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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue, Argonne, Illinois 60439

A MECHANISTIC MODEL FOR RADIATION-INDUCED CRYSTALLIZATION AND AMORPHIZATION IN U_3Si*

by

J. Rest

Energy Technology Division
Argonne National Laboratory
Argonne, Illinois U.S.A.

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Abstract

Of concern for the proposed Advanced Neutron Source and Research Reactors, which would use intermetallic fuels, are potential radiation-induced phenomena that could affect the physical and mechanical properties of intermetallic aluminum dispersion fuels. For this reason and because of observations of radiation-induced amorphization of U_3Si and U_3Si_2 during ion irradiation, the phenomenology of radiation-induced amorphization is assessed. A rate-theory model is formulated wherein amorphous clusters are formed by the damage event. These clusters are considered centers of expansion (CE), or excess-free-volume zones. Simultaneously, centers of compression (CC) are created in the material. The CCs are local regions of increased density that travel through the material as an elastic (e.g., acoustic) shock wave. The CEs can be annihilated upon contact with CCs (annihilation probability depends on height of the energy barrier), forming either a crystallized region indistinguishable from the host material, or a region with a slight disorientation (recrystallized grain). Recrystallized grains grow by the accumulation of additional CCs. Full amorphization is calculated on the basis of achieving a fuel volume fraction consistent with the close packing of spherical entities.

Amorphization of a recrystallized grain is hindered by the presence of the grain boundary. Preirradiation of U_3Si above the critical temperature for amorphization results in the observed formation of nanometer-size grains. In addition, the subsequent reirradiation of these samples at temperatures below the critical level shows that the material has developed a resistance to radiation-induced amorphization (i.e., a higher dose is needed to amorphize the preirradiated samples than for those that have not been preirradiated). In the model, it is assumed that grain boundaries act as effective defect sinks, and that enhanced defect annihilation is responsible for retarding amorphization at low temperature. The calculations have been validated against data from ion-irradiation experiments with U_3Si. To obtain additional validation, the model has also been applied to the ion-induced motion of the interface between crystalline and amorphous phases of U_3Si. The results of this analysis are compared to data and results of calculations for ion bombardment of Si.

1. Introduction

The bombardment of solids by energetic particles produces displacements of the host atoms and thus damage to the structure of the solids. If the damage energy is sufficiently high, displacement cascades containing hundreds of atoms each are produced. Molecular-dynamics simulations of ion collisions with a crystalline substrate show that the early stages of cascade development are characterized by the formation of shock waves [1], and that amorphous material is left after the cascades cool to ambient temperature [2]. Ion-induced crystallization and amorphization in Si has been extensively studied in the regime where these two processes occur at almost equal rates [3,4]. At low temperatures and high ion fluxes, amorphization dominates. At higher temperatures or lower fluxes, crystallization proceeds. Ion-irradiation-induced nano-scale polycrystallization of intermetallic and ceramic materials at temperatures above the critical temperature for amorphization was observed by in-situ and high-resolution transmission electron microscopy [5]. In addition, during a second irradiation at lower temperatures, the small crystallites retarded amorphization [6]. These observations suggest an intimate relationship between ion-induced amorphization and crystallization.

2. Model

A rate theory model for ion-induced crystallization and amorphization has been formulated on the basis of the following phenomenology. The bombarding ions produce clusters of amorphous material that are considered centers of expansion (CE), or excess free volume zones. Simultaneously, centers of compression (CC) are created in the material. The CCs are local regions of increased density that travel through the material as an elastic (e.g., acoustic) shock wave. The CEs can be annihilated upon contact with CCs (annihilation probability depends on height of the energy barrier), forming either a crystallized region that is indistinguishable from the host material, or a region with a slight disorientation (recrystallized grain). The CCs can also annihilate each other upon contact if close to vacancies or vacancy clusters, forming either oriented or slightly disoriented crystal structures. Recrystallized grains grow by accumulating additional CCs. Full amorphization is calculated on the basis of achieving a fuel volume fraction consistent with the close packing of spherical entities.

Amorphization of a recrystallized grain is hindered by the presence of the grain boundary. As discussed above, preirradiation of U_3Si above the critical temperature for amorphization results in the observed formation of nanometer-size grains. In addition, the subsequent reirradiation of these samples at temperatures below the critical temperature shows that the material has developed a

resistance to radiation-induced amorphization (i.e., a higher dose is needed to amorphize the preirradiated samples than for those that have not been preirradiated). In the model, it is assumed that grain boundaries act as effective defect sinks, and enhanced defect annihilation is responsible for retarding amorphization at low temperature.

The density of amorphous clusters, C_{ce}, evolves in time according to

$$\frac{dC_{ce}}{dt} = N_{ce} g \left(V_o^f + \frac{2R_g V_g^f}{3\delta} + \frac{V_\alpha C_g \Omega}{V_g} \right) - f_1 \frac{N_{ce}}{N_{cc}} v_a C_{cc} C_{ce} - \frac{C_{ce}}{\tau} , \qquad (1)$$

where N_{ce} and N_{cc} are the numbers of CEs and CCs created per ion, $g = d\phi$, where ϕ is the ion flux (ions m^{-2} s^{-1}) and d is the thickness of the material through which the ion beam is passing (see Sec. 3); V_α is the volume of amorphous material created per N_{ce}; V_o^f and V_g^f are the volume fractions of unaltered and crystallized material, respectively; and C_g, R_g, and V_g are the crystallized grain density, grain radius, and grain volume, respectively. δ is an effective grain-boundary thickness that provides a measure of the difficulty in amorphizing the boundary region by ion damage, T is the absolute temperature, and Ω is the atomic volume. v_a is given by

$$v_a = v_{cc} e^{-\varepsilon_a / kT} , \qquad (2)$$

where v_{cc} is the velocity of the shock wave in the material, ε_a is the activation energy for crystallization of an amorphous cluster by a CC, and , and τ is a waiting time for thermal crystallization given by

$$\tau = e^{-\varepsilon_a^t / kT} , \qquad (3)$$

where ε_a^t is the activation energy for thermal crystallization.

The corresponding equation for the density of the centers of compression, C_{cc}, is given by

$$\frac{dC_{cc}}{dt} = N_{cc} g \left(V_o^f + \frac{2R_g V_g^f}{3\delta} + \frac{V_\alpha C_g \Omega}{V_g} \right) - f_1 v_a C_{cc} C_{ce} - f_2 v_x C_{cc} C_g R_g$$

$$- f_3 v_{cc} C_{cc} C_{cc} , \qquad (4)$$

where v_x is given by

$$v_x = v_{cc} e^{-\varepsilon_x / kT} , \qquad (5)$$

where ε_x is the activation energy for grain growth due to interaction between a CC and a crystallized grain.

The first three terms on the right-hand side (RHS) of Eqs. 1 and 4 represent the gain of CEs and CCs due to production by ion damage in (a) the unaltered solid matrix, (b) the grain boundary of crystallized grains, and (c) the crystallized grain embryos. The fourth term on the RHS of Eqs. 1 and 2 represents the loss of CEs and CCs due to annihilation of the CEs by CCs. The last term in Eq. 1 is the loss of CEs by thermal dissociation. The last two terms in Eq. 4 represent the loss of CCs due to interaction with crystallized grain nuclei and CC pair annihilation, respectively.

The time rate of change of the density of crystallized grains, C_g, is given by

$$\frac{dC_g}{dt} = \beta_1 f_1 \frac{N_{ce}}{N_{cc}} v_a C_{cc} C_{ce} + \beta_3 f_3 v_{cc} C_{cc} C_{cc} - \frac{N_{ce} g V_\alpha C_g \Omega}{V_g} , \qquad (6)$$

where β_1 is the probability that a CE-CC annihilation results in a crystallized grain (instead of a resultant atom orientation that is in alignment with the original grain structure). The last term in Eq. 6 corresponds to the third terms on the RHS of Eqs. 1 and 2 and is the loss of crystallized grain nuclei due to destruction by an incoming ion. The radius of the crystallized grains is given by

$$R_g = \left(\frac{V_g}{\frac{4\pi}{3}} \right)^{\frac{1}{3}}, \tag{7}$$

where

$$V_g = \frac{V_g^f}{C_g}, \tag{8}$$

and

$$\frac{dV_g^f}{dt} = \frac{\beta_2 f_2 v_x C_{cc} C_g R_g^2 V_o^f A_{cc}}{2} - \frac{2 R_g V_g^f N_{ce} g V_\alpha}{3\delta}. \tag{9}$$

In Eq. 9, β_2 is the probability that an interaction between a CC and a crystallized grain results in the growth of the grain (as compared to formation of a region of the material adjacent to the crystallized grain whose atoms are in alignment with the crystal structure of the host atoms), and A_{cc} is the surface area of CC. The first term of Eq. 9 represents the conservation of surface area assumed for the growth of crystallized grains by accumulation of CCs. This is analogous to the physics associated with the growth of bubbles due to coalescence. The last term in Eq. 9 corresponds to the second terms on the RHS of Eqs. 1 and 2 and is the loss of crystallized grain volume due to amorphization by an incoming ion.

It is assumed here that interaction between the CEs, the CCs, and crystallized grains is facilitated by the presence of vacancies or vacancy clusters. Thus the rate constants, f_i, include not only the standard interaction cross sections, but the probability of finding an appropriate number of vacancies or vacancy clusters in the near vicinity of the interaction site.

It is also assumed that N_{ce} and N_{cc} are not independent, but are related by volume conservation. If it is assumed that a CE results in an average fractional density decrease η_{ce}, and a CC in a fractional density increase η_{cc}, then volume conservation requires

$$N_{cc}(1-\eta_{cc}) = N_{ce}(\eta_{ce} - 1). \tag{10}$$

3. Ion-Induced Crystallization and Amorphization in U_3Si

Table 1 lists the nominal values of the parameters used in Eqs. 1-10.

Parameter	Value	Parameter	Value
N_{ce}	69	ε_a	1.25 eV
δ	10^{-5} m	ε_x	0.1 eV
f_1	$5 \times 10^{-5} \Omega^{2/3}$ m^2	ε_a^t	1.44 eV
f_2	$1.6 \times 10^{8} \Omega^{2/3}$ m	η_{ce}	1.3
f_3	$2.3 \times 10^{-14} \Omega^{2/3}$ m^2	η_{cc}	0.98
v_{cc}	5×10^{3} m/s	Ω	10^{-28} m^3
β_1	3.125×10^{-4}	V_α	3×10^{-27} m^3
β_2	0.05	k	8.625×10^{-5} eV / K
β_3	0.0	d	5×10^{-8} m

Table 1. Values of parameters used in Eqs. 1-10.

Figure 1 shows the calculated and measured temperature dependence of the dose of 1.5 MeV Kr ions, at a flux of 2×10^{16} Kr m^{-2} s^{-1}, required to amorphize U_3Si with or without high-temperature irradiation treatments [6]. The calculated amorphization dose is based on achieving a close-packed structure of amorphous clusters: spherical entities will touch each other at a fuel volume fraction of about 0.652. The calculated dose follows the trend of the observations and clearly demonstrates the strong effect of grain refinement on ion-beam amorphization: pretreatment raises the amorphization dose and decreases the critical temperature (i.e., the temperature above which the material remains crystalline). A high temperature pretreatment dose of 5×10^{18} Kr m^{-2} raises the low temperature amorphization dose by a factor of about 5. Increasing the pretreatment dose by a factor of 2 raises the low-temperature amorphizaion dose by a factor of at least 40!

Calculated recrystallization during a high temperature (670 K) Kr irradiation treatment of U_3Si is shown in Fig. 2, where the density of recrystallized grains

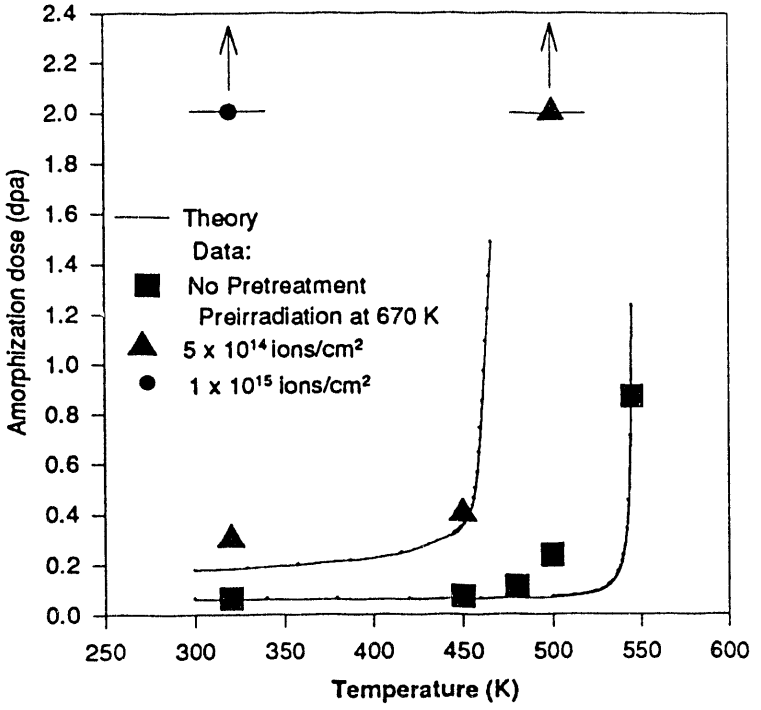

Fig. 1. Calculated and measured temperature dependence of dose of 1.5 MeV Kr ions required to amorphize U_3Si with and without high-temperature irradiation treatments.

and the average grain radius are plotted as functions of irradiation time: 100 s is equivalent to an ion dose of 5×10^{18} Kr m^{-2}. The calculated fuel volume fraction occupied by recrystallized grains increases rapidly during the first 200 seconds and approaches an asymptotic value of about 0.7. Close-packed spherical grains will touch each other at a fuel volume fraction of about 0.652. The recrystallized grain size shown in Fig. 2 increases rapidly in the first 200 s to about 120 Å diam eter, after which very little increase in grain size is predicted. During irradiation, the small grains increase in number until they fill the specimen. Experimentally, complete removal of the initial structure occurs by a dose of 3×10^{19} Kr m^{-2} (600 s in Fig. 2). In general, the calculated results shown in Fig. 2 are consistent with the experimental observations that the grain sizes are in the range of 100 – 200 Å, and that "During the course of irradiation the small grains increased in number and appear to increase very slowly in size." [6]

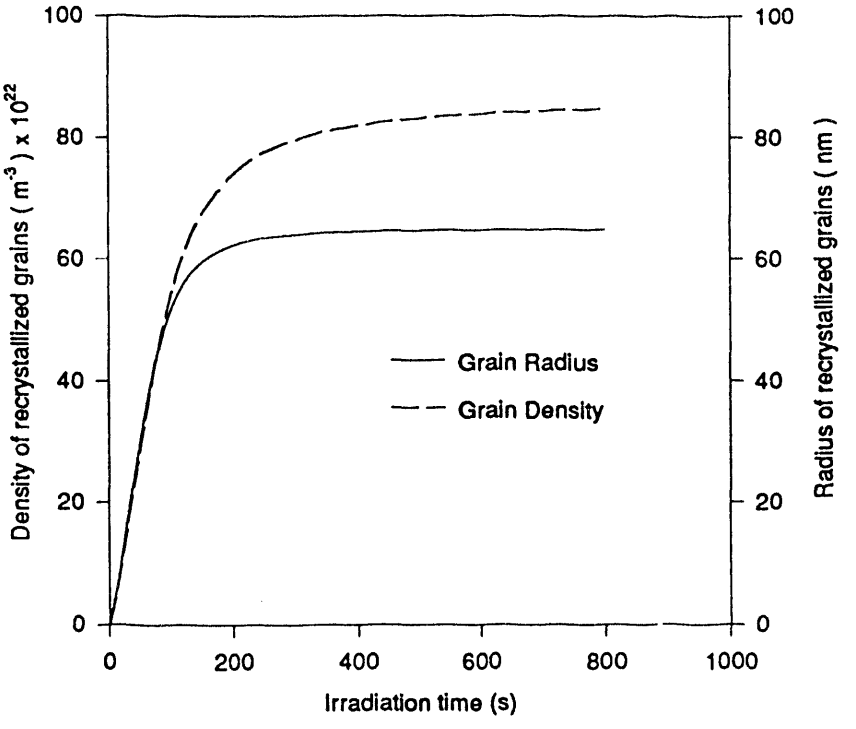

Fig. 2. Calculated recrystallization during Kr irradiation of U_3Si at 670 K.

4. Ion-induced Motion of Interface between Crystalline and Amorphous Phases of U_3Si: Comparison with Results from Si

For additional validation, the model defined by Eqs. 1-10 has been applied to the ion-induced motion of the interface between crystalline and amorphous phases of U_3Si. The reason for this assessment is the large body of data that exists for similar assessments and observations in Si [7]. Due to the unavailability of the values for many material properties, it is felt that applying the calculations to U_3Si and qualitatively comparing the results to the observations in Si is more meaningful than "guessing" the appropriate values for Si properties required for the Si calculations. Figure 3 shows the calculated normalized displacement rate in U_3Si plotted as a function of the reciprocal temperature for various dose rates. A starting composition of 50% crystalline and 50% amorphous material

was utilized. Also shown in Fig. 3 is the calculated normalized displacement rate in Si based on the defect model of Jackson [4]. As shown in Fig. 3, the crystal grows into the amorphous phase at high temperatures or relatively low dose rates, while the amorphous phase grows into the crystal at low temperatures or relatively high dose rates. The predictions of the theory for U_3Si are in qualitative

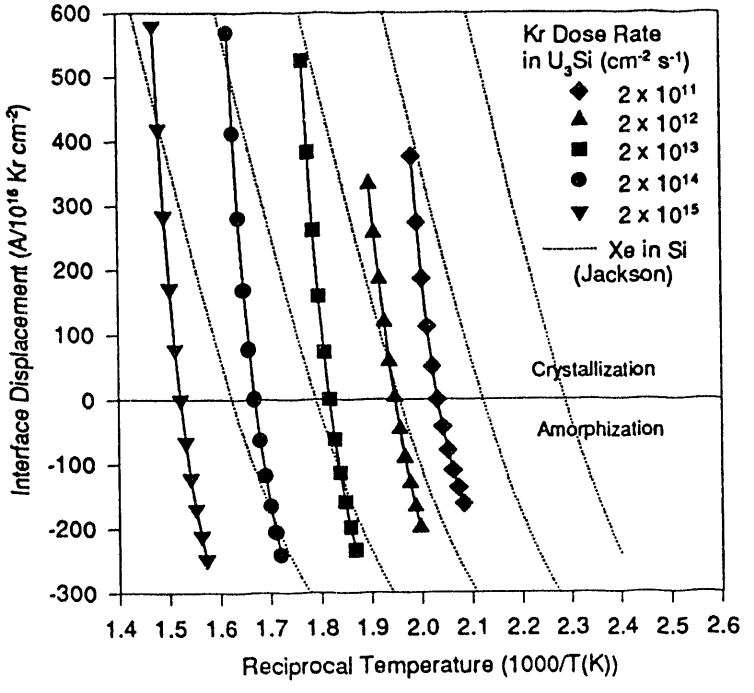

Fig. 3. Calculated normalized displacement rate in U_3Si plotted as a function of reciprocal temperature for various dose rates.

agreement with the Si results.

Figure 4 shows the calculated dose rate dependence of the temperature for zero growth rate for the Kr ion bombardments in U_3Si shown in Fig. 3. Also shown in this plot is the trend of the data for Kr ion irradiation in Si [7]. The predictions of the theory for U_3Si shown in Fig. 4 deviate from pure straight-line (Arrhenius)

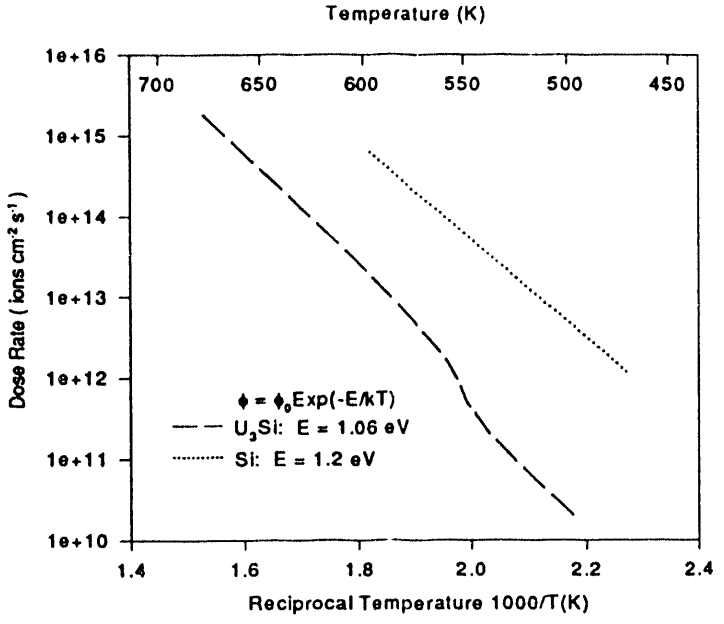

Fig. 4. Calculated dose rate dependence of temperature for zero growth rate for Kr ion bombardments in U_3Si shown in Fig. 3. Also shown is trend of data for Kr ion irradiation in Si [7].

behavior. This deviation which occurs at a recpriprocal temperature of about 2.0 x 10^{-3} K^{-1}, is due to a change in the mechanism of amorphous cluster loss from thermal crystallization to annihilation by irradiation-produced defects. This changeover in the mechanism of amorphous cluster loss is also responsible for the curvature of the calculated interface displacement vs. reciprocal temperature curves for U_3Si, shown in Fig. 3.

5. Conclusions

The fundamental difference between the model for ion-induced crystallization and amorphization presented in this paper and the model proposed by Jackson [4] for the ion-induced motion of the interface between the crystalline and amorphous phases of silicon is in the identity of the low-temperature recrystallization mechanism (i.e., below the temperature at which thermal crystallization occurs) . Jackson identifies this entity as a single defect believed to be a dangling bond in the

amorphous phase. These defects jump around in the interface region and create a volume Λ of crystal per jump. The theory presented here ascribes ion-induced recrystallization primarily to the annihilation of an amorphous cluster by a compressive shock wave created by the damage event. These shock waves can also annihilate each other if they interact in the presence of defects such as vacancies or vacancy clusters.

The values of the rate constants $f_1 - f_3$ and the parameters $\beta_1 - \beta_3$ are somewhat arbitrary. In principle, these constants could be evaluated in the context of generalizing the present model to include interaction with radiation-produced defects. However, such an evaluation is outside the scope of the present work. The methodology of value determination for various model parameters used in Eqs. 1-10 is based on a qualitative representation of the phenomenology. For example, the value of V_α was set by the amorphization dose at 300 K (no preconditioning); β_1 and f_1 were set by the asymptotic radius of recrystallized grains at the end of high-temperature irradiation; β_2 and f_2 were set by the volume fraction of recrystallized grains at the end of high-temperature irradiation; β_3 and f_3 were set by the low-T slope of amorphization dpa vs. T (no preconditioning); ε_a was set by the critical temperature; ε_a^t was set such that V_o^f decreases above the critical temperature, and such that the calculation is consistent with the measured amorphization dose just below the critical temperature; δ was set by the slope of amorphization dpa vs. T for irradiation of preconditioned material: value is constrained by the condition that grain radius and volume fraction show asymptotic behavior.

The present model has been shown to have a wider applicability than the Jackson model in that it not only provides an interpretation for the ion-induced motion of the crystalline/amorphous interface in Si, but provides an interpretation of the experiments of Birtcher and Wang [6] on the ion-induced nanocrystallization and amorphization of U_3Si. The key finding here is that amorphization of a recrystallized grain is hindered by the presence of the grain boundary.

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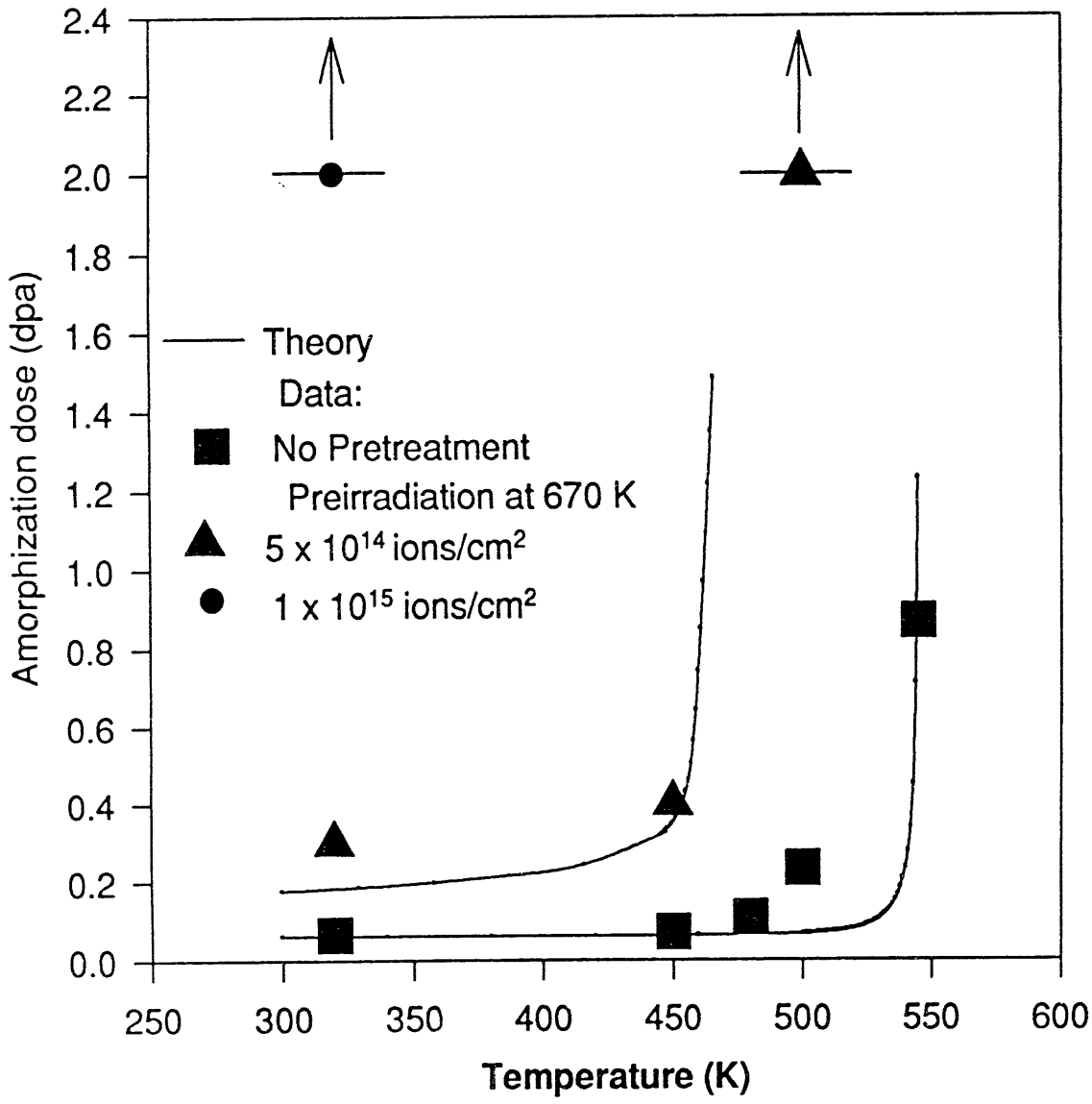
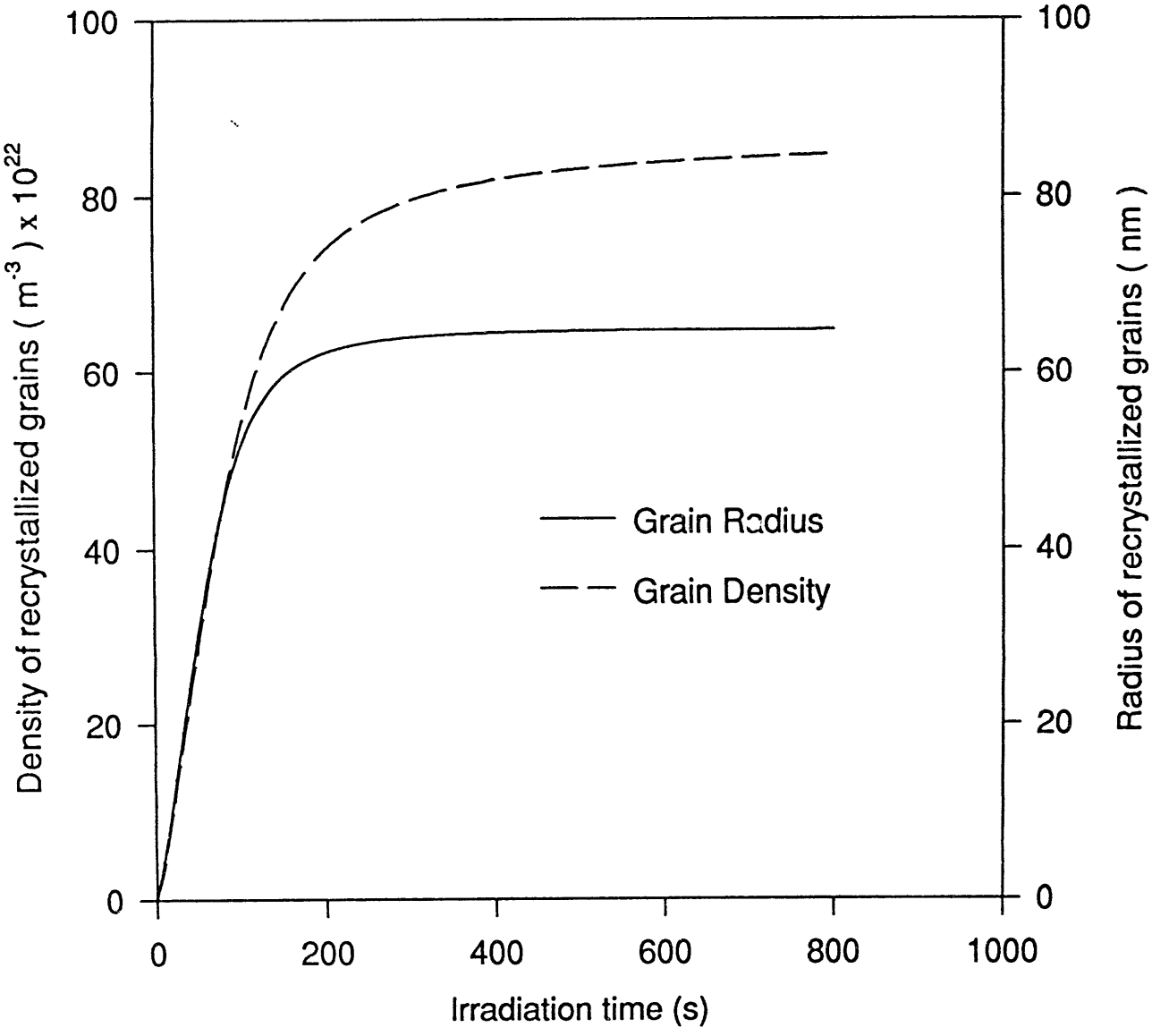
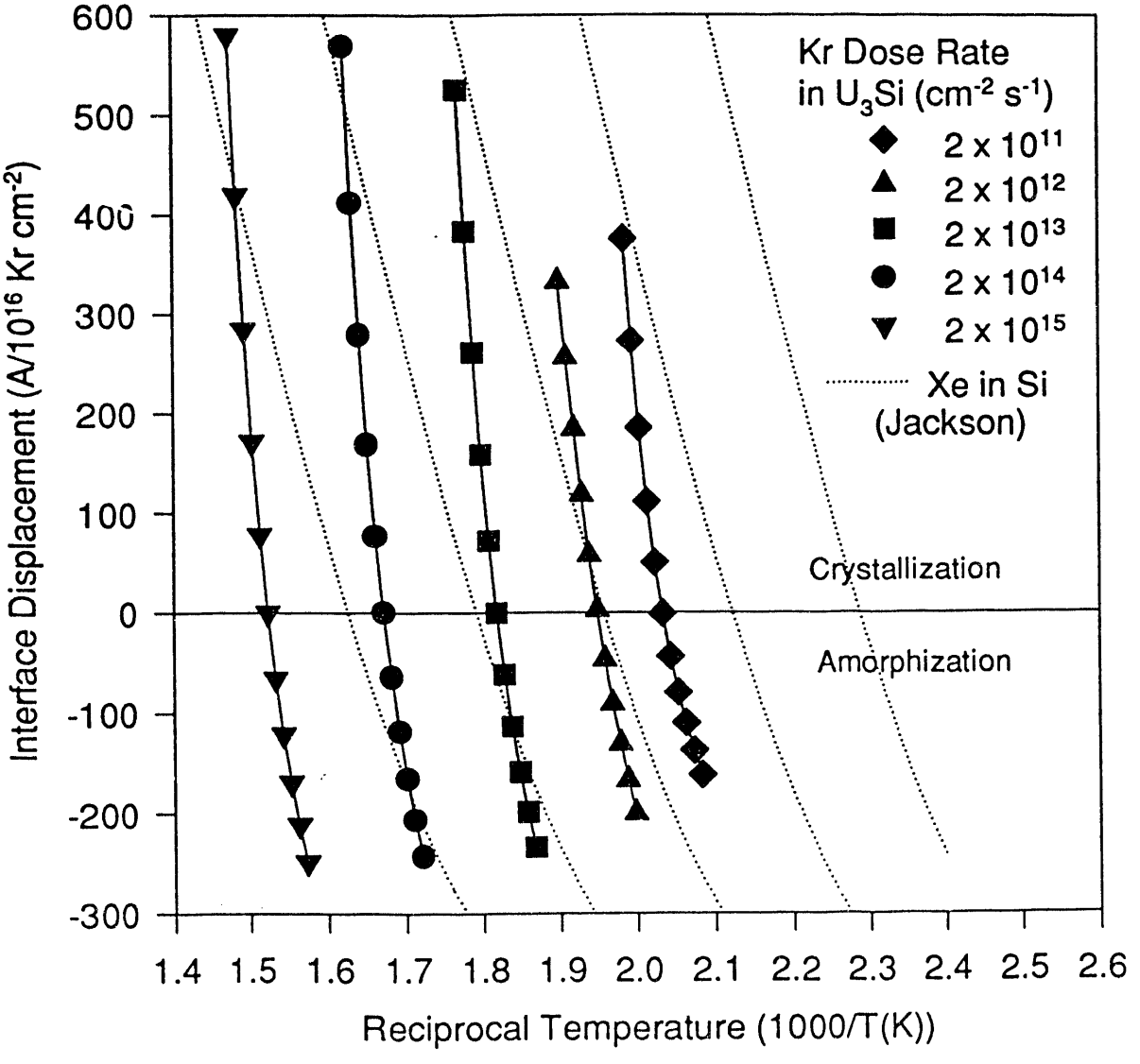
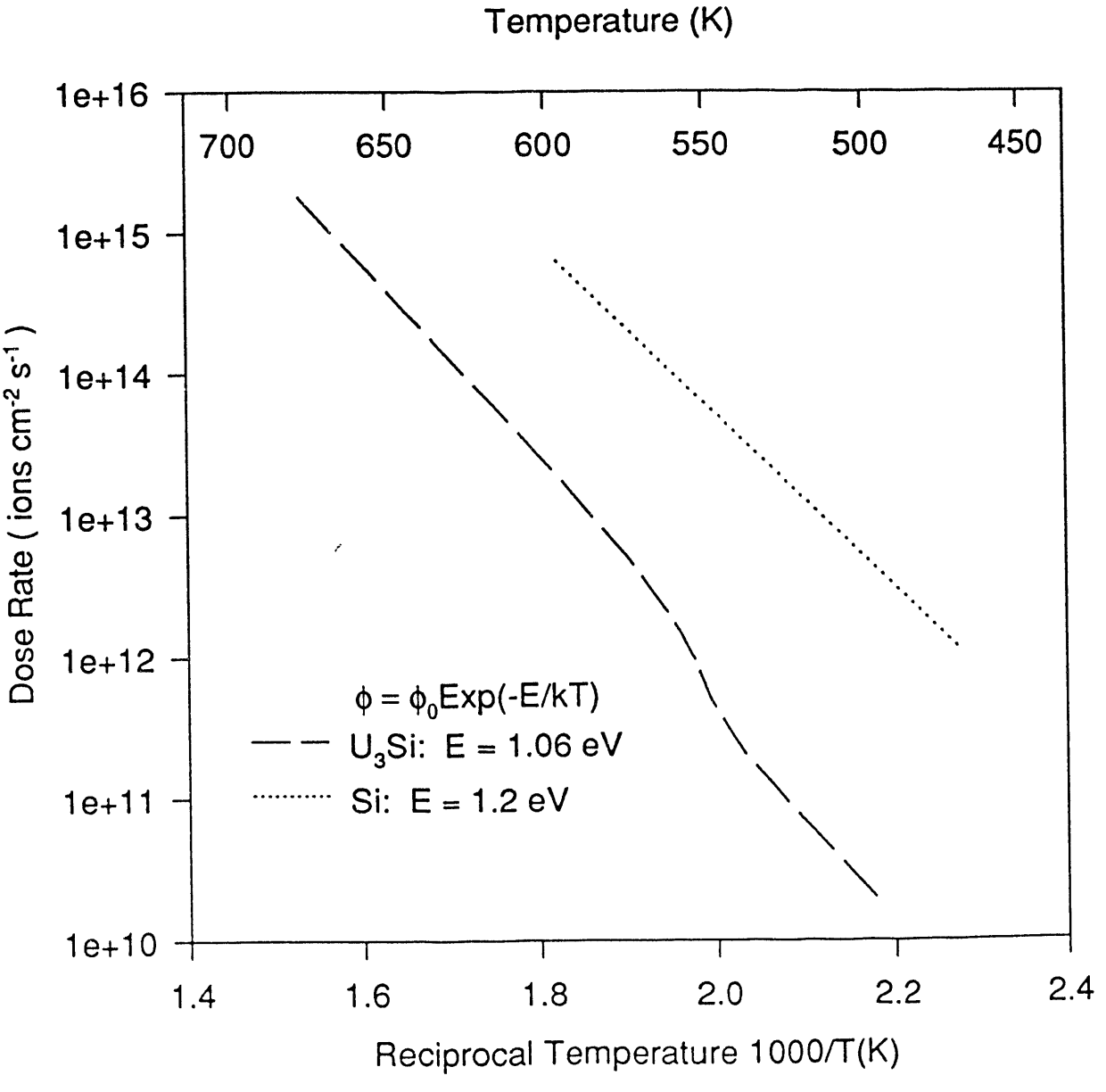
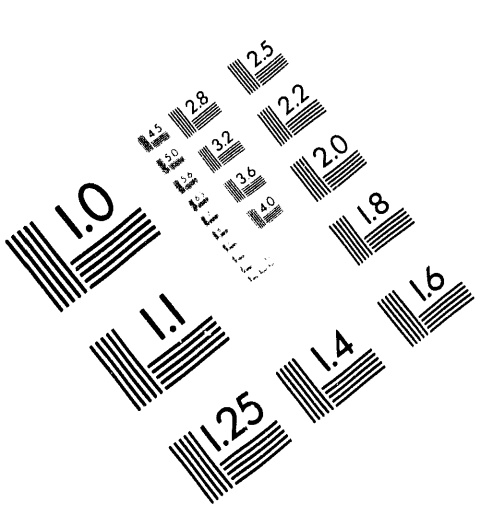

2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Amorphization dose (dpa)
Theory
Data:
No Pretreatment
Preirradiation at 670 K
5 x 10^14 ions/cm^2
1 x 10^15 ions/cm^2
250
300
350
400
450
500
550
600
Temperature (K)


100
80
60
40
20
0
0
200
400
600
800
1000
Irradiation time (s)
Density of recrystallized grains (m-3) x 10^22
Radius of recrystallized grains (nm)
Grain Radius
Grain Density


Kr Dose Rate
in U_3Si (cm^{-2} s^{-1})
2×10^{11}
2×10^{12}
2×10^{13}
2×10^{14}
2×10^{15}
Xe in Si
(Jackson)
Crystallization
Amorphization
Interface Displacement (A/10^{16} Kr cm^{-2})
600
500
400
300
200
100
0
-100
-200
-300
1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6
Reciprocal Temperature (1000/T(K))


Temperature (K)
700
650
600
550
500
450
1e+16
1e+15
1e+14
1e+13
1e+12
1e+11
1e+10
Dose Rate (ions cm-2 s-1)
ϕ = ϕ0Exp(-E/kT)
U3Si: E = 1.06 eV
Si: E = 1.2 eV
1.4
1.6
1.8
2.0
2.2
2.4
Reciprocal Temperature 1000/T(K)



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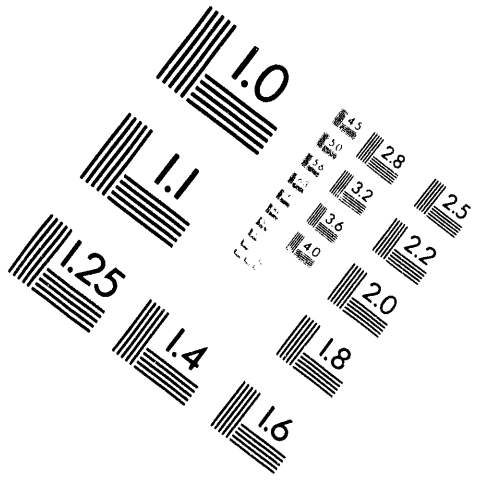

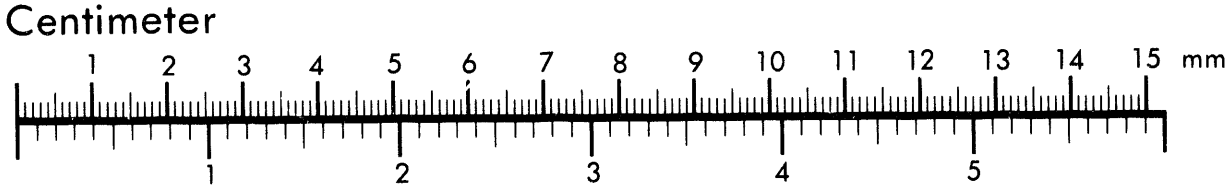

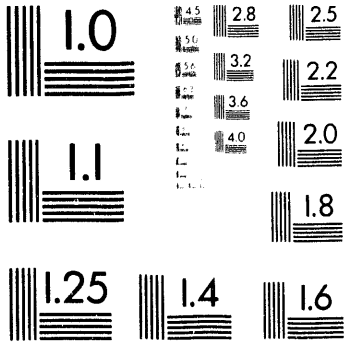

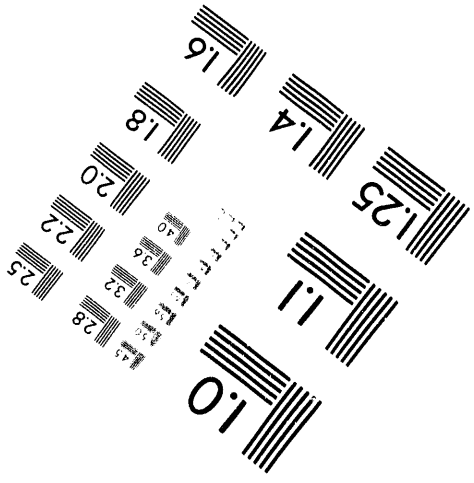

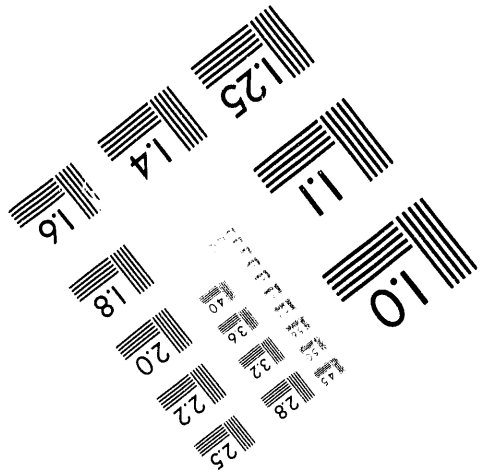

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