Electroluminescence and Lasing Properties of Highly Bi-Doped PbTe Epitaxial Layers Grown by Temperature Difference Method under Controlled Vapor Pressure

WATARU TAMURA,[1] ARATA YASUDA,[1] KEN SUTO,[1] OSAMU ITOH,[2] and JUN-ICHI NISHIZAWA[2,3]

1.—Department of Materials Science, Faculty of Engineering, Tohoku University, Aramakiaza Aoba, Sendai 980-0845, Japan. 2.—Semiconductor Research Institute, Kawauchi Aoba, Sendai 980-0862, Japan. 3.—E-mail: nishizawa@hanken.jp

Electroluminescence (EL) from PbTe pn homojunctions with a highly Bi-doped n-type emission layer with a concentration of $N_{Bi} > 10^{19}$ cm^{-3}, grown by the temperature difference method (TDM) under controlled-Te vapor pressure has shown a positive shift of the peak-photon energy, which coincides with the model that Bi atoms act as both donors and acceptors, and they make the nearest lattice-site or very close donor-acceptor (DA) pairs. Broad-contact pn junctions with highly Bi-doped layers easily cause laser emission compared to the difficulty in the lasing operation of undoped pn junctions, which suggests that the nearest lattice-site Bi-Bi DA pairs act as strong radiative centers in PbTe.

Key words: PbTe, Bi-doped, laser operation

INTRODUCTION

The PbTe and PbSnTe laser diodes are required for the detection of environmental pollution gases and for application to medicine and biology. Roller et al. have recently reported the measurement of exhaled nitric oxide (eNO) and carbon dioxide (CO_2) simultaneously in human breath with IV-VI mid-infrared laser.[1] For impurity doping in these laser diodes, Bi is usually used for obtaining n-type layers.[2–4] However, detailed knowledge of the behavior of Bi atoms in PbTe has yet been lacking.

Recently Prinz et al. have discussed the electron localization effects in Bi-doped PbEuTe layers grown by molecular beam epitaxy.[5] We have reported on the electrical properties of Bi-doped PbTe epitaxial layers grown by the temperature difference method under controlled vapor pressure (TDM-CVP) liquid phase epitaxy, as a function of Bi concentration in Pb solution, x_{Bi}, and as a function of Te vapor pressure applied on the solution.[6] Although Bi atoms were thought of as typical donor impurities, it is suggested that Bi atoms act as both donors and acceptors in highly Bi-doped layers as long as applied-Te vapor pressure does not exceed the optimum vapor pressure for stoichiometry. Moreover, with increasing x_{Bi}, Hall mobility has been found to drastically increase at $x_{Bi} > 0.4$ at.% at which Bi concentration in the crystal is thought to be $N_{Bi} > 10^{19}$ cm^{-3}. Also, Bi impurities form deep levels with $E_d = 0.06-0.08$ eV, only at a relatively low Bi-concentration region, i.e., $x_{Bi} < 0.2$ at.%, or, for Te vapor pressure exceeding the optimum value for stoichiometry.[6] From these results, it is suggested that at high Bi concentration, a Bi-donor atom located at the Pb site and a Bi-acceptor atom make a nearest-neighbor or very near donor-acceptor (DA) pair, which does not cause effective ionic scattering nor form a deep level.

In this paper, we report the electroluminescence (EL) and lasing properties of pn junctions formed with a highly Bi-doped PbTe epitaxial layer on a Tl-doped p-type epitaxial layer. We show that Bi doping causes efficient light emission, and emission wavelength shows a correspondence to the nearest-neighbor or very near DA pair model for Bi.

EXPERIMENTAL PROCEDURE

For the fabrication of pn junctions, a Tl-doped p-type layer and Bi-doped n-type layers are successively grown on a p-type undoped-PbTe substrate by TDM-CVP.[7–9] The growth temperature is 470°C. The substrate PbTe crystals have been grown with the Bridgman method under controlled-Te vapor pressure; they have a hole concentration of 7×10^{18} cm^{-3}. The Bi concentration in the solution, x_{Bi}, is 1 at.% so that the carrier concentration is about $1 \times$

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10^{17} cm^{-3}. However, Bi concentration incorporated in the epitaxial layer is 2.2×10^{19} cm^{-3}, which has been obtained by inductive coupled plasma (ICP) emission analysis.[6]

A Te vapor pressure of 2.3×10^{-4} Torr is applied on the growth solution to control stoichiometry.

In contrast, the carrier concentration in the p-type layer is 7×10^{18} cm^{-3}, which is higher than the electron concentration in the Bi-doped n-type layer.

Ohmic contacts are formed with Pt and Au successively deposited on both for the n-type layer and the p-type substrate by electric plating. Broad-contact structure laser diodes are obtained by cleaving a grown wafer to a width of 300 μm and length of 500 μm. No etching treatment is performed after cleaving.

The diode samples are placed in a cryogenic system in which the temperature can be controlled from 15.8–40 K. Width and duty ratio of the pulse current is 70 μsec and 1/267, respectively. Emission spectra are detected with a liquid nitrogen-cooled HgCdTe detector.

RESULTS AND DISCUSSION

The Bi-doped n region has a low electron concentration of 1×10^{17} cm^{-3}. Although Bi concentration is as high as 2.2×10^{19} cm^{-3}, self-compensation between Bi donors and Bi acceptors are thought to have occurred. In contrast, the Tl-doped p-region has a hole concentration as high as 7×10^{18} cm^{-3}. That is, the diodes are p^+n homojunctions, so the hole injection from the p-side to the n-side of the junction is almost two orders of magnitude higher than the electron injection from the n-side to the p-side. Therefore, we can reasonably assume that the observed light emission should be mainly due to the recombination of excess holes injected into the Bi-doped n side, occurring within the hole diffusion length from the pn-junction interface, and the electron injection to the p side can be neglected.

A typical example of the spontaneous emission spectra of highly Bi-doped pn junctions (x_{Bi} = 1 at.%) is shown in Fig. 1. A comparison is made with the earlier reported EL spectra from pn junctions with much lower Bi concentrations (1.6×10^{-3} at.% < $x_{Bi} < 6.2 \times 10^{-3}$ at.%).[10] A comparison is also made with the EL spectra of undoped pn junctions that were fabricated by Te vapor-pressure controlled growth of an undoped n-type epitaxial layer on an undoped p-type PbTe substrate. Figure 2 plots the peak-photon energies of these spectra as a function of temperature. For the undoped pn junctions, we showed that the peak at the high-energy side, denoted as A in the figure, nearly coincided with the bandgap energy determined from Ref. 11. Peak A becomes dominant, compared to peak B, at a current exceeding 100 A/cm^2. Therefore, peak A should correspond to the band-to-band transition.[10]

It is a remarkable fact that peak-photon energy for the highly Bi-doped pn junction is slightly larger than the bandgap energy, which is coincident

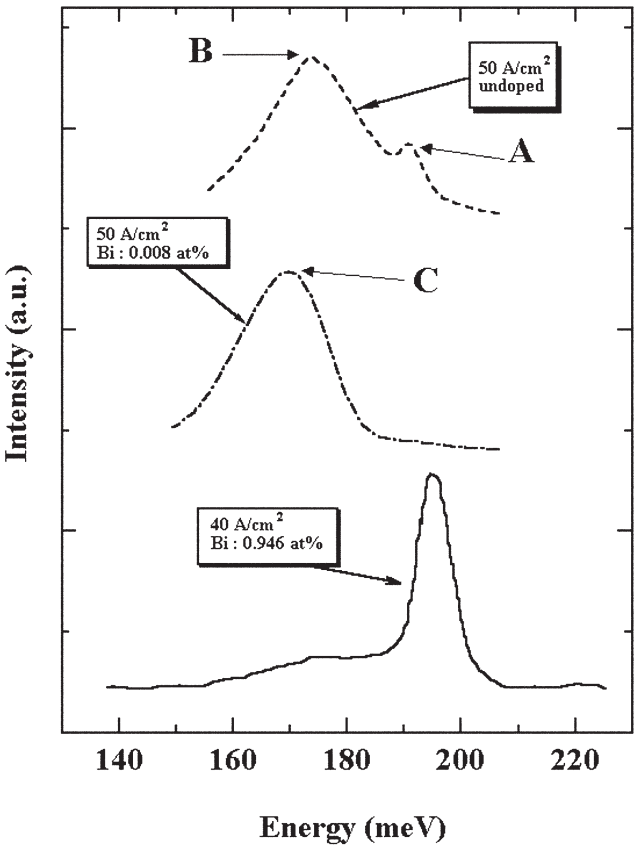

Fig. 1. The electroluminescence spectrum of a highly Bi-doped PbTe pn homojunction in comparison with those of lower Bi-doped and undoped pn junctions: (a) the band-to-band transition, (b) the DA pair transitions, and (c) through impurities levels or impurity band.

with the high-energy peak (A) of the undoped pn junction, in spite of a considerably longer wavelength shift for the lower Bi-doped pn junction. The energy is higher by about 3 meV than the bandgap energy. On the contrary, the EL peak-photon energy of the lower Bi-doped pn junction is lower by 20–25 meV than the bandgap energy (peak C). The latter energy difference was understood as an impurity level of Bi donors or onset of an impurity band caused by Bi donors.

In another paper,[6] we have reported the result that the Hall mobility is extraordinarily small for $x_{Bi} <$ 0.17 at.% (Bi concentration in the lattice $N_{Bi} < 4.4 \times 10^{18}$ cm^{-3}), which implies an impurity band formation by Bi donors or the formation of deep levels. Also, the result that the Hall mobility remarkably rises up at x_{Bi} = 0.4 at.% is coincident with the present result that the EL peak of a highly Bi-doped epitaxial layer up to x_{Bi} = 1 at.% is totally different from those for the lower Bi-doped layer. To explain such effects, we have proposed that, at high concentration of Bi impurities, a Bi atom occupying a Pb site and one occupying a Te site act as a donor and an acceptor, respectively, and most of them make up a DA pair at the nearest-neighbor Pb and Te lattice site, i.e., Bi_{Pb}-Bi_{Te} complexes are formed. Such a DA pair, having a distance with half the lattice spacing, will not cause strong ionic scatter-

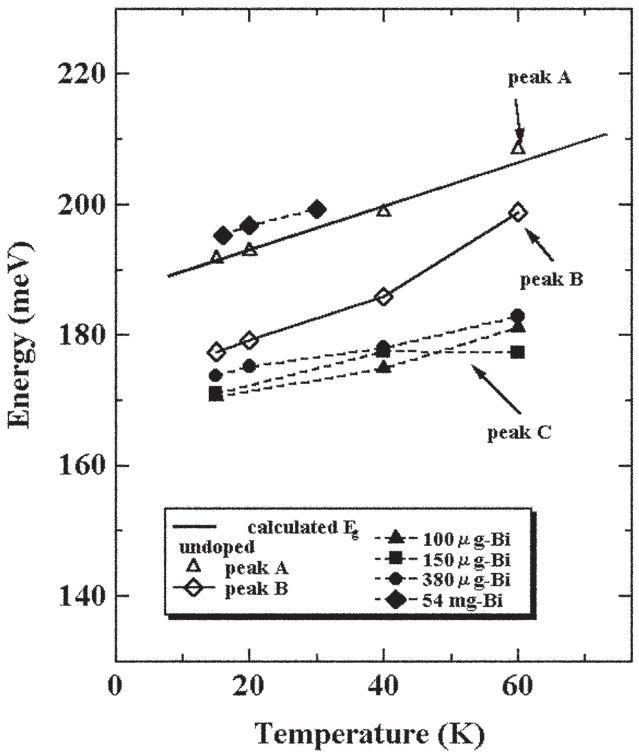

Fig. 2. The electroluminescence peak-photon energies versus temperature of a highly Bi-doped PbTe pn homojunction in comparison with those of lower Bi-doped and undoped pn junctions.

ing of charge carriers because the ionic charge is 0 as seen from carriers much more distant than the lattice spacing. In contrast, in an ordinary case in which ionized donors and acceptors are randomly distributed, strong ionic scattering should take place and Hall mobility should be greatly reduced at high Bi impurity concentration exceeding 10^{19} cm^{-3}. Therefore, the nearest lattice-site DA pair model for Bi impurities can explain the experimental result that the Hall mobility remarkably increased in the region $x_{Bi} > 0.4$ at.%.[6]

This model is consistent with the EL property of highly Bi-doped pn junctions. The emission photon energy for DA transition can be described as

$$h\nu = Eg - E_D - E_A + e^2/\varepsilon r$$

where E_g, E_D, and E_A are the bandgap energy and donor and acceptor binding energies, and r is the distance between a donor and an acceptor. The last term is the DA energy giving the positive shift to the emission energy. We estimate the DA energy for the nearest lattice-site pair; using r = 3.1 Å, half of the lattice constant, and the relative permeability of PbTe, $\varepsilon = 1400-1800$.[12] Then, we obtain $e^2/\varepsilon r = 42-32$ meV. Accurate comparison with the experiment cannot be made because the Bi acceptor energy is not known. However, the positive peak shift from the C peak arising from Bi impurities is 23–28 meV. Therefore, we can say that DA energy is roughly in agreement with the observed peak shift, considering the crudeness of the estimation.

Next, it is found that lasing oscillation easily takes place for pn junctions with a highly Bi-doped n-type layer, as is seen in Fig. 3. The threshold current for the broad-area diode structure is 800 A/cm^2 at 15 K, and 3 kA/cm^2 at 40 K (Fig. 4). The lasing wavelength shifts to a slightly longer wavelength than that of the spontaneous emission spectrum. This is a general feature because the absorption loss strongly increases at shorter wavelength for a homojunction laser.

In contrast, undoped pn junctions did not show any lasing oscillation as long as the same broad-contact diode structure is adopted. This fact indicates that the nearest lattice-site DA pairs of Bi act as efficient recombination centers. In the present experiment, the density of the Bi-Bi recombination center is thought to be as much as 1.3×10^{19} cm^{-3}. The applied-Te vapor pressure is the optimum vapor pressure for stoichiometry, i.e., $P_{Te} = 2.2 \times 10^{-5}$ torr for a growth temperature of 470°C, so the density of the defect deep levels should be minimized even though Bi concentration in the epitaxial layers is very high. On the other hand, the n-type layer in the undoped pn junction, the spectrum of which is shown in Fig. 1, was grown with a Te vapor pressure of 8.87×10^{-6} torr (growth temperature of 560°C), and the carrier concentration is 3×10^{17} cm^{-3}.[13] Its spontaneous emission spectrum reveals peak B, which shows a shift to higher energy with increasing current and, at the same time, the intensity saturation. Such behaviors are thought of as the features of the distant DA pair transition.[6] This fact means that any donor

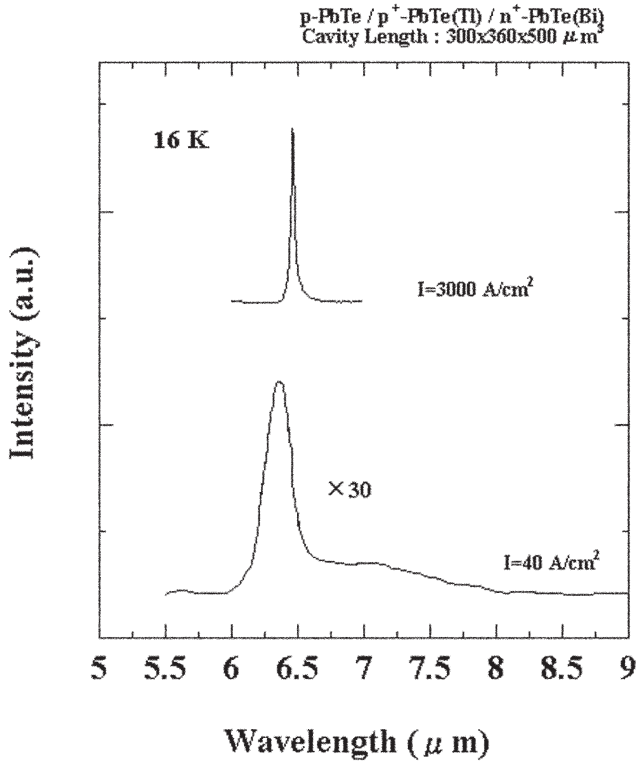

Fig. 3. The electroluminescence of a highly Bi-doped PbTe pn homojunction at a current density of 40 A/cm^2 and laser emission at 3000 A/cm^2 observed at 16 K.

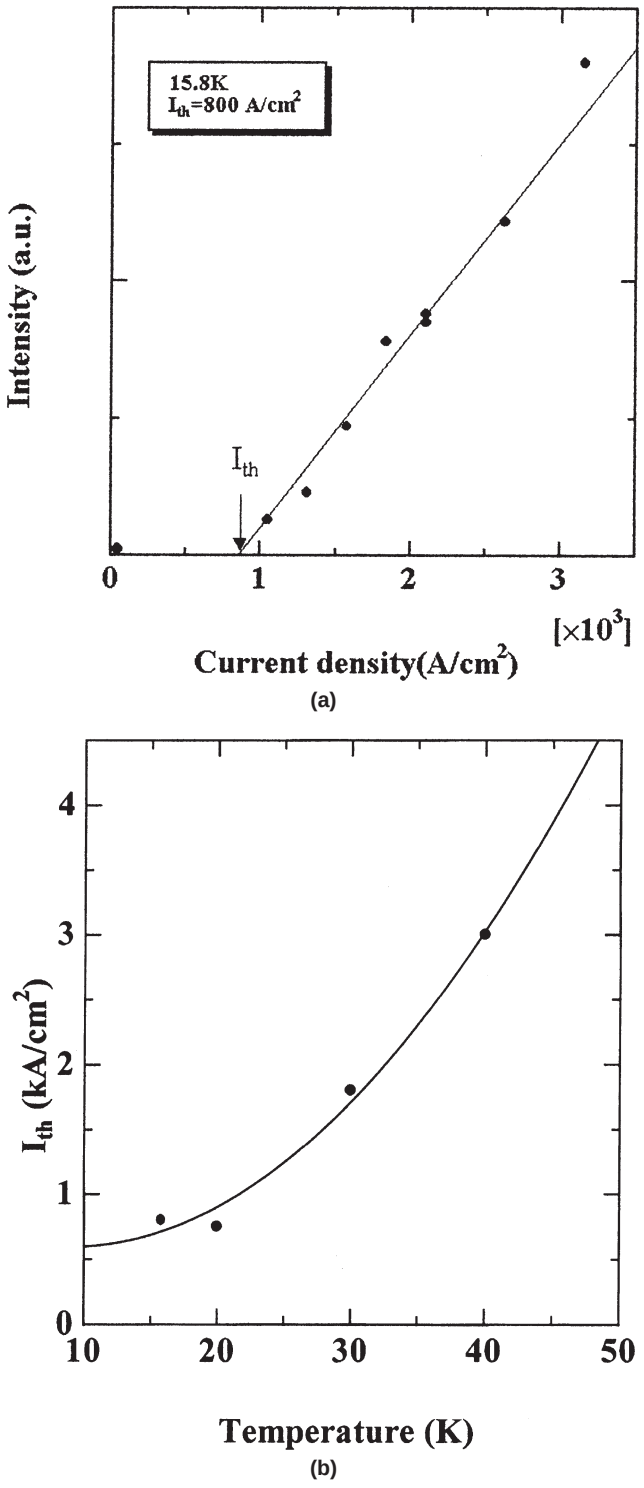

Fig. 4. (a) The intensity versus current density of a PbTe pn homojunction at 16 K showing the threshold current 800 A/cm^2. (b) Threshold current as a function of temperature.

and acceptor concentration in the undoped pn junction is not high enough for the lasing oscillation.

CONCLUSIONS

Electroluminescence and lasing from PbTe pn junctions with a Bi-doped n-type emission layer grown by the TDM-CVP has been investigated. Highly Bi-doped layers with $N_{Bi} > 10^{19}$ cm^{-3} show a positive shift of the EL peak-photon energy, opposed to those with lower Bi concentrations. This result coincides with the model that Bi atoms act as both donors and acceptors, and they make the nearest lattice-site or very close DA pairs in highly Bi-doped layers, which were derived from the measurement of the Hall coefficient. Broad-contact pn junctions with highly Bi-doped layers easily cause laser emission, while undoped pn junctions have not shown lasing operation as long as the same fabrication method is used. This result means that Bi-Bi DA pairs with the nearest lattice sites act as strong radiative centers in PbTe.

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