CONF-[illegible]623--11

CONF-900623--11

DE90 012294

TITLE OF SYMPOSIUM: 15th SYMPOSIUM ON RADIATION EFFECTS

AUTHORS' NAMES:

M. E. O'Hern[1], L. J. Romana[2], C. J. McHargue[3], J. C. McCallum[4], and C. W. White[3]

TITLE OF PAPER:

The Effect of Crystal Orientation on Damage Accumulation in Chromium-Implanted Al_2O_3

AUTHORS' AFFILIATIONS

[1] Research Associate, Oak Ridge National Laboratory, Oak Ridge, TN 37830-6118; current address: Nano Instruments, Inc., Knoxville, TN 37917.

[2] Post Doctoral Fellow, Oak Ridge Associated Universities, assigned to Oak Ridge National Laboratory, Oak Ridge, TN 37830-6118.

[3] Senior Research Staff Members, Oak Ridge National Laboratory, Oak Ridge, TN 37830.

[4] Post Doctoral Fellow, Oak Ridge Associated Universities, assigned to Oak Ridge National Laboratory, Oak Ridge, TN 37830-6118; current address: University of Western Ontario, Canada.

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

Abstract: Chromium-implantation of single crystal aluminum oxide (Al_2O_3) has been shown to be anisotropic with respect to damage accumulation. Ultra-low load indentation and Rutherford Backscattering Spectroscopy (RBS) have been used to demonstrate the dependence of radiation damage on fluence and crystal orientation. Single crystal Al_2O_3 specimens of c-axis ([0001] normal to the surface) and a-axis ($[11\bar{2}0]$ normal to the surface) orientations were ion-implanted simultaneously and found to possess different near-surface mechanical properties. Subsequent RBS-ion channeling examination indicated different amounts of disorder in both the aluminum and oxygen sublattices for the two orientations. These results imply a higher amorphization threshold in terms of implantation fluence for the a-axis oriented samples.

KEY WORDS: ceramics, alumina, ion implantation, mechanical properties, sapphire, Al_2O_3

Introduction

Ion implantation is now recognized as a reproducible and controllable technique to modify the microstructure of the near-surface region of ceramics. The microstructure can be altered by intrinsic defects induced by collisions between the incoming particles and the target atoms and/or extrinsic defects resulting from the presence of the ions implanted into the host lattice. Both of these processes lead to the formation of a non-equilibrium surface region which possesses different mechanical properties than the bulk material [1-3]. Three mechanisms seem to be responsible for this change: 1) the modification of the implanted layer composition due to the introduction of foreign atoms (an alloying effect), 2) point defect creation due primarily to ballistic collisions initiated by the incoming ion (defect hardening), and 3) a volume expansion of the implanted layer induced by this defect creation [4]. Since the surface can expand only in one direction (normal to the surface), a residual compressive stress state is produced in the near-surface region.

The first two of these mechanisms are thought to be responsible for the change in the near-surface hardness and elastic modulus as many previous studies have supported [1,2]. Although ion implantation induces a residual compressive stress in the near-surface regions concomitant with an increase in hardness for damaged (but still crystalline) material, there has been no evidence to date that directly links the increase in hardness to the compressive stress. This paper is a study of the hardness of the Al_2O_3 as a function of fluence and crystal orientation during implantation in terms of the first two of the three mechanisms outlined above (i.e., alloying and defect hardening effects).

The indentation hardness of materials has traditionally been determined by introducing a normal load to the material by means of an indenter with a given geometry (e.g., Knoop microhardness). Typically, after removal of the load the indentation left due to plastic flow about the indenter's contact area is measured optically. This area is considered the "projected contact area." Hardness is then calculated as the load divided by this projected contact area.

In relatively soft, ductile materials, such as most metals, this calculation of the hardness is a good approximation of the mean pressure the material will support since the area associated with elastic contact is small compared to the plastic contact area. However, hard, brittle materials such as ionic- and covalent-bonded ceramics possess different characteristics which complicate the determination of the indentation hardness. Problems such as elastic recovery after removal of load and cracking during indentation may make the "projected contact area" approximation for ductile materials inappropriate. The problem associated with making this approximation is dramatically illustrated by the example of rubber. Using the traditional hardness measurements, the hardness of rubber would be infinite.

The mechanical properties microprobe (MPM) negates the necessity of post-indentation imaging by recording the load applied by the indenter as well as its vertical displacement continuously during the indentation sequence, i.e., the entire time the indenter is in contact with the sample. From these data, representing the elastic-plastic response of the material, and a functional relationship between the indenter's displacement and contact area, the hardness and elastic modulus can be calculated. The mathematical relationship between the data and the results has been described in detail elsewhere [5,6].

In a previous paper O'Hern et al. [1] studied the near-surface mechanical properties of sapphire single crystals (c- and a-axis) implanted at 300 K with chromium ion fluences up to 1×10^{17} ions cm^{-2}. They reported an increase of the hardness and no change in the modulus of the implanted layer. For these fluences the sapphire lattice was still crystalline. In the present work the change in mechanical properties of sapphire implanted with chromium ions has been investigated over a larger fluence range ($3x10^{16}$ to $6x10^{17}$ ions cm^{-2}) including, then, the amorphous state. The effect of the crystal orientation has been studied using the same ion beam parameters to implant sapphire crystals with either c-axis or a-axis orientations. The ultra low load indentation results will be discussed with respect to the implanted layer structure determined by Rutherford Backscattering Spectroscopy (RBS).

Experimental Method

Ion Implantation

High purity α-Al_2O_3 single crystals of c-axis ([0001] normal to the surface) and a-axis ($[11\bar{2}0]$ normal to the surface) orientations with an optical grade polish were annealed in air at 1775 K (1500°C) for 5 days. The samples were subsequently implanted simultaneously at room temperature with chromium ions of 160 keV energy to fluences ranging from $3x10^{16}$ to $6x10^{17}$ ions cm^{-2}. In order to avoid ion channeling of the implanted ions, the incident beam direction was ~5° off the specimen normal. The mean projected range (R_p) and the range straggling (ΔR_p) calculated from an EDEP-1 code [7] are 80 nm and 25 nm, respectively.

Ion Channeling

The spatial distribution of the implanted ions and the distribution of the defects induced by implantation were characterized by RBS in random and channeling geometries using a beam of 2 MeV He^{++} ions issued from a tandem accelerator. The incident beam direction was near normal to the surface and a scattering angle of detection of 160° was used.

Mechanical Properties

A commercially available MPM was used for the measurement of the elastic modulus and hardness. The MPM is automated such that the locations of all of the indentations are chosen prior to testing. The indentations are then made sequentially in an enclosed chamber at constant temperature. The displacement of the indenter is measured with a capacitive displacement gauge with a resolution of 0.16 nm. The load is applied via a coil and magnet assembly. The resolution of the system is 0.3 μN.

A minimum of 10 indentations were made on each sample to total indenter displacements of 100 nm per indentation. Each indentation yields data for the calculation of the mechanical properties from total displacements of 25, 50, 75, and 100 nm. Determination of the plastic depth of the indentation (i.e., the depth to which the indenter is in contact with the specimen) is described in detail elsewhere [5,6]. The calculated plastic depths of the indentations are typically ~80% of the total displacement for Al_2O_3.

Results and Discussion

Ion Channeling

The RBS spectra of c-axis sapphire irradiated with fluences ranging from $3x10^{16}$ to $6x10^{17}$ Cr cm^{-2} are shown in Fig. 1. Only the aluminum and the oxygen signals are shown in Fig. 1. For each fluence the random and channeling spectra are plotted. As a reference, the virgin spectra is also presented with the $3x10^{16}$ Cr cm^{-2} curve. For the lowest fluences (up to $6x10^{16}$ Cr cm^{-2}), the aligned spectra exhibit a hump in a region extending from 50 to 150 nm which is a signature of the implantation damage. The experimental mean projected range, R_p, of chromium ions deduced from the chromium signal in the RBS spectra is about 80 nm. McHargue et al., using transmission electron microscopy examinations of sapphire implanted with chromium ions at 280 keV, have shown that most of the defects are points defect clusters and small dislocation loops [8].

In the spectra shown in Fig. 1 for 1×10^{17} Cr cm^{-2}, the random and channeling spectra are coincident near R_p (80 nm), which indicates the presence of a thin subsurface amorphous layer. This condition of amorphization corresponds to a peak damage energy deposition of 14 keV/atom (according to the EDEP-1 code calculation) and an average concentration ratio of chromium to aluminum atoms of 20%. As the fluence increases, the amorphous layer extends and reaches the surface at a fluence of 6×10^{17} Cr cm^{-2}. The thickness of this amorphous layer is about 100 nm at the highest fluence.

The RBS spectra of the a-axis sapphire samples are shown in Fig. 2. The fluence required to form an amorphous layer is three times higher (3×10^{17} Cr cm^{-2}) than that for the c-axis orientation. It is important to note that prior to amorphization, analysis of the chromium spectra indicate that the substitutional fraction of chromium is the same for both orientations. The spatial distribution of the chromium is also independent of the substrate orientation.

To further analyze the sapphire damage accumulation as a function of fluence, the ratio of the scattering yield of the aligned spectrum to the scattering yield of the random spectrum measured at R_p has been calculated. The degree of disorder, χ_{Al}, in the aluminum sublattice for different fluences is plotted in Fig. 3. The residual damage in the cation (aluminum) sublattice is about the same for the two substrate orientations at the lower fluences, although the critical fluence for amorphization (χ = 1) is significantly different.

This result indicates that for the same implantation conditions, the c-axis orientation is more easily rendered amorphous than the a-axis. In the present study, this difference originates in the late stages of damage accumulation. Similar tendencies in terms of critical dose for sapphire amorphization have previously been reported for titanium implantation at 300 K [9] and chromium implantation at 77 K [10]. However, at low temperature the degree of disorder for a given fluence is strongly dependent on the sapphire crystallographic orientation and the discrepancy between the amorphization critical dose of c-axis and a-axis is higher (one order of magnitude). Anisotropic effects on amorphization processes are hence reduced as the substrate temperature during irradiation increases. Such behavior could be explained by the different mechanisms involved in the process of amorphization with respect to the implantation temperature. At low temperature (77 K) sapphire amorphization has been shown to result mainly from intrinsic defects produced during the collision cascades [11]. Since for that temperature the dynamic recovery processes are not operant, the critical amount of residual defects required to amorphize the sapphire is reached at very low fluences [11-13]. On the other hand, at room temperature most of the defects created by ballistic collisions are annihilated and higher fluence is necessary to amorphize the sapphire. The impurity concentration can no longer be neglected and appears to play a role in the amorphization process [14,15].

Mechanical Properties

Determination of the mechanical properties on the nanometer scale is complicated in the case of ion-implanted materials due to the continuous change of properties as a function of depth from the free surface. In general, though, it has been shown that the mechanical properties (hardness and elastic modulus) of ion implanted ceramics are dependent upon the resultant microstructure of the material. In the case of Al_2O_3, implantation damage increases the hardness if the Al_2O_3 remains crystalline, whereas both the hardness and the elastic modulus are lower for the amorphous material relative to the crystalline state [2].

Figure 4 shows the apparent relative hardness as a function of indenter depth for various fluences near the critical fluence for amorphization. This plot of relative hardness (implanted/unimplanted hardness ratio taken at each plastic depth) versus plastic depth demonstrates two important points. First, the increase in hardness of damaged but crystalline Al_2O_3 is not usually detected at plastic depths as low as 20 nm due to the indentation size effect (ISE). The ISE is much larger in the unimplanted Al_2O_3 single crystals than in the implanted samples. This leads to a higher apparent hardness for the reference state, and, hence, a lower relative hardness for the implanted region. The data used for studying the effects of fluence in this study were calculated for plastic depths of 35nm or greater in order to minimize this effect.

Second, the presence of even a thin amorphous subsurface layer has a significant influence on the measurements. For example, the amorphous layer for the sample implanted with 1×10^{17} Cr cm^{-2} is less than 2 nm wide and is centered at about 70 nm from the surface. Note that the entire hardness versus depth curve is shifted downward (relative to the curve for 6×10^{16} Cr cm^{-2}). Likewise, substrate effects on the apparent hardness are observed even when the indentation depth does not penetrate the amorphous/crystalline interface (6×10^{17} Cr cm^{-2}).

To study the effect of implantation fluence on the hardness of the material, the relative hardness at a total displacement of 50 nm for each sample was used. In this case, the plastic depth is small enough to remain well within the damaged region, and large enough to avoid the uncertainties associated with the ISE.

Ion implantation increases the hardness in both the a-axis and c-axis materials until a critical fluence at which the hardness drops precipitously. Figure 5 shows the relative hardness of the c-axis implanted Al_2O_3 as a function of fluence. This rather well-behaved curve demonstrates the gradual increase in relative hardness from 1.1 at $1x10^{15}$ Cr cm^{-2} [1] to 1.2 at $6x10^{16}$ Cr cm^{-2} . The drop to 0.95 at $1x10^{17}$ Cr cm^{-2} reflects a composite hardness of the surface material (damaged crystalline) and the thin subsurface amorphous layer. Higher fluence (larger amorphous regions) measurements show increasing influence of the softer material on the apparent hardness values.

Despite the anomalous hardness value at $1x10^{15}$ Cr cm^{-2}, the a-axis implanted Al_2O_3 shows a curve similar to that of the c-axis material in Fig. 6. A point to note is the drop in hardness at a fluence of $1x10^{17}$ Cr cm^{-2}. This raises an interesting question as to the critical fluence for the hardness peak in Al_2O_3. The RBS data shows that there is no amorphous region at that fluence, yet the hardness is shown to drop from the peak value to about 1.15. Likewise, data for the c-axis specimens suggest the peak hardness may occur at a fluence slightly lower than the onset of amorphization. It is clear, though, that there does exist a peak hardness at some fluence close to the critical fluence for amorphization.

Conclusions

The critical fluence at which sapphire (single crystal a-Al_2O_3) amorphizes is lower for chromium ion implantation along the c-axis than for implantation along the a-axis. The critical fluence for c-axis implantation appears to be at $1x10^{17}$ Cr cm^{-2} while the critical fluence for a-axis sapphire is close to $3x10^{17}$ Cr cm^{-2}. The hardness of the region damaged by the implantation increases to a value approximately 20% higher than that of the unimplanted material, and exhibits a precipitous drop in hardness near the onset of amorphization for both axis orientations.

Acknowledgements

Research sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References

[1] O'Hern, M. E., McHargue, C. J., White, C. W., and Farlow, G. C.," The Effect of Chromium Implantation on the Hardness, Elastic Modulus and Residual Stress of Al_2O_3," Nuclear Instruments and Methods in Physics Research, Vol. B46, 1990, pp.171-175.

[2] McHargue, C. J., White, C. W., Sklad, P. S. , O'Hern, M. E., Joslin, D. L., and Farlow, G. C., "Structure-Mechanical Property Relationships in Ion Implanted Ceramics," Proceedings 2nd International Seminar on Surface Engineering with High Energy Beams, CEMUL, Lisbon, 1989, pp. 566-575.

[3] McHargue, C. J., O'Hern, M. E., White, C. W., and Lewis, M. B., "Ion Implantation in Ceramics – Residual Stress and Properties," Materials Science and Engineering, Vol. A115, 1989, pp.361-367.

[4] EerNisse, E. P., "Sensitive Technique for Studying Ion-Implantation Damage," Applied Physics Letters, Vol. 18, 1971, pp. 581-583.

[5] Pethica, J. B., Hutchings, R., and Oliver, W. C., "Hardness Measurement at Penetration Depths as Small as 20 nm," Philosophical Magazine, Vol. A48, 1983, pp.593-606.

[6] Doerner, M. F., and Nix, W. D., "A Method for Interpreting the Data from Depth-Sensing Indentation Instruments," Journal of Materials Research, Vol. 1, 1986, pp.601-609.

[7] Davisson, C. M., and Manning, I., Naval Research Laboratory Report 885, Washington, DC, 1986.

[8] McHargue, C. J., Lewis, M. B., Appleton, B. R., Naramoto, H., White, C. W. , and Williams, J. M., in: Science of Hard Materials, eds. Viswanadham, R. K., Rowcliffe, D. J., and Gurland, J., Plenum Press, New York, 1983, pp.451-466.

[9] Bull, S. J. , "The Mechanical and Tribology of Ion Implanted Ceramics," Ph. D. Dissertation, Cambridge University,1988.

[10] Farlow, G. C., Sklad, P. S., White, C. W., McHargue, C. J., and Appleton, B. R., "The Formation and Annealing of Amorphous Layers of Al_2O_3,"Material Research Society Symposia Proceedings, Vol. 60, 1986, pp. 387-394.

[11] Sklad, P. S., McHargue, C. J., White, C. W., and Farlow, G. C., "Analytical Electron Microscopy of Ion Beam Modified alpha-Al_2O_3," High Technology Ceramics, ed. P. Vincenzini, Elsevier, Amsterdam, The Netherlands, 1987, pp. 1073-1082.

[12] White, C. W., Farlow, G. C., McHargue, C. J., Angelini, P., Sklad, P. S., Lewis, M. B., and Appleton, B. R., "The Formation of Amorphous Layers in Al_2O_3 by Ion Implantation," Nuclear Instruments and Methods in Physics Research, Vol. B7/8, 1985, pp.473-478.

[13] Romana, L., Thevenard, P., Canut, B., Massouras, G., Brenier, R., and Brunel, M., "Phase Formation Study in α-Al_2O_3 Implanted with Niobium Ions," Nuclear Instruments and Methods in Physics Research, Vol. B46 , 1990, pp. 94-97.

[14] McHargue, C. J., Sklad, P. S., McCallum, J. C., White, C. W., Perez, A., Abonneau, E., and Marest, G., "The Residual Charge State of Tin Implanted into Sapphire," Nuclear Instruments and Methods in Physics Research, Vol. B46, 1990, pp. 74-78.

[15] McHargue, C. J., Farlow, G. C., White, C. W., Williams, J. M., Appleton, B. R., and Naramoto, H.,"The Amorphization of Ceramics by Ion Beams," Materials Science and Engineering, Vol. 69, 1985, pp.123-127.

Figure Captions

FIG. 1-- RBS-ion channeling spectra for α-Al_2O_3 single crystals (c-axis orientation) implanted at room temperature with 160 keV Cr to indicated fluences.

FIG. 2-- RBS-ion channeling spectra for α-Al_2O_3 single crystals (a-axis orientation) implanted at room temperature with 160 keV Cr to indicated fluences.

FIG. 3-- Disorder in Al-sublatice (χ_{Al}) as a function of chromium fluence.

FIG. 4-- Indicated relative hardness (implanted/unimplanted) for c-axis Al_2O_3 implanted with 160 keV as a function of depth of indenter penetration.

FIG. 5-- Relative hardness of c-axis Al_2O_3 crystals as a function of chromium fluence. Hardness values were taken for a plastic depth of 35 nm.

FIG. 6-- Relative hardness of a-axis Al_2O_3 crystals as a function of chromium fluence. Hardness values were taken for a plastic depth of 35 nm.

ORNL-DWG 90-9333

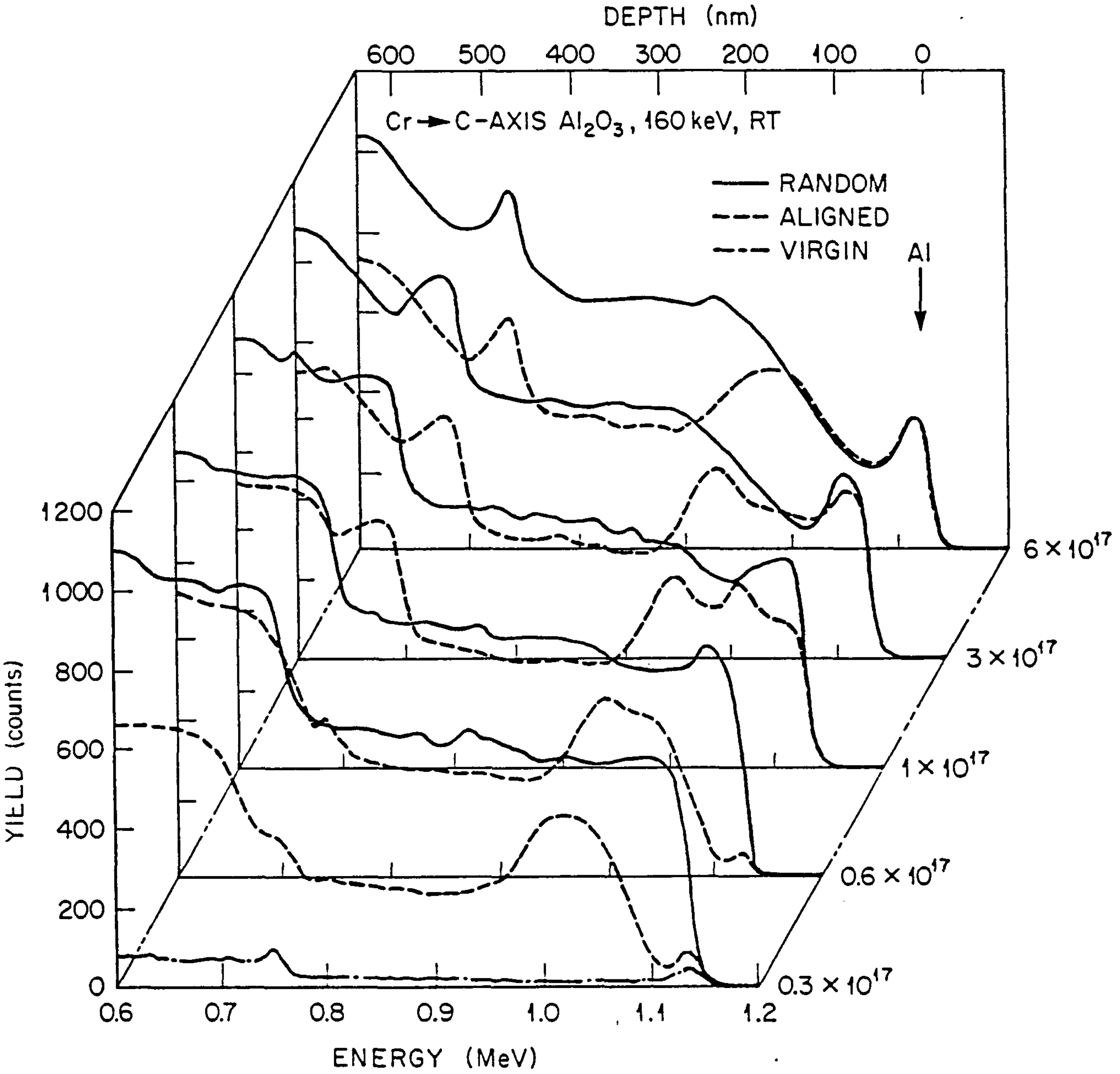


fig. 1

ORNL-DWG 90-9334

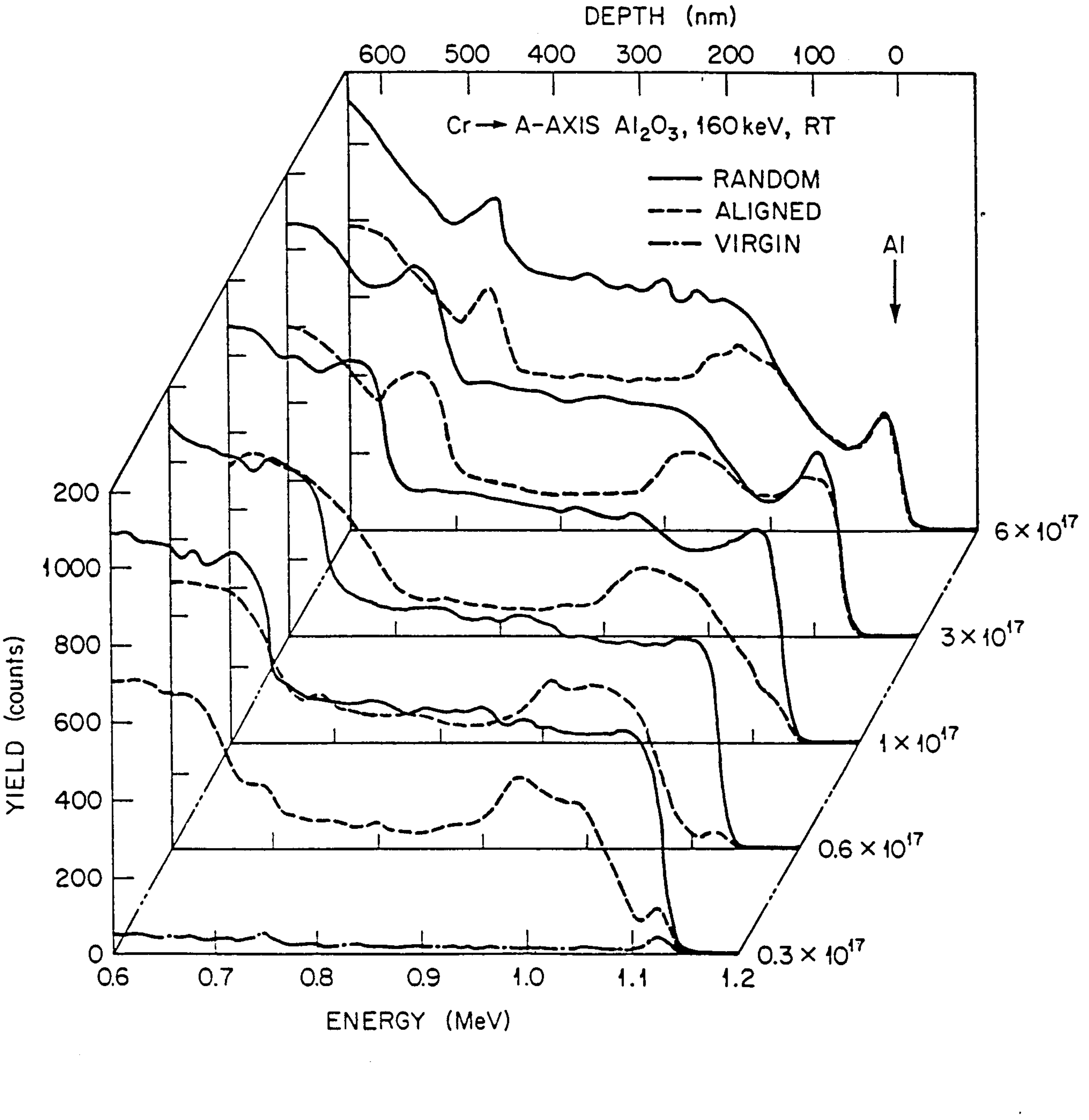


fig. 2

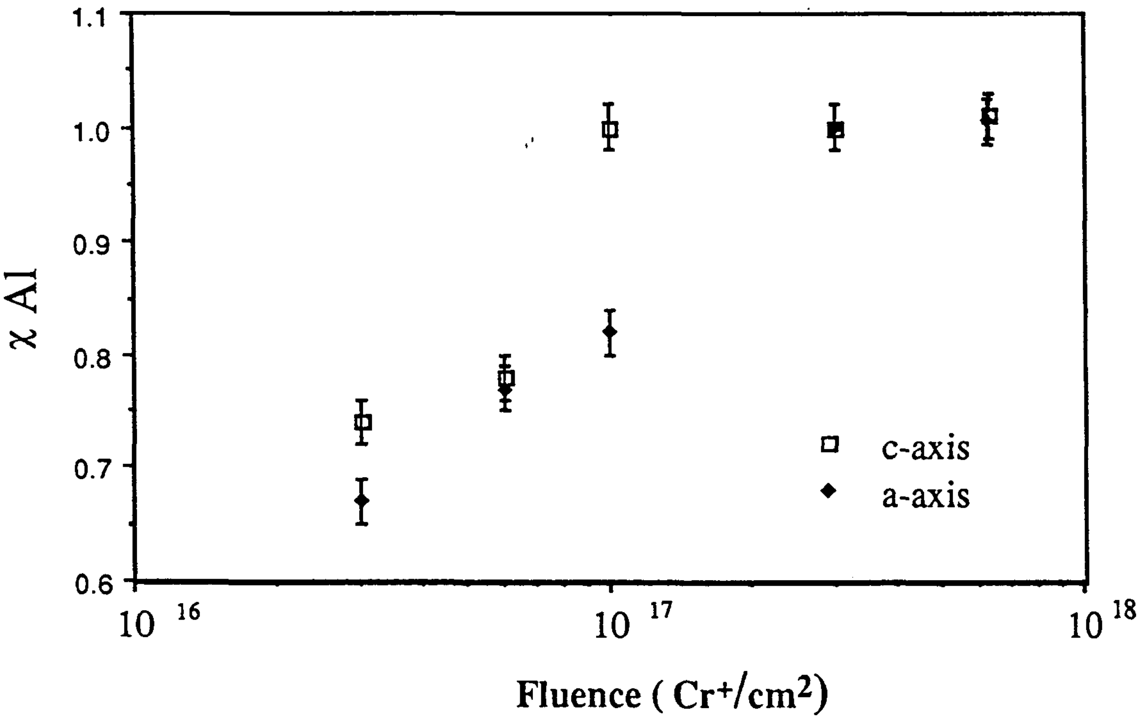


Figure 3

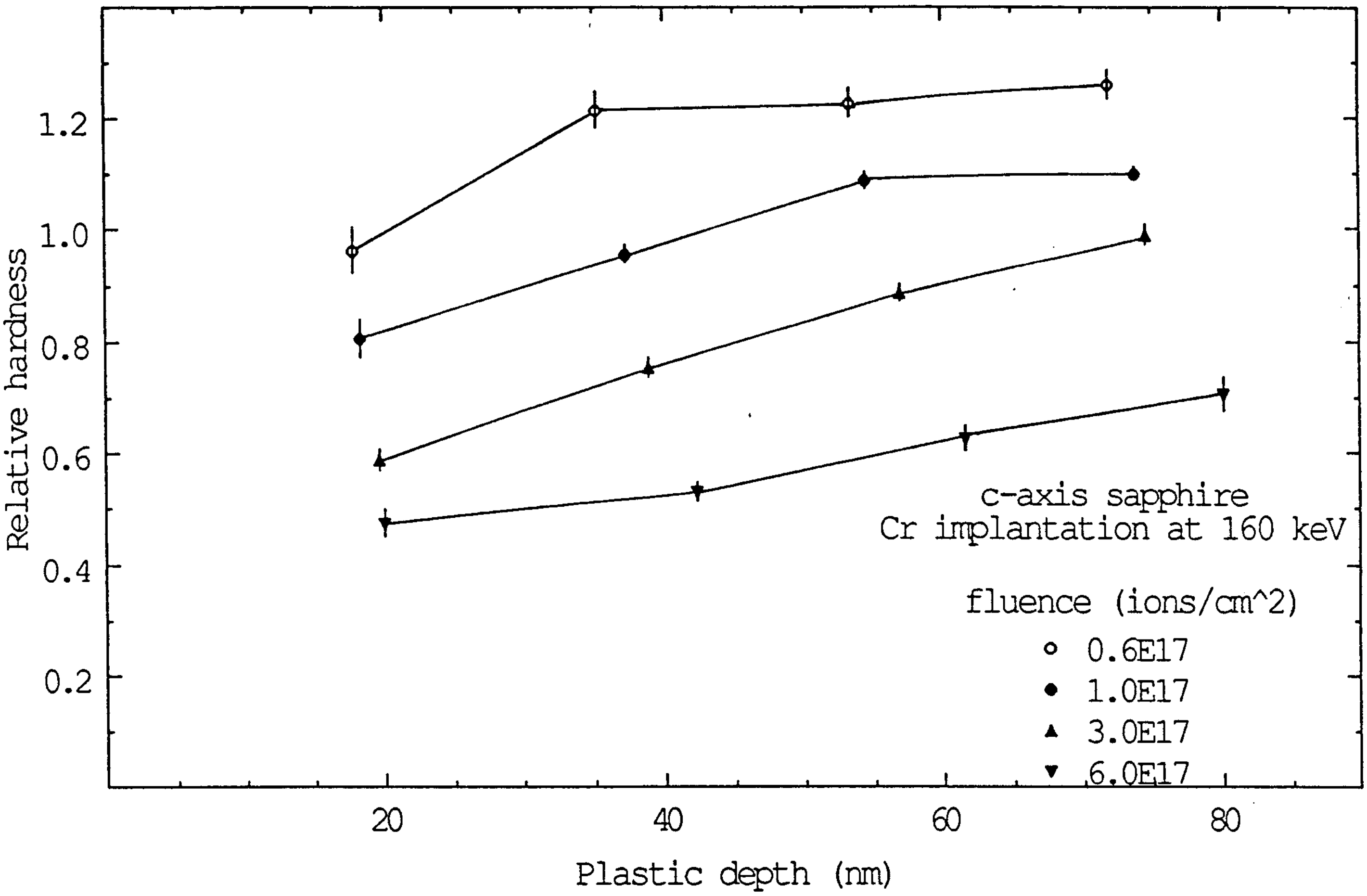

Relative hardness
1.2
1.0
0.8
0.6
0.4
0.2
20
40
60
80
Plastic depth (nm)
c-axis sapphire
Cr implantation at 160 keV
fluence (ions/cm^2)
○ 0.6E17
● 1.0E17
▲ 3.0E17
▼ 6.0E17

fig. 4

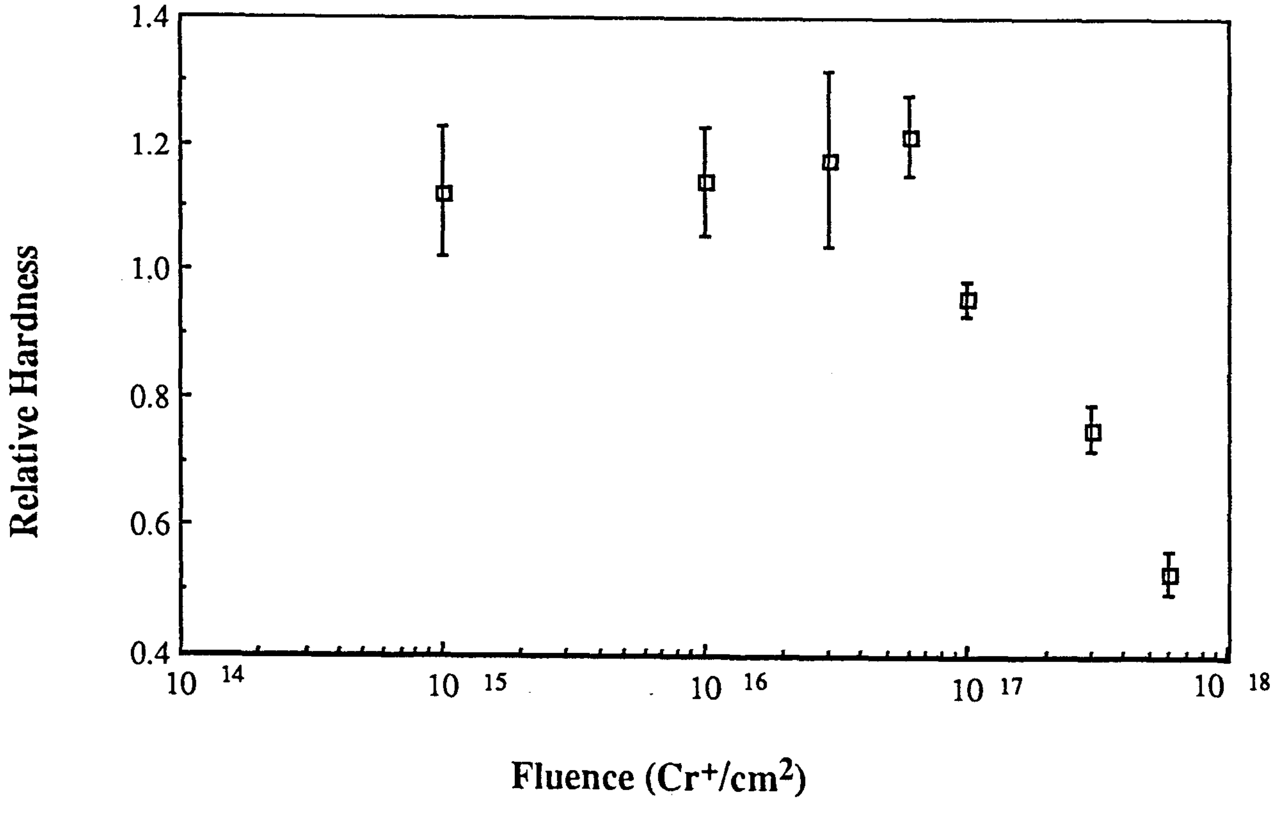
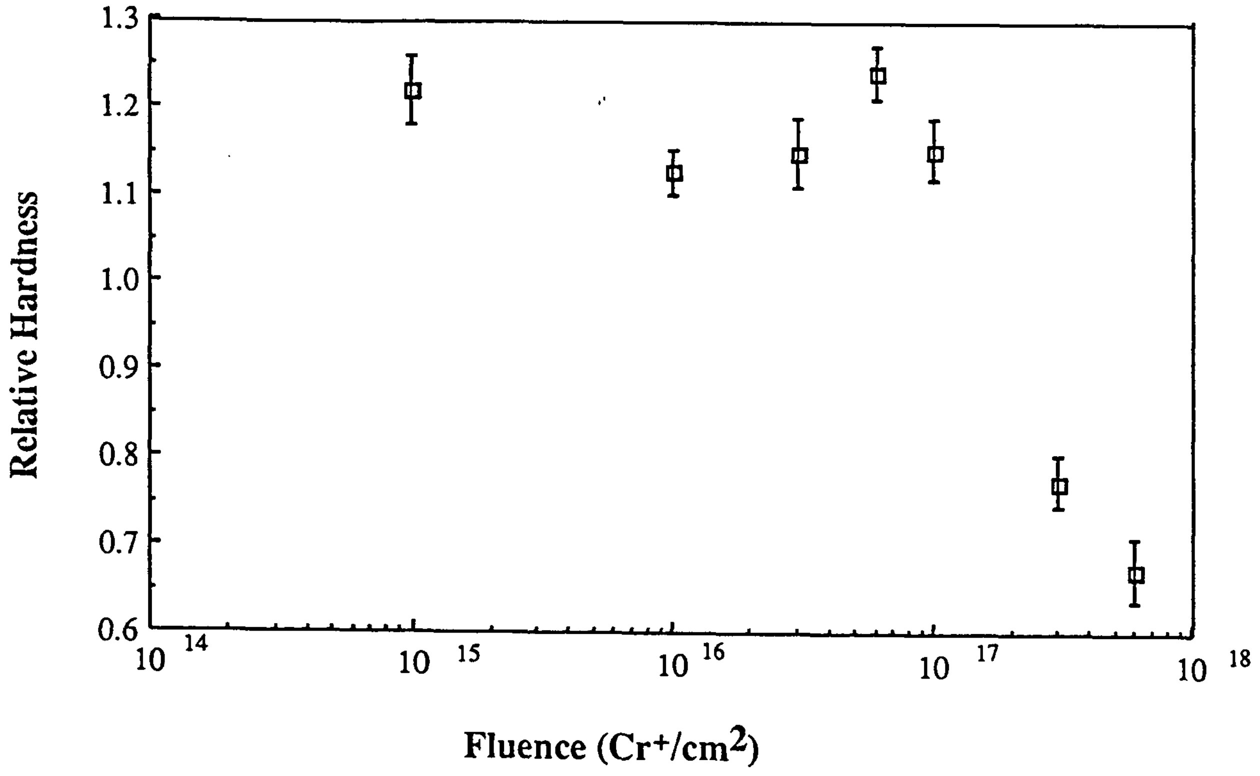

1.4
1.2
1.0
0.8
0.6
0.4
Relative Hardness
10 14
10 15
10 16
10 17
10 18
Fluence (Cr+/cm2)

Figure 5



1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
Relative Hardness
10 14
10 15
10 16
10 17
10 18
Fluence (Cr+/cm2)

Figure 6