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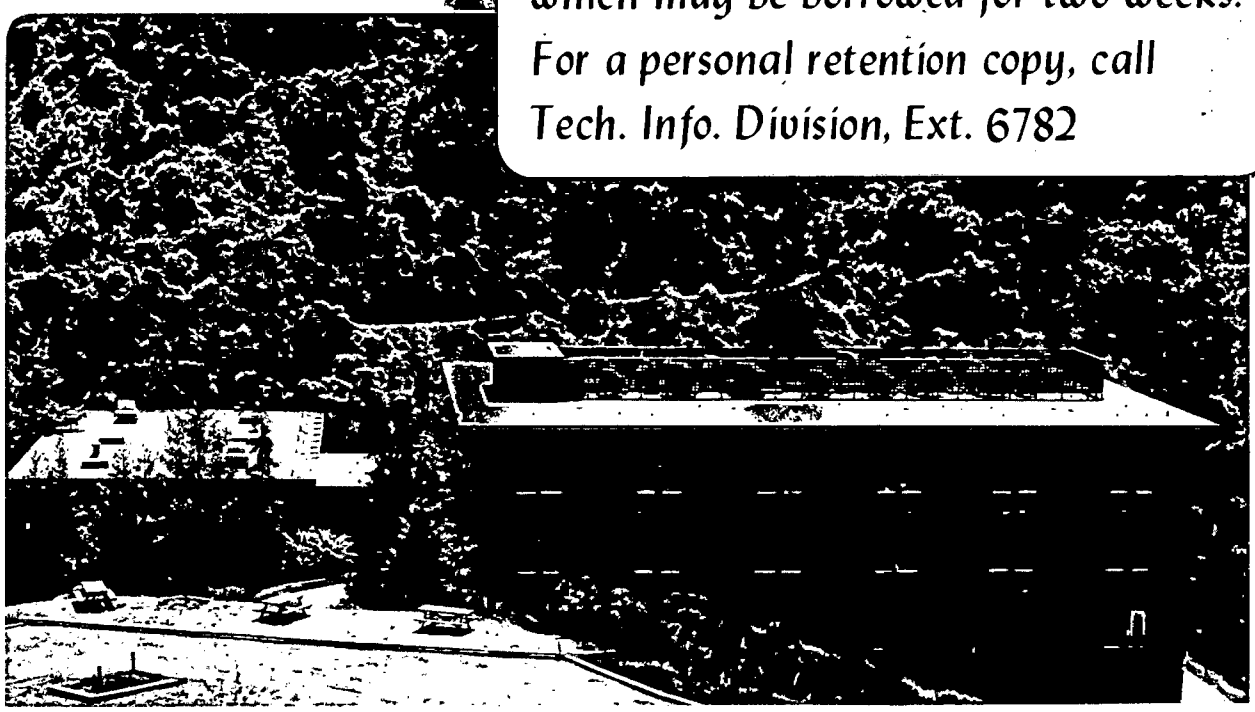

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DIRECT EVIDENCE OF Cr-STRUCTURAL DEFECT-OXYGEN INTERACTION IN ION-IMPLANTED GaAs

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Abstract

The redistribution of Cr in GaAs implanted with either Ga and As, or Ga, As and O and subsequently furnace annealed was studied by secondary ion mass spectrometry. The depth distribution of the residual damage was obtained by cross-sectional transmission electron microscopy. At annealing temperatures of $\leqslant 600°C$, there was a one to one depth correlation between the positions of the damage layers and peaks in the atomic profile of Cr. However, at annealing temperatures of $\geqslant 800°C$ such correlations were complicated by oxidation effects.

Introduction

The redistribution of Cr in ion-implanted and subsequently furnace-annealed GaAs has been studied extensively.[1-6] Although gettering of Cr at structural defects has been suggested,[1,2,4,6] none of the published work has been able to fully explain the anomalous redistribution of Cr in the implanted region. Understanding this phenomenon is important for the device manufacturing industry because of the degradation in the electrical behavior associated with Cr segregation if it is in the active region of the device. In this paper, direct depth correlations between the Cr and structural defects are presented for the first time and the anomalous redistribution of Cr is explained by considering a combined Cr-structural defect-oxidation interaction during the annealing.

Experimental

Dual implantation of Ga and As was carried out at 550 and 575 keV, respectively (two different energies were used to match the projected ranges, R_ps for the two ions), into (100) GaAs at room temperature. In some cases, O was also implanted at two energies (80 and 240 KeV, respectively) together with Ga and As to study the influence of O on Cr redistribution and damage annealing. The dual energies in the case of O

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implants were used to obtain a nearly flat distribution of O in the implanted region. The doses used were $5 \times 10^{14}/cm^2$ of Ga, $5 \times 10^{14}/cm^2$ of As and $2 \times 10^{15}/cm^2$ of O, respectively. The samples without and with O implant will be referred to as sample X and sample Y, respectively, in the text from here onwards. The implanted samples were then capped with SiO_2 at 410°C by chemical vapor deposition before furnace annealing to temperatures up to 840°C. The structural damage in the as-implanted and annealed samples was analyzed both in cross-sectional and plan views by transmission electron microscopy (TEM), using bright field diffraction contrast. The Cr and O distributions in the same samples was measured by secondary ion mass spectrometry (SIMS) using O-ion and Cs-ion bombardment, respectively.

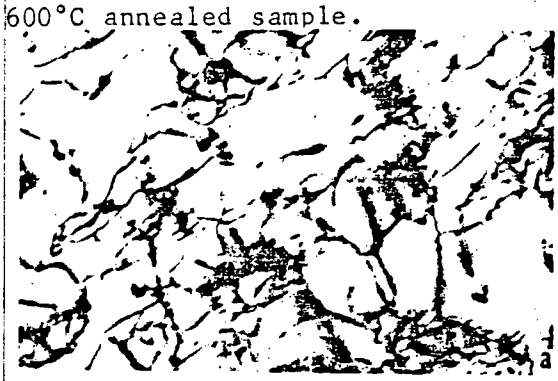
Results

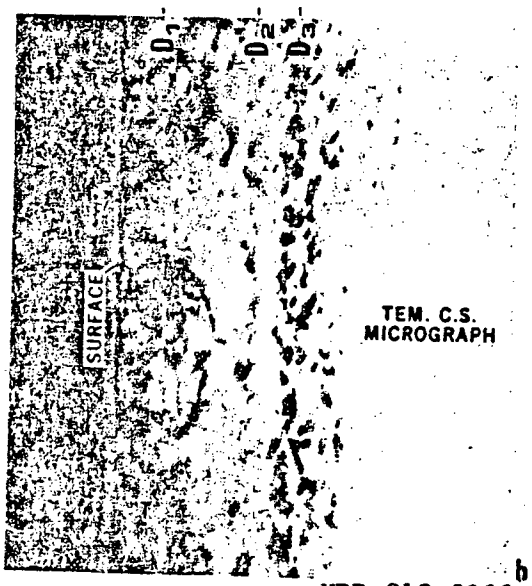
The cross-sectional TEM micrograph from the unannealed sample X (not included) showed a damaged layer of width 0.28μm below the surface. The transmission electron diffraction pattern from the plan view specimen showed a diffuse ring pattern indicating that the damaged layer contained amorphous material. The Cr atom distribution from this sample was found to be the same as for the unimplanted and unannealed sample.

Subsequent annealing of the sample X at 600°C for 15 minutes in a N_2 ambient gave a complicated distribution of defects as revealed by the cross-sectional TEM micrograph shown in Fig. 1b. The micrograph showed three distinct defect layers. The first layer, D_1 contained entangled dislocations looping from the surface to a depth of 0.2μm. The second damage layer, D_2, was very narrow and contained small dislocation loop (~ 0.03μm across) at a mean depth of 0.275μm. The third damage layer, D_3, again contained small dislocation loops, but in a band that was 0.12μm wide situated at a mean depth of ~ 0.36μm. The regions between D_1 and D_2 and between D_2 and D_3, were relatively free from "visible" damage. The term "visible" damage refers to the damage observable in a conventional TEM. The corresponding plan view micrograph (Fig. 1a) gave complimentary results, i.e., it also showed entangled dislocations and the dislocation loops. Comparison of Figs. 1a and 1b demonstrates the power of cross-sectional TEM because the complicated distribution of the defects revealed by Fig. 1b is not evident in Fig. 1a. The Cr atoms distribution from the same sample, but from a different area, showed three peaks and two shoulders (Fig. 1c). The first shoulder occurred within 0.03μm of the surface. The peaks A_1, A_2, and A_3 at depths of 0.13μm, 0.29μm and to 0.39μm, respectively, correspond precisely to the high defect density layers observed in the TEM micrographs. Similar depth correlation between the defects and atomic profile have been reported earlier.[7] The second shoulder at a depth of 0.6μm occurred in the region below D_3 in the TEM micrograph. For comparison, the Cr distribution in the as-implanted sample is shown by a broken line in Fig. 1c.

Figure 2b shows a cross-sectional TEM micrograph of sample X after annealing at 840°C for 10 minutes. The damage in this case consisted of only a single layer S of dislocation loops at a mean depth of 0.36μm from the surface. The corresponding plan view TEM micrograph (Fig. 2a) showed similar defects. Occasionally, looping dislocations near the surface were also present (Fig. 2b). The Cr atomic distribution from the same sample but from a different area showed two distinct peaks, P_1 and

P_2, at depths of 0.18μm and 0.375μm, respectively. The second peak P_2 corresponds precisely to the position of high dislocation density, layer S, in the TEM micrograph (Fig. 2b). There was no discrete "visible" damage region corresponding to the first Cr peak P_1. However, this peak was in the vicinity of peak A_1 in Fig. 1c of the 600°C annealed sample.





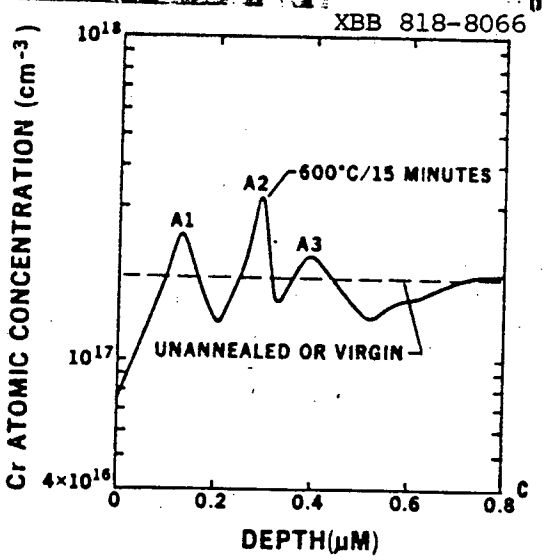


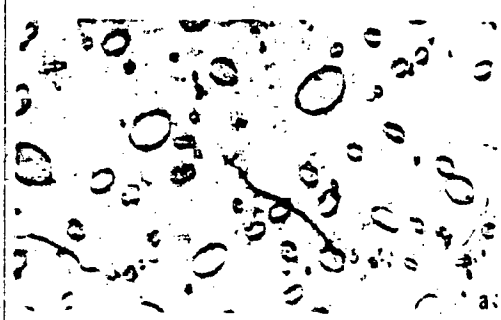
Fig 1a & b TEM plan view and cross-section micrographs showing the defects distribution in the 600°C annealed sample. (c) Cr atoms-depth distribution from the same sample as in Fig. 1a and b.

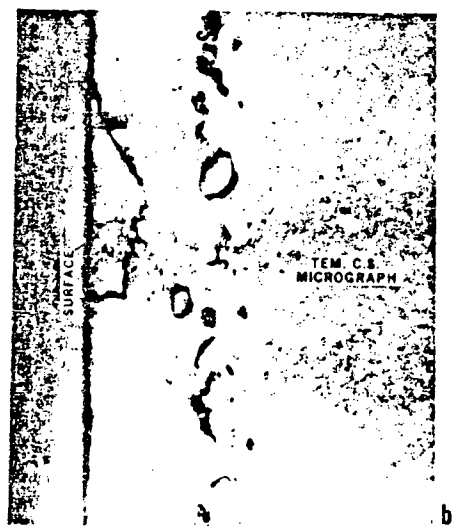
Figure 3a shows a plan view TEM micrograph from sample Y that was annealed at 840°C for 15 minutes. The micrograph shows dark patches consisting of entangled dislocations. The corresponding cross-sectional TEM micrograph showed two separate regions of damage L_1 and L_2, respectively. The region L_1 corresponded to the dark patches in Fig. 3a and extended from the surface to a depth of 0.2 μm. The region L_2 showed a band of small dislocation loops, 0.28 μm wide, and was located at a mean depth of 0.53 μm. The SIMS data from the same sample showed three Cr peaks C_1, C_2, and C_3, respectively. Peaks C_1 and C_2 corresponded to the damage regions L_1 and L_2 in Fig. 3b, however, peak C_3, which has the highest magnitude, was present in a region below L_2. The O profile was also obtained from this sample and is shown by a broken line in Fig. 3c. Note that not only are the three O peaks O_1, O_2, and O_3 located precisely where peaks C_1, C_2 and C_3 are present, but also the shapes of the two profiles are identical.

Discussion

The detailed recrystallization mechanism of amorphous GaAs has been described elsewhere.[8,9] Layer D_1 in Fig. 1b arises due to the solid phase expitaxial growth of amorphous GaAs generated by Ga and As implantation. The sharpness and location of layer D_2 at a depth corresponding precisely to the original amorphous/crystalline GaAs interface indicate that it might have originated because of small differences in the Rps of Ga and As in GaAs, although the two different implantation energies (550 and 575 keV) used were expected to match the Rps. Layer D_3 below the original amorphous crystalline

interface is typical of any ion implantation into Si or GaAs followed by furnace annealing. This is attributed mainly to (i) a small fraction (2-3%) of implanted ions that are steered into open channels at the end of their implantation trajectories and (ii) high mobility of interstial point defects at RT that is further enhanced during radiation damage, especially in the case of GaAs. At 840°C, layers D_1 and D_2 are completely





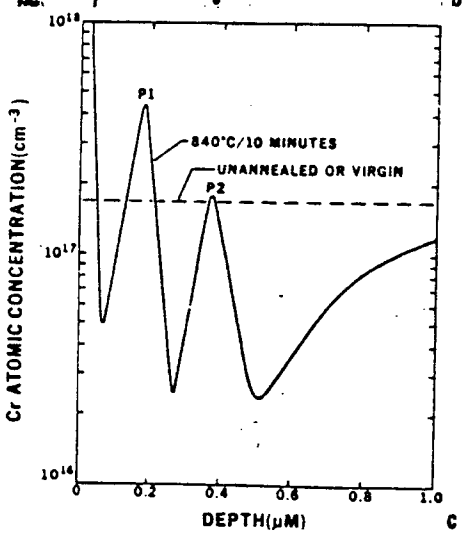


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Fig. 2a & b TEM plan view and cross-section view micrograph showing a discrete layer of dislocation loops in the 840°C annealed sample. (c) Cr atoms distribution from the same sample as in Fig. 2a and b.

layers D_1 and D_2 are completely annealed out (Fig. 2b) with only a few looping dislocations remaining. Layer S (Fig. 2b) results from the growth of the loops in layers D_3 of Fig. 1b. However, as is evident from Fig. 3, the annealing out of the dislocations is considerably retarded in the presence of high concentration of O. This is believed to be due to the formation of fine Ga-O, Cr-O As-O precipitates and/or their complexes that pin the dislocations.

It is clear from Figs. 1b and 1c that there is an excellent correlation between the presence of "visible" damage and Cr segregation in the implanted region. However, Figs. 2 and 3 show that after high temperature anneals (≥ 800°C) Cr segregation does not necessarily correspond to the regions containing "visible" damage. All of these results can be explained by the following model.

At the lower annealing temperature (600°C), when the amorphous layer of sample X recrystallized and dislocations formed, Cr segregated at high dislocation density regions because of its binding to dislocation cores and the reduced activation energy for pipe diffusion. It seems likely that some oxidation in sample X (the source of oxygen may be the ambient or the SiO_2 cap used to prevent the decomposition of the GaAs surface) occurs simultaneously with the segregation, and Cr then forms Cr-oxygen complexes. This oxidation is expected to be confined to the near-surface region at the annealing temperature used. Due to the presence of the dense entangled dislocation network, oxygen can migrate via pipe diffusion to depths where the dislocation network extends. Therefore, the

first peak A_1 in Fig. 1c could contain Cr-oxygen complexes but the deeper lying peaks probably arise simply due to Cr gettering to the damage regions. The presence of peak P_1 in the 840°C annealed sample, (Fig. 2c) without a corresponding well-defined visible damage layer (Fig. 2b) is consistent with the hypothesis that Cr-oxygen complexes are formed near the surface during the early stages of annealing in the region D_1. This may explain why the Cr in the form of complexes stays at peak P_1 (originally A_1 at 600°C) even when the dislocations have annealed out. The formation of relatively stable Cr-oxygen complexes is further suggested by the fact that annealing for 5 minutes at 840°C produces practically the same Cr atom concentration vs depth profile as does annealing for 40 minutes at 840°C.

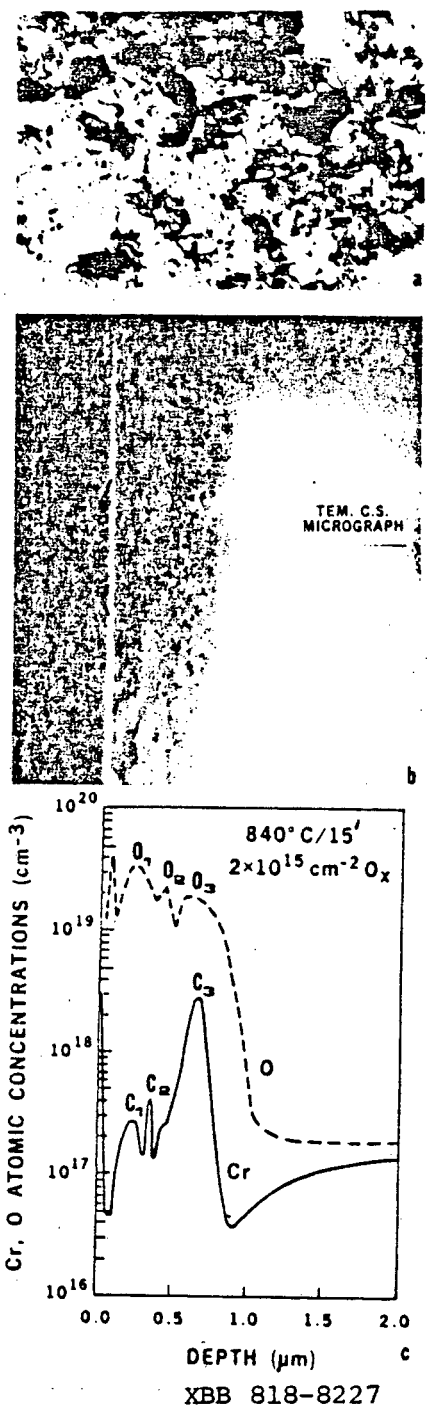

Fig. 3a & b. TEM plan view and cross-section view micrographs showing the defects distribution in 840°/15' annealed sample containing O. (c) Cr and O atoms distributions from the same sample as in Fig. 3a and b.

More direct evidence of oxygen involvement in the Cr redistribution process can be seen in Fig. 3 which corresponds to sample Y in which O was deliberately introduced by ion implantation. In this case the Cr and O profiles look identical except for the magnitude of the peaks. These results are also consistent with the hypothesis of Cr-O complexes formation as explained below. Because of a high concentration of dislocations near the surface, Cr starts to out-diffuse from the bulk at low annealing temperatures. However, at annealing temperatures above 800°C, the formation of Cr-O complexes may define the Cr distribution as indicated by the identical shapes of Cr and O profiles. If this is true, then at higher annealing temperatures the Cr should no longer be able to out-diffuse beyond the region where it first meets the O atoms. This is precisely what seems to happen in Fig. 3, where the out-diffusing Cr atoms first meet the O atoms at a depth of 0.53 μm (peak C_3). This also explains the occurrence of the highest Cr peak in a region beyond L_2 (Fig. 3b). The presence of O in the deeper regions act as a trap for Cr as far as its out-diffusion towards the

surface is concerned. Because of the chemical affinity of Cr for O, the Cr-O complexing does not saturate in the high O concentration regime. The height of the Cr peak was also found to be related to the oxygen dose. For example, when an O dose of $2.0 \times 10^{15}/cm^2$ was used, the Cr peak concentration was $3 \times 10^{18}/cm^3$ while a Cr peak concentration of $5 \times 10^{17}/cm^3$ occured when an O dose of $4 \times 10^{13}/cm^2$ was used. Thus, x50 less dose of oxygen gives x6 smaller Cr peak. This is again in agreement with the Cr-O complexing model. The detection of the Cr peak at the surface in almost all the annealed GaAs samples in this study as well as in the earlier reported work[1-6] is also consistent with the formation of stable Cr-oxygen complexes at the external surface.

Conclusions

1. Direct evidence of Cr segregation at high defect density regions has been obtained.
2. The complex Cr redistribution for annealing at temperatures 800°C can be explained in terms of Cr-oxygen complexing combined with segregation at dislocations. The model is also consistent with much of the earlier published results on Cr redistribution in GaAs.

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