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TEMPERATURE AND ION-MASS DEPENDENCE OF AMORPHIZATION DOSE FOR ION BEAM IRRADIATED ZIRCON ($ZrSiO_4$)

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ABSTRACT

The temperature dependence of amorphization dose for zircon under 1.5 MeV Kr ion irradiation has been investigated using the HVEM-Tandem Facility at Argonne National Laboratory. Three regimes were observed in the amorphization dose-temperature curve. In the first regime (15 to 300 K), the critical amorphization dose increased from 3.06 to 4.5 ions/nm^2. In the second regime (300 to 473 K), there is little change in the amorphization dose. In the third regime (> 473 K), the amorphization dose increased exponentially to 8.3 ions/nm^2 at 913 K. This temperature dependence of amorphization dose can be described by two processes with different activation energies (0.018 and 0.31 eV respectively) which are attributed to close pair recombination in the cascades at low temperatures and radiation-enhanced epitaxial recrystallization at higher temperatures. The upper temperature limit for amorphization of zircon is estimated to be 1100 K. The ion-mass dependence of the amorphization dose (in dpa) has also been discussed in terms of the energy to recoils based on data obtained from He, Ne, Ar, Kr, Xe irradiations and a ^{238}Pu-doped sample.

INTRODUCTION

Zircon ($ZrSiO_4$, $I4_1/amd$, Z = 4) is an orthosilicate of both mineralogical and technological interest. The structure of zircon (Fig.1) consists of edge-sharing dodecahedra forming chains parallel to [010]. The chains are cross-linked by SiO_4 tetrahedral monomers. Because zircon typically contain 5 to 4,000 ppm U and 2 to 2,000 ppm Th, it is an important phase used in U-Th-Pb dating [1]. Zircon experiences the radiation-induced crystalline to amorphous transition in nature due to radioactive decay of the radionuclides and their daughter products in the ^{238}U, ^{235}U, and ^{232}Th decay series. This process, metamictization [2], can lead to increased solubilities [3] and fracturing [4]. In addition, the zircon structure type is an actinide-bearing phase in proposed crystalline, polyphase, ceramic nuclear waste forms [5], and natural zircons

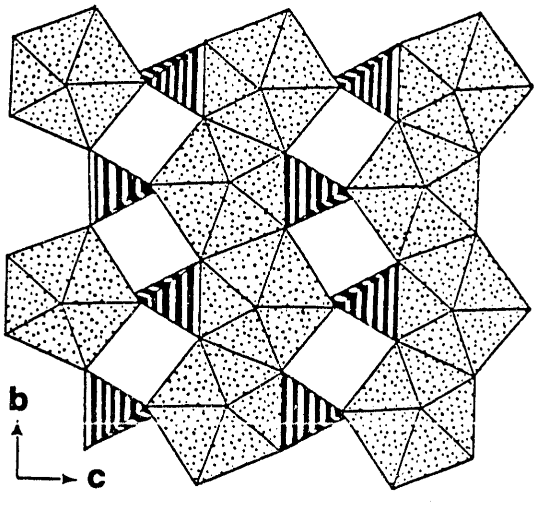

Fig. 1. Structure of zircon down [100] axis. Edge-sharing dodecahedra (8-coordinated Zr, dotted) form chains parallel to [010]. The chains are cross-linked by SiO_4 tetrahedra (striped).

have been used to evaluate elemental loss from waste-form phases under repository conditions [6]. For this reason, an important area of research has been the comparison of radiation damage effects in ^{238}Pu-doped synthetic zircon [7] with those observed in natural zircon [8]. This comparison allows for the determination of dose-rate effects (which differ by a factor of 10^8) and long-term annealing kinetics under ambient conditions. Also, ion-beam modified zircon (with a buried amorphous layer) has been used as a novel material for optical wave guides [9].

Recently, in situ transmission electron microscopy (TEM) during ion irradiation has been used to determine the critical amorphization dose of zircon, and it was found that zircon becomes amorphous at a nearly constant dpa under Kr and Xe ion irradiations, regardless of the differences in ionization energy deposition at room temperature [10]. Also by in situ TEM studies, amorphization dose has been found to be strongly dependent on the irradiation temperature for intermetallics [11], semiconductors [12], and, more recently, a wide variety of silicates [13]. In this study, the temperature and ion-mass dependence of the critical amorphization dose of zircon is investigated.

EXPERIMENTAL PROCEDURES

The zircon sample from Mud Tanks, Australia is completely crystalline [8]. Although zircon may contain U and Th up to several thousand ppm, no U and Th were detected via electron microprobe analysis [14]. TEM specimens were made by Ar ion milling from well polished (010) thin sections. The as-milled TEM discs were examined with high resolution TEM (HRTEM) and lattice fringe images showing no damage were obtained.

Irradiations with 0.8 MeV Ne$^+$, 1.5 MeV Ar$^+$, 0.7 and 1.5 MeV Kr$^+$, and 1.5 MeV Xe$^+$ were conducted with in-situ TEM using the HVEM-Tandem Facility [15] at Argonne National Laboratory. The Ar$^+$, Kr$^+$ and Xe$^+$ ion irradiations were performed with a flux of ~3.5×10^{-3} ions/nm^{2}s, and higher fluxes were used for Ne$^+$ (2.4×10^{-2} ions/nm^{2}s) and He$^+$ (4.25×10^{-2} ions/nm^{2}s) irradiations. 1.5 MeV Kr$^+$ irradiation was performed in a temperature range of 15 K to 913 K using either a liquid He cooling stage or a heating stage. The other irradiations were all performed at room temperature. The selected area electron diffraction pattern (SAD) was monitored during the course of ion irradiation to follow the crystalline to amorphous transformation. Amorphization was indicated by the development of diffuse halo(s) in SAD and complete amorphization was defined by the total disappearance of diffraction maxima. Sample temperature was monitored during irradiation, and the maximum temperature increase due to beam heating was ~30°C. 1.5 MeV Kr$^+$ irradiations at selected temperatures were repeated to check the accuracy of the critical ion dose determination. The error is generally within 10%. The recorded ion fluences for complete amorphization were converted to dose in dpa based on TRIM calculations [16] and a displacement energy of 25 eV was used in these calculations.

RESULTS AND DISCUSSION

Figure 2 is a typical series of electron diffraction patterns obtained from the in situ experiment. The effect of temperature on the dose for complete amorphization in ZrSiO$_4$ is shown in Fig. 3. Three regimes are identified. In the first (15 to 300 K), critical amorphization dose increased from 3.06 to 4.5 ions/nm^2. In the second (300 to 473 K), there is no apparent change in the amorphization dose. In the third (> 473 K), the amorphization dose increased exponentially to 8.3 ions/nm^2 at 913 K. The increase of amorphization dose shows the effects of thermally activated defect annealing processes at elevated temperatures. The two separated stages (Fig. 3) in which the amorphization dose increased significantly with temperature suggest two different defect annealing processes.

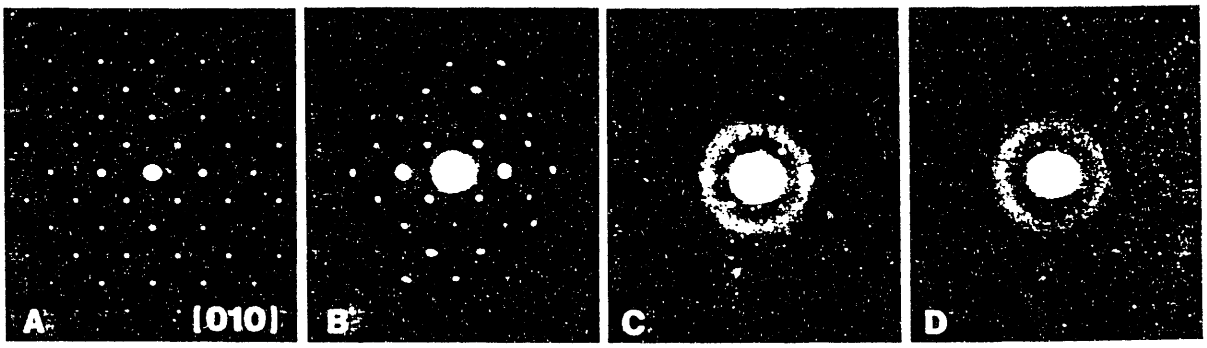

Fig. 2. Electron diffraction patterns of zircon obtained during in-situ 1.5 MeV Kr ion irradiation at 300 K: (A) original, (B) 1.3 ions/nm^2, (C) 3.2 ions/nm^2 and (D) 4.5 ions/nm^2.

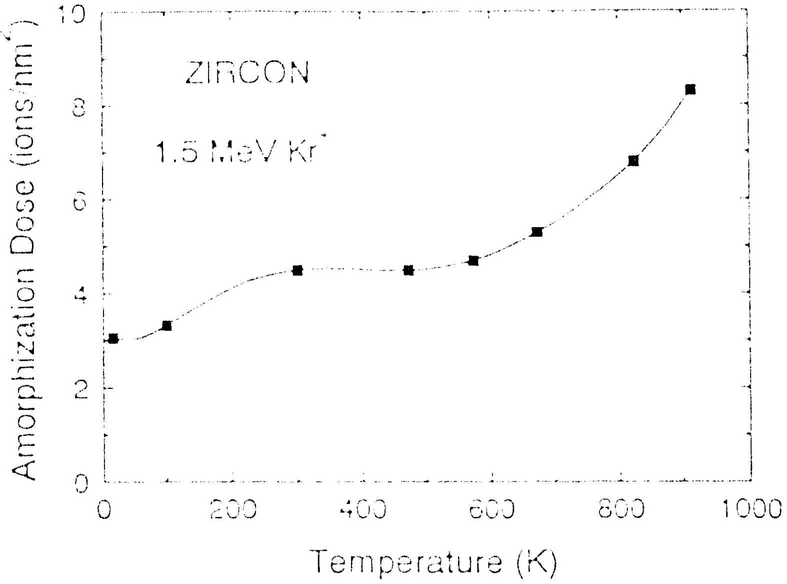

Fig. 3. Temperature dependence of critical amorphization dose of 1.5 MeV Kr ion irradiated zircon.

Using a method of analysis described in more detail by Weber and Wang [17], an activation energy, E_a, associated with the exponentially dependent annealing stages and a critical temperature, T_c, above which amorphization does not occur can be determined from the data in Fig. 2. The relationship between temperature and dose required for complete amorphization is given by:

$$\ln(1 - D_0/D) = C - E_a/kT \qquad (1)$$

where C is a constant dependent on ion flux and amorphization cross section and D_0 is the amorphization dose at T = 0 K associated with each annealing process. An Arrhenius plot of $\ln(1 - D_0/D)$ versus 1/kT yields $-E_a$ as the slope (Fig. 4).

The critical temperature, T_c, defined where $D = \infty$ in equation (1) can be determined once C and E_a are known. The expression for T_c is given by:

$$T_c = E_a/kC \qquad (2)$$

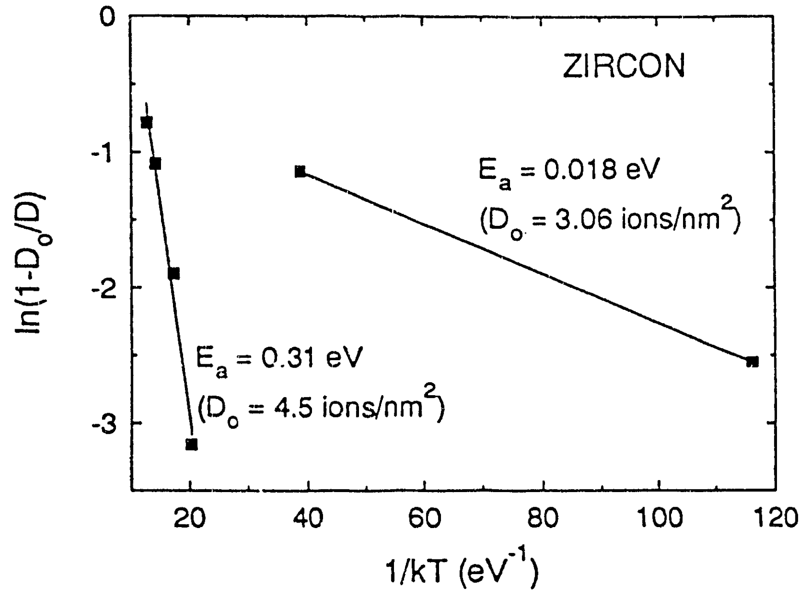

Fig. 4. Arrhenius plot of ln(1 - D_o/D) versus 1/kT deduced from the dose-temperature curve for zircon (Fig. 3).

The initial annealing stage in zircon is assumed to be associated with an intra-cascade close pair recombination process at low temperatures that is effective up to ~300 K where all close pairs recombine instantaneously. This process, which is insufficient to prevent complete amorphization, slightly decreases the amount of residual disorder that survives each ion cascade at temperatures above 300 K. Because of the limited data for this first stage, the estimated activation energy, 0.018 eV, is only approximate. Additional data, to be obtained at low temperatures, will allow a more accurate determination of this activation energy. The second annealing stage is assumed to be an irradiation-enhanced epitaxial recrystallization process associated with irradiation-enhanced defect mobility [11-13]. This annealing process competes with irradiation-induced amorphization and dominates above T_c, thus preventing amorphization. A temperature dependence study of amorphization in Ni^+- and N^+-implanted Ni_xTi_{1-x} alloys has revealed two very similar processes with distinct activation energies occurring at low and high temperature regimes, respectively [18]. In the case of zircon, the activation energy associated with irradiation-enhanced epitaxial recrystallization, 0.31 eV, is nearly identical to an earlier measurement, 0.30 eV, [13]; however, it is considerably less than the activation energy for fission fragment track annealing (epitaxial recrystallization) in zircon, 3.6 eV [19], and the activation energy for the bulk recrystallization of fully amorphous zircon, 5.1 eV [7].

The critical temperature for amorphization, T_c, is determined to be ~1100 K for zircon by equation (2). This value is much higher than that reported for semiconductors, intermetallics and other ceramic materials. For example, the T_c for Ge [12], U_3Si [20] and CuTi [11] are all estimated to be below 573 K, and the T_c for $Ca_2La_8(SiO_4)_6O_2$ has been determined to be 711 K [17]. The unusually high critical amorphization temperature of zircon implies a high thermal stability of amorphous phase, which is an important concern for the wave guide applications [21]. Indeed, amorphous zircon has been found to be stable at 1023 K in a two day annealing experiment [8].

Irradiation with 0.8 MeV Ne, 1.5 MeV Ar, 1.5 MeV Kr, 0.7 MeV Kr and 1.5 MeV Xe ions at room temperature resulted in complete amorphization at 0.38, 0.26, 0.51, 0.57 and 0.58 dpa, respectively. One major difference in defect production related to ion mass is that the energy transferred to recoils is generally much higher for larger ions, thus resulting in larger displacement cascades. For the Kr irradiations, 700 keV ions transfer more energy to the recoils through collision than 1.5 MeV ions in the thickness of study (~200 nm) according to the TRIM calculations. The effect of average recoil energy per ion (calculated at 100 nm) on amorphization dose is illustrated in Fig. 5. Also included in Fig. 5 is the amorphization dose reported for the low-dose-rate (3 x 10^{-9} dpa/s) 92 keV U recoils in polycrystalline Pu-doped $ZrSiO_4$ (0.48 dpa) by Weber [7], and that for 2 MeV He^+ in bulk $ZrSiO_4$ (2.3 dpa) by Babsail et al. [9].

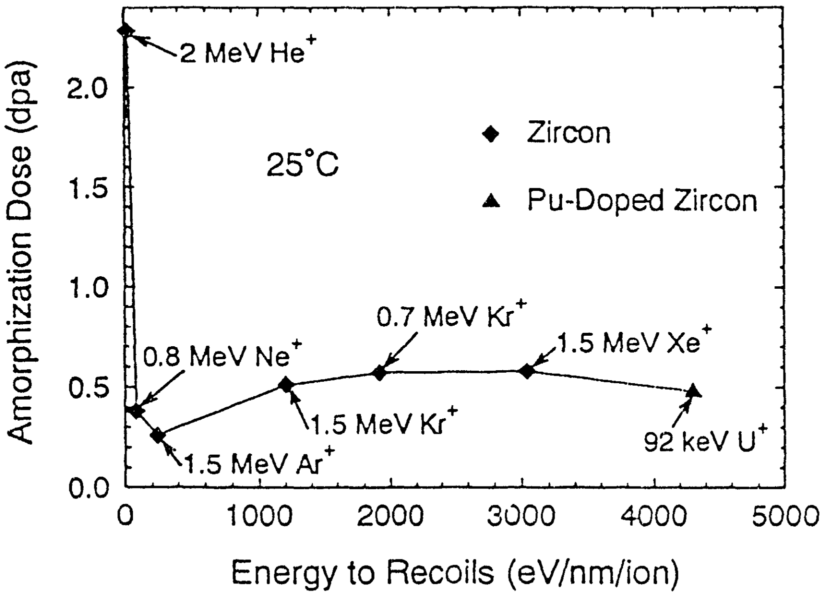

Fig. 5. Dependence of amorphization dose at room temperature on average energy transferred to recoils per ion.

The similarity in amorphization doses for Pu-doped and the heavy ion irradiated samples (10^{-4} to 10^{-3} dpa/s) indicate that the dose rate effect is small, and so is the effect of average recoil energy above 1000 eV/nm/ion. The reduction in amorphization dose for the Ar^+ irradiated sample as compared to that of Kr^+ and Xe^+ perhaps reflects the greater "survivability" of point defects from intra-cascade recombination in the smaller cascades created with a lower recoil energy [22, 23]. Since the cascades created by Ne^+ and He^+ are much smaller in size and further apart, substantial cascade overlap, especially for the He^+ irradiation, is required to achieve the critical defect density for amorphization [11]. Also, isolated mobile point defects may disappear during the interval between overlapping cascade events. Thus, one may expect an increase in amorphization dose for Ne and He as compared to Ar. The amorphization dose for the 2 MeV He^+ irradiation is about a factor of 4 higher than for the heavier ions, which may indicate that the large fraction of isolated displacements created by He ions anneal more easily under continued irradiation. Thus, as Koike and others [11] have emphasized, the kinetics of amorphization are qualitatively different for lighter and heavier ions because of fundamental differences in cascade structure.

CONCLUSIONS

Two defect recovery processes in Kr ion irradiated zircon have been suggested by the temperature dependence of amorphization dose. One with an activation energy of 0.018 eV is believed to be due to close pair recombination and is mainly effective at temperatures below

300 K; the other, with an activation energy of 0.31 eV, is assumed to be due to irradiation-enhanced epitaxial recrystallization associated with irradiation-enhanced defect mobility and is significant only at temperatures above 473 K. The critical temperature above which zircon does not become amorphous is 1100 K.

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