ION-BEAM MIXING OF CERAMIC ALLOYS — PREPARATION AND MECHANICAL PROPERTIES*

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ABSTRACT

Techniques used to produce unique states of pure metals
mixed into ceramic materials are presented. The samples were
prepared by irradiating a 1-MeV Fe^+ beam on Al_2O_3 crystal
surfaces over which a thin chromium or zirconium film had
been evaporated. The limitations of using noble gas ion
beams are noted. Micro Knoop hardness tests performed
near the surfaces of the samples indicated a significant
increase in the hardness of most samples prepared by ion
beam mixing.

INTRODUCTION

One of the results of ion implantation studies carried out over the past few
years has been the recognition that ion beams induce interactions between atoms
even at temperatures well below thermal activation temperatures. Such ion pro-
cessing techniques as ion-beam mixing (IBM) initiate atomic interactions leading
to equilibrium and metastable surface alloys as well as amorphous materials. As
ions pass through interfaces of, for example, two distinct chemical regions in
a sample, some energy is deposited by these primary ions in a region surrounding
the interface. The combination of the ionization, lattice vibrations, and
Frenkel pairs produced by the primary ion stimulate atomic migration across the
interfacial boundary. Some atoms experience direct collision with the primary
ions, and this process is referred to as "recoil implantation" [1], whereas the
atomic motion associated with the radiation cascades is referred to as "cascade
mixing" [2-4]. The atomic cascades can initiate large concentration gradients
of both interstitials and vacancies, which enhance diffusion [5-6], lead to
solute migration [7] and phase transformations [8], or dissolution of
precipitates [9]. A review of some of these processes has recently been given
by Myers [10]. Final states produced in this way may be unique low energy
states or new metastable phases. Reference [11] contains a review covering ion
implantation studies outside of semiconductor technology with special emphasis
on material properties.

Ceramics have a special importance in modern technology. In addition to
refractory fissionable fuels, the electrical properties of ceramics will see
broad application in fusion reactors such as first wall coatings, blanket gaps,
injectors, divertors, limiters, magnetic insulation, and windows. These
applications require a high degree of mechanical stability.

In this work we are continuing an investigation of the changes in mechanical
properties of ceramics due to ion beam irradiation [12]. In particular, we have
examined the hardness changes near the surface of Al_2O_3 when chromium or
zirconium are introduced by the mechanism of ion beam mixing.

Ion bombardment of Al_2O_3 has been carried out by Drigo et al. and Carnera et al. [13-14] who determined lattice disorder and atom locations created by implanting 20-100 keV Pb^+ ions. Other investigators have studied defect structure produced by the implantation of H, He, Ar, Kr, and Xe as well as self ion implantation of aluminum and oxygen [15-20]. Although no data on mechanical properties have been reported, a group at Sandia National Laboratory has calculated surface stress produced in Al_2O_3 from a measurement of the deflection of a cantilever beam specimen during implantation [21].

MATERIALS AND METHODS

Single crystals of Al_2O_3 were obtained from two sources, Union Carbide Corporation (Crystal Products Division, 888 Balboa Avenue, San Diego, CA 92123) and Crystal Systems, Inc. (P.O. Box 1957, Salem, MA 01970). Both materials had high-purity, low-dislocation density and were oriented within ±2 of (0001). Before implantation, each specimen was annealed for five days at 1200°C in air to remove any mechanical damage introduced during sample preparation.

Chromium or zirconium films of ≈160 Å were evaporated on the (0001) surface of most of the crystals. The remaining crystals were irradiated without the evaporated layer. Irradiations were carried out with 1 MeV Fe^+ ions in a UHV target chamber at a pressure of 10^{-8} torr. The ion beam was normal to the crystal surface and limited to maintain a specimen temperature $\lesssim 300$°C. Inert gas ions were not used because surface blisters formed at high fluence. Following the irradiation, the excess metal film was etched away with hot potassium permanganate.

Rutherford backscattering and channeling (0001 axial) techniques were applied to the irradiated targets in order to characterize the atomic migration and radiation damage. The energy of the backscattered ^4He particles was measured by a silicon surface barrier detector with energy resolution 15 keV (FWHM) positioned 140° with respect to the incident beam. The beam energy was 1.6 or 0.5 MeV in the case of the channeling experiments. The beam current was limited to a few nanoamps to minimize pulse pileup distortion of the spectra. An electronic pileup rejector was also used. Details of simple film targets such as gold evaporated on Si were examined in order to characterize the remaining pileup effects and the ion beam degradation by finite apertures. This procedure increased our certainty of the magnitude of the metal ion concentrations in regions where the magnitude is only of the order of 100 appm. The actual depth profiles were calculated from the backscattering spectra by direct deconvolution [22]. The data were normalized by the Al component in Al_2O_3 substrate backscattering.

Mechanical properties were evaluated by microhardness measurements. In all cases, only half of a specimen surface was implanted so that property measurements of unimplanted and implanted regions could be made under identical conditions. The hardness properties will be presented as relative values, i.e., ratio of implanted value to unimplanted value. The Knoop hardness technique was used with a force of 0.147 N in order to confine the impression to the near surface region. Typical impression depths were about 3000 Å.

RESULTS

The depth profile measurement for the Cr film on Al_2O_3 is given in Fig. 1. The range of the Fe^+ ions is about 4000 Å and is mostly off scale. Also shown in the figure is a profile following a thermal anneal for 3 h at 600°C but without any ion irradiation (except for the ^4He analysis which results in orders of magnitude less dpa than the Fe irradiation). The background profile is one taken on a virgin Al_2O_3 sample. The ion mixed profile is quite

different from the annealed-only in two ways: (a) the distinct broadening
of the near surface $\lesssim 500$ Å profile and (b) a much larger and nearly featureless
concentration in the depth region >500 Å. A similar measurement on Fe
irradiated Zr is shown in Fig. 2. These results differ from the Cr case only
in the deeper minimum around 1200 Å. Finally, it was noted in all irradiations,
crystals darkened. By etching the surface it was found that the discoloration
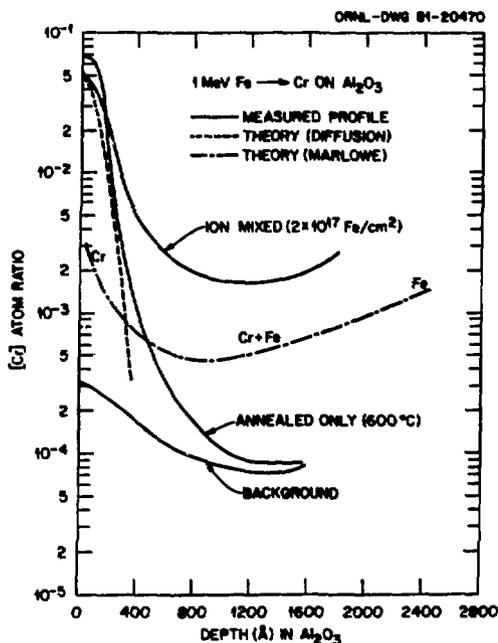occurred throughout the depth of the implant to approximately 1 μm

Fig. 1. Depth-concentration profiles
of Cr coated Al_2O_3 samples following
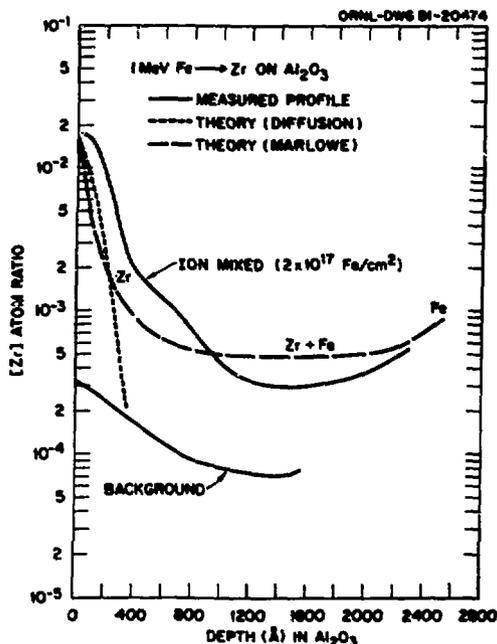Fe^+ ion irradiation at T $\lesssim$ 300°C.

Fig. 2. Depth concentration profiles
of a Zr coated Al_2O_3 sample following
Fe^+ ion irradiation at T $\lesssim$ 300°C.

Channeling spectra corresponding to the profiles in Figs. 1 and 2 are given
in Fig. 3 for Cr and Zr. The near surface region in Fig. 1 corresponds to
channels near 250 for Cr and 125 for Al backscattering in Fig. 3. The yield
(counts/channel) in both surface regions for the aligned spectrum are much
lower than in the random spectrum. In addition, the Al backscattering from the
deeper regions of the crystal corresponding to channels below 100 shows little
difference between the aligned (irradiated) curve and the virgin (unirradiated)
case. A similar relationship can be seen in Fig. 3 for the analysis of the
irradiation of the Zr film. Quantitative values are given in Table I.

The χ_{Al} (channeling minima) values shown in Table I were used along with
χ_{Cr} and χ_{Zr} minima in order to estimate the fraction of substitutionality of
the ion mixed metal atoms. These results are given in the right-hand column of
Table I. The result of the hardness tests indicated that the hardness
increased 21% for the Cr mixed surface and 28% for the Zr mixed case. An
irradiated surface without evaporated film showed a hardness increase of 15%.
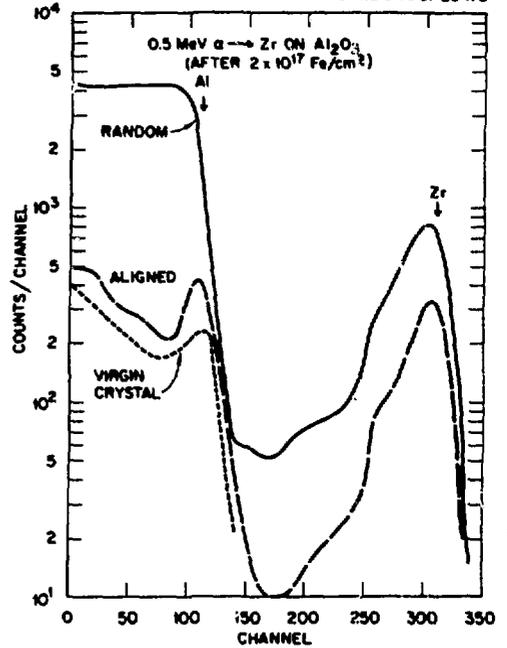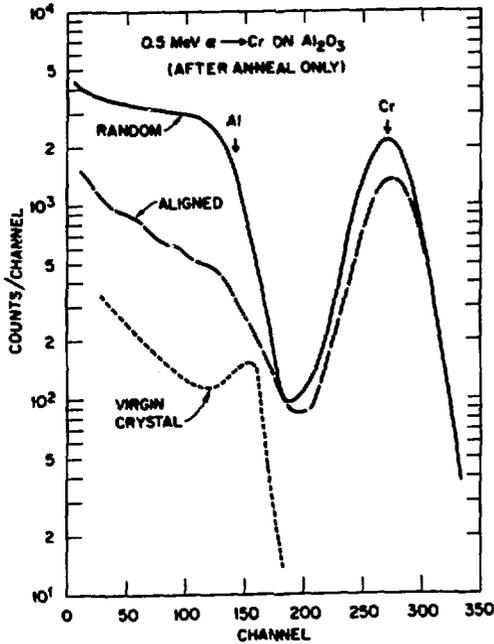
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Fig. 3. Rutherford backscattering channeling (0001) spectra corresponding to the Cr (left) sample in Fig. 1 and the Zr (right) sample in Fig. 2.

TABLE I
A summary of the results of the (0001) channeling measurements. In column 3, χ refers to the minimum yield for Al in the substrate; in column 4, f_s is the fraction of metal film atoms found in substitutional type sites which would be consistent with the results of the Cr, Zr, and Al channeling minima.

Film	Fluence (Fe/cm^2)	χ_{Al}	$f_s \; (= \dfrac{1 - \chi_M}{1 - \chi_{Al}} \%)$
Cr	2×10^{17}	0.04	85
Zr	2×10^{17}	0.04	66
Zr	4×10^{17}	0.14	58

DISCUSSION

Currently, the degree of lattice disorder in Al_2O_3 per unit fluence appears much less than in previous studies [13-21]. For example, the increase in the aligned spectra minima for the 40 keV Kr bombardment [20] occurs at about two orders of magnitude lower dose (10^{15}/cm^2) than our 1 MeV Fe irradiations (10^{17}/cm^2). In these previous studies, the ranges of the implanted ions were much shorter than the present experiments. Thus the surface disorder caused by the presence of ions themselves (as opposed to the atomic displacements

created by the ions) may be largely responsible for the dechanneling or back-
scattering in the aligned spectra. Using the energy deposition code
E-DEP [23], we investigated this quantitatively by calculating the displace-
ments (dpa) in specific cases. The results indicated that the near surface
region displacement damage was about 2 dpa for 10^{15} Kr/cm^2, but was about
70 dpa for 2×10^{17} Fe/cm^2. An additional reason for the low lattice disorder
in the present case is that the ratio of ionization to atomic displacement
events is relatively large for the 1 MeV beam in the near surface regions.
There is evidence to suggest that such ionization processes anneal displacement
damage in Al_2O_3 near room temperature [15,16].

The fraction of substitutional Cr or Zr atoms resulting from ion beam mixing
is more than half, even for a beam fluence of 4×10^{17} Fe/cm^2. This is consist-
ent with the results of Drigo [13] who found a high degree of Al substitutional
site occupancy for implanted Pb ions. The degree of substitutionality is some-
what greater for Cr than Zr and is fluence dependent for the Zr in the
$\sim 10^{17}$/cm^2 range.

Another aspect of using higher energy beams in ion beam mixing experiments
is the larger contribution of recoiling ions. This is shown in Figs. 1 and 2
where calculations of migration profiles are compared. The diffusion curve is
based upon the simple assumption [10] that the temperature independent diffusion
constant is

$$D = \frac{1}{6} \lambda^2 P , \qquad (1)$$

where the jump distance λ is taken as 20 Å, and P is given by the Kinchin-Pease
relation in which the energy deposition is calculated by E-DEP [23]. The
resulting diffusion profile takes the form of an error function. For fluences
2×10^{17} Fe/cm^2, the resulting diffusion length in Al_2O_3 is about 100 Å so that
the resulting concentration profile is significant in the first 200 Å but
nearly vanishes beyond 400 Å.

In contrast to the diffusion approach, binary-collision calculations were
made using the code MARLOWE [24]. The advantage of this method is that the
ion energies resulting from high momentum transfer between the primary (Fe)
ions and secondary (Cr or Zr) ions can be calculated. Using stopping powers
in Al_2O_3 estimated by E-DEP [23], we approximated the ranges of these primary
and secondary ions making a small angular correction for "projected" range.
The results are shown in Figs. 1 and 2 where a superposition of Cr and Fe are
shown (as previously mentioned, the measured profile does not distinguish
between Cr and Fe or Zr and Fe at large Zr or Cr depths). The deeper regions
($\gtrsim 2000$ Å) consist mostly of Fe ions degraded by collisions in the Cr film
while the shallow regions ($\lesssim 1000$ Å) are mostly Cr atoms. The nearly featureless
region (1000-2000 Å) is the overlap between the low energy Fe "tail" and the
high energy Cr "tail". The corresponding Zr + Fe curve in Fig. 2 is quali-
tatively similar.

Although neither the diffusion curve alone nor the binary collision curve
alone fits the data well, there is reason to believe that a coherent addition
of the theories may explain the data. If we add to the Fe component the
energy degradation of the primary beam by the substrate, the deeper regions
will more closely agree with the data. The diffusion equations should contain
a generator source term, $G_r(x,t)$, given by the Cr or Zr transmission or recoil
profile of the binary collision calculations:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C}{\partial x^2} (x,t) + G_r(x,t) . \qquad (2)$$

The Knoop impression depths (~ 3000 Å) exceed the depth of the high (ion
mixed) metal concentration region. As a result, the relative hardness values
indicate the direction of property changes, but they may underestimate the
magnitude of the effects in the implanted region. Nevertheless, this data
indicates that the Fe$^+$ ion beam itself made a major contribution to the surface

hardness. It is not clear if the hardness in this case is from the radiation damage caused by the beam or due to the implanted ions themselves, although evidence supports the latter. The channeling measurements indicated only slight surface disorder caused by the Fe fluence. The range of the Fe ions is about 4000 Å while the Knoop indentation is only slightly less, about 3000 Å, and probably senses a somewhat deeper surface region. The Cr and Zr presence in the surface layers increased the hardness. The Zr atoms, while showing a lower degree of substitutionality, manifested a greater effect toward increasing the surface hardness.

SUMMARY

We have used the ion beam mixing technique to prepare Cr and Zr enriched surfaces on Al_2O_3. Ions of 1 MeV Fe^+ were used to irradiate the evaporated metal coatings on Al_2O_3 producing metal concentrations up to a few atomic percent. Channeling measurements suggest that most of the Cr or Zr atoms migrated into substitutional sites. The surface disorder in the Al_2O_3 substrate appeared minimal even for an ion beam fluence of 2×10^{17} Fe/cm^2. Binary collision calculations were used to investigate recoil effects in this high energy ion beam mixing. Knoop microhardness tests were made on the irradiated surfaces. The results showed significant increases in surface hardness compared to unirradiated surfaces.

ACKNOWLEDGMENTS

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