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Mid-infrared transmission imaging and spectroscopy with PbSnTe laser diodes grown with stoichiometry-controlled liquid-phase epitaxy

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HIGHLIGHTS

- A PbSnTe/PbTe double-hetero laser structure was fabricated using TDM-CVP LPE.
- Lasing and wavelength tuning of the fabricated LD were achieved.
- Mid-IR images of benzoic acid and Si wafers were obtained.
- Absorbance peaks of organic materials were observed in the resulting spectra.

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ABSTRACT

Bi- or In-doped *n*-PbTe/*p*-PbSnTe/Tl-doped *p*-PbTe double-hetero (DH) diode structures were fabricated using the temperature difference method under controlled vapour pressure (TDM-CVP) liquid-phase epitaxy (LPE). We fabricated a PbSnTe/PbTe DH-junction laser diode (LD) using TDM-CVP LPE and subsequently obtained sharp lasing spectra between 7.2 (1390 cm^{-1}) and 9.4 μm (1070 cm^{-1}) by varying the ambient temperature of the diode. When the fabricated $Pb_{0.89}Sn_{0.11}Te$/PbTe LD was used to image Si wafers with different resistivities, we obtained a clear contrast between the wafers. We also obtained the mid-infrared imaging spectrum of benzoic acid (BA) using the fabricated $Pb_{0.89}Sn_{0.11}Te$/PbTe LD, and the absorbance image obtained using the fabricated LD showed good agreement with a Fourier transform infrared (FTIR) spectrum. We observed sharp lasing spectra between 7.20 (1390 cm^{-1}) and 7.80 μm (1280 cm^{-1}) by varying the ambient temperature of the diode sample. We observed some absorption peaks in the obtained infrared absorption spectra of *para*-nitrobenzoic acid (PNBA) and BA; a peak at approximately 7.45 μm (1345 cm^{-1}) in the spectrum of PNBA originated from NO_2 symmetric stretching bands. Moreover, we observed that the other peaks in these spectra also match peaks from conventional FTIR spectra.

1. Introduction

The 6.70–16.7-μm (1500–600-cm^{-1}) mid-infrared region is well known as a fingerprint region for identifying organic materials [1]. It is possible to construct a molecular map using only images obtained at absorption frequencies in this region. Thus, mid-infrared semiconductor lasers with such emission wavelengths are expected to be more compact and to provide higher resolution infrared fingerprint region analysis than conventional Fourier-transform infrared (FTIR) spectroscopy.

In particular, group IV–VI compound materials, such as PbSnTe systems, are narrow- (0.04–0.3 eV, 30–4 μm) and direct-bandgap semiconductors. Therefore, these compounds are candidate materials for use in high-spatial-resolution mid-infrared lasers. Such PbSnTe lasers were already commercially available in the 1970s, however, these laser diode (LD) structures were fabricated by conventional slow-cooling liquid-phase epitaxy (LPE) [2–5]. A disadvantage of this method is that it is difficult to adjust the stoichiometry during crystal growth. Therefore, such conventional devices with non-stoichiometric defects in the semiconductor crystals suffered from poor performance. Recently, III–V semiconductor super lattice quantum cascade lasers (QCLs) have been developed as candidates for mid-infrared laser devices [6–8], and are now commercially available. These QCLs have high

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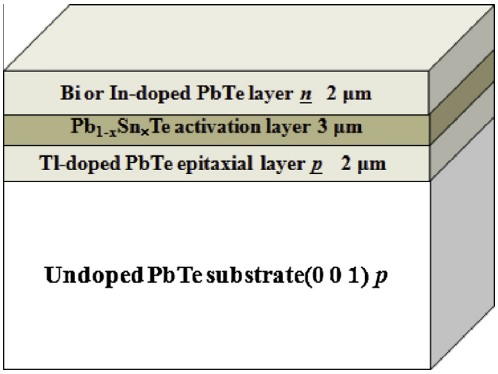

Fig. 1. Schematic of the PbSnTe/PbTe DH laser diode structure fabricated via TDM-CVP LPE.

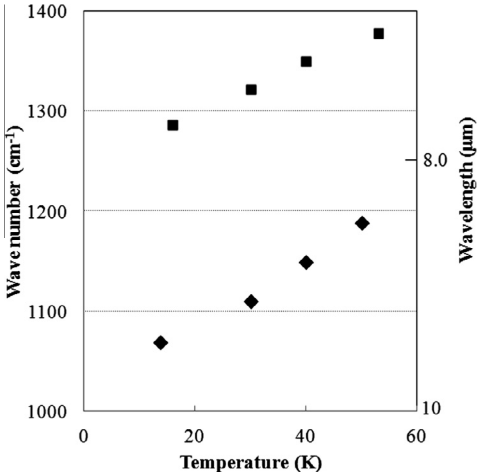

Fig. 2. Wavenumber and wavelength of the PbSnTe/PbTe DH lasing spectrum peak as a function of temperature.

performance related to emission power, sharpness and stability, however, they have very complicated structures and the wavelength cannot be easily tuned by varying the temperature (although they require only Peltier-cooled temperatures and not cryogenics).

In this study, we present simple, high performance and easily-tunable PbSnTe mid-infrared lasers prepared by stoichiometry-controlled crystal growth. As we reported previously [9–11], although our fabricated double-hetero (DH) laser diodes have a simple broad contact structure, the threshold current density for lasing was as low as approximately 200 A/cm^2. In addition, the emitting wavelength of such LDs could be tuned by varying the operating temperature (although cryogenic temperatures are required).

Gas sensing of environmental pollutants is a very popular application of these LDs [12–15]. Hinkley et al. reported gas spectroscopy using high performance PbEuSnTe DH lasers grown using the normal cooling LPE method [12], and Reddy et al. demonstrated high resolution gas spectroscopy [15]. However, little has been reported on the analysis of solids and organic materials using such lasers. Previously, we have reported transmission spectroscopy of glycine using our fabricated mid-infrared LD [10].

In this paper, as a first step for the application of such lasers for spectroscopy of solids and organic materials, we report the fabrication of a longer-lasing broad-contact *pn*-PbSnTe/PbTe DH LD and its lasing properties. We also demonstrate the infrared transmission imaging and spectroscopy of some Si wafers with different resistivities and two organic compounds (*para*-nitrobenzoic acid (PNBA) and benzoic acid (BA)) using the tunable $Pb_{1-x}Sn_xTe$/PbTe DH LD. We then discuss these results with respect to those obtainable using state-of-the-art techniques.

2. Materials and methods

Un-doped *p*-type PbTe crystals for the substrate were grown via the Bridgman method under controlled Te vapour pressure [16,17] where the hole concentration of the crystals was $p \approx 7 \times 10^{18}$ cm^{-3}. The substrate surfaces were polished and etched with a Norr etch solution (20 g KOH + 45 ml H_2O + 30 ml glycerol + 20 ml ethanol) to remove surface damage and to reveal a mirror-like surface [18]. For fabricating diode structures, epitaxial layers were grown by the temperature difference method under controlled vapour pressure (TDM-CVP) LPE. TDM-CVP LPE has been used to grow epitaxial layers with controlled stoichiometry [19–22]. First, Tl-doped PbTe was grown as a *p*-type cladding layer where the Tl concentration in the melts was 0.03 at.%. Next, a PbSnTe activation layer was grown. Finally, Bi-doped ($x_{Bi} \approx 8 \times 10^{18}$ cm^{-3}, $n \approx 1.0 \times 10^{17}$ cm^{-3}) or In-doped ($x_{In} \approx 1 \times 10^{19}$ cm^{-3}, $n \approx 8.0 \times 10^{18}$ cm^{-3}) PbTe was grown as an *n*-type cladding layer. The epitaxial thicknesses of the Tl-doped *p* cladding layer, activation layer, and Bi-doped or In-doped *n* cladding layer were approximately 2 μm, 3 μm, and 2 μm respectively. The growth temperature was 470 °C measured using a thermocouple positioned under the substrate. A nearly optimum Te vapour pressure for stoichiometry was applied to the growth solution during epitaxial growth to control the stoichiometry of the epitaxial layers [23–25]. Fig. 1 shows a schematic of the fabricated PbSnTe/PbTe DH LD structure.

Au/Pt were deposited as ohmic contacts via electro-plating on both the *n*-type layer side and the *p*-type substrate. Broad contact structure LDs were obtained by scribing to chips.

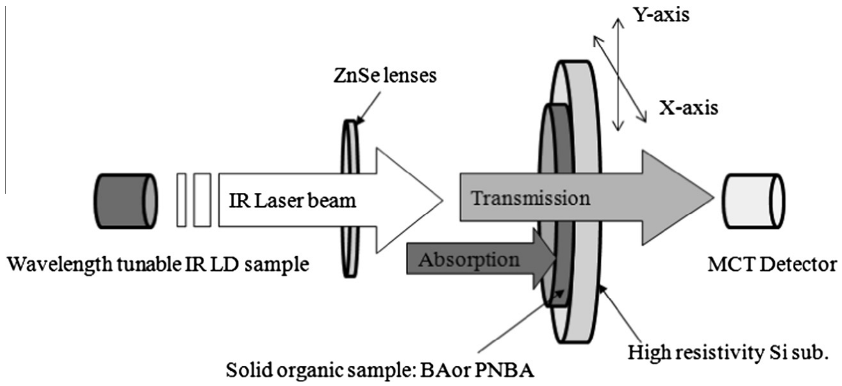

Fig. 3. Apparatus used for IR transmission imaging and spectroscopy with the tunable PbSnTe/PbTe DH LD.