

# INFLUENCE OF OXYGEN ION IMPLANTATION ON THE DAMAGE AND ANNEALING KINETICS OF IRON-IMPLANTED SAPPHIRE

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## Abstract

The effects of implanted oxygen on the damage accumulation in sapphire which was previously implanted with iron was studied for (0001) sapphire implanted with iron and then with oxygen. The energies were chosen to give similar projected ranges. One series was implanted with a 1:1 ratio ( $4 \times 10^{16}$  ions/cm<sup>2</sup> each) and another with a ratio of 2:3 ( $4 \times 10^{16}$  Fe<sup>+</sup>/cm<sup>2</sup>;  $6 \times 10^{16}$  O<sup>+</sup>/cm<sup>2</sup>). Retained damage,  $\chi$ , in the Al-sublattice, was compared to that produced by implantation of iron alone. The observed disorder was less for the dual implantations suggesting that implantation of oxygen enhanced dynamic recovery during implantation. Samples were annealed for one hour at 800 and 1200° C in an oxidizing and in a reducing atmosphere. No difference was found in the kinetics of recovery in the Al-sublattice between the two dual implant conditions. However, the rate of recovery was different for each from samples implanted with iron alone.

## 1. Introduction

There is interest in the formation of nanometer-sized phases in insulator matrices due to the possibility of producing quantum confinement effects as the particle size approaches the scale of electron scattering. Nanometer-sized elemental phases and

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compounds have been produced by ion implantation. Compound formation is achieved by the implantation of two or more chemical species, often followed by annealing.

Because of the very low solubility of impurities, sapphire makes an excellent host for such studies. White and co-workers [1,2] have prepared a number of nanometer-sized semiconducting compounds (e. g., SiGe, GaAs, GaP, GaN, CdS, CdSe, ZnS, PbS) in sapphire by sequential implantation and post-implantation annealing.

The present study explores the amount of the residual damage and the possibility of compound formation for sequential implantation of iron and oxygen into sapphire at room temperature (~300 K) and the effect of annealing temperature and atmosphere on damage recovery.

According to the phase diagrams,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  are soluble in each other to 5 - 10% at 1100° C [3], thus, a solid solution,  $(\text{Al}_x\text{Fe}_{1-x})_2\text{O}_3$  may form during the oxygen implantation. Other iron oxides,  $\text{Fe}_{1-x}\text{O}$  and  $\text{FeAl}_2\text{O}_4$ , should appear as second phase precipitates [4].

## 2. Experimental Procedures

High purity single crystals of  $\text{Al}_2\text{O}_3$  with the c-axis normal to the surface were obtained from Crystal Systems, Inc. with optically polished surfaces. Samples were annealed for 120 h at 1500° C in flowing  $\text{O}_2$  to remove any residual polishing damage and surface contamination. One set was implanted at room temperature with  $4 \times 10^{16} \text{ Fe}^+ / \text{cm}^2$  (160 keV) followed by implantation of  $4 \times 10^{16} \text{ O}^+ / \text{cm}^2$  (54 keV), giving an implanted Fe:O ratio of 1:1. Another set was implanted with  $4 \times 10^{16} \text{ Fe}^+ / \text{cm}^2$  followed by implantation of  $6 \times 10^{16} \text{ O}^+ / \text{cm}^2$ , giving an implanted Fe:O ratio of 2:3. The energies

were chosen such that the ranges were similar. Because of differences in longitudinal straggling, the concentration ratios may vary slightly with depth and differ slightly from these ratios. In order to avoid channeling of the implanted ions, the incident beam direction was 5-7° from the crystal axes.

Samples of each set were annealed for 1 hour at 800 and 1200° C in an oxidizing (oxygen or air) or reducing (Ar-4% H<sub>2</sub>) atmosphere. A few samples were annealed at 500 and 1500° C.

The residual damage was determined from Rutherford backscattering-ion channeling using a beam of 1.6 MeV He<sup>+</sup>. The incident beam direction was normal to the specimen surface and the scattering angle of detection was 140°. The residual damage,  $\chi$ , was scaled to that produced by implantation of  $4 \times 10^{16}$  Fe/cm<sup>2</sup> (160 keV) using the value of deposited damage energy ( $S_D$ ) calculated with the code E-DEP-1 (P-5.0) [5]. Experimental values for samples implanted with only iron were taken from a previous study [6].

### 3. Results

#### 3.1 Effects of Oxygen-implantation on Residual Damage

There were no significant differences in the RBS-ion channeling spectra from the as-implanted samples having different Fe:O ratios. Values of  $\chi$  for the Al-sublattice (0.62 and 0.60, 4:4 Fe:O and 4:6 Fe:O, respectively) were lower than for the sample implanted only with  $4 \times 10^{16}$  Fe/cm<sup>2</sup>, (0.68). These results are shown in Fig. 1. Also shown in Fig. 1 are the values scaled with total deposited damage energy ( $S_D$ ). If the disorder scaled directly with damage energy, values of 0.86 and 0.95 would be expected. However, dynamic recovery during implantation makes a linear extrapolation of  $\chi$  with damage

energy unlikely. A previous paper [6] reported  $\chi$  as a function of iron fluence for similar implantation conditions. Using those data as a basis of extrapolation for the dual implanted samples gives values of  $\chi = 0.73$  and  $0.75$  for the 4:4 and 4:6 samples, respectively.

The observed values are significantly lower than values projected by either method, suggesting that the subsequent implantation of oxygen enhanced recovery in the Al-sublattice.

### 3.2 Damage Recovery during Post-implantation Annealing

Values of  $\chi$  were determined after annealing for one hour at 500, 800, and 1200° C in an oxidizing or reducing atmosphere. The data, normalized by dividing  $\chi_{\text{annealed}}$  by  $\chi_{\text{as-implanted}}$ , are summarized in Table 1 and plotted in Fig. 2 as the fraction damage remaining vs. annealing temperature. Data for samples implanted with iron only, taken from reference [6], are shown for comparison.

The curves of Fig. 2a show that recovery of disorder in the Al-sublattice during annealing in the oxidizing atmosphere is essentially the same at temperatures below 800° C for samples implanted with iron only, 4:4 Fe:O and 4:6 Fe:O. As indicated in Table 1, the fraction of retained damage after the 800° C treatment was slightly higher in the 4:6 Fe:O sample than in the others. Little additional recovery of the Fe-implanted sample occurred in the temperature range of 800 to 1200° C. This observation is consistent with the two-stage recovery process reported earlier [7]. Lattice damage in the dual implanted samples continued to anneal in this temperature range, and similar fractions of the as-implanted disorder remain after the 1200° C anneal.

Figure 2b shows that disorder for both dual implanted conditions recovered at about the same rate in the reducing atmosphere. The samples implanted only with iron

recovered at significantly slower rates at 800 and 1200° C than did the dual implanted samples.

### 3.3 Iron Redistribution During Annealing

The RBS-ion channeling spectra for the iron peak are shown in Figs. 3 and 4. There were no significant differences among the samples annealed at 800° C. All exhibited increased channeling in the aligned spectra, but no shift in the position of the peak. No iron was lost from the implanted zone. These observations are in marked contrast to the results for samples implanted only with iron and annealed in oxygen [7]. In that case, a surface peak was present after the 800° C anneal in oxygen, indicating a migration of the implanted iron to the surface.

The 4:4 sample annealed in air at 1200° C developed a surface peak in the iron spectrum but there was no change in the position of the peak for the 4:6 sample annealed under the same conditions. A slight (~5%) amount of iron was lost from the 4:4 sample but there was no detectable loss of iron from the 4:6 sample.

The spectra for the 4:4 sample annealed in Ar-4%H<sub>2</sub> at 1200° C suggest that some iron diffused into and toward the surface of the sapphire during this anneal. There was reduced channeling at the peak position than after the 800° C anneal. On the other hand, the aligned curves were identical for the 4:6 samples annealed in the same atmosphere at 800 and 1200° C. The peak position did not shift from the as-implanted position; there was only a broadening of the peak. The position of the peak did not change in samples implanted with only iron annealed under similar conditions [7].

Many of the iron atoms, either as isolated implanted atoms or in iron-containing compounds are shielded by the aluminum atoms as viewed along the c-axis. The value of  $\chi_{\text{Fe}}$  for iron was lower for the dual implanted samples than for the iron implanted samples in the as-implanted and each annealing treatment. Earlier studies found that iron

oxides formed during annealing in oxygen have a high degree of coherency in the [0001] direction but not along other crystallographic axes [7]. Iron nanocrystals formed during high fluence implantation and during reducing anneals are also highly oriented along the c-axis [8].

#### 4. Discussion

The reduced disorder in the dual as-implanted samples, compared to the single implant of iron, could be due to in situ compound formation or to the implanted oxygen replacing oxygen displaced by knock-ons. At this fluence, most of the iron is present as  $\text{Fe}^{2+}$  with a small amount present as nanometer size metallic iron precipitates [9]. It was proposed that the  $\text{Fe}^{2+}$  was present as iron-oxygen vacancy clusters. Oxygen implanted after the iron may annihilate these vacancies, causing the iron to precipitate. The oxygen could also promote the formation of iron oxides. Studies in progress using transmission electron microscopy and grazing angle x-ray diffraction should define the location of the iron.

The lower values of  $\chi_{\text{Fe}}$  for the dual implanted samples is consistent with the formation of coherent second phases.

A previous study [7] of Fe-implanted sapphire found recovery of the disorder in the Al-sublattice had a plateau between 800 and 1200° C (see Fig. 2b). Annealing in oxygen at 700° C produced small precipitates of  $\text{FeAlO}_4$  in regions near the peak iron concentration. Precipitates of  $\alpha\text{-(Fe,Al)}_2\text{O}_3$  were formed at and near the surface during a 1200° C anneal. The plateau in the recovery curve was thought to be controlled by the in-diffusion of oxygen to reach a level where the mixed Fe-Al oxide could form. The implantation of oxygen after the iron may provide sufficient oxygen for in situ

precipitation. Removal of Fe from the Fe-O vacancy clusters in the presence of implanted oxygen should promote recovery of the Al<sub>2</sub>O<sub>3</sub> lattice.

The increased recovery of the dual implanted samples for the 800° C anneals in the reducing atmosphere may also be due to the presence of the implanted oxygen in the region where Fe<sup>2+</sup> is being reduced to Fe<sup>0</sup>, thereby releasing oxygen vacancies from the charge compensating clusters, allowing reformation of the sapphire lattice.

## 5. Summary

The amount of disorder in the Al-sublattice is less than expected for the implantation of Fe followed by the implantation of oxygen, compared to the results for implantation of Fe only.

The recovery of disorder in the Al-sublattice during post-implantation annealing was enhanced by the dual implantation in both oxidizing and reducing atmospheres. It is suggested that the implanted oxygen reacts with the iron to form iron (or iron-aluminum) oxides which are coherent with the sapphire lattice as viewed along the c-axis.

## Acknowledgments

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### Figure Captions

Fig. 1. Damage ( $\chi$ ) in the Al-sublattice measured by RBS-ion channeling and as scaled with calculated damage energy deposition and with damage observed in reference 6..

Fig. 2. Recovery of disorder in Al-sublattice during post-implantation annealing; (a) Oxidizing atmosphere; (b) Reducing atmosphere.

Fig. 3. Iron spectra for 4Fe:4O annealed in (a) air, (b) Ar-4% H<sub>2</sub> ( $\square$  = random for as-implanted and 800° C;  $\blacktriangle$  = random for 1200° C;  $\blacksquare$  = aligned, as-implanted;  $\circ$  = aligned, 800° C;  $\blacklozenge$  = aligned, 1200° C).

Fig. 4. . Iron spectra for 4Fe:6O annealed in (a) air, (b) Ar-4% H<sub>2</sub> ( $\square$  = random for as-implanted and 800° C;  $\blacktriangle$  = random for 1200° C;  $\blacksquare$  = aligned, as-implanted;  $\circ$  = aligned, 800° C;  $\blacklozenge$  = aligned, 1200° C).

**Table 1. Fraction Damage Remaining after Annealing**

Temperature	Oxidizing			Reducing		
	Fe only	4:4	4:6	Fe only	4:4	4:6
500° C	0.9	0.89	0.88	0.9	0.89	0.89
800° C	0.2	0.19	0.26	0.53	0.19	0.22
1200° C	0.19	0.10	0.13	0.14	0.08	0.05
1500° C	0.05			0.05		

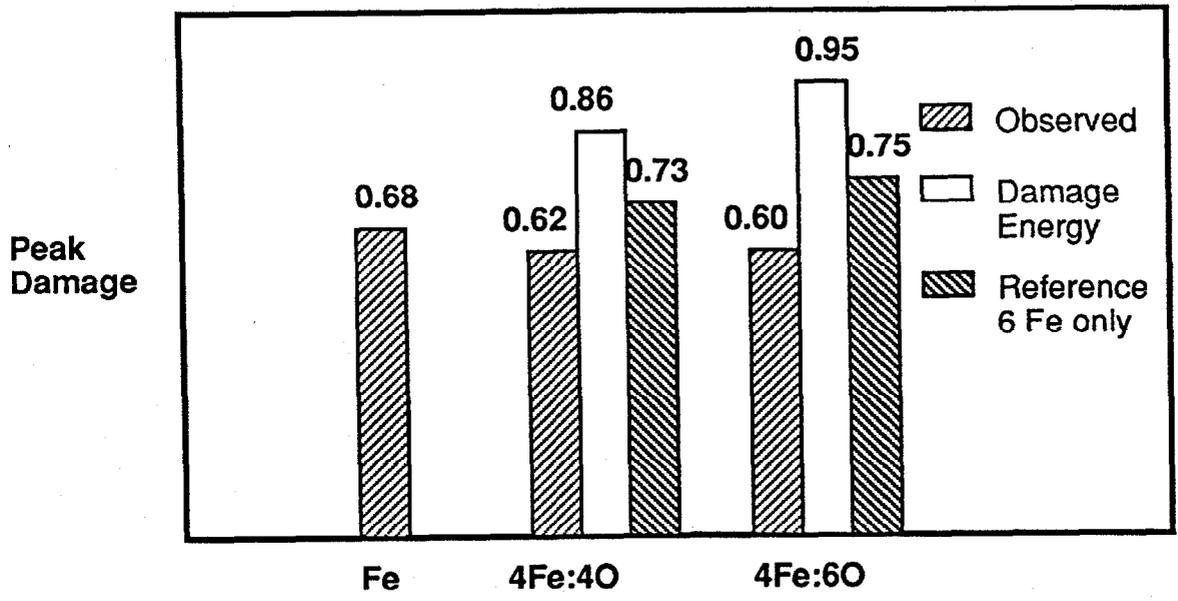
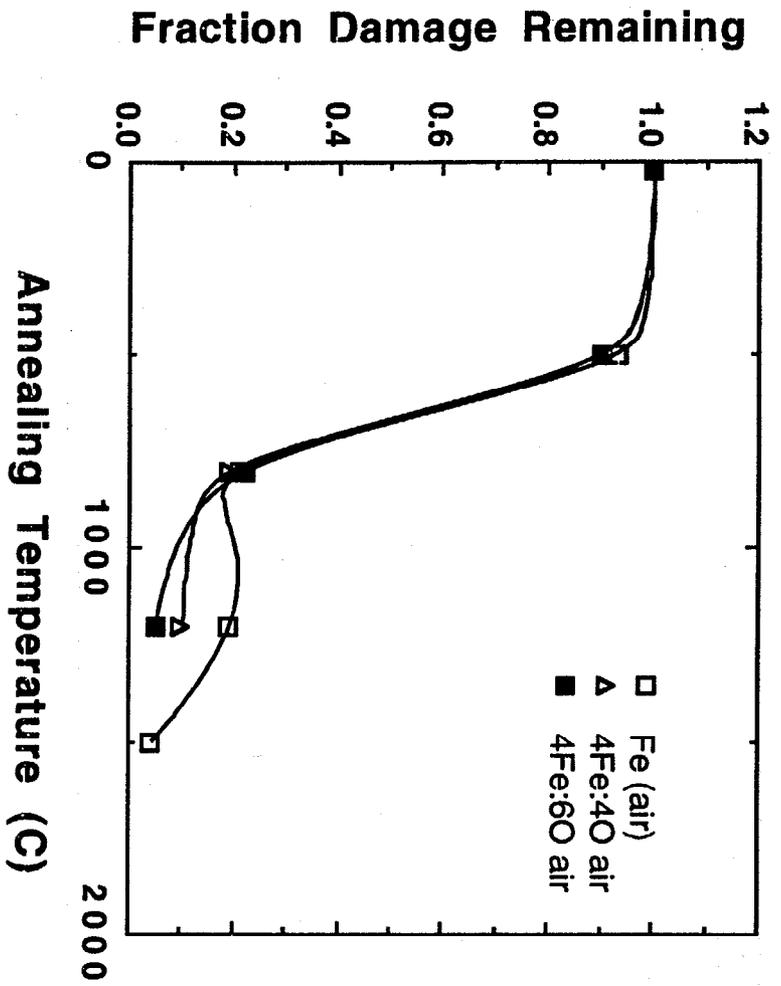


Fig. 1

Fig 2e



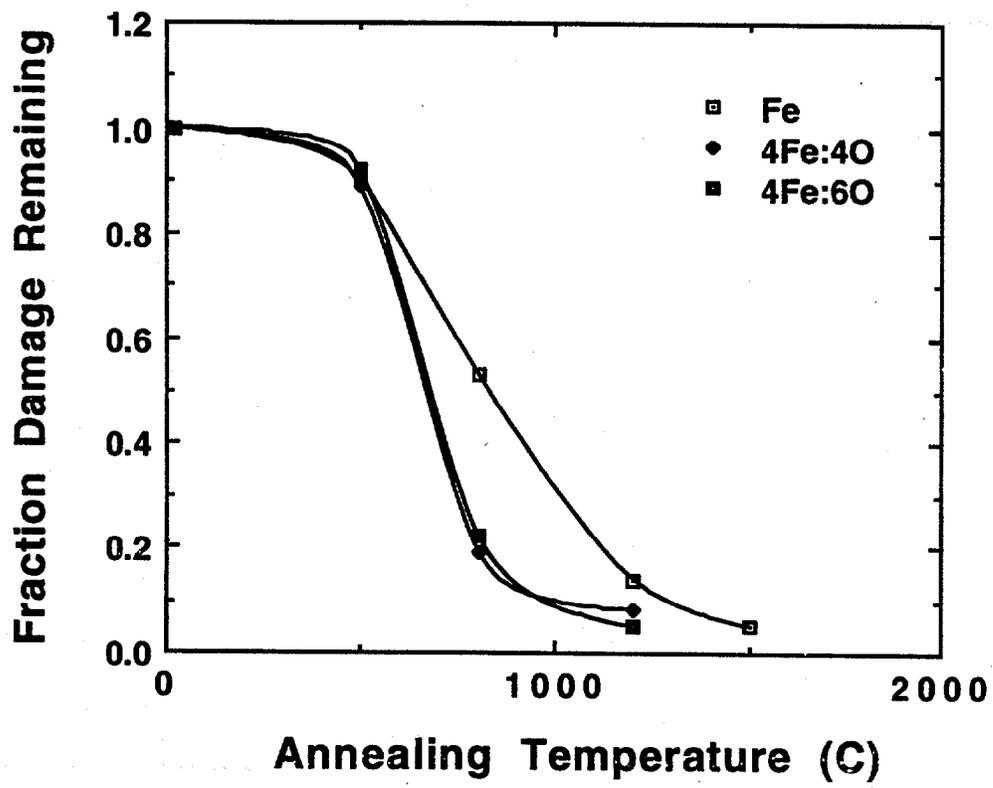


Fig 2b

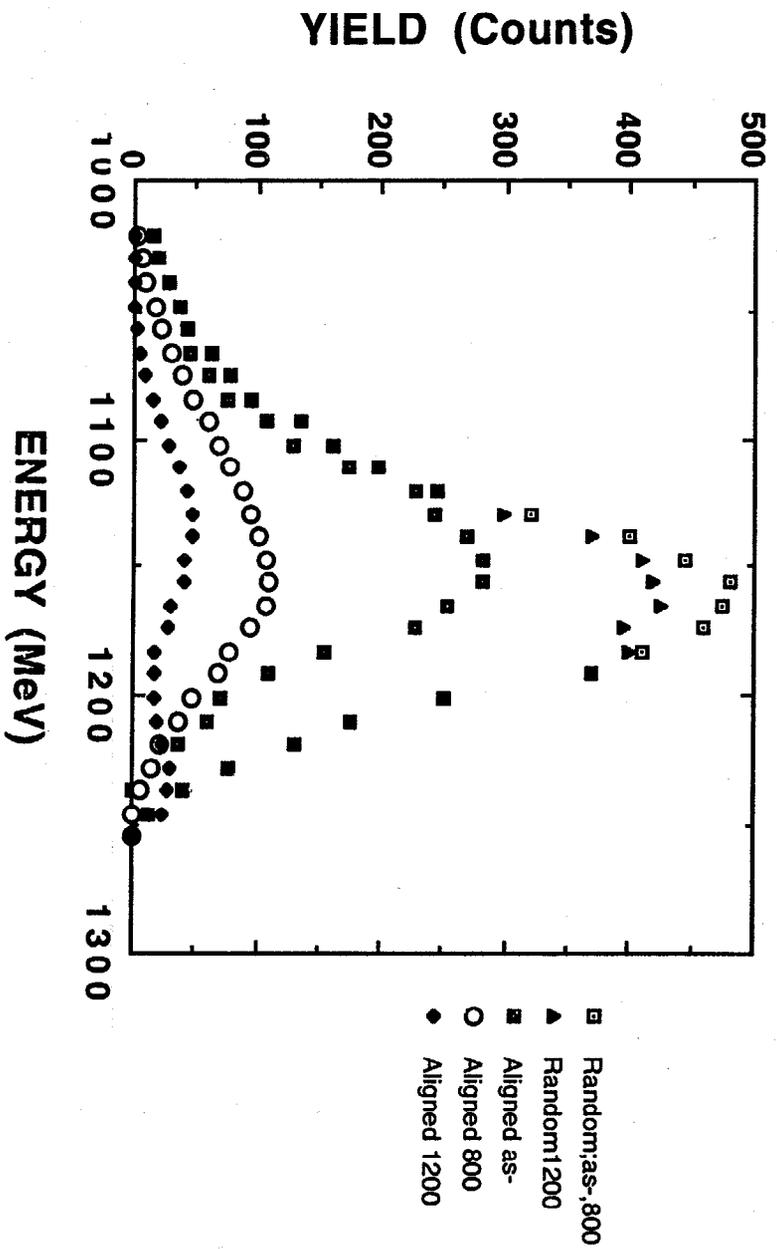


Fig 3a

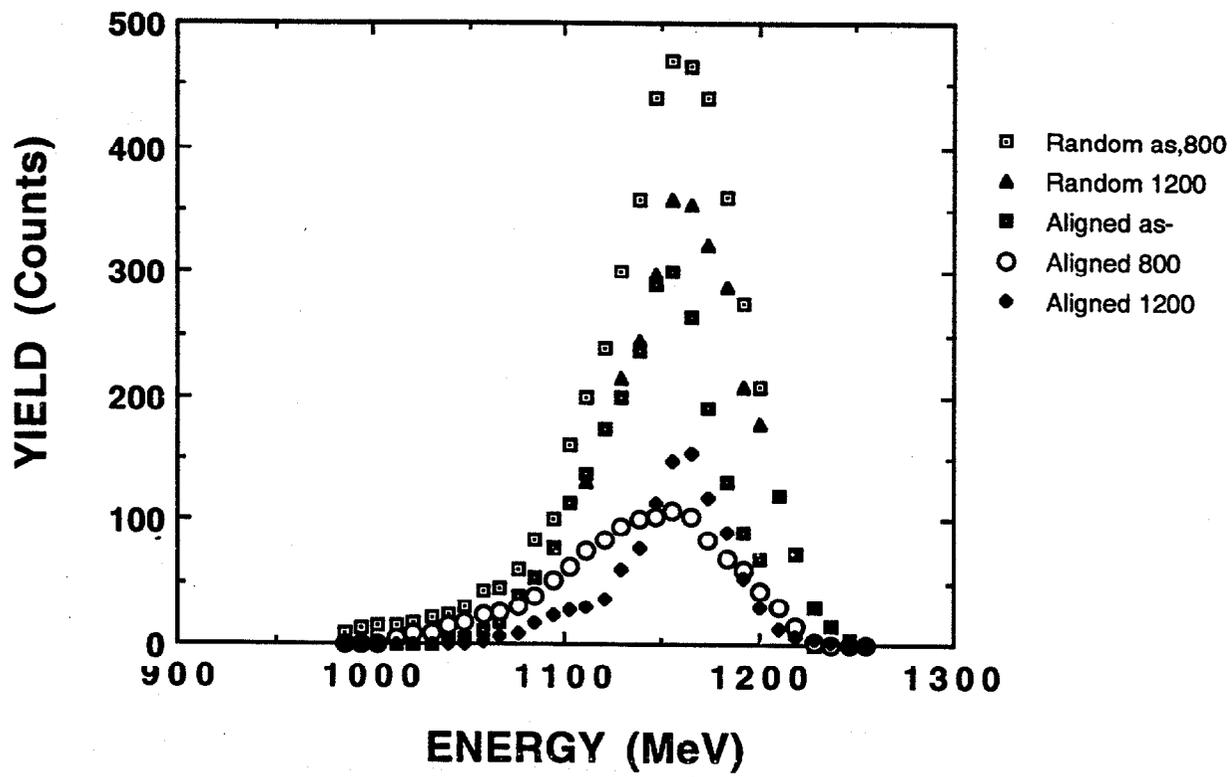


Fig 2b

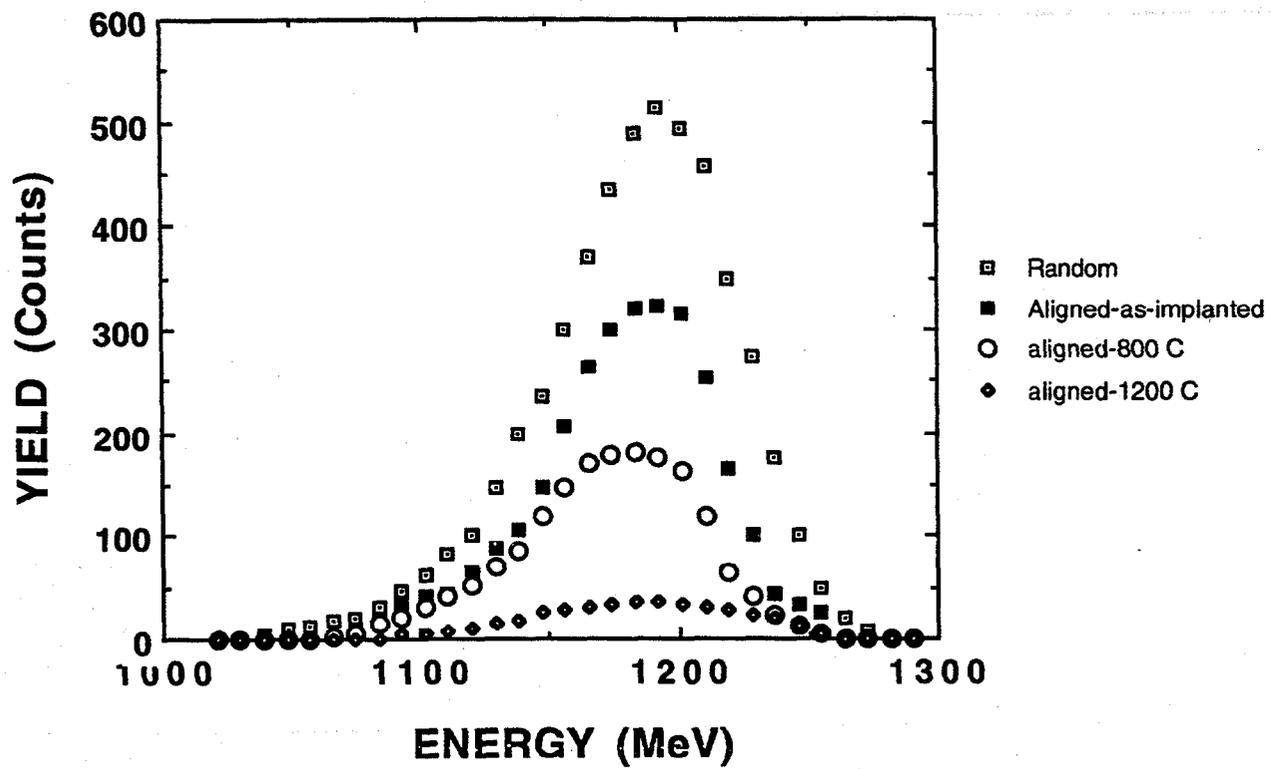


Fig 4a

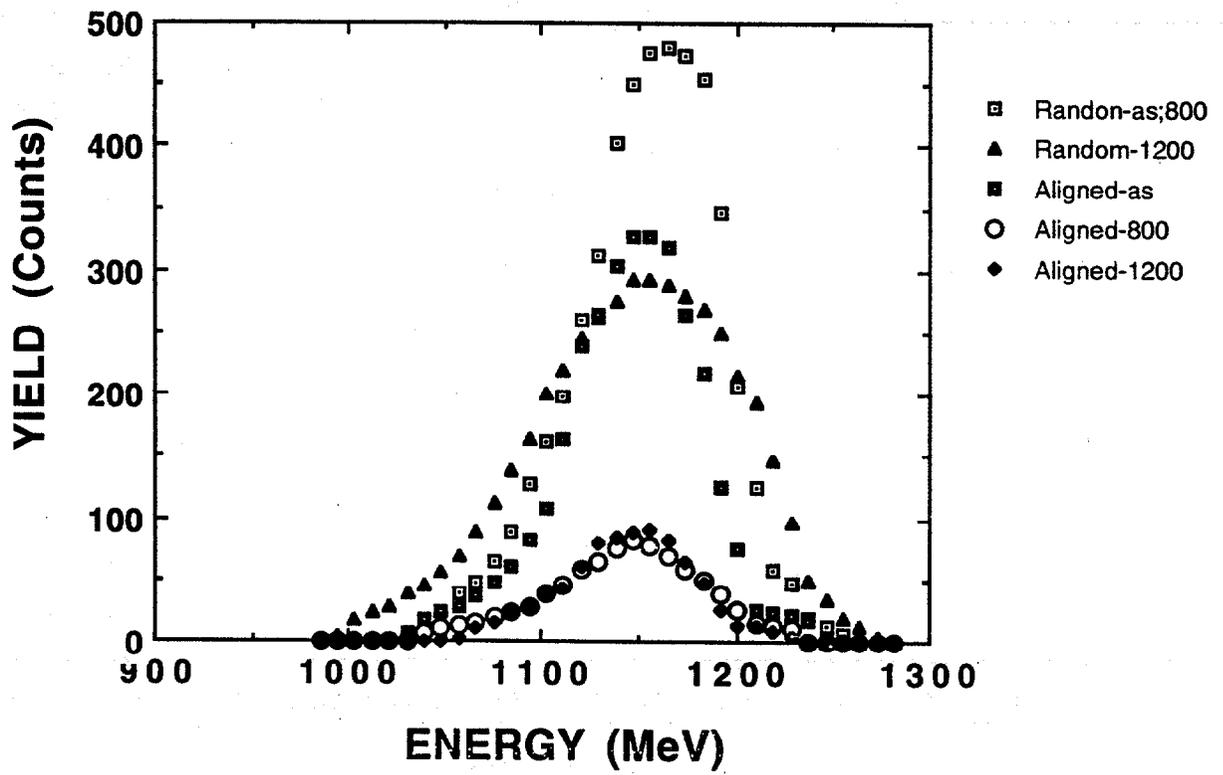


Fig 4b