Close-space sublimation growth and characterization of ZnTe epitaxial thick film

Jiawei Li, Gangqiang Zha*, Yadong Xu, Shouzhi Xi, Yingrui Li, Rui Yang, Wanqi Jie
State Key Laboratory of Solidification Processing
Key Laboratory of Radiation Detection Materials and Devices, Ministry of Industry and Information Technology,
School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China

Abstract—**ZnTe epitaxial film with thickness of 200μm was grown on the GaAs substrate by close-space sublimation（CSS）. The surface topography of ZnTe film was analyzed by SEM, and the evolution of growth pit was observed, which revealed the mechanism of epitaxial growth. The structure was analyzed by X-ray radiation diffraction (XRD) θ-2θ scan and rotary Φ-scan, and the results suggested that the ZnTe thick film is epitaxial film. The crystalline quality of ZnTe thick film was characterized by X-ray rocking curve and Raman spectrum, and the results suggested that ZnTe epitaxial film obtained by CSS could be as a replacement of ZnTe single crystal, especially for thinner and larger requirement.**

I. INTRODUCTION

ZNTE offers interesting properties at potential application in terahertz (THz) device. X.C. Zhang [1, 2] result shows a thin sensor crystals (<30μm) allow the range of electric-optic detection extend into mid-infrared range. Considered to obtain certain thickness of crystals, mechanical polishing process which greatly introduced surface stress damage is the only way. H.G. Roskos[3] results promote the use of larger emitter crystals in amplifier-laser-based THz systems in order to minimize saturation effects. Moreover, the generation of an initially larger THz beam also provides improved spatial resolution at intermediate foci between emitter and detector. Thus, the fabrication of large-size（>25mm） ZnTe crystals becomes significant. Traditional crystal growth method is hard to obtain large-area sample. The epitaxial growth of ZnTe film on certain substrate could cover such shortages that have received considerable interest. Various growth techniques such as hot wall epitaxy（HWE）[4], molecular beam epitaxy（MBE）[5], metal-organic vapor phase epitaxy (MOVPE)[6] have been explored. However, such growth techniques are hard to prepare thicker, fast-growing and lower cost epitaxial film. Close-space sublimation, of which growth condition is easily controlled, is a promising growth method for obtaining ZnTe epitaxial film with high-quality and controllable thickness ranging from 10μm to 400μm.

In this article, hetero-epitaxial ZnTe layers on (100) GaAs substrate were fabricated by CSS. The surface morphology evolution mechanism was presented by SEM and the epitaxial property was confirmed by X-ray diffraction with Φ-scan mode. Raman spectrum and X-ray rocking (XRC) curve show that the ZnTe epitaxial film has a high crystalline quality on the GaAs substrate.

II. RESULTS

ZnTe layer was grown by a co-developed close-space sublimation furnace at atmospheric pressure with different thickness. The main features of this method are that the growth speed and the growth condition could be easily controlled, which could obtain high quality epitaxial film. ZnTe bulk was used as source and GaAs (100) 2° off towards [110] was used as substrate. Before performing the experiment, the ZnTe bulk was pretreated in acetone, anhydrous ethanol and double distilled water, using an ultrasonic cleaner for 20 min. The GaAs substrate was corroded by corrosive liquid (H_2SO_4:H_2O_2:H_2O=3:1:1) for 90s, and was cleaned following the same steps as ZnTe bulk. After dried by nitrogen respectively, the ZnTe bulk and GaAs substrate was put in the vacuum drying chamber for thermal treatment, and then transfer to the CSS growth chamber.

Before sublimation process, GaAs substrate was heated up to 823K for 30min, as a cleaning treatment to remove the surface oxide layer. The ambient pressure was 100Pa in static Ar and the source-substrate separation distance was 5 mm in order to keep a proper deposition rate and film uniformity. The ZnTe films were deposited with the source temperature of 1073 K and substrate temperature of 673 K for 2h, and the thickness of film is 200μm, the growth rate is up to1.67μm/min.

The surface morphology of the film was studied with a field emission scanning electron microscopy (FE-SEM, ZEISS SUPRA-55). The structure was studied with XRD θ-2θ scan and rotary Φ-scan. Both an X-ray θ-2θ scan in the range of 20^o-80^o and Φ-scan for the (511) set of planes. The crystalline quality of the ZnTe films was evaluated by Raman spectra and X-ray rocking curve (XRC) of a high resolution double-crystal method.

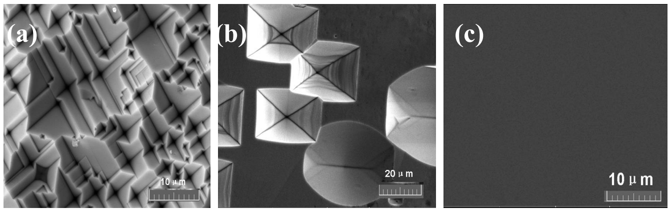

Fig.1. SEM images of ZnTe(100) epitaxial growth on (100) GaAs.

(a) ZnTe growth step, (b) ZnTe growth pit,(c) ZnTe smooth surface

Fig. 1 displays the morphology evolution of the ZnTe film, characterized by FE-SEM with deposit thickness varying, which clearly shows that the film is growth at the beginning based on the heredity of GaAs(100) growth steps, and then the growth pit formed, deposited clusters fulfill the growth pit, and finally developed into an epitaxial layer with smooth surface.

The XRD θ-2θ spectrum of the film shown in Fig. 2 has two diffraction peaks corresponding to the (200) and (400) planes of zinc blende ZnTe, respectively. (400) diffraction from

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*Author to whom correspondence should be addressed. Electronic mail: zha_gq@hotmail.com.

the GaAs substrate located at 65.88° is also observed. Fig. 3 shows the XRD rotary Φ-scan for the (511) set of planes. Four 90° equally separated diffraction peaks are observed in the spectrum of Φ-scan, seen in Fig. 3, indicating the film has single in-plane orientation and four-fold symmetry, which is consistent with the cubic crystal structure [7].

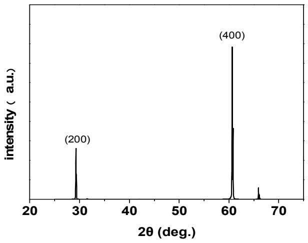

Fig.2. XRD θ-2θ scan in the range of 20°-80°.

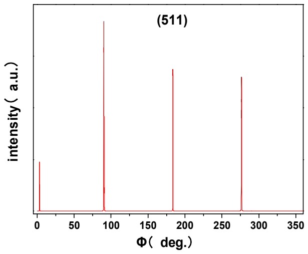

Fig.3. XRD Φ-scan for the (511) set of planes.

XRC should be a generally accept test method to evaluate the crystalline quality. Fig.4 shows a typical XRC result for (400) reflection from ZnTe films with a full width at half maximum (FWHM) value of 264arcsec (compared other growth method (HWE: 107arcsec, MOVPE: 103arcsec) [4, 8]. Optical property has a close relationship with crystalline quality especially for the requirement of electric-optic sample. Raman spectra result is shown in Fig.5, Low longitudinal optical phonon mode: 1LO (206cm^{-1}), 2LO (410cm^{-1}), are clearly observed [9]. The Raman scattering of phonons in crystals can be explained by interactions of phonons and photons. It has been shown that Raman spectroscopy is a sensitive method for characterize the crystalline quality for the extent defect could give rise to a broadening of Raman peak [10]. The FWHM of 1LO peak was calculated as 0.722meV. For CSS growth ZnTe film, thermal stress is the main stress affection to crystal quality.

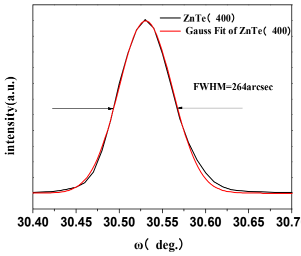

Fig.4. X-ray rocking curves for (400) reflection.

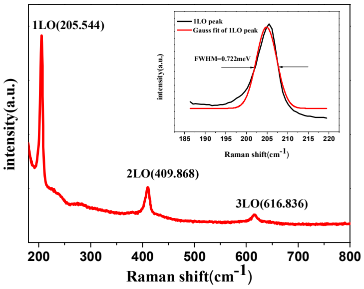

Fig.5. Raman spectra of ZnTe epilayer and the FWHM of 1LO by Gauss fitting.

Compared with ZnTe thermal expand coefficient, GaAs is smaller, and the mismatch between film and substrate is 34%. Expansion stress becomes bigger as the cooling process going for ZnTe film from substrate temperature (623K). For the further fabrication of ZnTe film, the crystalline quality of film will be improved by lowering the substrate temperature or better designing the cooling process.

III. SUMMARY

ZnTe epitaxial film with a well controlled thickness was successfully prepared by CSS. The surface topography of ZnTe film was analyzed by SEM, and the evolution of growth pit was observed, which revealed the mechanism of epitaxial growth. XRD θ-2θ and Φ-scan analysis confirmed the epitaxial growth mechanism respectively. The X-ray rocking curve result shows the FWHM is 264arcsec. The low longitudinal optical modes were clearly observed and the FWHM of 1LO is 0.722meV, such results suggested that ZnTe epitaxial film could be as a replacement of ZnTe single crystal, especially for thinner and larger requirement.

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