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Low-temperature ion beam mixing of Pt and Si markers in Ge

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The mixing of Pt and Si marker atoms in Ge during 750-keV Xe irradiation was measured at temperatures between 6 and 500 K. The low-temperature measurements show that the mixing parameter for Pt is nearly twice that for Si. This result is in strong contradiction to the collisional theory of ion beam mixing. A weak temperature dependence in the mixing is found for both markers.

The mechanisms underlying diffusion during ion irradiation of metals and semiconductors are proving very elusive to theoretical understanding. Such basic aspects of ion beam mixing as its magnitude,¹ the movement of marker atoms relative to matrix atoms,² and the formation of various compound and amorphous phases,³ remain unexplained. This situation is somewhat of an enigma since the theories of both atomic collisions in solids and radiation-enhanced diffusion are now well developed. Apparently atomic motion within cascades is more complex than originally thought, and an improved theory is necessary. To help delineate the form of such a theory, a data base which provides systematic trends of ion beam mixing would be useful. We have begun such a set of experiments, the first using Ge as the matrix. Although we have completed measurements for only two markers, Si and Pt, they represent a very light and very heavy marker atom relative to Ge, and serve to test the collisional theory of ion beam mixing proposed by Matteson *et al.*⁴

This theory for mixing is based on a random flights model in which the marker atoms are impacted by recoiling matrix atoms and thereby knocked from their initial sites. The basic equation for this collisional diffusion model is

$$Dt = 1/6 N \langle r^2 \rangle, \quad (1)$$

where N is the number of times a marker atom is relocated, and $\langle r^2 \rangle$ is the average of the squared relocation distance. Since a whole spectrum of recoil energies is possible, Eq. (1) must be integrated over all possible energies, i.e.,

$$Dt = \frac{1}{6} \int_{E_d}^{E_{\max}} dE \frac{dN}{dE} \langle r^2(E) \rangle. \quad (2)$$

Expressions for dN/dE and $\langle r^2(E) \rangle$ based on linear transport

theory can be found in Ref. 4. The lower limit of integration, E_d , is the minimum energy necessary to displace an atom from its initial site. Figure 1 illustrates the results for several different markers in Ge. The important feature of the plot is that the mixing increases rapidly with decreasing atomic number for atomic numbers less than 20. A simple test of the

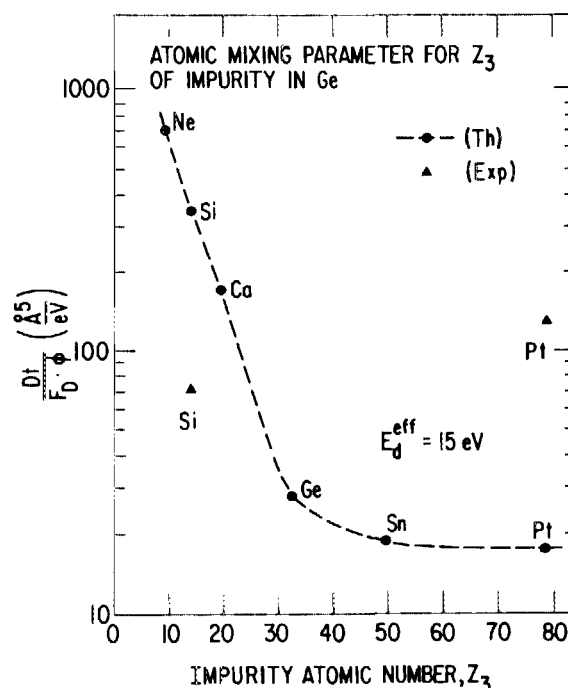


FIG. 1. Calculated values for the "mixing parameter" in Ge as a function of the atomic number of the marker atom according to Eq. (2). Experimental values for Si and Pt markers are also indicated.

theory can therefore be effected by measuring Dt for a heavy and a light marker atom in a given matrix.

Ge was chosen as the matrix as both heavy and light markers could be readily analyzed by backscattering spectrometry. Moreover, Ge can be deposited in the amorphous state which is an assumption in the theory; crystal structure, however, does not seem to strongly influence the magnitude of mixing.^{5,6} The specimens were prepared by vapor deposition onto oxidized Si substrates. The Pt and Si layers had average thicknesses of 10 and 30 Å, and were located in the deposited Ge at depths of 330 and 380 Å, respectively. The specimen temperature during both the mixing and analyzing irradiations was held near 6 K in order to minimize radiation-enhanced diffusion, i.e., diffusion caused by the thermal motion of radiation-induced defects. The specimens were cooled by clamping them to an aluminum plate which was in contact with a liquid helium bath. Indium strips were placed between the specimens and clamps to prevent the Si wafers from cracking. The beam power was kept below 0.05 W to avoid beam heating; the estimated temperature rise in our specimens was 0.1 K. Dose measurements were performed with a Faraday cage which could monitor the beam flux during irradiation. Its calibration was checked prior to each irradiation by slipping a Faraday cup between it and the specimen. The accuracy is ~5%.

The results for the ion beam mixing during 750-keV Xe irradiation at 6 K are shown in Fig. 2. Only the Si and Pt portions of the spectra are shown. For Pt, no deviation from a Gaussian distribution is observed. For Si, interference of the Si yield in the SiO₂ substrate with the low-energy side of the marker Si yield, prevents making a similar determination of the symmetry. However, the distribution between the

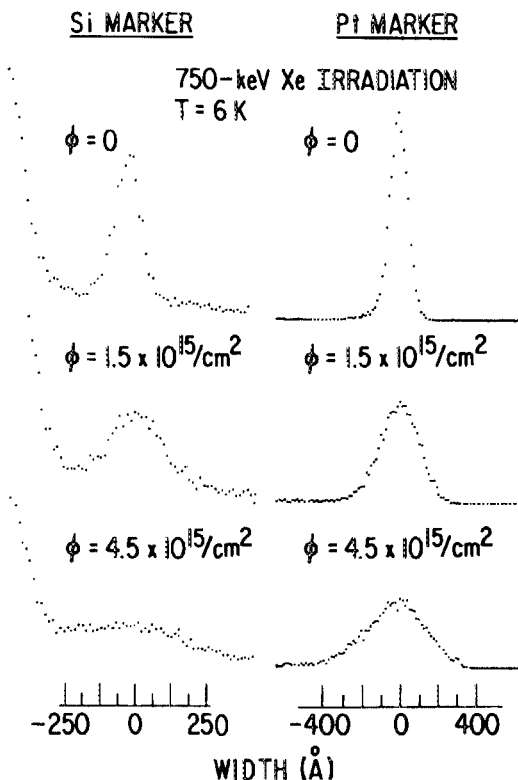


FIG. 2. RBS spectra illustrating the mixing of Pt and Si markers in Ge for 750-keV Xe irradiation at 6 K.

Table I. Compilation of ion beam mixing results for Si and Pt markers in Ge.

Z_3	ϕ ($10^{15}/\text{cm}^2$) ^a	T (K)	$Dt/F_D\phi$ ($\text{\AA}^2/\text{eV}$) ^b
Si	1.5	6	77
Si	4.5	6	71
Si	1.5	77	109
Si	4.5	77	102
Si	1.5	300	143
Si	3.0	300	131
Pt	1.5	6	133
Pt	4.5	6	120
Pt	1.5	300	291
Pt	4.5	300	236
Pt	1.5	493	289

^a 750 keV Xe.

^b $F_D = 201 \text{ eV/\AA ion}$.

marker peak maximum and the high-energy portion of the distribution is Gaussian to within the statistical accuracy. The mixing Dt was determined from the measured variances Ω in the backscattering spectra, converted to units of depth:

$$Dt = (1/2)\sigma^2, \quad (3)$$

$$\sigma^2 = \Omega^2 / (N [\epsilon])^2 \quad (4)$$

and

$$\Omega^2 = \Omega_{\text{irr}}^2 - \Omega_{\text{unirr}}^2. \quad (5)$$

Here Ω_{irr} and Ω_{unirr} are the measured variances after and before irradiation, and N and $[\epsilon]$ are the atomic number density and the stopping cross-section factor of the material for backscattering, respectively. The results are tabulated in Table I. In addition to Dt , the mixing parameter Dt/ϕ is shown. The ion dose for this column is expressed in units of damage energy per \AA^3 . These units were employed to facilitate comparisons with other irradiations of Ge as well as comparisons with other matrices. A Monte Carlo computer simulation, TRIM,⁷ was employed for the conversion to damage energy. A small correction for the incorporation of Pt or Si atoms in the matrix was neglected as it was estimated to be less than 15% once the variances became larger than ~50 Å. Although the correction is small in this case, it can be large for heavy markers in light matrices, like Si, if the marker layer thickness is not small.

The results show that Dt/ϕ is nearly independent of dose for both markers at all temperatures; this is indicative of a stochastic diffusional process. There is some temperature dependence in the mixing; it is small, however, and will be discussed later. The important result shown in the table is that the mixing parameter for the Pt marker is approximately 50% greater than for the Si marker. This is in contradiction to the prediction of the collisional random flight theory, according to which Dt/ϕ for the Si marker should be a factor of 20 greater than that for the Pt marker.

Whether these results in Ge signify that collisional mixing is not the primary mechanism of atomic motion during low-temperature irradiation or that other aspects of collisional mixing are important (see for example, Ref. 1) is not yet certain. We note in this regard that the values of Dt/ϕ for the two markers in Ge are 50% different. An even larger

dependence on the type of marker atom was reported in Si irradiated at 80 K.⁸ If these variations are real, and not an artifact of the preparation of the marker specimens (all specimens were prepared at the Caltech laboratory), they indicate that the specific marker plays a role in the mixing, and mixing is not a function of the composition of the matrix alone. This could be due to either chemical or kinematic processes. Chemical processes could be important if diffusion within the cascade is not determined entirely by binary collisions of atoms. During the cooling of a cascade, atoms within the vicinity of the cascade region have considerable kinetic energy; this phenomenon is sometimes referred to as a "thermal spike." Regardless of whether a thermal spike is an accurate description or not, it has been demonstrated by molecular dynamic computer simulations^{9,10} and to some extent by experiment,¹¹ that considerable defect motion takes place within the highly agitated region of an energetic cascade. If this stimulated defect motion is the primary diffusion mechanism in ion beam mixing, then it is reasonable that, like thermal diffusion, the chemical nature of the marker would be important. Unfortunately, we have no good way of estimating the magnitude of this stimulated diffusion process. Consistent with this thermal spikelike model is the observation that increasing the energy density within cascades significantly enhances the mixing.¹² Chemical processes would also be important if defects are already mobile in Ge at 6 K. Kinematic processes cannot be ruled out as a possible explanation for variations in the mixing parameter for different markers in the same matrix; however, the results of the present experiment and the large difference in the mixing for W, Au, and Pt markers in Si (Ref. 8) suggest that processes other than those of pure collisional mixing are also important. To sort out the main effects will require reliable data on a large number of systems.

Table I shows that between 6 and 300 K there is a small temperature dependence in the mixing, and that it is approximately the same for both markers. This temperature dependence seems to be correlated with a change in the morphology of the amorphous Ge during high-dose irradiation at temperatures above 80 K. It has been reported that the near-surface region in Ge acquires a "honeycomb-like" structure at room temperature due to ion irradiation.¹³ This structure was reported to be accompanied by a "blackening" of the specimen. Blackening was also observed for the present irradiations at room temperature and at 500 K. No changes in the morphology were observed at 80 K until the doses were more than an order of magnitude greater than those employed for the experiments discussed here.¹³ Thus the change in morphology may play a role in the high-temperature mixing experiments but should not affect those at 6 K.

Whether it is actually the change in morphology that causes the mixing to change with temperature, or whether it is some diffusion process that causes both the morphology and the mixing to change, is not known. In this connection we note that our result for the mixing of the Si marker at 80 K is in contradiction with a similar experiment by Clark *et al.*¹⁴ They observed a mixing parameter at 34 K very similar to that observed here at 6 K; however, they observed nearly no mixing at 80 K. We can only surmise that the difference lies in the preparation of the different marker specimens. It is interesting that at the temperature where changes in the morphology begin to occur, specimen quality also appears to become important; this may indicate the onset of thermally induced defect motion.

In summary, we have found that the relative magnitude of mixing of Pt and Si markers in Ge at 6 K strongly contradicts the theory of simple collisional mixing. The 50% difference in the mixing parameter between Si and Pt markers indicates that the chemical nature of the markers may be important to the mixing process. No definite explanation for this effect can presently be given although chemical processes associated with "thermal-spike" induced defect motion are a possibility. The mixing for both markers in Ge increase weakly from 6 to 500 K.

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