used in §3.2, namely non-doped LEC GaAs made by direct synthesis method. The contacts are stripe-shaped 100 µm-gap Au-Ge-Ni and show the ohmic characteristics up to the field of 100 V/cm.

Figure 6(a) shows the distribution of the extrinsic photocurrent excited by the focused YAG laser measured at intervals of 100 µm along the <110> direction from the center of the wafer. Figure 6(b) shows that of the intrinsic photocurrent excited by He-Ne laser. The photon flux and spot size are 8.7×10^{20} $cm^{-2}s^{-1}$ and about 180 µm for (a), 3.4×10^{15} $cm^{-2}s^{-1}$ and 120 µm for (b). We find; (1) the fluctuation with a small pitch is observed in both of the figures and the peak in Fig. 6(a) corresponds to the valley in (b) and vice versa, (2) the gradual U-shaped distribution which is observed in the extrinsic photocurrent is not observed in the intrinsic photocurrent. From the discusson in §3.1, it is

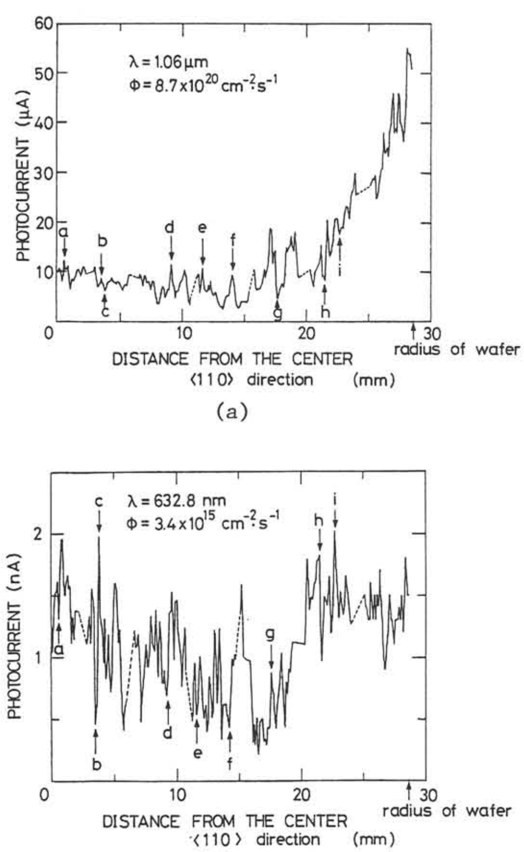

Fig. 6. Radial distribution of photocurrent in the semi-insulating wafer, measured at intervals of 100 µm and at 292 K. Arrows with the same alphabet indicate the same position. Dashed lines indicate the regions which could not be measured for sample preparation. (a) for extrinsic excitation. (b) for intrinsic excitation.

deduced that (1) is due to the variation of the trap density in the region where the trap density is much larger than the shallow acceptor density, while (2) is due to the change of the shallow acceptor density. As a result, it is suggested that a 0.79eV main compensator fluctuates with a small pitch in a wafer, while a shallow acceptor varies gradually towards the periphery in this sample.

This highly non-uniform distribution of the trap in semi-insulating GaAs is the same as that observed in semi-conductive GaAs described in §2.

§4. Summary

In semi-conductive LEC GaAs, the mid gap deep level has not a unique origin but has a family. The variation of the characteristics in depth and in radial direction and the annealing behavior of them show that one group in the family is unstable and highly fluctuating in a wafer. The fluctuation of the main compensator also observed in semi-insulating GaAs by the photocurrent method. Such fluctuations of the mid gap level can be considered to be related with the non-equilibrium growth condition which is due to the temperature fluctuation caused by convection in a melt.

Acknowledgement

This work is partially supported in "Nano-meter Structure Electronics" project by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) G. M. Martin, J. P. Farges, G. Jacob, J. P. Hallais and G. Poiblaud: J. Appl. Phys. 51 (1980) 2840.
2) D. E. Holmes, R. T. Chen, K. R. Elliot, and C. G. Kirkpatrick: Appl. Phys. Lett. 40 (1982) 46.
3) M. Taniguchi and T. Ikoma: Inst. Phys. Conf. Ser. No. 65 (1982) p.65
4) G. M. Martin, A. Mitonneau, and A. Mircea: Electron. Lett. 13 (1977) 191.
5) M. Taniguchi, T. Ikoma, K. Kikuchi and T. Oyoshi: to be published in Appl. Phys. Lett.
6) D. E. Holmes, R. T. Chen, and J. Yang: Appl. Phys. Lett. 42 (1983) 412.
7) T. Fukuda and T. Iizuka: to be published in the Post-Conf. Meeting on Integrated Optics and Optical Fiber Communication, 1983, Kobe, Japan
8) H. Noge, Y. Adachi and T. Ikoma: to be published
9) A. Mitonneau, A. Mircea, G. M. Martin and D. Pons: Rev. Phys. Appl. 14 (1979) 853.
10) A. Mitonneau and A. Mircea: Solid State Commun. 30 (1979) 157.

Extended Abstracts of the 15th Conference on Solid State Devices and Materials, Tokyo, 1983, pp. 153-156

Growth and Electrical Properties of Gallium Arsenide Single Crystal by Magnetic Field Applied LEC Technique

T.Fukuda, K.Terashima ,T.Katsumata, F.Orito and T.Kikuta

Optoelectronics Joint Research Laboratory
1333 Kamikodanaka, Nakahara-ku, Kawasaki 211

Undoped 2inch in diameter GaAs single crystals with low dislocation density (3000~ 8000/cm^2) have been successfully grown by MLEC technique. The electrical measurements revealed that resistivity of undoped GaAs abruptly changed from being semi-conductive (10^{1}ohm.cm) to semi-insulating (10^8 ohm.cm) under the magnetic field (1300 Oe), by increasing the pulling speed above 18 mm/h (PBN crucible), 36 mm/h (SiO_2 crucible) and also by doping the super low Cr concentration at around 0.007 wt ppm, whereas the resistivities were always semi-conductive under the magnetic field at the pulling speed 9 mm/h.

1.Introduction

Recently it has been well recognized that whether one can achieve large scale integration of electronic circuits or, in that matter, of optoelectronic devices on GaAs substrates depends largely on how one can obtain high quality GaAs single crystals. For this reason it is quite understandable that major efforts throughout the world have been concentrated on how to develop the reproducible growth techinque of large and high quality undoped semi-insulating GaAs single crystals particularly by the LEC technique.

We have developed a new magnetic field applied LEC (MLEC) apparatus using superconducting magnets [1] and have successfully grown GaAs single crystals of 2 inch in diameter in the presence of magnetic field for the first time [2]. The electrical measurements on the MLEC crystal revealed that the electrical resistivity of undoped GaAs has changed depending strongly on the magnetic field[3] and on the pulling speed . We have considerably improved reproducibility and homogeneity of semi-insulating GaAs crystals in the LEC technique by applying the magnetic field.

In this paper we report MLEC growth and electrical properties of GaAs single crystals. The relation between growth conditions and electrical properties are examined and discussed based on the impurity analysis by SIMS, photoluminescence spectroscopy (PL) and deep level transient spectroscopy (DLTS) measurements.

2. Experimantal

The MLEC apparatus used consists of an in-house modified high pressure puller and a superconducting magnetic field generator. ⟨100⟩ oriented GaAs single crystals of up to 2 inch diameter were grown in 20 atm of Ar atmosphere by direct synthesis LEC technique using either a PBN or a SiO_2 crucible with the 1300 Oe magnetic field. Crystal pulling speed was from 9 to 36mm/h. Some crystals were grown with Cr doping, while others were grown with undoped. The doped Cr concentration was from 0.005 to 0.1 wt.ppm. The electrical properties of samples were measured by the van der Pauw method and direct resistivity measurement technique[4]. The resulting crystals were characterized by etching technique, SIMS analysis, PL and DLTS measurements. The dislocation density was examined assuming they are equal to etch pit density (EPD) revealed by KOH etchant.

3.Results and discussions

The temperature fluctuation of the GaAs melt in the crucible was markedly suppressed from 18 deg to 0.1 deg by applying more than 1250 Oe[5], which may be due to the suppression of the fluid flow by the magnetic field[6]. As a result, $\langle 100\rangle$ GaAs single crystal of high quality with inclusion-free could be grown at the fast pulling speed up to 36mm/h, which is 3 to 4 times as fast as that of conventional LEC

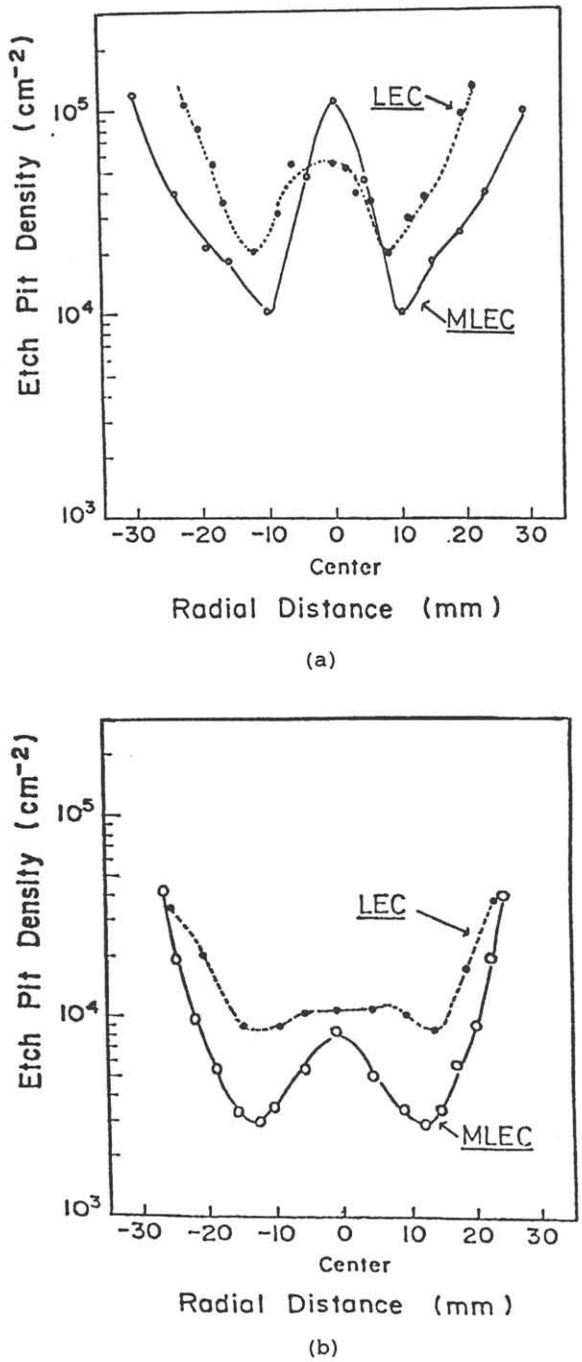

Fig.1 E.P.D. distribution on (100) wafer of MLEC crystals grown under the relatively high temperature gradient (a) and low temperature gradient, as compared with those grown by LEC technique.

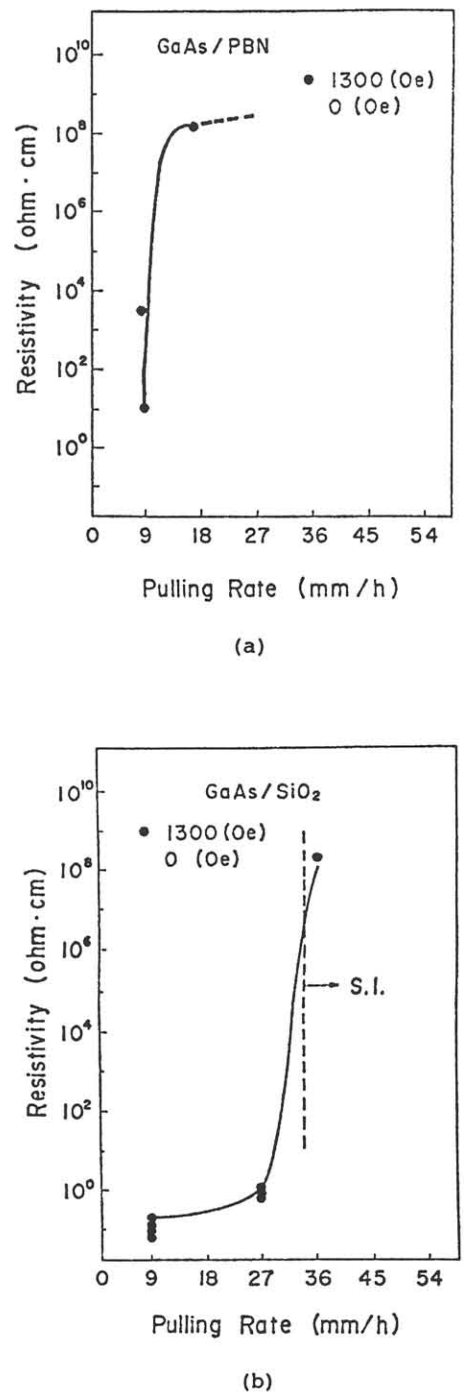

Fig.2 Pulling speed dependence of resistivity of undoped MLEC GaAs single crystal. (a) PBN crucible (b) SiO_2 crucible.

technique. The EPD distribution on ⟨100⟩ wafer of MLEC crystals grown under the relatively high temperature gradient (90°C/cm) and low temperature gradient (25 °C/cm) are shown in Fig.1 (a) and Fig.1 (b), respectively, as compared with those grown conventional LEC technique. It was observed that the tendency of W-spaped EPD was intensified and the density was reduced at the low temperature gradient. This results may be explained to be due to the increase of radial temperature gradient on the surface of GaAs melt by applying the magnetic field and due to the smooth growth with the decrease of climb motion of dislocation and suppress point defects under the magnetic field. Figure 2 (a) and (b) shows the resistivity of the MLEC crystals against the pulling rate, in the case of using PBN crucible and SiO_2 crucible , respectively, as compared with those grown by conventional LEC at pulling rate 9mm/h. At the pulling rate of 9 mm/h, the undoped MLEC crystal obtained from PBN showed n-type conductive properties , whreas the undoped GaAs single crystals grown from a PBN crucible

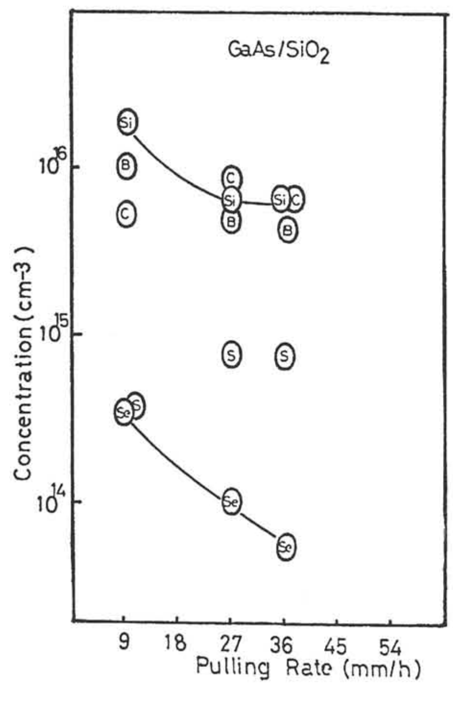

Fig.3 Residual impurity concentration of MLEC crystals grow from a SiO_2 crucible corresponding to Fig.2(b).

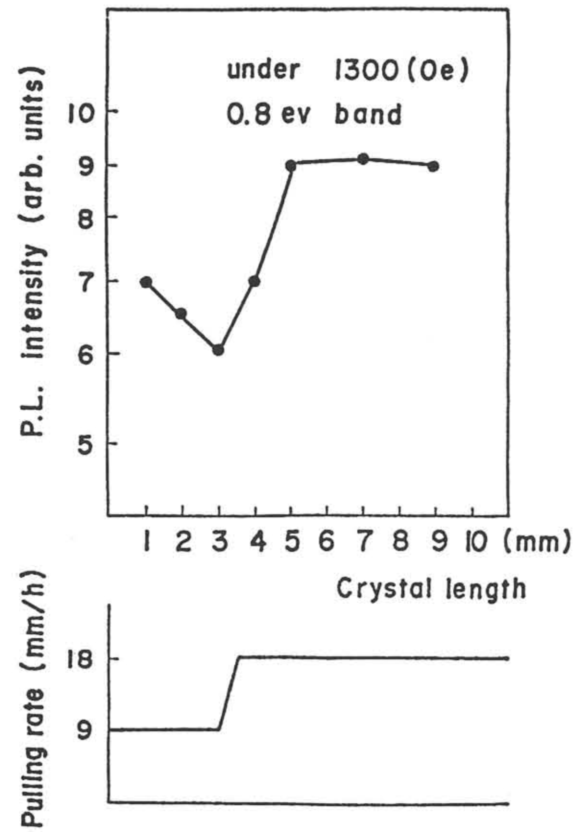

Fig.4 PL intensity of 0.8 eV band dependence on crystal pulling speed.

by conventional LEC technique showed semi-insulating property. However the resistivity could be changed from semi-conductive ($10^1 \sim 10^2$ ohm.cm) to semi-insulating (10^8 ohm.cm) by increasing the pulling rate to 18mm/h , as shown in Fig.2 (a). The same tendency of conversion from semi-conductive to semi-insulating was observed in the case of using a SiO_2 crucible but much higher pulling rate of 36 mm/h as shown in Fig.2 (b).

In order to clarify the dependence of pulling effect on resistivity under the magnetic field, the residual impurity and deep level concentrations were measured by SIMS and PL measurements, respectively. Fig.3 shows the impurity concentration of MLEC crystal grown from a SiO_2 crucible corresponding to Fig.2 (b). Significant difference in concentration of impurities among the crystals grown at variouse pulling speeds was not detected which sufficiently explain the large increase of resistivity. Fig.4 shows the 0.8eV deep level intensity band ,which is related to undoped

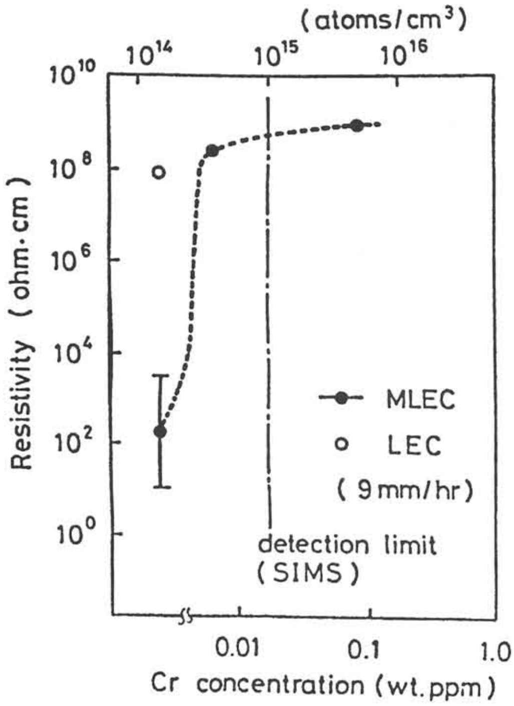

Fig.5 Resistivity of MLEC crystal is plotted against the doping concentration of Cr, compared with that of conventional LEC crystal grown from a PBN crucible.

semi-insulating property,of MLEC crystal grown from a PBN crucible along the crystal length, corresponding to Fig.2 (a). The PL intensity increases with the increase of the resistivity. These results, given in Fig.3 and Fig.4, support that the abrupt increase in resistivity at the fast pulling speed shown in Fig.2 must be mainly due to the increase in deep level traps.

Figure 5 shows the resistivity of a MLEC crystal doped with Cr grown at low pulling speed of 9 mm/h. The Cr concentration was calaulated from the amount of dopant and segregation coefficient k_{eff}= 6.4 X10^{-4} . When doping level of Cr concentration was brought down to 0.007 wt.ppm, which was lower than the detection limit of Cr concentration by SIMS, the resistivity increased abruptly from conductive to semi-insulating with high resistivity 5X10^8 ohm.cm, as is given in Fig.5. The resistivity of this super low Cr doped crystals was markedly uniform from top to tail, while in the case of conventional undoped LEC GaAs crystals the resistivity of tail always decreased more than one order of magnitude.

4. Summary and conclusion

We have grown GaAs single crystals by magnetic field applied LEC technique and measured their electrical and optical properties. Undoped 2inch in diameter GaAs single crystals with low dislocation density (3000~8000/cm^2) have been successfully grown by MLEC technique. The electrical measurements revealed that resistivity of undoped GaAs changed from being semi-conductive to semi-insulating under the magnetic field (1300 Oe), by increasing the pulling speed up to 18 mm/h (PBN crucible), 36 mm/h (SiO_2 crucible) and doping the super low Cr concentration up to 0.007 wt.ppm, whereas the resistivity was semi-conductive under the magnetic field at the pulling speed 9 mm/h. These results are suggestive of that the resistivity of undoped GaAs single crystal is strongly dependent on the stability in the vicinity of the freezing interface.

Aknowledgement

This work is supported by the agency of Industrial Science and Technology, MITI of Japan in the frame of the National Research and Developement.

References

1) K.Terashima and T.Fukuda:submitted to J.Cryst. Growth
2) K.Terashima and T.Fukuda: Spring meeting of E.C.S, (1983) Abstract No. 326
3) K.Terashima , T.Katsumata, F.Orito, T.Kikuta and T.Fukuda: Jpn. J. Appl.phys.22 (1983)L401
4) T.Matsunura, H.Emori, K.Terashima and T.Fukuda: Jpn.J.Appl.Phys.22(1983)L154
5) S.Chandrasekhar: Phil.Mag. 42(1954) 1177
6) D.T.J. Hurle:Phil.Mag.13(1966)305