文章编号:1001-9014(2009)01-0001-03

THz EMISSION AND DETECTION OF ZnTe BULK CRYSTALS GROWN BY Te SOLVENT METHOD

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Abstract: <110> oriented ZnTe crystals were grown by Te-solvent method and tested by X-ray diffraction (XRD) and Raman scattering measurements. THz generation and detection characteristics of the Te-solvent-grown ZnTe electro-optic crystals were studied in detail in Terahertz-time domain spectroscopy. Our results show that the <110>-oriented ZnTe crystals can emit high signal noise ratio THz signal pumped by Ti: sapphire laser, and the THz pulse's width is over 3 THz at the room temperature.

Key words: ZnTe crystal; terahertz-time domain spectroscopy (THz-TDS); Te-solvent method
CLC number: 0472+.3 **Document**: A

碲-熔剂方法生长 ZnTe 单晶的太赫兹辐射及探测

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摘要:通过Te熔剂方法生长出<110>晶向的ZnTe单晶,利用X射线衍射(XRD)及拉曼光谱对该材料进行了测试.详细研究了太赫兹时域光谱系统中该ZnTe单晶作为激发和探测晶体的辐射和探测特性.结果表明在钛-宝石激光器的泵浦下,Te熔剂方法生长的<110>晶向的ZnTe晶体表现出良好的THz辐射性能,室温下激发频谱可达3THz以上.

关 键 词:ZnTe单晶;太赫兹时域光谱系统(THz-TDS);Te溶剂方法

Introduction

Photoconductive method and optical rectification method are often used to generate wide-band THz pulses [1]. In recent years, optical rectification has received extensive attention for its potential application in THz microscopy techniques [2]. In optical rectification method, a very short optical pulse is focused on a nonlinear crystal, which causes a time-dependent polarization of the material due to the electro-optic effect. The induced polarization radiates a broadband THz pulse[3].

Several materials, including ZnTe, ZnSe, CdTe, $LiTaO_3$, $LiNbO_3$, and organic DAST crystal, have been proved proper as THz sensor crystals. Data in literature[4] shows that ZnTe crystal appears to be the best choice for THz pulse generation by 800 nm laser pumping, since ZnTe crystal has a large 2nd order

Received date: 2008-02-13, **revised date**: 2008-08-15   **收稿日期**:2008-02-13, **修回日期**:2008-08-15
Foudantion item: supported by The National High Technology Research and Development (No. 2006AA12Z135), National Nature Science Foundation of China (Nos. 10334030 and 60225004), Knowledge Innovation Program of Chinese Academy of Sciences (Nos. C2-38 and C2-22).
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nonlinear susceptibility $\chi^{(2)} = 1.6 \times 10^{-7}$ esu and large electro-optic coefficient $\gamma_{41} = 4.04$ pm/V at this wavelength. Since the phase matching condition in the <110> orientation is more favorably met, the <110> oriented ZnTe crystal yields more powerful THz pulse than any other orientations.

It is rather difficult to grow high-quality ZnTe single crystal used in THz apparatus. In this paper, we report the Te-solvent method to grow ZnTe single crystal. Te-solvent method takes advantage of the reduction of crystal growth temperature and the growth equipment in the Te-solvent method is relatively simple. We also report the characteristics of the ZnTe crystals and the detailed information of the Terahertz emission and detection using ZnTe crystals.

1 EXPERIMENT

Zn-Te binary phase diagram[5] indicates that the melting point of ZnTe crystal is about 1300℃ at 1:1 mole ratio. The crystallization temperature of ZnTe crystal decreases with the increase of Te mole ratio and the solubility of ZnTe in liquid tellurium can be calculated from the phase diagram. Crystallization temperature of ZnTe is as low as 1060℃ when the mole ratio of Zn: Te reaches 3:7. To get high purity ZnTe crystals, 7N zinc (Zn) and 7N tellurium (Te) were charged into quartz crucible and the crucible was exhausted down to a pressure less than 1×10^{-4} Pa and then sealed off by a quartz plug. The crucible of 25 mm diameter and 250 mm length was placed in the vertical furnace and heated up to 1060℃. The highest temperature was set at 1100℃ to ensure complete melting of ZnTe. The temperature gradient of the vertical furnace was controlled at 10℃/cm.

<110>-oriented ZnTe single crystal wafers were cut from the grown ingot. After being polished on both surfaces, the ZnTe wafers became relatively transparent and exhibited orange color, as shown in Fig. 1. Crystallization quality of ZnTe crystals was characterized by Philip X' pert Pro X-ray diffraction (CuKα radiation source, 0.2 mm Ni filter). Fig. 2 gives XRD pattern of the <110> -oriented ZnTe crystal and the data are presented with a 2θ/ω scan mode. The main peaks are due to the second and the fourth order diffractions of

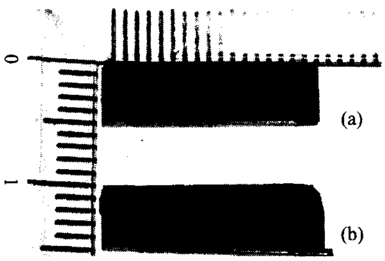

Fig. 1 <110> oriented ZnTe crystals with a size of 5 × 16 mm^2 (1.05 mm in thickness) used as detector (a) and as emitter (b)
图1 5×16 mm^{2}的<110> ZnTe 单晶(1.05 mm 厚)(a)探测晶体 (b)激发晶体

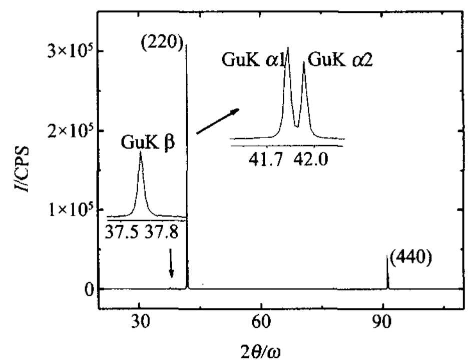

Fig. 2 X-ray diffraction of ZnTe crystal (I is X-ray intensity)
图2 ZnTe 晶体的 X-射线衍射图谱

the ZnTe crystal, indicating that the material is single crystal with a <110> -oriented surface. The XRD result demonstrates that the Te-solvent method can be adopted to grow ZnTe crystal with good crystalline quality.

Terahertz-Time Domain Spectroscopy (THz-TDS) was measured on the ZnTe crystal grown by Te-solution method. The schematic information of the THz-TDS system is presented in Fig. 3. In this THz-TDS setup, THz pulses are generated with optical rectification in a ZnTe nonlinear crystal and detected with another ZnTe electro-optic crystal. Two <110> -oriented ZnTe crystals, grown by Te-solvent method, with the same thickness are selected as the emitter and detector.

Ultra-short laser pulses are generated from a regenerative Ti: sapphire amplifier using chirped pulse amplification technique (RegA 9000, Coherent Inc.). The output pulse with central wavelength at 800 nm has pulse duration of 120 fs, repetition rate of 250kHz. After passing through the chopper, the pulse energy density is about 30 μJ/cm^2. A beam splitter was used to split the laser beam into two: a pump beam (~90%) and a weak probe beam (~10%). The strong pump beam goes through an optical delay line and is then focused onto a ZnTe emitter to generate pulsed THz electric-magnetic wave. The weak beam is focused onto a ZnTe detector to detect THz radiation from the ZnTe emitter. A silicon slice is used as a filter for blocking the pump light. The transmitted THz beam was collimated with a parabolic mirror first and then focused onto the ZnTe detector with another parabolic mirror. After passing through a quarter wave plate (λ/4) and a Wollaston prism, the probe beam is focused on the same spot of the ZnTe detector as the THz wave is. A differential detection with balanced photodiodes was used to measure the different intensities of the probe beam caused by generated THz waves. The final differential signal from balanced photodiodes was collected with a lock-in amplifier.

2 RESULTS AND DISCUSSION

Raman spectroscopy can be used as an effective tool for structural characterization of semiconductors. Among many applications in semiconductor studies, Raman measurements provide a means of probing the lattice dynamics of disordered solids, thus giving insight into the structure, bonding and nature of the disorder. The room-temperature Raman spectrum of ZnTe was investigated by a 50mW He-Ne laser operating at 632.8 nm and the results are presented in Fig. 4 Several Raman lines are observed and two main lines are found at 175 cm^{-1} and 202 cm^{-1}, both being the first-order Raman peaks that are assigned as transverse optical (TO) mode (at 175 cm^{-1}) and longitudinal optical (LO) mode (at 202 cm^{-1}). The other observed frequencies in Fig. 4 are attributed to the second-order Raman modes of ZnTe single crystal [6]. No Raman peaks associated with Te are observed, indicating that the density of Te precipitates is low in the ZnTe crystal.

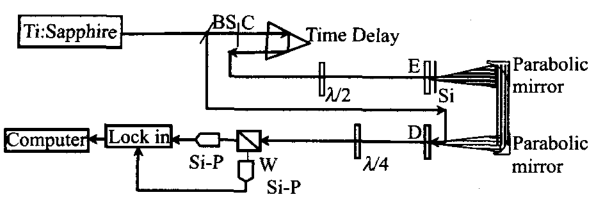

Fig. 3 Schematic of THz-TDS system. BS: beam splitter; C: chopper; E: ZnTe emitter; D: ZnTe detector; W: Wollaston prism; Si-P: silicon photodiode
图 3 太赫兹时域光谱系统图示. BS: 分束器; C: 斩波器; E: ZnTe 太赫兹发射器; D: ZnTe 太赫兹探测器; W: 渥拉丝顿棱镜; Si-P: 硅光探测器

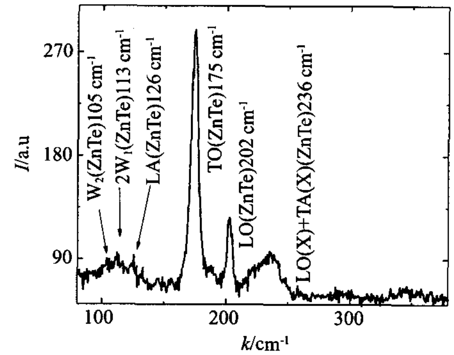

Fig. 4 Room-temperature Raman spectrum of ZnTe crystal (k is wavenumber and I is intensity)
图 4 室温 ZnTe 的拉曼光谱

Fig. 5 (a) presents the temporal waveform of a THz pulse with ZnTe optical rectification emission and ZnTe electro-optic detection, while Fig. 5 (b) shows the frequency waveform Fourier-transformed from the temporal waveform. In Fig. 5, sample. 1 ZnTe crystal (dashed line) was grown by the high pressure Bridgman method bought from II-VI Company (U. S.), while sample. 2 ZnTe crystal (solid line) was grown by Te-solvent method in this work. Since the thickness of the sample. 2 (1.05mm) is thicker than that of sample. 1 (1mm), the pulse of sample. 2 arrives later than that of sample. 1, i. e., it takes a little more time (about 0.39 ps) to propagate through sample. 2. As the measurements were performed in the atmosphere without dry N_2 purging, the water vapor absorption is rather strong. There are many absorption peaks in the Frequency waveform (Fig. 5(b)). We can see that the temporal waveform and the frequency waveform of sample. 2 (solid line) are as good as those of sample. 1 (dashed line). It can be seen that the ZnTe single crystal grown by Te-solvent method can emit and detect THz signal as well as the ZnTe single crystal grown by high pressure Bridgman method. Moreover, the Te-solvent method can reduce the temperature and pressure of the crystal growth com-pared with the high pressure Bridgman method. How-

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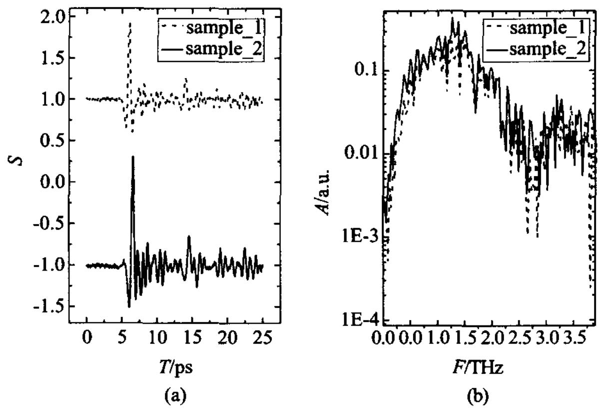

Fig. 5 THz pulse spectrum (a) temporal waveform (b) frequency waveform(*T* is time and *F* is frequency, *S* is THz signal and *A* is THz amplitude)
Sample_1: <110> ZnTe crystal emitter, <110> ZnTe crystal detector (II-VI Company)
Sample_2: <110> ZnTe crystal emitter, <110> ZnTe crystal detector (This work)
图 5 THz 脉冲光谱 (a)时域光谱 (b)频域光谱
Sample_1: <110>晶向 ZnTe 晶体激发, <110>晶向 ZnTe 晶体探测(II-VI 公司)
Sample_2: <110>晶向 ZnTe 晶体激发, <110>晶向 ZnTe 晶体探测(本实验)

ever, more information needs to be explored on the THz characteristics of ZnTe crystal grown by Te-solution method in our future study.

3 CONCLUSION

Te - solution method was introduced to grow ZnTe single crystal. The experimental analysis was performed on THz pulse characteristics and beam propagation of the Te-solvent-grown ZnTe electro-optic crystals. The TDS results confirm that Te-solvent method is a useful method for the growth of ZnTe crystals which are used to generate and detect the THz waves.

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