

Diffusion of Zinc into GaAs Layers Grown by Molecular Beam Epitaxy at Low Substrate Temperatures

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We report the diffusion of zinc into low temperature (LT) GaAs grown by MBE at 200° C, the problems associated with using a silicon nitride film directly deposited on the LT GaAs as a Zn diffusion mask, and several schemes to avoid the problems. The Zn diffusion coefficient is measured (sealed-ampoule technique) to be about one order of magnitude higher in the LT GaAs than in normal GaAs, attributed to a large quantity of defects including arsenic antisites (As_{Ga}) in the LT GaAs. The effectiveness of silicon nitride as a Zn diffusion mask depends if the mask is deposited directly on the LT GaAs. The failure of the nitride directly deposited on the LT GaAs to stop the Zn is attributed to arsenic atoms outdiffusing from the As-rich LT GaAs (about 1 at. % excess As) into the nitride. Several structures are introduced including a 100-Å thick GaAs layer on the LT GaAs that are effective in preserving the diffusion mask properties of the silicon nitride.

Key words: Zn diffusion, LT GaAs, Si_3N_4 , MBE

1. INTRODUCTION

In recent years, GaAs layers grown by molecular beam epitaxy (MBE) at low substrate temperatures (200° C, LT GaAs) have found an increasing number of applications both in electronics and optoelectronics. The LT GaAs layers have been employed as buffer layers for GaAs metal-semiconductor field-effect transistors (MESFET's).¹⁻³ GaAs MESFET's with a low temperature buffer layer (LTBL) exhibited reduced sidegating effects, increasing the packing density of transistors. Sidegating is the reduction in the drain-source current of a FET as a result of a bias applied to an adjacent device.^{4,5} More recently, a substantial enhancement of the breakdown voltage of a GaAs MESFET has been demonstrated by using LT GaAs surface layers.⁶ LT GaAs has also been used in optoelectronic devices such as photoconductors and a very high-speed photoconductive response was observed.⁷⁻⁹

Some remarkable features of the LT GaAs include (1) very weak photoluminescence (PL),^{1,2} (2) very high resistivity,^{1,2} (3) an As-rich stoichiometry ($\text{GaAs}_{1.01}$),¹⁰ (4) a large quantity (greater than $10^{19}/\text{cm}^3$) of an EL2-like deep level (probably As_{Ga}),¹⁰⁻¹² and (5) a density of $10^{17} - 10^{18}/\text{cm}^3$ of arsenic precipitates.¹³

This paper reports the diffusion of zinc into LT GaAs grown by MBE at 200° C. We also investigate the use of a silicon nitride film directly deposited on the LT GaAs as a Zn diffusion mask and offer several schemes to avoid problems associated with using such a film.

2. EXPERIMENTAL METHODS

The samples used in this study were all grown by molecular beam epitaxy (MBE, Varian 360). The control sample (sample A) was an undoped liquid-encapsulated Czochralski (LEC) GaAs substrate. The LT GaAs samples were grown at 200° C and the growth rate was about 1 $\mu\text{m/hr}$. The growth temperature was measured accurately using a thermocouple imbedded in the heater block. After the LT GaAs was grown, a stop growth was employed to anneal the sample at 580° C for 10 min under As overpressure and then the next layers were grown successively. Four samples were grown as follows. Sample B - a 3- μm thick LT GaAs layer on an undoped GaAs substrate, sample C - a 1- μm thick GaAs layer on a 3- μm thick LT GaAs layer grown on a Si-doped GaAs substrate, sample D - an 87-Å GaAs quantum well sandwiched by 0.5- μm thick $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ layers on a 0.2- μm thick LT GaAs layer grown on an undoped GaAs substrate, and sample E - a 100-Å thick GaAs layer on a 2- μm thick LT GaAs layer grown on a Si-doped GaAs substrate.

The silicon nitride was deposited by plasma enhanced chemical vapor deposition (PECVD). The deposition temperature was fixed at 350° C for all of the samples throughout this experiment. The refractive index and thickness of the silicon nitride films were about 2.0 and 1500 Å, respectively. Standard photolithography was employed to define stripe patterns (windows for Zn diffusion, the width of the stripe was about 150 μm) and the silicon nitride films were etched by reactive ion etching (RIE) with a mixture of CF_4 and O_2 . In addition, the LT GaAs layer was etched with deionized (DI) water-diluted clorox (clorox:DI water = 1 : 4) and the etching

rate was about 10 \AA/sec at room temperature without agitation.

Zinc was diffused by a sealed-ampoule technique. ZnAs_2 was used as a Zn diffusion source, and a weight of about 5 mg of ZnAs_2 (to provide an As-overpressure of about 450 Torr, see Ref. 14) was used for an ampoule of about 4 cc. The amount of the source material was kept to about 1 mg/cc, so equal Zn diffusion rates were expected regardless of the size of the samples. Zn was diffused in a furnace at 650°C for 12 hr for all of the samples used in this study. After the Zn diffusion was performed, the sample was cleaved and stained with an A-B etchant,¹⁵ and the Zn diffusion profile was observed with a Nomarski-contrast optical microscope.

In preparation for 77K PL (photoluminescence) measurements, small sections of the samples were pressed into a layer of indium on a copper plug¹⁶ and cooled to 77K in a liquid nitrogen dewar. An argon laser beam ($\lambda = 5145 \text{ \AA}$) was focused on the sample surface, and the luminescence was measured using a 0.5-m spectrometer and a cooled S-1 photomultiplier.

3. RESULTS AND DISCUSSION

3.1 Zn Diffusion Coefficient in LT GaAs

The Zn diffusion profile for sample B is shown in Fig. 1. The left-hand side was etched for the ease of comparing Zn diffusion rates in undoped GaAs and LT GaAs. The two-boundary diffusion model with constant diffusion coefficient was used to calculate the Zn diffusion rates in the LT GaAs and undoped GaAs.^{17,18} The Zn diffusion rate in the undoped GaAs could be evaluated in the region where the LT GaAs was completely etched. As shown in the schematic diagram of Fig. 1, the Zn diffused all the way through the $3\text{-}\mu\text{m}$ thick LT GaAs into the undoped GaAs substrate. The Zn diffusion rate in the LT GaAs layer ($D_{\text{Zn}} = 1.3 \times 10^{-11} \text{ cm}^2/\text{sec}$) was calculated to be about nine times faster than that in undoped GaAs ($D_{\text{Zn}} = 1.5 \times 10^{-12} \text{ cm}^2/\text{sec}$). The faster Zn diffusion rate in the LT GaAs is attributed to the presence of a large number of defects including arsenic antisites (As_{Ga}) in the GaAs layer grown at the low substrate temperature of 200°C . Zn has been shown to diffuse much faster in GaAs with a lot of defects than in GaAs with fewer defects because the defects provide high diffusivity paths or short circuit paths.¹⁹ The dependence of Zn diffusion rate on the number of defects is also evidenced by the fact that a slower Zn diffusion rate was observed in an In-doped AlGaAs layer compared to AlGaAs,²⁰ attributed to a reduced defect density (fewer Ga vacancies, for example) made possible by isoelectronic In doping.²¹ A similarly slow Be diffusion rate was observed from In-doped AlGaAs.²²

3.2 Photoluminescence (PL)

The 77K PL data were taken for sample B before and after the Zn diffusion at 650°C for 12 hrs. The

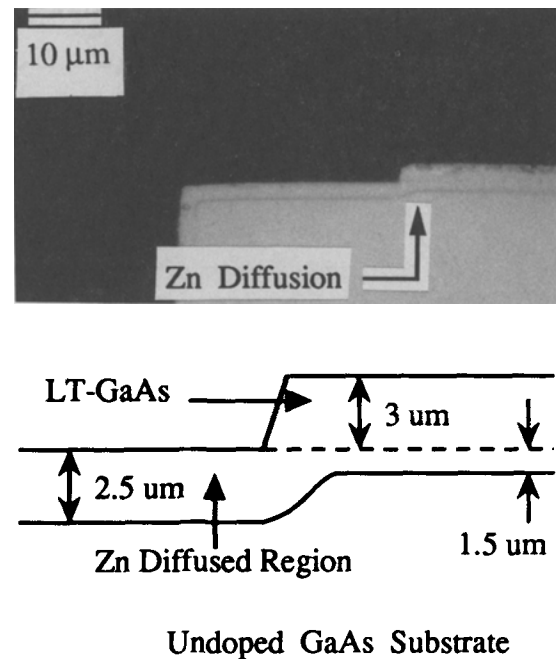


Fig. 1 — Optical photomicrograph of a cleaved and stained cross-section of a sample with a $3\text{-}\mu\text{m}$ thick LT GaAs layer on an undoped GaAs substrate (sample B) after Zn diffusion. On the left-hand side of the sample, the LT GaAs was etched for the purpose of estimating the Zn diffusion coefficient in the LT GaAs. Schematic cross-section is also shown with thicknesses of the layers labeled.

PL peaks were measured at 8500\AA (1.462 eV) for both cases. The full widths at half maximum (FWHM's) for the as-grown and Zn-diffused LT GaAs layers were measured to be 307 and 211 meV, respectively. A high input power of 250 mW from the argon ion laser was focused on the surface of the sample to obtain reasonable data, which may account for why we could observe PL and others could not. The PL intensity was about twice as strong from the Zn-diffused sample. For LT GaAs layers grown at $300\text{--}450^\circ \text{C}$, the near band gap PL peak has been measured at approximately 1.5 eV at 5 K .¹ The difference of about 160\AA in the wavelength in the PL peaks between two measurements can be explained by more defects in the layers grown at a lower growth temperature of 200°C .

High temperature annealing experiments were also performed on the other LT GaAs samples grown at different times. Annealing was done by the same sealed-ampoule technique under no-, As-, and Ga-overpressure conditions at 850°C for 10 hr. These annealing conditions seem to remove the optical defects responsible for the very weak PL intensity from the as-grown LT GaAs. The 77 K PL peak was observed at 8500\AA after an anneal under no overpressure, whereas the 77 K PL peaks were measured at 8280\AA after an anneal under As or Ga overpressure. The wavelength of 8280\AA corresponds to a slightly *p*-doped GaAs.

3.3 Electrical Resistivity

Electrical resistivities of the LT GaAs were measured before and after the Zn diffusion of sample B with a four point probe. A reduction in resistivity was observed after the Zn diffusion. Prior to the diffusion the resistivity was too high to accurately measure, but after the Zn diffusion the LT GaAs had a resistivity of $2 \times 10^{-3} \Omega\text{-cm}$ that corresponded to a hole mobility of $31 \text{ cm}^2/\text{V-sec}$ assuming a Zn concentration of 10^{20} cm^{-3} (see Ref. 23). Another group reported no reduction in resistivity from LT GaAs doped with Si (greater than $10^{18}/\text{cm}^3$) after annealing at 600°C .²⁴

3.4 Silicon Nitride as a Zn Diffusion Mask

Cleaved and stained cross-sections of samples A and B after the Zn diffusion are shown in Fig. 2. The samples shown in Fig. 2(b) and (c) underwent the plasma nitride deposition and Zn diffusion at the same time for a fair comparison. As shown in Fig. 2(c), the nitride film on the undoped GaAs substrate was a good Zn diffusion mask. However, as can be seen from Fig. 2(a) and (b), the nitride on the LT GaAs was unable to stop the Zn, and this

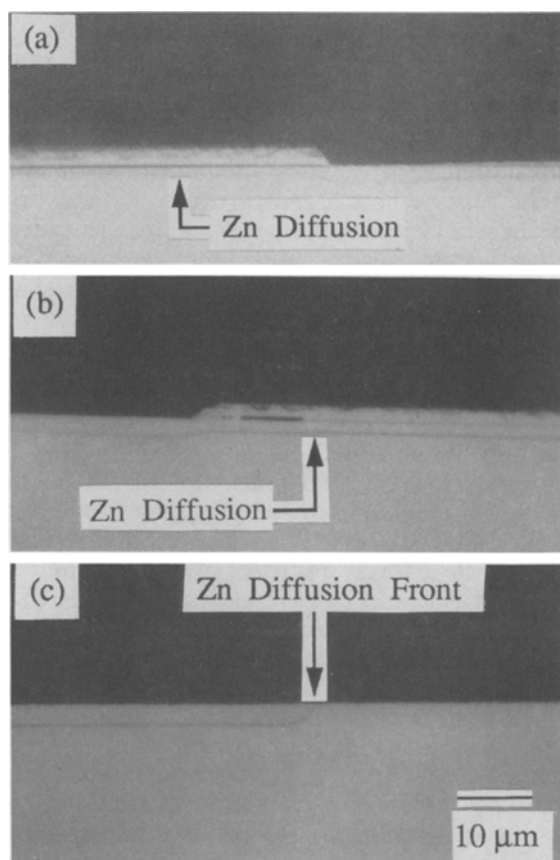


Fig. 2 — Optical photomicrographs of cleaved and stained cross-sections of samples A and B. Sample A is a control sample, an undoped GaAs substrate (Fig. 2(c)). Figure 2(a) and (b) are from sample B with the $3\text{-}\mu\text{m}$ thick LT GaAs layer. Two separate processing runs were performed for (a), and (b) and (c), respectively. The nitride on the LT GaAs was unable to stop the Zn (Fig. 2(a) and (b)), whereas the nitride on undoped GaAs substrate could stop the Zn.

result was observed several times on different wafers with different silicon nitride depositions. A schematic diagram of the Zn diffusion profile for sample B is shown in Fig. 3. The failure of the nitride film on the LT GaAs to stop the Zn is attributed to arsenic atoms outdiffusing from the As-rich LT GaAs ($\text{GaAs}_{1.01}$ or about 1 at. % excess arsenic) into the nitride. The outward diffusion of arsenic atoms from the underlying GaAs into the nitride has previously been reported as one of the reasons for the failure of nitride as an encapsulant on stoichiometric GaAs.²⁵ Adding impurities to dielectrics has profound effects on their diffusion mask characteristics as evidenced by one group's findings that the amount of Zn lateral diffusion could be changed by adjusting the amount of P_2O_5 added to the silicon oxide film.²⁶ They found that the lateral diffusion of Zn was typically an order of magnitude larger than the junction depth for all oxide compositions, but showed a marked reduction for oxides with 17-20% P_2O_5 by weight.

Several methods were tried to find ways to avoid the above problem. Cleaved and stained cross-sections of samples C and D after the Zn diffusion are shown in Fig. 4(a) and (b). As shown in Fig. 4(a), the $1\text{-}\mu\text{m}$ thick GaAs layer deposited on the LT GaAs was effective in preserving the diffusion mask properties of the silicon nitride. Likewise the $1\text{-}\mu\text{m}$ thick AlGaAs layer was also very effective as shown in Fig. 4(b). Schematic diagrams of the Zn diffusion profiles for samples C and D are shown in Fig. 5. A structure with a $100\text{-}\text{\AA}$ thick GaAs layer on the $2\text{-}\mu\text{m}$ thick LT-GaAs layer (sample E) was also studied (data not shown here). Like samples C and D, the $100\text{-}\text{\AA}$ layer of GaAs in sample E was also effective in preserving the diffusion mask properties of the silicon nitride. A portion of sample E was etched with a solution of $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O} = 8:1:100$ for 30 sec to remove approximately $250\text{-}500 \text{ \AA}$ from its surface.²⁷ The samples with and without the top $100\text{-}\text{\AA}$ thick GaAs layer underwent processing at the same time, and the two samples were compared. The nitride on the sample with the $100\text{-}\text{\AA}$ thick GaAs layer was effective in stopping the Zn, whereas the

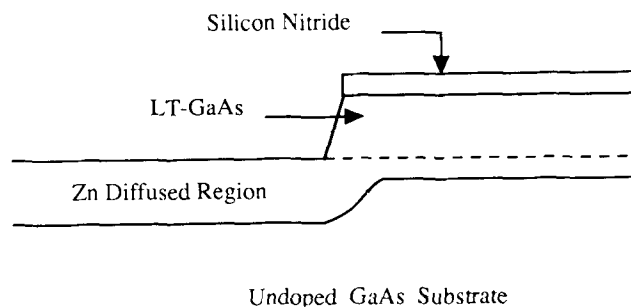


Fig. 3 — Schematic cross-section of the Zn diffused sample with the $3\text{-}\mu\text{m}$ thick LT GaAs layer (Fig. 2(a) and (b)). The diagram illustrates that the nitride on the LT GaAs could not stop the Zn.

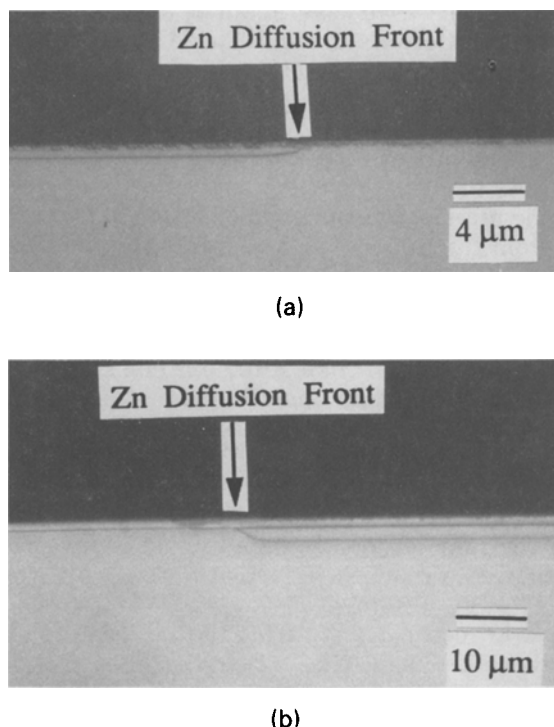


Fig. 4 — Optical photomicrograph of cleaved and stained cross-sections of samples C and D. With 1 μm of GaAs on top of 3 μm of LT GaAs (Fig. 4(a), sample C), or an AlGaAs/GaAs heterostructure on top of 0.2 μm of LT GaAs (Fig. 4(b), sample D). The nitride acts as a good diffusion mask.

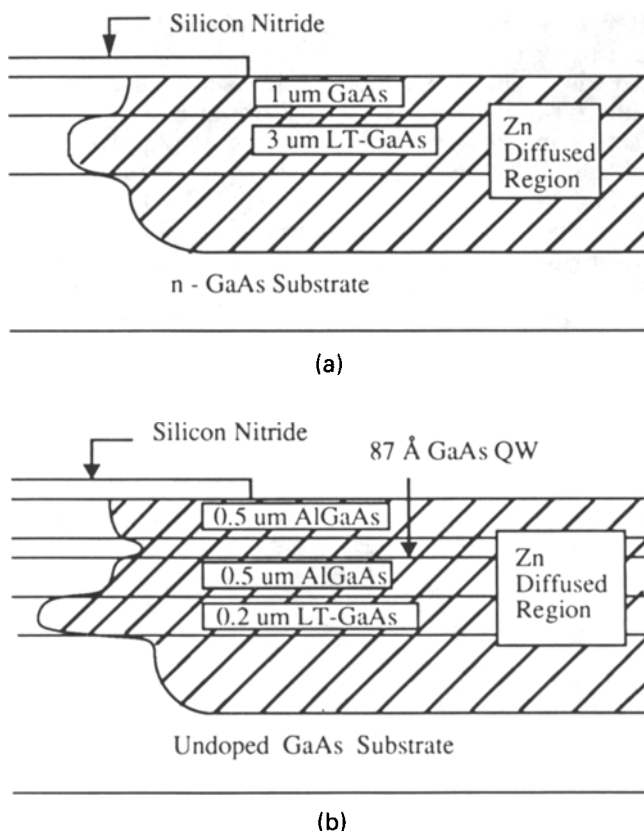


Fig. 5 — Schematic cross-sections of the Zn-diffused samples shown in Fig. 4. Figure 5(a) corresponds to sample C (1 μm of GaAs on top of 3 μm of LT GaAs) and Fig. 5(b) corresponds to sample D (an AlGaAs/GaAs heterostructure on top of 0.2 μm of LT GaAs).

nitride on the same wafer but without the 100-Å thick GaAs layer was unable to stop the Zn.

To see if 100 Å of GaAs can make such a big difference consider the self-diffusion coefficient (D) of As which is given by,²⁸

$$D = D_0 \exp(-Q/kT)$$

where D_0 is a temperature independent factor and Q is the activation energy for the atomic jump mechanism. For As diffusion in GaAs, D_0 and Q are 0.7 cm^2/sec and 3.2 eV, respectively.²⁸ The self-diffusion coefficient of As in GaAs is estimated to be $3 \times 10^{-18} \text{ cm}^2/\text{sec}$ at 650° C from the above equation. Thus, the diffusion length of As in GaAs is about 40 Å after the Zn diffusion at 650° C for 12 hrs. It would appear that allowing the excess As to reach the silicon nitride film severely degrades its usefulness as a Zn diffusion mask.

3.5 Device Applications

Two facts suggest that LT GaAs will be very useful for semiconductor lasers since current confinement and heat dissipation are very critical for a low laser threshold, high modulation speed, and high power operation in these devices. First, a much higher electrical resistivity is obtained from LT-GaAs compared to undoped GaAs.¹ And, secondly, better thermal conductivity²⁹ and a better thermal expansion coefficient are expected from LT GaAs compared to dielectrics such as silicon nitride or silicon dioxide. Also, a better temperature dependence of laser threshold and lasing wavelength is expected due to a better thermal impedance. We are now in the process of developing laser diodes with the LT GaAs and the results will be published elsewhere.

4. SUMMARY

The Zn diffusion coefficient in LT GaAs has been measured using the two-boundary diffusion model and found to be about one order of magnitude higher than in undoped GaAs. The faster Zn diffusion is attributed to a large quantity of defects including arsenic antisities in the LT GaAs. The 77K photoluminescence data taken before and after Zn diffusion have the same emission peaks at 8500 Å but the diffusion reduces the halfwidth of the emission peak. Electrical resistivities measured before and after the Zn diffusion show a reduction in the resistivity. The failure of the silicon nitride film directly deposited on the LT GaAs to stop the Zn is attributed to arsenic atoms outdiffusing from the As-rich LT GaAs into the nitride film. Several structures were grown including samples with a 100-Å thick GaAs, a 1- μm thick GaAs, and about a 1- μm thick AlGaAs layer separating the LT GaAs from the silicon nitride. All of these layers grown on the LT GaAs were effective in preserving the diffusion mask characteristics of the silicon nitride. This success, with as little as 100 Å of GaAs, is consistent

with the assumption that As outdiffusion is responsible for the failure of the SiN mask.

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