Pergamon

0038-1101(95)00152-2

Solid-State Electronics Vol. 39, No. 1, pp. 1–5, 1996

0038-1101/96 $9.50 + 0.00

PLASMA-INDUCED DAMAGE AND HYDROGENATION OF $Al_xGa_{1-x}P$

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(Received 17 May 1995; in revised form 14 July 1995)

Abstract—Highly C-doped $Al_xGa_{1-x}P$ was exposed to electron cyclotron resonance (ECR) Ar and H_2 plasmas to investigate dry etch damage and hydrogen passivation effects. The $Al_xGa_{1-x}P$ is much more resistant to plasma damage than InGaP or AlInP across the entire range of x-values investigated ($x = 0$–0.7). For example, under plasma conditions that induce $\approx 10^{10}$ cm^{-2} dislocation loops in InGaP, no defects are observed in AlGaP. These results are understood in terms of the high stability of the Al–P bonds in addition to the higher bond strengths of Ga–P relative to In–P. The hydrogen passivation of C acceptors is lower in the alloys compared to GaP, and exposure to an ECR H_2 plasma creates a band of defects ≈ 200 Å deep at the AlGaP surface.

1. INTRODUCTION

The AlGaInP material system is currently under investigation for use in short wavelength photonic devices and microelectronics with improved characteristics relative to the more conventional AlGaAs alloys[1–3]. While there is a significant understanding of the processing of the ternary compounds InGaP and AlInP[4–9], there are no reports on the response of AlGaP to dry etch-induced damage, or on the role of hydrogen in this material. Since AlGaP will generally be grown by a gas-phase technique like metal organic chemical vapor deposition (MOCVD)[2], there is concern about electrical passivation of dopants by residual hydrogen in the layers from the metal organic or hydride precursors[10,11]. Moreover, it is well-established that AlGaAs is more resistant to introduction of damage during ion implantation or dry etching than is GaAs[12], and therefore there is interest in the response of AlGaP relative to the other ternaries InGaP and AlInP.

In this paper we detail experiments on the change in electrical and structural properties of $Al_xGa_{1-x}P$ exposed to electron cyclotron resonance (ECR) Ar or H_2 discharges under a range of different powers, pressures and times. For the entire set of material compositions investigated ($x = 0$–0.7) we did not observe any significant change in conductivity after exposure to the Ar plasmas, and transmission electron microscopy (TEM) could not detect any dislocation loops. This is very different from the cases of InGaP or AlInP, both of which display severe changes ($> 10^4$ decrease) in conductivity as a result of high ion density Ar plasma treatments[13]. $Al_xGa_{1-x}P$ is therefore an attractive candidate as a robust etch-stop layer material in multi-layer device structures. One could employ high ion energies during dry etching of overlayers without fear of point defects propagating through the AlGaP and into underlying layers.

2. EXPERIMENTAL

The $Al_xGa_{1-x}P$ layers ($x = 0$–0.7) were grown on Si substrates by metal organic molecular beam epitaxy (MOMBE) using dimethyl-ethylamine alane, triethylgallium and phosphine as the chemical precursors[3]. The growth temperature was 525°C and the growth rate was ≈ 1 μm h^{-1}. Each of the films was ≈ 1 μm thick. Due to efficient incorporation of C under the particular set of growth conditions employed, the $Al_xGa_{1-x}P$ is strongly p-type ($\approx 10^{19}$ cm^{-3}) for all compositions. Sheet resistances before and after Ar or H_2 plasma exposures were obtained from Van der Pauw geometry Hall measurements using alloyed (420°C, 3 min) HgIn contacts on the corners of 5×5 mm^2 samples.

The damage and hydrogenation studies were performed in a Plasma-Therm SLR 770 system in which the plasma is generated in an ECR source operating at 2.45 GHz (Astex 4400). The sample position can be negatively biased through application of 13.56 MHz r.f. power, which therefore controls the energy of ions emerging from the ECR source. The effect of Ar plasma exposure on the samples was investigated to measure the susceptibility of AlGaP to ion-induced damage during dry etching. The use of a purely physical etch chemistry like Ar enables us to study only the effects due to ion bombardment of the

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AlGaP surface. The electrical passivation due to hydrogen incorporation was examined by exposing the samples to ECR H_2 plasmas under various conditions.

3. RESULTS AND DISCUSSION

3.1. Ion damage

Figure 1 shows the ratio of sheet resistance of $Al_{0.45}Ga_{0.55}P$ layers after Ar plasma exposure to their initial sheet resistance (R_0) as a function of r.f. power applied to the cathode during 1 min exposures. The process pressure was 1.5 mtorr, and either 0 or 750 W of ECR power was applied. In the case of r.f. power only, where the ion density in the discharge is in the 10^9 cm^{-3} range, we do not see any change in the resistance of the layer for any r.f. power, indicating that deep level electron trap introduction under these conditions must be $\ll 10^{17}$ cm^{-3}, or else we would observe an increase in the ratio R/R_0. Under these same Ar plasma conditions, InGaP for example shows increases of 2–3 times in sheet resistance. When ECR power is applied, the ion density in the discharge rises to $\approx 5 \times 10^{11}$ cm^{-3}, but even under these conditions the sheet resistance only increases by 20%. By sharp contrast, *n*- and *p*-type InGaP exposed to Ar discharges under the same conditions show increases from a factor of 3 (*p*-type) to $> 10^4$ (*n*-type). Therefore, AlGaP appears to be much more resistant to the introduction of damage than InGaP. This is analogous to the situation with GaAs and AlGaAs, discussed earlier and results from the higher bond strength of the Al–P bond (51.8 kcal mol^{-1}) relative to that of In–P (47.3 kcal mol^{-1}). Given the resistance to ion-induced damage it is not surprising that we observed no effect of changing pressure (1.5–10 mtorr), the time of exposure (1–5 min) or the AlP mole fraction in the AlGaP. Figure 2 shows that over the entire Al composition range investigated there was no measurable change in sheet resistance of the AlGaP, even for high ECR and r.f. powers. Since the Ga–P bond strength is also very high (54.9 kcal mol^{-1}), this result is consistent with expectations.

ECR plasma exposure generally creates a high density ($\approx 10^{10}$ cm^{-2}) of small dislocation loops in materials like GaAs and InGaP due to the coalescence of point defects generated at the surface

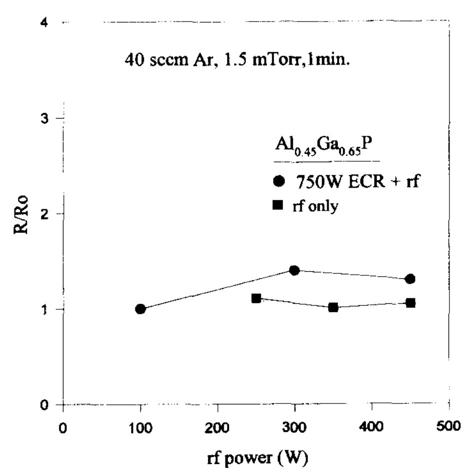


Fig. 1. Sheet resistance ratio increase in AlGaP after exposure to Ar plasmas, as a function of r.f. power.

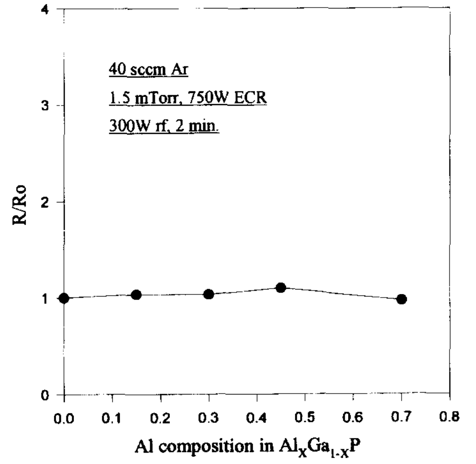
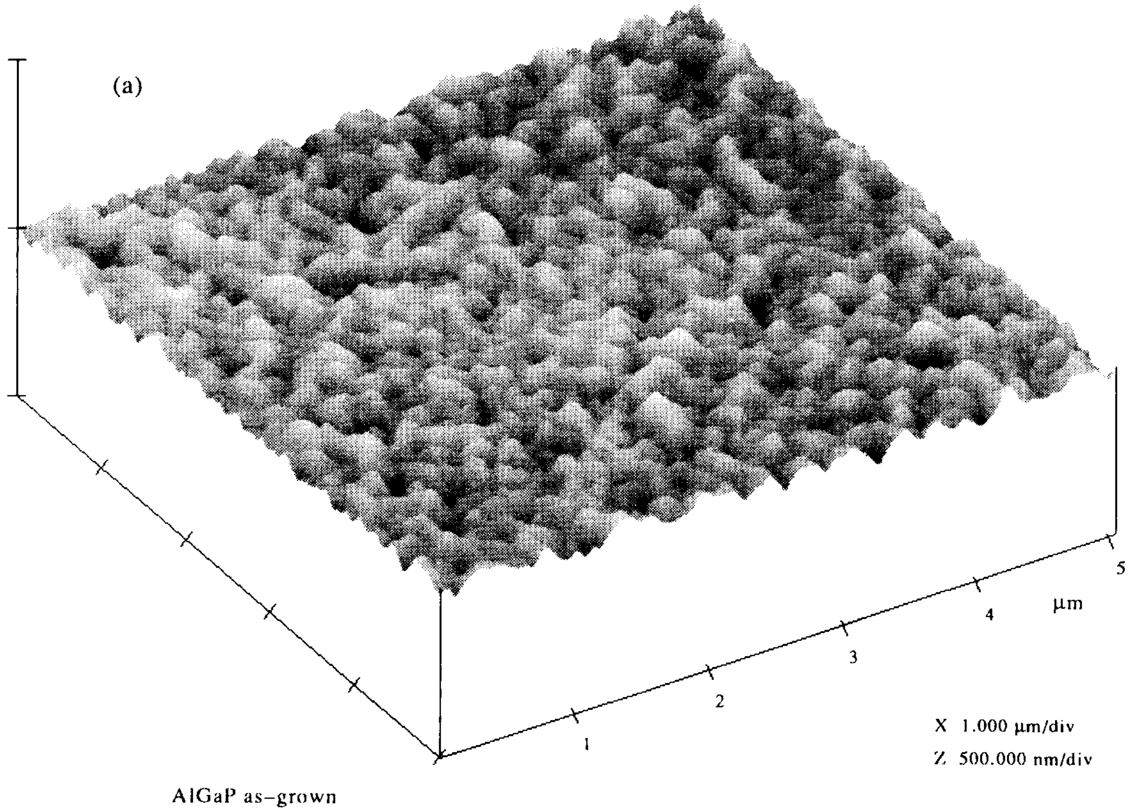


Fig. 2. Sheet resistance ratio increase in $Al_xGa_{1-x}P$ as a function of Al composition.

Fig. 3. TEM cross-sections of (top) Ar r.f. plasma exposed AlGaP and (bottom) Ar ECR plasma exposed AlGaP.



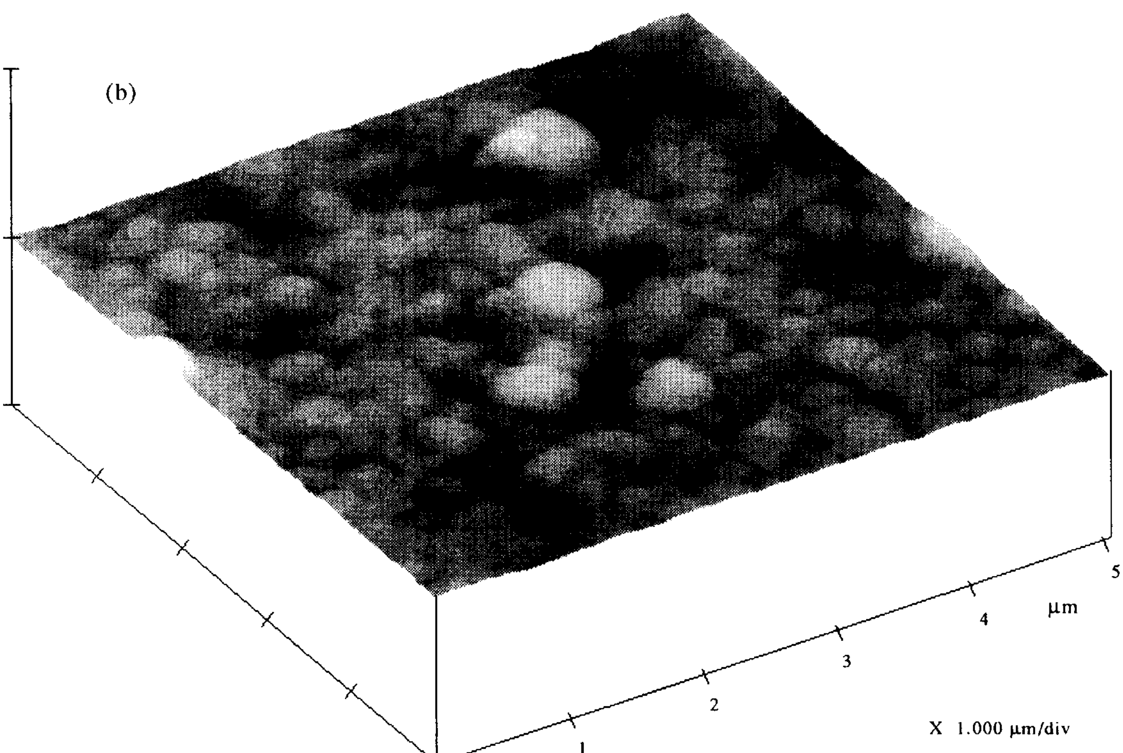


Fig. 4. (a) AFM scan as-grown AlGaP; (b) AFM scan of ECR Ar plasma-treated AlGaP.

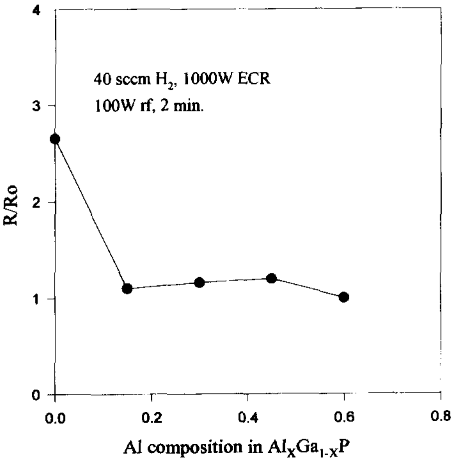


Fig. 5. Sheet resistance ratio increase in AlGaP after hydrogen plasma exposure, as a function of Al composition.

by ion bombardment[13]. However in $Al_{0.45}Ga_{0.55}P$ exposed to either r.f.-only Ar plasmas or with additional ECR power, we could not detect any extended defects created by ion bombardment. Figure 3 (top) shows a cross-sectional transmission electron microscopy (TEM) of the AlGaP after a 1 min exposure to a 300 W r.f. discharges, while Fig. 3 (bottom) shows a sample after a 750 W (microwave), 300 W (r.f.) treatment. In neither case do we observe any dislocation loops associated with ion damage, and the extended defects present are a result of the island growth mechanism of the AlGaP on Si. The only change to the physical properties of the AlGaP is a slight smoothing of the surface as a result of the Ar plasma treatment. Figure 4(a) shows an atomic force microscope scan of an as-grown sample, displaying a root-mean-square roughness over a 5×5 μm^2 area of 16.5 nm. While bombardment with an r.f. plasma did not alter the morphology (RMS value of 16.3 nm), an ECR Ar plasma exposure for 1 min significantly reduced the surface roughness. Figure 4(b) shows the AFM scan from this sample, which now has an RMS roughness of only 6.04 nm. We attribute this change to the fact that ion milling is faster for incidence angles between 45–70°[14], and that the as-grown surface morphology presents features with these angles to vertically-incident ions from the plasma. The ion milling rate of the AlGaP under ECR conditions is ≈ 400 Å min^{-1}, and therefore in a 1 min exposure erosion of the sharply angled surface features at a faster rate than the flat sections of the surface leads to a general smoothing of the morphology.

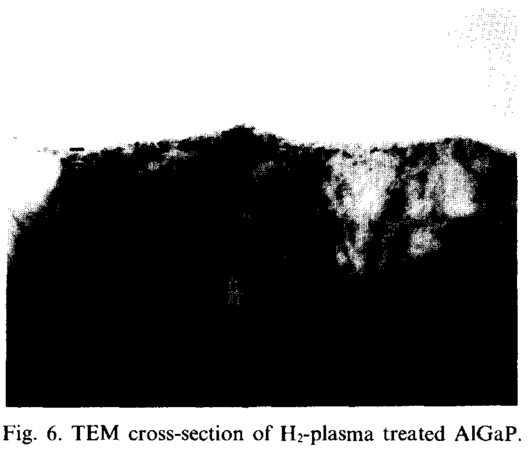


Fig. 6. TEM cross-section of H_2-plasma treated AlGaP.

3.2. *Hydrogen passivation*

Deactivation of C acceptors by association with atomic hydrogen to form neutral C–H complexes is well-established in GaAs, $Al_xGa_{1-x}As$, InGaAs and GaP[15], but no data is available for $Al_xGa_{1-x}P$. Samples with different Al compositions were exposed to H_2 plasmas at near room temperature and the change in sheet resistance measured. Figure 5 shows that under these conditions only GaP showed significant hydrogen passivation of the carbon. It is probable that higher hydrogenation temperatures are required in order to incorporate enough hydrogen into the alloys to affect their conductivity, and this study will be reported at a later date. The microwave power level or process pressure also had no effect on the sheet resistance, at least for the 2 min exposures we carried out.

We did observe a shallow (≈ 200 Å) band of defects in AlGaP after exposure to H_2 plasmas, as shown in the cross-sectional TEM micrograph of Fig. 6. The origin of this defect band is not clear at present, but it could result from two mechanisms. The first would be preferential loss of P by formation of PH_3. This is a common problem in hydrogenation experiments with III–V, and leads to the presence of group III droplets on the surface. However, AFM scans of the AlGaP surface after ECR H_2 plasma exposure did not show any evidence for roughening. Figure 7 shows the morphology, and the RMS roughness of 13.53 nm is actually smoother than that of the as-grown material. Therefore loss of P from the AlGaP surface does not appear to account for the defects observed by TEM since one would expect the morphology to become much poorer. The other possible mechanism for defect formation is precipitation of hydrogen into the type of clusters seen in H^+-implanted GaAs[16–18], or in H_2-plasma Si[19]. In these materials the hydrogen forms a variety of different extended defects where structure changes with annealing. We do not believe the defects seen in the AlGaP are related to ion bombardment damage, since they are not observed in the Ar-treated material. If this is indeed the case, then the formation of extended hydrogen-related defects near the surface could impede the diffusion of the atomic species into the bulk and thereby account for the low passivation efficiency in the alloys. This assertion can be checked by performing secondary ion mass spectrometry measurements of the incorporation depth of hydrogen into $Al_xGa_{1-x}P$ of different compositions.

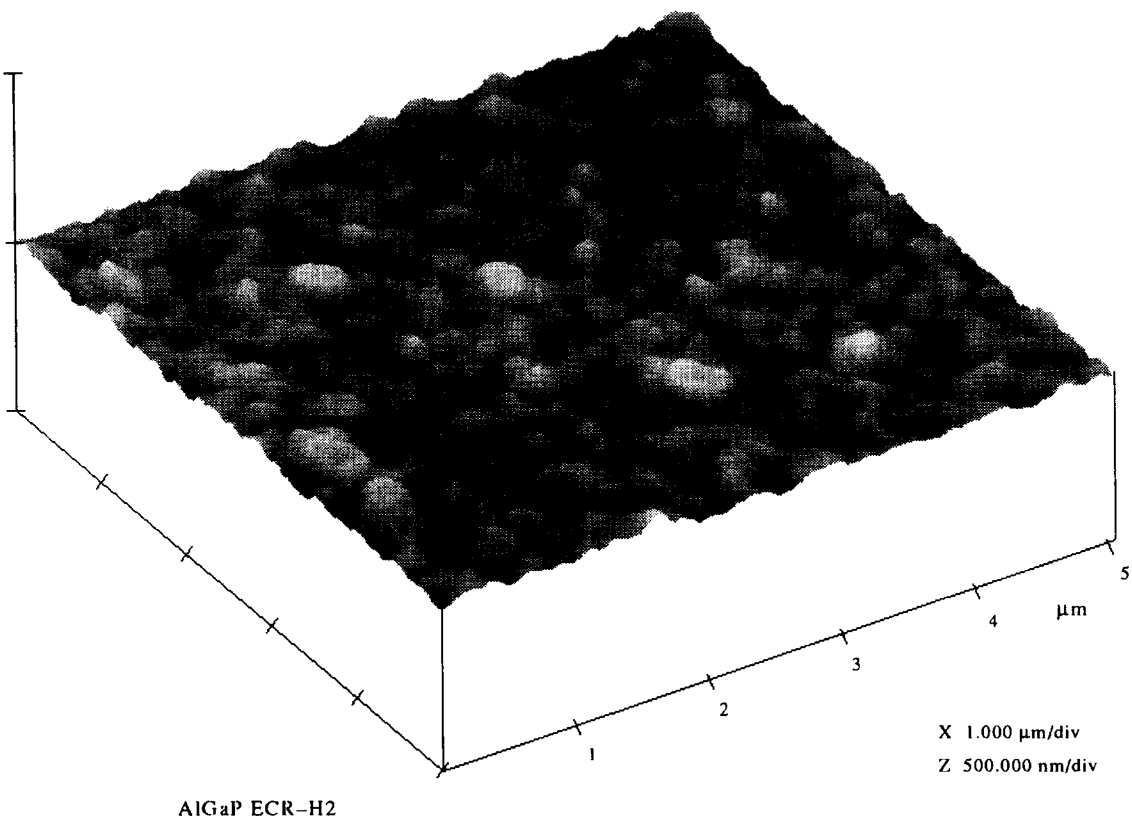


Fig. 7. AFM scan of H_2 plasma treated AlGaP.

4. CONCLUSION

AlGaP is more resistant to plasma-induced damage than InGaP and other III–V materials. There is minimal change in the electrical and structural properties of the AlGaP for a wide range of ECR plasma conditions. Similarly, hydrogen passivation of C acceptors in the material is weak under conditions which lead to extensive passivation in *p*-type InGaP. Both of these results suggest that AlGaP is an attractive etch-stop layer and hydrogen filter in multilayer structures based on the AlGaInP material system.

Acknowledgements—This work is partially supported by a grant from Hughes Aircraft Company (Dr C. S. Wu) and an AASERT grant from the U.S. Army Research Office (Dr J. M. Zavada). The work is performed in the Microfabritech facility—the support of the staff is greatly appreciated.

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