Study and application of the mass transport phenomenon in InP

T. R. Chen, L. C. Chiu, A. Hasson, K. L. Yu, U. Koren, S. Margalit, and A. Yariv
California Institute of Technology, Pasadena, California 91125

(Received 2 November 1982; accepted for publication 25 January 1983)

A study of the mass transport phenomenon in InP is presented. Conditions and possible explanation for the transport process are discussed. Characteristics of the mass transported InP homojunctions are described and compared with those in the InP–InGaAsP heterojunctions. Effects of the mass transported junction on laser performance are discussed.

PACS numbers: 66.90. + r

INTRODUCTION

The recently discovered mass transport phenomenon in InP (Refs. 1,2) has been generating considerable interest. Application of this technique to laser fabrication has resulted in very low threshold devices.[2,3] For quaternary InGaAsP/InP lasers, this technique eliminates the critical regrowth step necessary in some structures, most notably the buried heterostructure (BH), thereby simplifying the entire fabrication process. The mass transport technique also provides greater flexibility in diode laser fabrication, as demonstrated in the control of active layer widths in Refs. 2 and 3. The simplicity of the mass transport process makes it an attractive technique in the fabrication of other InP based semiconductor devices and in integrated optoelectronics. The viability of this technique in device fabrication will depend on its consistency and reproducibility. In our work, the process has been found to be highly reproducible and quite controllable over the entire wafer.[3,4] In view of its potential, a better understanding of the process itself would be desirable. In this paper, a study of the mass transport process is presented. The properties of the resultant mass transport *p–n* junctions in laser structures are described. Some advantages and disadvantages of the mass transport technique in laser fabrication and consequent effects on laser performance are also discussed.

MASS TRANSPORT PROCESS

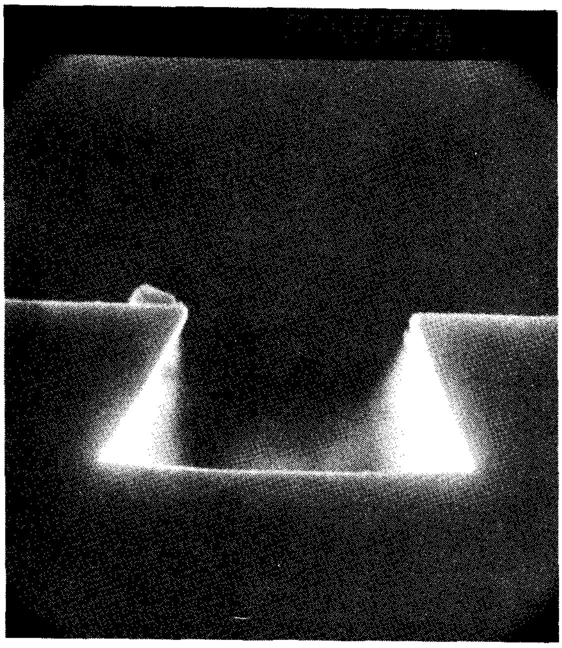
The mass transport process referred to in this paper was first observed by Liau and Walpole in the fabrication of a heterostructure laser with integrated passive waveguide.[1] It was found that when part of a quaternary layer sandwiched between InP layers was selectively etched away and the wafer heated to about 670 °C in an LPE system in an atmosphere of H_2 and PH_3, the original air space adjacent to the quaternary layer was filled with InP [see Fig. 1(a) of Ref. 1 and Fig. 2 of Ref. 2]. This InP mass transport phenomenon should be distinguished from the conventional LPE growth of InP, in which the InP is introduced from specially prepared growth solution. This new technique was successfully employed in the fabrication of a very low threshold buried heterostructure laser.[2]

However, the origin and kinetics of the mass transport phenomenon thus observed was still unclear. In this paper, a systematic study was conducted to provide information on the origin and dynamics of the mass transport process, and also to probe the characteristics of mass transported InP homojunctions to gain information on the crystalline quality of the mass transported region.

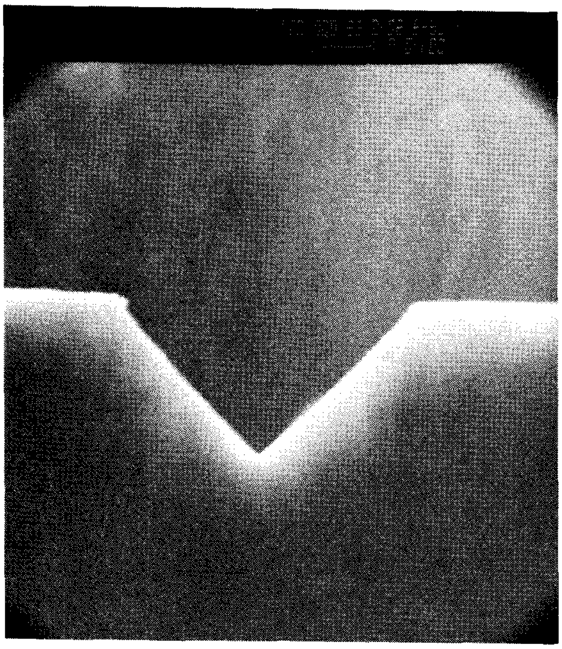
In the original work,[1,2] mass transport of InP was observed in a liquid phase epitaxial (LPE) system in an atmosphere of H_2 and PH_3. In the present work, however, PH_3 was not used, and the LPE system was merely flushed with hydrogen. In most of the cases studied, an InP cover wafer and a thick graphite plate were employed.[3] To accomplish the mass transport process, the system was heated to around 675 °C and maintained at that temperature for a period of time depending on the desired experimental conditions and circumstances.

To facilitate the study of the transport kinetics, U- and V-shaped grooves were etched with iodic acid along the (011) and (01$\bar{1}$) crystallographic directions respectively on an InP substrate. The width and depth of the U-shaped groove were $\sim 10\,\mu$m and $\sim 4.5\,\mu$m, respectively, and the corresponding values are $\sim 5\,\mu$m and $\sim 2.5\,\mu$m for the V-shaped groove. After cleaning, the wafers were placed in a shallow slot on a conventional sliding graphite boat and loaded into the LPE system for mass transport. Experiments were performed in the temperature range of 670–740 °C and with heating times between 40 min and 3 h. Figures 1 and 2 compare the shapes of the grooves before and after heating. The shapes of the grooves were clearly deformed by the heating. In addition to the rounded corners, the depth of the V-shaped groove was $\sim 0.3\,\mu$m shallower after transport, and the width of the top opening was slightly wider. The bottom width of the U-shaped groove was $\sim 1.4\,\mu$m narrower, and the slightly curved bottom became flat after transport. Notice that the convex corners were slightly rounded and materials were clearly "grown" at the concave corners, thus changing the width and depth of the groove.

A qualitative understanding of the mass transport process through the vapor phase could be gained by considering the variation of equilibrium vapor pressure with the curvature of the solid surface in equilibrium with its vapor. Denoting this pressure for a flat surface by P, then the deviation ΔP from P near a curved surface could be expressed as[5]



(a) 1 μm



(b) 1 μm

FIG. 1. SEM pictures of the (a) U-shaped, and (b) V-shaped grooves before mass transport.

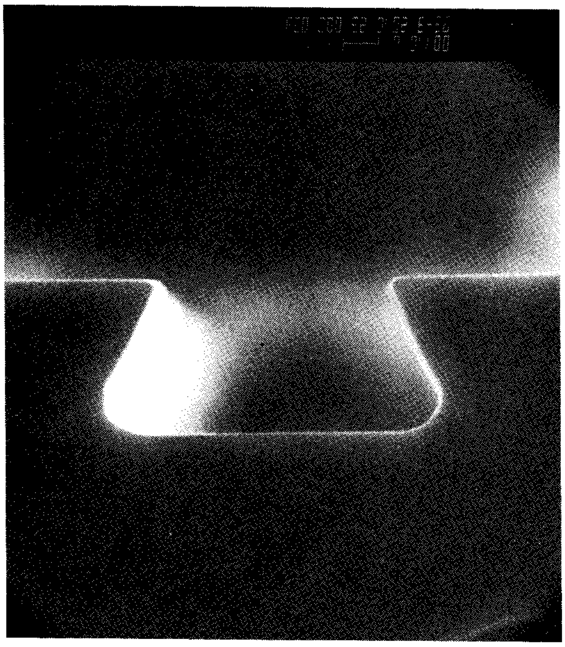
$$\frac{\Delta P}{P}=\frac{C}{T}\frac{1}{R}, \quad (1)$$

where C is a constant, T the temperature and R the radius of curvature. For a convex surface, R is positive and the equilibrium vapor pressure at the surface exceeds P. Therefore, materials at such places are more prone to be evaporated. Conversely, near a concave surface with negative R, the equilibrium vapor pressure is lower and material could be grown. This seems to be consistent with experimental observations of Figs. 1 and 2 and also Fig. 2 of Ref. 2. In our experiments, a few tiny In droplets were always found on the surface of the wafer after the transport process. This is most probably the result of the dissociation of InP during the heating period.

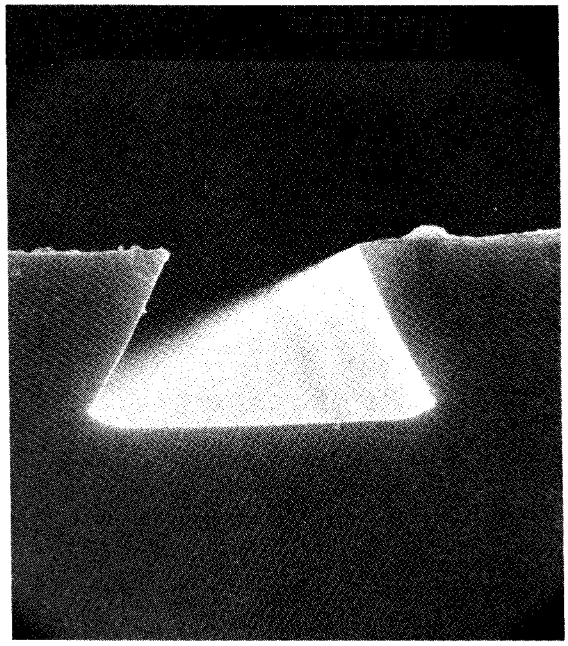
Unfortunately, these observations alone do not eliminate other possible mass transport mechanisms, including the movements of InP molecules over the crystal surfaces in the solid phase or other solid phase mass migration processes. However, when a very thin layer of Si_3N_4 was deposited over the entire substrate, no discernible change in shape was observed after heating. This may indicate that the possibility of solid phase mass migration processes was quite remote. We recognize that the presence of the Si_3N_4 layer alters the surface property of the wafer and the above mentioned processes, though unlikely, cannot be positively ruled out.

To probe further, two experiments were performed. These employed the terrace structure with a long and narrow etched channel described in Ref. 3. In the first experiment, the substrate and some phosphorous powder were placed in an evacuated ampule ($\sim 10^{-6} - 10^{-7}$ mm Hg). The mass of the phosphorous powder was estimated to produce a pressure slightly higher than one atmosphere. No mass transport was observed after heating at 700 °C for an hour. In the second experiment, a substrate and an InP wafer, separated by about 10 cm, were loaded into an evacuated ($\sim 10^{-7}$ mm Hg) ampule. In this experiment, a temperature difference of ~ 30 °C was created along the axis of the ampule between the substrate (at 700 °C) and InP wafer (at 730 °C). After an hour, the InP wafer was decomposed with a drastic change in surface condition, but the surface of the substrate remained clean and free from In droplets. Moreover, mass transport was observed on the substrate and the etched channel was completed filled. These experiments provided strong support for the vapor phase transport mechanism.

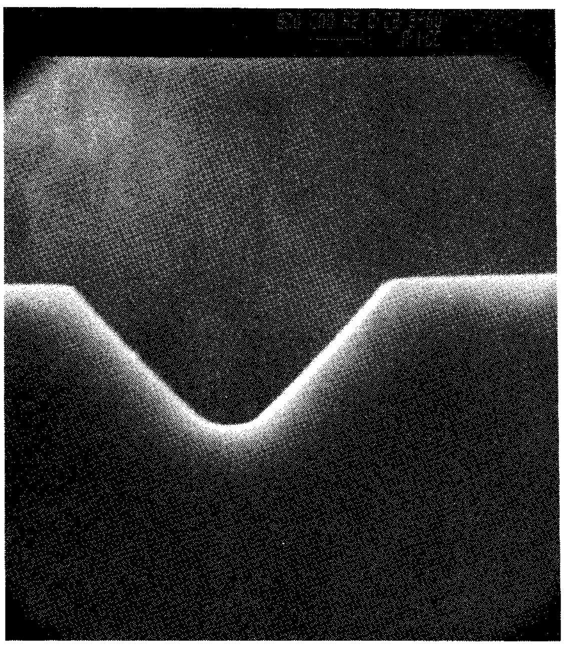
The transport process was found to be a very sensitive function of temperature and less sensitive to the time of heating. Figure 1 consists of SEM photographs of the grooves before heating, and Figs. 2(a) and 2(b) show the grooves after heating at 720 °C for 3 h, and Fig. 2(c) after heating for 3 h at 670 °C. In contrast to Fig. 2(a), Fig. 2(c) shows only minute deformation in the shape of the groove. Conditions for mass transport were also studied in the terrace structure described in Ref. 3. In these laser structures, the active InGaAsP layer was selectively etched away, resulting in an undercutting into the quaternary layer. After the mass transport process, a "burying layer" was "grown" next to the exposed quaternary layer, giving rise to a buried laser structure. Here, besides the temperature and time, the process also depended on the thickness of the active layer. The width of the transported region was found to vary directly with temperature and time but inversely with the thickness. Figure 3 shows the different widths under a number of different conditions, where the temperature and time were 675 °C, forty five minutes and 740 °C, 1.5 h for Figs. 3(a) and 3(b), respectively. It can be seen that for lower temperature and shorter heating time, the mass transport process only occurred in the thin constricted region, where the vapor pressure could be high-



(a) 1 μm



(c) 1 μm



(b) 1 μm

FIG. 2. SEM pictures of the (a) U-shaped, high temperature: (b) V-shaped, high temperature: and (c) U-shaped, low temperature grooves after mass transport.

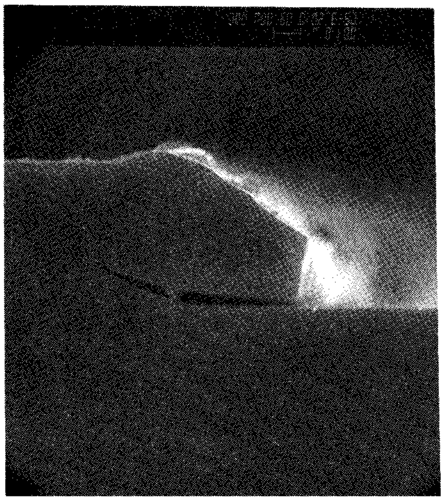
er. From Fig. 3(a) it was apparent that in the thin constricted regions, the mass was transported from regions adjacent to the quaternary layer. In the absence of the InP cover wafer and thus exposing the wafer directly to the reducing atmosphere of the LPE system, mass transport also occured next to the quaternary layer. However, thermal etching was observed in this case and large In droplets were found on the surface of the wafer. In view of the results of this and the two experiments in ampule described above, it seems that in the presence of the InP cover wafer and graphite plate, the vapor pressure was automatically adjusted to a condition suitable for mass transport. Moreover, they also protect the wafer from problems of thermal etching. Thus, the cover wafer provides a convenient and practical way to obtain reproducible and controllable mass transport process.

PROPERTIES OF *P–N* JUNCTIONS 'GROWN' BY MASS TRANSPORT PROCESS

Properties and quality of a p–n junction are important factors influencing the performance of a semiconductor laser. Characteristics and effects of the transported region on the laser performance will be described in the following sections. By etching away the quaternary layer completely in the terrace structure described in Ref. 3, an InP–InP homojunction results after mass transport. These junctions were then compared with the InP–InGaAsP junctions in both the cases with (InP–Q MT) and without (InP–Q NMT) a mass transported region grown next to the InGaAsP layer. In each of the three cases, characteristics of 6–8 diodes from the same wafer were measured and an average value was taken. Figure 4 shows the typical forward I–V characteristic at low voltages. Assuming the diodes obey the equation:

$$J = J_s\,(e^{qV/n\mathrm{kT}} - 1), \tag{2}$$

where J and J_s are the current and reverse saturated current densities, respectively, q the electronic charge and V the applied voltage, and the values of n and j_s were found to be 2.3 $(1.2 \pm 0.59)\times 10^{-6}$ A/cm^2 (InP), 2.1 $(1.59 \pm 0.57)\times 10^{-4}$ A/cm^2 (InP–Q MT), and 2.3 $(1.58 \pm 0.21)\times 10^{-4}$ A/cm^2 (InP–Q NMT), respectively, for the three cases. The values of n were indicative of generation-recombination dominated process. The deviation at higher voltage was due to the effect of the series resistance. In Fig. 5 is shown the curve tracer photograph where the difference in turn-on voltages for the



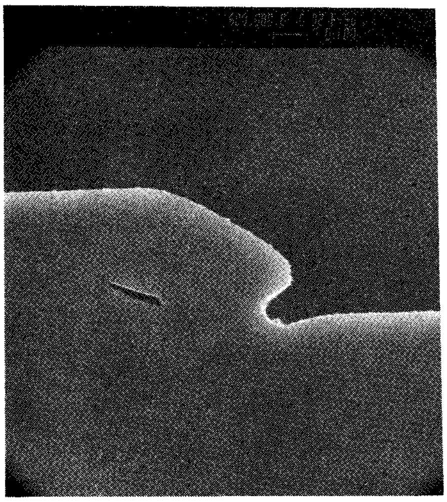


FIG. 3. SEM pictures of the mass transported terrace structure: (a) lower temperature and shorter heating time: (b) higher temperature and longer heating time.

hetero and homojunctions was clearly displayed. The larger turn-on voltage for InP is a direct consequence of the much smaller J_s which in turn is due to the smaller n_i (larger band gap E_g), the intrinsic carrier concentration of InP as compared with InGaAsP.

Figure 6 shows a typical C–V characteristics of the three different types of diodes. The linear relationship of $1/C^2$ vs V justifies the classification of these as abrupt junctions. From these measurements, values of the built-in voltages (V_b) and doping concentrations could be extracted. Assuming these to be one-sided abrupt junctions, the doping concentrations in the active layers were estimated to be $(1.0 \pm 0.3)\times 10^{17}$ cm^{-3} (InP), $(1.5 \pm 0.5)\times 10^{18}$ cm^{-3} (InP–Q MT), and $(5.0 \pm 1.0)\times 10^{17}$ cm^{-3} (InP–Q nMT). These values are consistent with the approximate values calculated from the semiempirical expression of Sze[6]

$$V_B = 60\left(\frac{E_g}{1.1}\right)^{3/2}\left(\frac{N}{10^{16}}\right)^{3/4}, \quad (3)$$

where E_g is the band-gap energy in eV and N the concentration in cm^{-3}. The values of the reverse breakdown voltages were found to be 14 V (InP–InP), 1.8 V (InP–Q MT) and 3.6 V (InP–Q NMT). The higher doping concentration in the quaternary layer after heating is most probably due to the Zn diffusion when the wafer was heated at around 675 °C during the transport process.[7]

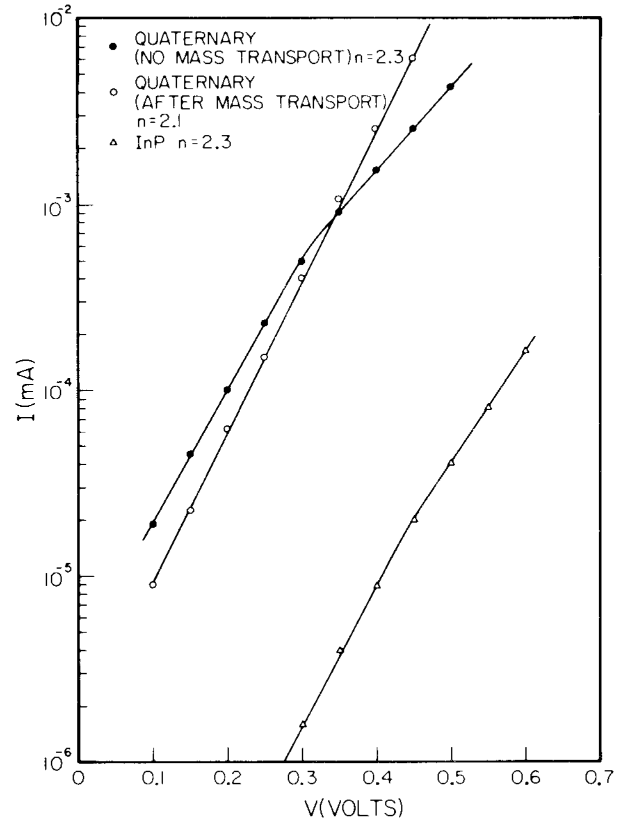


FIG. 4. Forward I–V characteristics of the diodes.

The junction characteristics are summarized in Table I. The InP mass transport homojunction is indistinguishable from grown junctions, indicating the high crystalline quality of the transported region.

APPLICATION AND EFFECTS ON LASER PERFORMANCE

The mass transport technique has been applied in laser fabrication, resulting in extremely low threshold lasers.[2,3] In

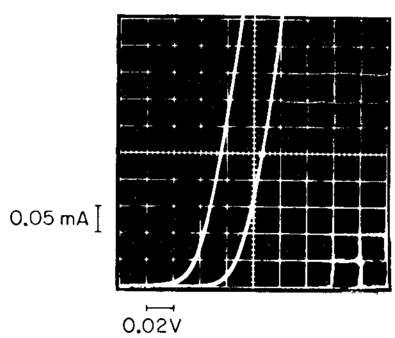


FIG. 5. Curve tracer photograph showing the difference in I–V characteristics of the hetero- and homojunctions. The homojunction has a larger turn-on voltage.

TABLE I. Comparison of the properties of the InGaAsP–InP heterojunction and InP–InP homojunction.

Junction type	InP–Q (NMT) abrupt	InP–Q (MT) abrupt	InP–InP (MT) abrupt
n	2.3	2.1	2.3
$J_s (A/cm^2)$	$(1.58 \pm 0.21)\times 10^{-4}$	$(1.59 \pm 0.57)\times 10^{-4}$	$(1.2 \pm 0.59)\times 10^{-6}$
$V_{\text{turn-on}} (V)$	0.6–0.7	0.6–0.7	0.9–1
$V_{\text{breakdown}} (V)$	3.6	1.8	14
$V_{\text{built-in}} (V)$	1.1	1.2	1.0
$N (cm^{-3})$	$(5.0 \pm 1.0)\times 10^{17}$	$(1.5 \pm 0.5)\times 10^{18}$	$(1.0 \pm 0.3)\times 10^{17}$

the BH structure of Ref. 2, the otherwise necessary and critical regrowth process is completely eliminated. In the terrace structure of Ref. 3, this technique offers the added flexibility of controlling the desired width of both the active and the burying layers. The mass transport technique can also find application in the fabrication of other devices, such as LED's and superluminescent diodes, to name a few. However, it should also be mentioned that mass transport process can give rise to undesirable results. For example, in the fabrication of distributed feedback lasers, the corrugation grating on the substrate could be smeared due to the transport process, and special care has to be taken to prevent the transport process.[8]

The effects of the mass transported region on the laser have been described briefly in Ref. 4, where the performance of the terrace mass transport (T-MT) lasers was compared with the terrace mesa (T-ME) lasers. Figure 3(a) showed the SEM photograph of the cross-section of the T-MT laser. The T-MTs and T-MEs were identical in all respects except that the mass transport step was skipped in the T-MEs, resulting in active layers which were not "buried" and were exposed directly to air. (Schematics of the T-MT and T-ME lasers can be found in Fig. 1 of Refs. 3 and 4.) It has been found that for comparable active volumes, the T-MEs had lower average threshold current than the T-MTs. Thus, it is possible that the transported region forms an undesirable current leakage path under high injection condition. In view of this, to obtain low threshold lasers, it would be essential to have narrow transported region so as to minimize current leakage. Also, the T-MEs had better linearity in the light versus current characteristics and also higher external quantum efficiency.

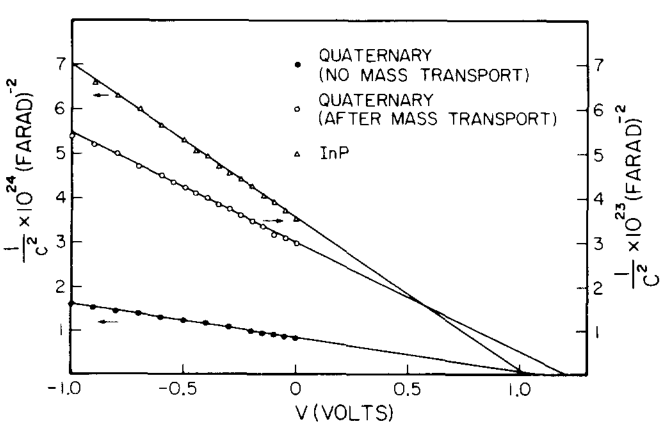


FIG. 6. C–V characteristics of the diodes.

In addition, the T-MEs were found to be less temperature sensitive. Using the empirical relation for the temperature dependence of threshold current:

$$I_{th} = I_0 e^{T/T_0}, \tag{4}$$

the T_0's for the TM-E and T-MT lasers were found to lie in the range of 60–70 and 40–50 °K, respectively. This could be due to the current leakage discussed above or the higher doping concentration in the active layer.[4] In any case, this is unavoidable in a laser fabricated by utilizing the mass transport technique. Thus, it is important that in lasers, the width of the transport region should be narrow, which could be realized by executing the transport process at lower temperatures as shown in Fig. 3(a). This would then reduce both the leakage current and doping concentration in the active layer. Although the presence of such layers seems to cause slight degradation in the performance of the laser, it is an excellent way to protect the InGaAsP surface and reduce scatterings from the side wall.

CONCLUSION

The mass transport process in InP was studied. Experiments performed in this work provide strong support for the interpretation of a vapor phase mass transport mechanism. The transport process was found to depend on the temperature and time duration of heating, with the former the more sensitive factor. The properties of mass transport InP homojunction was studied and compared with those of the InP–InGaAsP heterojunctions. Effects of the transported region on laser performance was also discussed. It was found that the transported region probably provides a channel through which current could bypass the active region in a laser structure, thereby degrading the laser performance. Nevertheless, a narrow mass transported layer would serve as an excellent way to passivate and protect the surface.

ACKNOWLEDGMENT

This work is supported by the National Science Foundation and the Air Force Office of Scientific Research.

[1] Z. L. Liau and J. N. Walpole, Paper WB 3, Technical Digest, Topical Meeting on Integrated and Guided Wave Optics, Optical Society of America, 1982.

[2] Z. L. Liau and J. N. Walpole, Appl. Phys. Lett. **40**, 568 (1982).

[3] T. R. Chen, L. C. Chiu, K. L. Yu, U. Koren, A. Hasson, S. Margalit, and A. Yariv, Appl. Phys. Lett. **41**, 1115 (1982).

[4]T. R. Chen, L. C. Chiu, K. L. Yu. U. Koren, A. Hasson, S. Margalit, and A. Yariv, IEEE J. Quant. Electron. (to be published).
[5]J. W. Cahn, and D. W. Hoffman, Acta Metal. **22**, 1205, 1974.
[6]S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981), Chap. 2.
[7]C. B. Su, J. Schlafer, J. Manning, and R. Olshansky, Electron. Lett. **18**, 595, 1982.
[8]K. Utaka (private communication).