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BY ION BEAMS

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and N.W. Cheung

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RECRYSTALLIZATION OF AMORPHOUS GALLIUM ARSENIDE BY ION BEAMS

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Abstract

An 11 megavolt arsenic beam was used to amorphize approximately 3.9 μm of GaAs surface layer at liquid nitrogen temperature. It was found that apparently amorphous gallium arsenide can be reconverted to single crystal by subsequent implantation at higher temperature. The recrystallization by the ion beam proceeded simultaneously from the amorphous surface and the deep amorphous/crystalline interface. Growth of dendrites and/or microtwins occurred at the recrystallizing interfaces.

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The defect structures (point defects and their complexes) created by ion implantation in GaAs are quite complicated in nature and are far from being understood. It is not clear at present whether the structure of amorphous GaAs and Si are comparable. The difference in the amorphousness of the two materials is suggested indirectly by the results of annealing experiments. The damaged GaAs recrystallizes at a much lower temperature ($\approx 150^\circ\text{C}$) than Si ($\approx 450^\circ\text{C}$). Correlation of structure-electrical depth profiles suggest that the electrical properties of GaAs are influenced much more by point defects than by secondary defects such as dislocation loops or dislocations. (1)

The electrical properties of ion implanted and annealed GaAs are especially poor (1-10% activation) when the dose is such that the as-implanted material becomes amorphous (medium to high dose case). Better electrical results have been reported for elevated temperature implantation. It is therefore apparent that better characterization of amorphous GaAs created by ion implantation is of great concern. In this communication, annealing of apparently amorphous GaAs due to MeV ion beams has been reported. The energy density needed to transform crystalline GaAs into amorphous state has also been obtained.

Eleven MeV arsenic ions were implanted into (100) semi-insulating GaAs to a dose of 10^{15} cm^{-2} at liquid nitrogen (LN) temperature. These same substrates were subsequently implanted at room temperature (RT) up to a dose of 10^{15} cm^{-2} . Pulses of $\approx 1 \mu\text{A As}^{+++++}$ were extracted

at 2.2 MeV in a Lawrence Berkeley Laboratory dynamatron at a rate of 5 cycles/sec. The ion source was a conducting crystal of gallium arsenide from which 5^+ charge state As ions were sputtered and extracted into the accelerator column.⁽²⁾ Taking into consideration the average power of the beam (10 watts cm^{-2}) in the present experiment, the localized substrate heating should cause a temperature rise of $\leq 200^\circ\text{C}$.⁽³⁾ The structural examinations of the damage layer was carried out in a Philips 301 transmission electron microscope (TEM) operating at 100 keV. The specimens of both plan and cross-sectional (X) geometries were examined. It should be noted that a 100 keV electron beam is capable of imaging defects present only within 1 μm of the thin GaAs specimens. Therefore, while the interfaces extending several microns into the material can be revealed in thin cross-section specimens, the information from plan view specimens is limited only to 1 μm skin of the surface.

Figure 1a shows the damage-depth distribution in the LN implanted GaAs sample. The diffraction pattern taken from the plan view specimen of this sample (Fig. 2a) showed that the surface region ($\leq 1 \mu\text{m}$) of the dark band in Figure 1a consisted of amorphous material. Subsequent RT implantation of the sample of Fig. 1a to a dose of 10^{14} cm^{-2} produced rather striking results. Not only did the amorphous layer begin to recrystallize from the deep amorphous/crystalline interface, but also from the surface which was apparently amorphous (Figure 1b). The amorphous $\rightarrow$ crystalline transformation at the surface was confirmed by the electron diffraction pattern from a plan view

specimen corresponding Fig. 1b. The pattern consisted of single crystal spots of (100) orientation which were superimposed on the amorphous pattern (Figure 2b). This indicates that the regrown layer retained the original substrate orientation. However, the TEM micrographs of Fig. 2b shows that the regrown surface region contains a high density of dark blobs type defects which could be related to the formation of a second phase (such as Ga or As precipitation). Further increase in the dose (10^{15} cm^{-2}) of subsequent implantation at RT accelerated the in situ annealing process. The regrowth front from the surface moved $2.2 \text{ } \mu\text{m}$ while the deep amorphous/crystalline front moved only $0.5 \text{ } \mu\text{m}$. This is believed to be due to the differences in the amorphousness of GaAs in the surface region and that in the deeper parts as indicated by the displacement damage curve (Fig. 1d). Due to the smaller component of the nuclear stopping near the surface, the amorphous GaAs may consist of a mixture of tiny crystallites ($<20 \text{ } \text{\AA}$) and amorphous zones. This case is difficult to detect by bright-field TEM such as that employed to obtain Figs. 1-3. On the other hand, the amorphous GaAs near the lower interface is expected to have fewer tiny crystallites, if any. Some of the amorphous material was still sandwiched between the two fronts. Another striking feature of the regrowth was the nucleation of dendrite-like structures and their protrusion from both of the interfaces along $\langle 110 \rangle$ and $\langle 112 \rangle$ directions into the sandwiched amorphous GaAs layer.

Similar two step implantation methods at lower energies (120 keV) in Si showed only small regrowth of the amorphous material. No dendrites or microtwins were found to nucleate even in (111)

Si for second implantations conducted at temperatures up to 450°C (3). The detailed crystallographic information obtained in Figure 1c pertaining to epitaxial regrowth of GaAs is unique. Because of the extremely high regrowth rate of amorphous GaAs at the annealing temperatures generally used, partly recrystallized amorphous GaAs has not previously been observed. The 'dendrite-like' structures have been found to be microtwins on further annealing. Microwinning in implanted and annealed GaAs has been reported many times in the literature. (4-6)

Indirect evidence of regrowth occurring from an apparently amorphous surface has also been obtained from the cross-sectional TEM micrographs of self (Ga and As) and Cr (10^{15} cm^{-2}) implanted GaAs samples that were furnace annealed at 600°C (see Fig. 3a and b for implantation details). The boundary marked B in Fig. 3b indicates that the regrowth fronts from the apparently amorphous surface and amorphous-crystalline interface met there.

We now propose a qualitative model that correlates the observed results. The free energy change associated with crystalline→amorphous transformation in GaAs is expected to be smaller than that in Si because of the higher ΔS (change in entropy) created by each entering ion. Therefore, at lower temperature (LN) where the mobility of point defects in GaAs is restricted, a lower dose compared with Si should be sufficient to amorphize the implanted region in GaAs. This was found to be true when nuclear stopping energy deposition curves generated from Brice's tables (Fig. 1d) were compared with the cross-sectioned TEM micrograph of Fig. 1a. The threshold

value for converting crystalline GaAs into amorphous GaAs was between $2-5 \times 10^{20} \text{ keV cm}^{-3}$. Under similar LN implantation conditions for Si, the threshold value was $2 \times 10^{21} \text{ keV cm}^{-3}$ (2). On the other hand, because of the partly ionic nature of the bonding in GaAs, Ga atoms will have a tendency to occupy sites near to As atoms or vice versa, even in the amorphous state. Therefore, there may be short range order even immediately after implantation. At higher temperatures (greater than RT) long range ordering should take place with the aid of mobile point defects. Single crystal growth during the room temperature implant from the surface suggests that even long range order at the surface had not been completely destroyed by the low temperature implant.

It is not clear from these results whether migration of amorphous-crystal interfaces was caused simply by heating that may have occurred during the room temperature implant, although the wafers were water cooled and heat conducting silver paint was used to ensure good thermal contact of the GaAs substrate to the wafer mount, or whether atomic displacements near the amorphous/crystal interfaces due to the energetic ions played a more direct role.

The formation of dendrite-like structures which protuded into amorphous GaAs in Fig. 1c is reminiscent of constitutional supercooling in metal alloys. It may be that the growth rate at the tip of a sharp protusion is favored by the possibility of spherical rather than linear diffusion of rejected excess As.

Another possibility is that the interface between a microtwin and the matrix crystal provides a particularly advantageous growth site. This effect has been observed in silicon (7).

In conclusion, it appears that (i) the amorphous surface region of GaAs created by ion implantation can be reconverted to single crystal by ion beams even without monocrystalline seeds. It is not clear whether it is predominantly a thermal effect or a direct atomic displacement effect and (ii) the threshold displacement energy for crystalline to amorphous transformation in GaAs ($2 \times 10^{20} \text{ keV cm}^{-3}$) is an order of magnitude less than that for Si ($2 \times 10^{21} \text{ keV cm}^{-3}$) under comparable implantation conditions.

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REFERENCES

1. D. K. Sadana, J. Washburn, M. D. Strathman, G. R. Booker and M. H. Badawi, Defects in Semiconductors 2 515 (1981), Mat. Res. Soc. Symp. Boston 1980. (Ed. J. Narayan and T. Y. Tan).
2. P. F. Byrne, N. W. Cheung and D. K. Sadana, App. Phys. Lett. 41 537 (1982).
3. P. D. Parry, J. Vac. Sci. Technol. 15 111 (1978).
4. D. K. Sadana, J. Washburn, P. F. Byrne and N. W. Cheung Defects in semiconductor 2 511 (1983), (Mat. Res. Soc. Sym. Boston 1982, Ed. S. Mahajan and J. W. Corbett).
5. S. S. Kular, B. J. Sealy, K. G. Stephens, D. K. Sadana and G. R. Booker, Solid State Elec. 23 831 (1980).
6. R. S. Bhattacharya, A. K. Rai, P. P. Pronko, J. Narayan, S. C. Ling and S. R. Wilson, J. Phys. & Chem of Solids, 44, 61 (1983).
7. M. G. Grimaldi, B. M. Paine, M. A. Nicolet, D. K. Sadana, J. App. Phys. 52 4038 (1981).
8. R. Drosd and J. Washburn, J. App. Phys. 53 397 (1982).

FIGURE CAPTIONS

Figure 1 Recrystallization of amorphous GaAs by an 11 MeV As beam as revealed by cross-sectional transmission electron micrographs.

11 MeV As $\longrightarrow$ (100) GaAs, (a) LN only, (10^{15}cm^{-2}),
(b) LN(10^{15}cm^{-2}) + RT (10^{14}cm^{-2}),
(c) LN (10^{15}cm^{-2}) + RT (10^{15}cm^{-2}), and
(d) theoretical displacement energy absorption vs. depth curve.

Figure 2 Plan view TEM micrographs corresponding to the surface regions ($\leq 1\text{ }\mu\text{m}$) of Fig. 1(a) and 1(b). Diffraction patterns inset.

Figure 3 Recrystallization of triple ion (Ga, As and Cr) implanted GaAs on furnace annealing. Ga (550 KeV, $5 \times 10^{14}\text{cm}^{-2}$), As (575 KeV, $5 \times 10^{14}\text{cm}^{-2}$) and Cr (300 KeV, 10^{15}cm^{-2}) $\longrightarrow$ (100) GaAs, all implanted at room temperature (a) unannealed and (b) capped and annealed in N_2 at 600°C for 15 minutes. The dotted line B indicates where the surface and amorphous/crystalline fronts met on annealing.

Fig. 1

XBB 841-75

LN

LN + RT (10^{14})

a)

b)

0.2 μm

XBB 820-9453

Fig. 2

Fig. 3

XBB 841-74

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