Effect of Partial Dissolution During LPE Growth of $Al_xGa_{1-x}As$ on the Efficiency of Diffused Light-Emitting Diodes

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ABSTRACT

Light-emitting diodes have been prepared by Zn diffusion to form p-n junctions in Te-doped $Al_xGa_{1-x}As$ layers grown by liquid phase epitaxy. When the growth process is interrupted by a partial dissolution cycle, the external quantum efficiencies for junctions formed in the material grown after dissolution are about five times greater than those obtained without a dissolution cycle. Efficiencies of about 1 x 10^{-3} have been measured at about 6750Å for uncoated diodes. Electron microprobe analysis shows that in the regrown material there is a sharp initial drop in Al concentration, after which the Al concentration gradient becomes considerably less than in layers grown without dissolution. In addition the dislocation density in the regrown layers is about a factor of two lower than in material grown without dissolution.

Efficient visible light emission has been obtained (1) from $Al_xGa_{1-x}As$ p-n junctions grown by the liquid phase epitaxial (LPE) method. It is important to develop a simple diffusion process as an alternative technique for making high efficiency $Al_xGa_{1-x}As$ light-emitting diodes. This would make it possible to prepare planar monolithic structures and therefore enable the economical fabrication of high density monolithic arrays. Linden (2) has made diodes by Zn diffusions into $Al_xGa_{1-x}As$ crystals grown by the LPE method, but these diodes had very low quantum efficiencies (about 10^{-5} at 7000Å).

We have studied the diffusion of Zn into $Al_xGa_{1-x}As$ epitaxial layers grown by the LPE method. By optimizing the diffusion processes and doping levels of the material, slight improvements of quantum efficiency in diffused diodes have been achieved. More important, a substantial improvement in efficiency has been obtained by using a dissolution cycle during the LPE growth of the material into which Zn is subsequently diffused to form the diodes. This cycle dissolves a thin surface layer of the epitaxial overgrowth prior to the regrowth of another thin layer. In order for the improvement in efficiency to be realized, the p-n junction must be formed in the regrown layer near the region where the dissolution takes place.

In order to grow $Al_xGa_{1-x}As$ crystals for diffusion studies the vertical growth method described by Rupprecht *et al.* (1) was employed. N-type GaAs single crystals with (100) orientation were used as substrates. Te was added as the n-dopant. A typical solution composition is 20g Ga, 3g GaAs, 3 mg Te, and a variable amount of Al depending on the desired composition. The cooling cycle I shown in Fig. 1 was used to grow one epitaxial layer. The solution was heated to 955°C and then cooled in contact with the GaAs substrate to about 860°C at a rate of about 0.4°C/min. The AlAs concentration of the epitaxial layer was about 50 mole per cent (m/o) at the interface with the substrate and about 25 m/o at the surface. To prepare diodes, this layer, which was about 60-80 μm thick, was etched into five steps at about 6 μm intervals as depicted in the insert in Fig. 1, and Zn was diffused into the surface of these steps at 700°C for 30 min. The diffusion junction depth is about 3-5 μm. The external quantum efficiencies and wavelengths of the diodes made from each step were measured at 300°K, and the data are plotted as solid circles in Fig. 2.

Cooling cycle II with a dissolution cycle during the growth process, as shown in Fig. 1, was used to grow another $Al_xGa_{1-x}As$ n-type epitaxial layer. In this case, the solution was first cooled at a rate of 0.4°C/min from 955° to 900°C. The temperature was then raised five degrees to 905°C, kept there for 5 min, and finally lowered to 860°C again at a rate of 0.4°C/min. (This cooling cycle is the same as the one which Woodall *et al.* (1, 3) used to grow $Al_xGa_{1-x}As$ p-n junctions with high efficiencies, but they added Zn during the process to form the grown junctions.) As before, the epitaxial layer was etched into five steps, and Zn was diffused into the surfaces of the steps at 700°C for 30 min. The diode results are shown by open circles in Fig. 2. In the region where dissolution had taken place, the diodes are substantially more efficient than those made from the epitaxial layer grown by cooling cycle I.

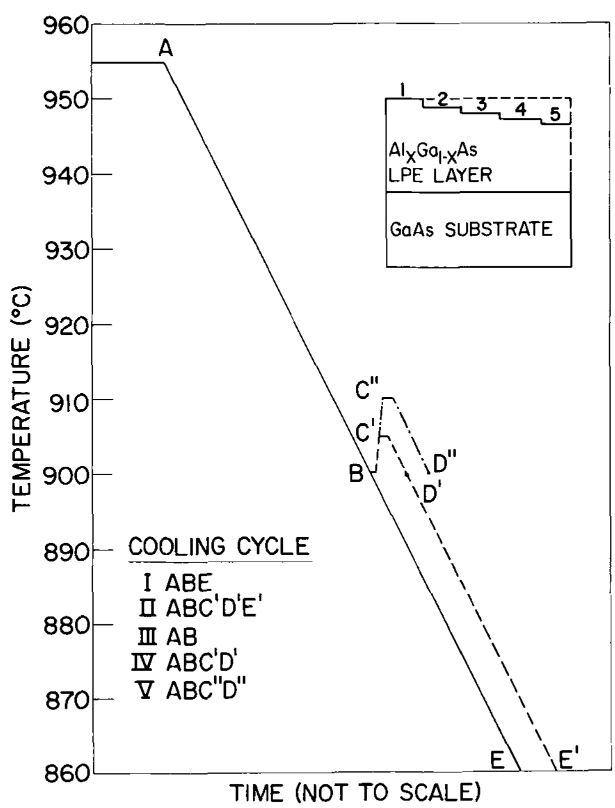

Fig. 1. Schematic representation of cooling cycles for $Al_xGa_{1-x}As$ LPE. Cooling rate 0.4°C/min.

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Key words: $Al_xGa_{1-x}As$, liquid phase epitaxy (LPE), dissolution, regrowth, diffusion, light-emitting diodes, III-V alloys.

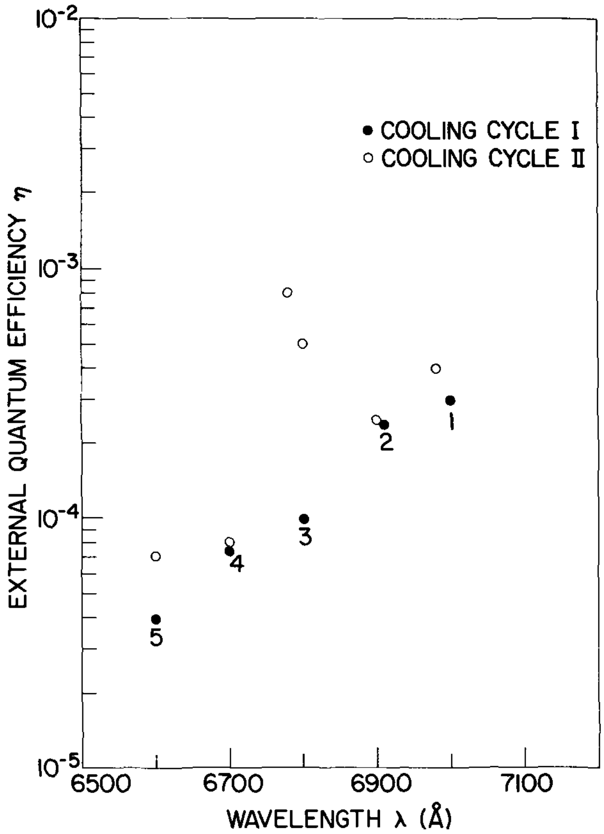

Fig. 2. The external quantum efficiency of $Al_xGa_{1-x}As$ diffused diodes as a function of diode emission energy at 300°K. Solid and open circles correspond to diodes made from epitaxial layers grown with cooling cycles I and II in Fig. 1, respectively.

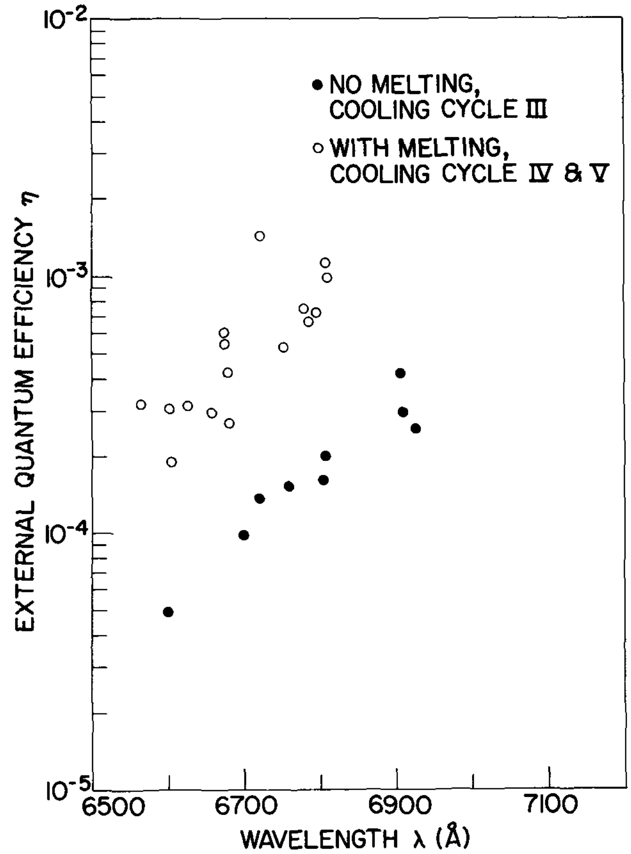

Fig. 3. The external quantum efficiency of $Al_xGa_{1-x}As$ diffused diodes as a function of diode emission energy at 300°K. Solid and open circles correspond to diodes made from epitaxial layers grown without and with a dissolution cycle, respectively.

In order to confirm that the dissolution cycle during the LPE growth of the $Al_xGa_{1-x}As$ is responsible for the improvement in the quantum efficiency of diodes made by subsequent diffusions, many additional layers using the same composition of solution but different amounts of Al have been grown by using the cooling cycles III, IV, or V shown in Fig. 1. In cooling cycle III the solution was heated to 955°C and cooled at a rate of about 0.4°C/min to 900°C. For layers grown with a dissolution cycle, after cooling to 900°C, the temperature was raised 5°C (cycle IV) or 10°C (cycle V). After 5 min at the higher temperature, the solution was cooled again to 900°C. The initial concentration of Al in each of the solutions was different. The AlAs concentration in the epitaxial layers varied between 50-54 m/o at the interface with the substrate and between 32-36 m/o at the surface, and the total thickness of the layers was about 30-50 μm. Zn was subsequently diffused into the surface of these layers at 700°C for 30 min. Figure 3 shows the external quantum efficiencies of the $Al_xGa_{1-x}As$ diffused diodes as a function of the diode emission energy, both measured at 300°K. Solid circles represent the diodes made from layers grown by using cooling cycle III, and open circles represent the diodes made from layers grown by using cooling cycles IV and V. The efficiency decreases as the wavelength decreases because the direct-indirect bandgap composition is approached. The efficiency of diodes made from material grown with a dissolution cycle is improved by a factor of about five, but this value is about a factor two lower than that of the grown junctions (1, 3).

The electron microprobe has been used to measure the composition profiles of epitaxial layers along the growth axis. The mole fraction of AlAs, x in $Al_xGa_{1-x}As$, is plotted in Fig. 4 as a function of dis-

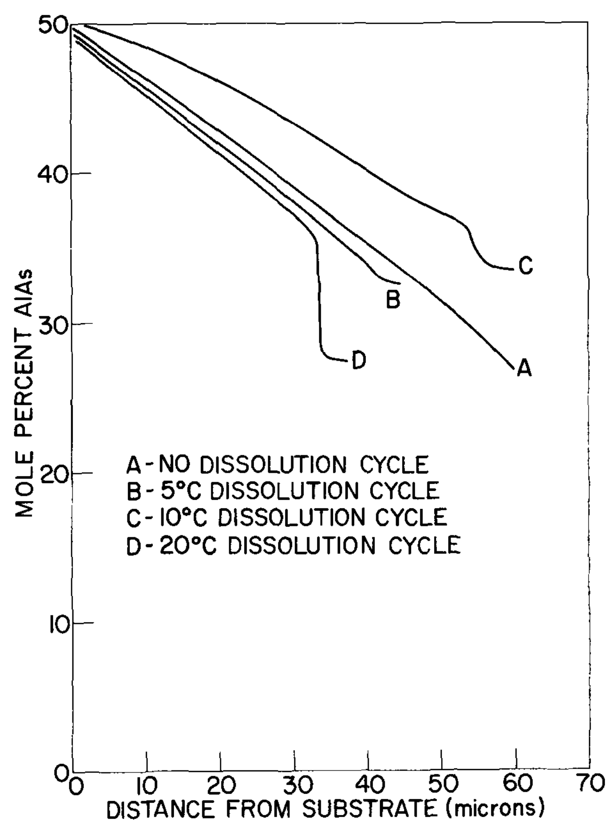

Fig. 4. Aluminum composition profiles of epitaxial layers grown with or without a dissolution cycle.

tance from the substrate for four representative layers. Because of the high segregation constant of Al (3), the concentration of Al decreases with increasing distance from the substrate. Curve A is a typical Al profile of a layer which was grown by using cooling cycle III in Fig. 1. Curves B and C are typical Al profiles of layers grown by using 5° and 10°C dissolution cycles, respectively, corresponding to cooling cycles IV and V in Fig. 1. It is apparent that consequences of dissolution on the material grown after this step are twofold: there is a sharp drop in Al concentration, after which the rate of decrease of the Al concentration with distance is much smaller than the rate of decrease prior to the dissolution cycle. An epitaxial layer with a 20°C dissolution cycle was grown and its profile (curve D) exhibits an even larger initial decrease in Al concentration. A kinetic effect must be responsible for the observed composition profiles, since under equilibrium conditions dissolution and regrowth would not cause any change in the Al concentration profile.

The two changes in the Al concentration profile are probably the major factors which contribute to the large increase in quantum efficiency of diodes made from material grown with a dissolution cycle. The regrown region is about 5 μm thick. The diffused p-n junction, which is about 3-5 μm deep, is normally located in the regrown region after the abrupt drop in Al concentration. Since the radiative recombination occurs on the p-side of the junction, the sudden decrease in bandgap due to the drop in Al concentration, which is about 0.02 eV for a 5°C dissolution step, may increase the radiative recombination by enhancing the injection of electrons and confining the holes in the p-region. The result would be similar to the effect observed in $Al_xGa_{1-x}As$-GaAs heterojunction lasers, where a marked decrease in current threshold is attained using the heterostructure to increase carrier confinement with suppression of the onset of hole injection (4-6).

The diode efficiency may also be increased by the flattening of the Al concentration profile in the regrown region. Because of this change in profile, the Al concentration and therefore the average bandgap are greater in this region (curves B, C, and D in Fig. 4) than in the corresponding region grown without a dissolution step (curve A in Fig. 4). This will reduce the fraction of the light emitted at the junction which is absorbed by the regrown region. In order to determine the degree of improvement one could expect from the flattening effect a rough estimate has been made of the degree to which the absorption is reduced. The photon energy emitted by $Al_xGa_{1-x}As$ diodes is approximately 0.03 eV less than the bandgap at the junction (7), and a 5°C dissolution step causes an increase of about 0.03 eV in the bandgap at the surface of the epitaxial layer. On the basis of these values, together with the slope of the intrinsic absorption edge for direct bandgap material such as GaAs and InP (8, 9), the average absorption coefficient at the emitted wavelength was assumed to be 5×10^2 cm^{-1} for the regrown region and 5×10^3 cm^{-1} for the corresponding region grown without a dissolution step. For a junction depth of 3 μm, the absorption by the regrown region would then be about one-fourth that of the region grown without dissolution. Such a reduction would make a significant contribution to the increase of about a factor of 5 in diode efficiency obtained by using a dissolution cycle.

The effect of the dissolution cycle on the dislocation density of the grown $Al_xGa_{1-x}As$ was also investigated. Dislocations were observed by using the etchant described by Abrahams and Buiocchi (10) to etch 5° angle-lapped surfaces which had been mechanically polished to a mirror finish. The dislocation density of the typical epitaxial layer is of the order of 10^4-10^5 cm^{-2}, and it decreases by about a factor of two in the regrown region. The dislocation density may be reduced in the regrown regions because the dissolution and waiting provides more time for establishing a better liquid-solid interface. This reduction in dislocation density may improve the quality of devices produced by subsequent diffusions.

In conclusion, it was found that the external quantum efficiency of $Al_xGa_{1-x}As$ diodes made by Zn diffusion into layers which were regrown after a 5°-10°C dissolution step is improved by about a factor of approximately five. This may be attributed to the abrupt change of Al concentration so that the injection of electrons into the p-side is enhanced, the leveling effect of the Al concentration gradient in the regrown region so that the absorption of emitted light is reduced, and the reduction in dislocation density.

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