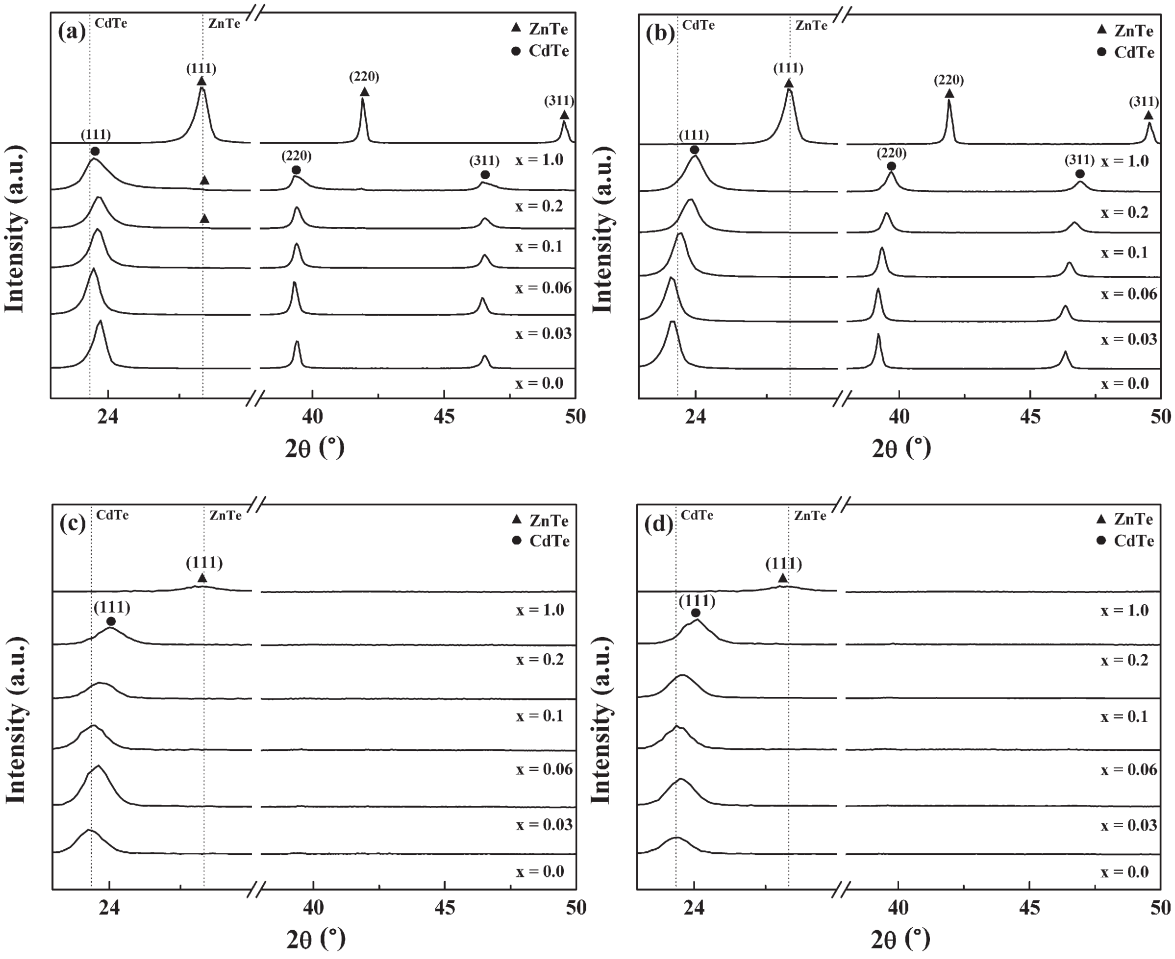

Fig. 1. X-ray diffraction patterns of $Cd_{1-x}Zn_xTe$ targets and films with various compositions: (a) hot-pressed targets, (b) annealed targets, (c) films deposited from hot-pressed targets, and (d) films deposited from annealed targets.