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Mössbauer effect of ^{73}Ge in laser-processed Si and Ge crystals

Loren Pfeiffer, T. Kovacs, G. K. Celler, J. M. Gibson, and M. E. Lines
Bell Laboratories, Murray Hill, New Jersey 07974
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The first observation of the 13.3-keV Mössbauer resonance of ^{73}Ge nuclei located at substitutional sites in a single-crystal Si host lattice is reported. Mössbauer sources are made using laser melting to incorporate volatile ^{73}As radioactive parent nuclei into (111) crystals of Si or Ge. Laser-induced diffusion (LID) of As into Si is found to be an order of magnitude more efficient than conventional oven diffusion. Possible lattice damage resulting from the laser processing is studied by ^{73}Ge Mössbauer effect, Rutherford backscattering, and transmission electron microscopy (TEM). With the LID ^{73}As:Si source the Mössbauer resonance is broadened to 118 μm/sec full width at half maximum, of which ~ 106 μm/sec is attributable to the laser processing of Si. Mössbauer evidence indicates that this broadening is due not to a distribution of isomer shifts, but to an electric field gradient (EFG) induced at most Ge daughter nuclei by bulk strain. TEM measurements indeed reveal a high density of dislocations. Bond-orbital calculations are reported of the EFG induced at substitutional ^{73}Ge nuclei by deforming the Si host lattice in uniform tension in the plane of the (111) surface. The strains required are as large as the average bulk strain arising in the entire lattice contraction undergone by the Si as it cools from 1412 °C to 20 °C following pulsed laser melting, $\Delta l/l = 0.56\%$. Even with this maximal assumed strain the calculated broadening is insufficient to fully account for the observed effect if the unknown ^{73}Ge 13.3-keV nuclear quadrupole moment Q_e is near zero. Assuming maximal strain, the ^{73}As:Si data allow us to estimate the value $Q_e = -0.4(3)$ b for this moment. In addition, with simple scaling we are able to account for the EFG observed in two other independent ^{73}Ge Mössbauer experiments involving stressed lattices. In one of these the strain deduced from Mössbauer broadening was directly confirmed by x-ray diffraction.

I. INTRODUCTON

A comparison of the Mössbauer resonances of ^{73}Ge nuclei at substitutional sites in single crystals of Si and Ge has long been a goal for ^{73}Ge Mössbauer spectroscopy.[1,2] The close similarity of the tetrahedral bonding and structure of these two diamond lattices holds the promise of an eventual first-principles calculation of the detailed differences in electronic bonding to the two lattices, which would lead to predictions for the expected Mössbauer isomer shift between the two hosts.

Until this work, however, no ^{73}Ge:Si Mössbauer experiment has succeeded, because of the difficulty of diffusing the ^{73}As parent radioactivity into a Si lattice with sufficient efficiency to make a useful ^{73}As:Si Mössbauer source. A film of ^{73}As on Si invariably evaporates during a furnace anneal (even if capped with a closely fitting SiO_2 wafer) before more than about 1–2 % of the ^{73}As is diffused into the Si lattice. In this paper we report a useful laser-melting method[3] for incorporating ^{73}As into the lattice of Si. The method can readily be extended to other valuable but volatile dopants and other high-melting-point hosts. For ^{73}As:Si the laser method relocates as many as 80% of the ^{73}As atoms from a surface film to substitutional sites in a Si host crystal. The unique benefits of laser-induced diffusion (LID) are accompanied, however, by concerns that the laser processing introduces some damage to the host lattice.

The main emphasis of this paper is to address this issue of laser-processing damage. After describing the LID method we will discuss Rutherford backscattering (RBS), Mössbauer effect, and transmission electron microscopy (TEM) experiments which allow us to assess the extent and nature of the laser damage. We will then describe a bond-orbital calculation which relates the strain in a deformed Si lattice to the electric field gradient (EFG) expected at a ^{73}Ge nucleus site. Next we give a simple model of how a maximal strain due to differential thermal contraction could be introduced during laser processing. We then relate the EFG-strain calculation to the Mössbauer data and are able to use our maxi-

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mal strain model to estimate the value of the electric quadrupole moment of the 13.3-keV ^{73}Ge nuclear state from the data. The last section contains conclusions and applications of our model to several independent experiments involving strained lattices, which confirm its validity.

II. METHOD OF LASER-INDUCED DIFFUSION

The ^{73}As radioactivity (half-life 80 d, initial strength 110 mCi) was obtained from the reaction ^{74}Ge$(p,2n)^{73}$As by bombarding a 0.27-g/cm^2 natural Ge target with protons at 50 μA for 50 d at the Brookhaven linear isotope producer.[4] The targets were aged for 100 d to allow the 19-d—half-life ^{74}As from ^{74}Ge(p,n) to decay and were then dissolved in a 3:1 HCl:HNO_3 solution. The solution was then slowly brought to 110 °C and additional 10:1 HCl:HNO_3 solution was added to make up for evaporation. This procedure volatilized the 5 g of Ge as $GeCl_4$ over 4 d (as monitored by the several millicuries of ^{68}Ge produced during the bombardment), leaving the ^{73}As behind in the HNO_3 solution as As^{5+}. The ^{73}As radioactivity was separated from the several millicuries of ^{65}Zn produced during the bombardment and from the remaining solid residues by an arsine evolution procedure in a Marsh apparatus.[5] The As:HNO_3 solution was taken to near dryness, added to 1.5 ml of H_2SO_4 and fumed for 15 min to volatilize the HNO_3. Water was added to bring the solution to 5 ml, and this was added to a vessel of the Marsh apparatus containing 5 g of Zn granules at 100 °C. When the acid and Zn were combined, the gases AsH_3 and H_2 were immediately formed and carried along with the purge gas N_2, through a Dryerite moisture trap and a 0.5-μm mesh filter, to a furnace maintained at 1000 °C with an exit tube ~70 cm long. The AsH_3 was decomposed in the furnace producing a high-purity ^{73}As coating on the 3-mm-diameter inner surface of the exit tube. The ^{73}As coating was dissolved in 10:1 H_2O:HNO_3, brought to dryness, and redissolved in a few microliters of water or HF. This solution was then dropped onto the surface of the host Si or Ge crystal and dried to form an ^{73}As coating 3 mm in diameter.

At this stage the samples were ready for laser diffusion. To eliminate possible radioactive contamination of the laser laboratory, the ^{73}As coated samples were placed in a small stainless steel chamber 5 mm deep and sealed with a Suprasil quartz cover. The chamber was then evacuated, backfilled with Ar gas and sealed. Laser irradiation was carried out with a frequency-doubled *Q*-switched Nd-YAG (yttrium aluminum garnet) laser beam at 532 nm focused through the quartz cover to a 40-μm-diameter spot on the sample. The laser was pulsed at a 2000-Hz rate, with individual pulses 125 nsec long. The sample along with the entire chamber was moved in a raster scan pattern in 10-μm steps between pulses so that a sample area 4×4 mm^2 centered on the ^{73}As coating was laser irradiated.

In Ref. 3 we showed for a given host material that the As incorporation efficiency increased directly with increasing laser-power density (until cratering of the host occurs), with increasing numbers of rescans of the laser (up to about eight), and with increasing initial purity of the As surface coating. We also found, comparing Ge and Si hosts, that the power required for a given laser-doping efficiency scales as one would expect with the melting point of the host. Based on this information the Mössbauer and test sources of ^{73}As:Si were laser scanned at 8.0 J cm^{-2} for four to six raster repeats, and the ^{73}As:Ge sources scanned in four repeats at 3.2 J cm^{-2}. We note that even single-scan laser-energy densities used here are 3$\times$ higher than those typical in laser annealing. Therefore, we might well expect to see significantly more lattice damage than is commonly observed in other laser-processing work, particularly after multiple laser passes.

III. RBS, MÖSSBAUER, AND TEM ANALYSIS

A sensitive measure of the quality of the As incorporation in Si is given by the Rutherford backscattering and channeling spectra shown in Fig. 1. This test sample was prepared by laser irradiating a Si(111) sample coated with 6×10^{16} As atoms/cm^2 of which 1% were the radioactive tracer ^{73}As. The laser incorporation efficiency was 18% resulting in a total laser doping of 1×10^{16} As atoms/cm^2. From the spectra one calculates the channeling to random backscattering ratios $\chi_{\min}(\mathrm{Si})=0.037$ and $\chi_{\min}(\mathrm{As})=0.05$, which allow[6] the calculation

$$\frac{1-\chi_{\min}(\mathrm{Si})}{1-\chi_{\min}(\mathrm{As})}=0.987$$

for the fraction of As atoms located on Si substitutional sites. From the As and Si RBS data in the nonchanneling direction we find[6] that the As doping level is 0.11 at. % and that the As atoms are distributed uniformly from the Si front surface to a depth of more than 8500 Å. Another backscattering spectrum of this sample taken using 3.0-MeV ^{4}He shows that the As laser doping is approximately uniform to more than 1.7 μm. This diffusion depth, larger than ever reported in laser-annealing experiments, results from the very-high-energy densities and the multiple scans. Nevertheless, the RBS channeling experiments reveal no extensive damage to the Si during laser processing, and they show further that

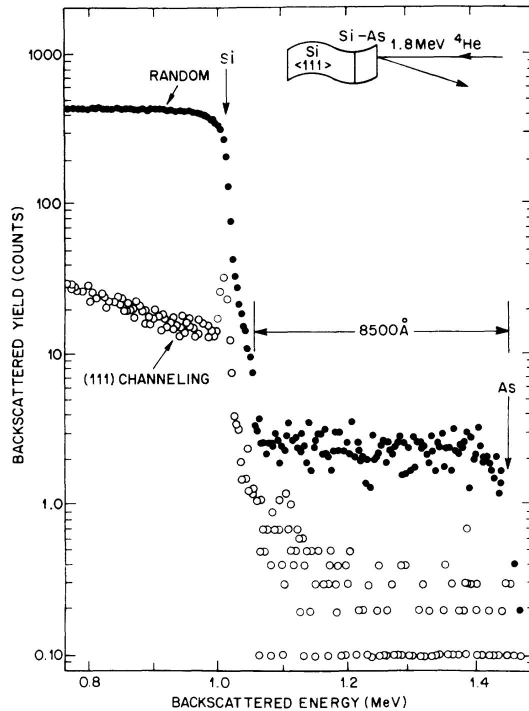

FIG. 1. Rutherford backscattering and channeling spectra using 1.8-MeV ^{4}He ions incident on a Si(111) crystal which was coated with 6×10^{16} As atoms/cm^{-2}, and then laser scanned as described in the text at 8.0 J cm^{-2} for six complete raster scans.

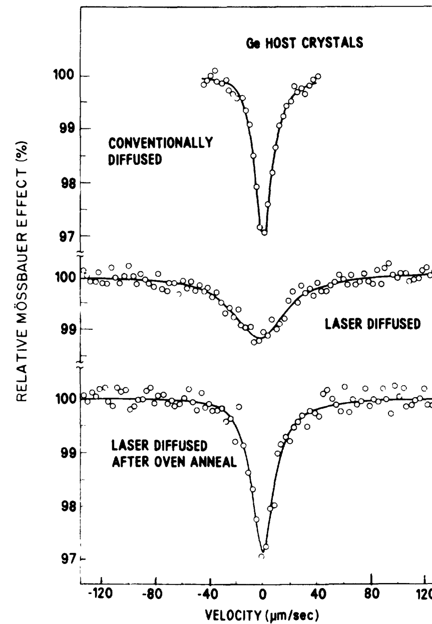

FIG. 2. High-resolution ^{73}Ge Mössbauer spectra of ^{73}As sources diffused by various procedures into Ge(111) host crystals. All spectra were taken with the same enriched absorber crystal of ^{73}Ge. This absorber is known (Ref. 2) to broaden the Mössbauer resonance to 16 μm/sec FWHM for an unbroadened source. Top curve: ^{73}As diffused into a Ge(111) crystal by conventional furnace anneal at 850 °C. Resonance linewidth 15.6(6) μm/sec FWHM, line position $+0.3(3)$ μm/sec. Center curve: ^{73}As diffused into a Ge(111) crystal by Nd:YAG laser at 3.2 J cm^{-2} in four raster scans. Resonance linewidth 48(4) μm/sec FWHM, line position $-0.5(9)$ μm/sec. Bottom curve: The same laser-diffused ^{73}As in Ge crystal source used to obtain the center spectrum, but after a subsequent oven anneal in flowing Ar gas at 850 °C for 15 min. Resonance linewidth 19(2) μm/sec FWHM, line position $+0.3(5)$ μm/sec.

the laser melting relocates the As atoms to substitutional Si sites at a uniform density well below the As:Si solid solubility limit.

The Mössbauer data taken with laser-diffused ^{73}As sources in Si and Ge reveal a rather different picture. In the upper portion of Fig. 2 we compare the ^{73}Ge Mössbauer spectra of a conventionally diffused ^{73}As:Ge oven source with the middle spectrum obtained with a similar ^{73}As:Ge laser-diffused source. The total area of the two resonances is about the same, but the resonance obtained with the laser-processed source is broadened by a factor of 3 over the conventional source. This broadening is clear evidence that the laser processing damaged the local environment of the ^{73}Ge daughter atoms. The lower spectrum of Fig. 2 demonstrates that a 15-min oven anneal at 850 °C is enough to remove this damage.

In Fig. 3 we report the first ^{73}Ge Mössbauer spectra employing a Si host crystal. In these experiments we find similar laser-induced damage and thermal healing effects as were found for Ge host crystals. The upper spectrum which was taken using a ^{73}As:Si source directly after LID reveals a single strongly shifted resonance line broadened to 118(23) μm/sec full width at half maximum (FWHM) over the 16 μm/sec width expected for an unbroadened source. The lower spectrum taken after annealing the above ^{73}As:Si source for 15 min at 1180 °C shows a sharper and deeper resonance at the same shift now broadened to only 49(11) μm/sec FWHM. The Mössbauer evidence suggests that the laser-induced ^{73}As diffusion damages the Si lattice also, and that this damage is at least partially healed by the subsequent oven anneal.

It is possible to make some conjectures about the nature of the laser-induced damage by noting the following: (i) the Si RBS channeling experiments reveal no damage to the Si lattice, and show that the ^{73}As parent and thus the ^{73}Ge daughter atoms are on

substitutional Si sites; (ii) the isomer shift between the Si and Ge hosts that we report in Fig. 3 is more than 100 natural ^{73}Ge linewidths, which is very large indeed, implying that any defect or vacancy near the ^{73}Ge atom would probably shift the Mössbauer resonance line drastically; and (iii) in both the Si and Ge source experiments the area under the Mössbauer resonance is not changed and the resonance positions are not shifted despite the substantial sharpening of the resonance width after the laser damage is oven annealed. These observations suggest that the resonance broadening associated with the laser damage is not likely due to a distribution of inequivalent sites of a slightly varying isomer shift. This follows because (i) and (ii) suggest that a distribution of distinct sites with closely spaced isomer shifts is unlikely, and (iii) adds the additional constraint that the closely spaced isomer-shift distributions for both Ge and Si must sharpen up exactly symmetrically about their centers as the result of the subsequent oven anneal.

On the other hand, the experimental facts do appear to be consistent with the proposals that (a) the laser-induced diffusion process succeeds in incorporating the ^{73}As dopant deeply because the host crystal is actually melted deeply by the laser, allowing the As to rapidly diffuse in the melt, that (b) strains in the host lattice are introduced during the rapid refreezing of this ^{73}As doped melt, and that (c) these strains in the host lattice induce a nonzero electric field gradient (EFG) at each daughter ^{73}Ge nucleus, which broaden the subsequently observed Mössbauer resonance through the ^{73}Ge electric quadrupole hyperfine interaction. With the use of the same logic as before it is unlikely that the required strain is local to each ^{73}Ge site as might result from a nearby defect bound to the parent ^{73}As, because in that case the Mössbauer resonance undoubtedly would also experience a large isomer shift due to the defect, and any such shift would be expected to change markedly in any subsequent anneal sufficiently potent to reduce the local EFG by a factor of 2 or more.

The transmission electron micrographs shown in Fig. 4 give an explicit picture of the strains introduced by laser processing. The upper micrograph is a part of the same ^{73}As:Si sample after LID which gave the RBS data of Fig. 1. The dark lines are dislocations introduced by laser processing. Unprocessed Si shows no dislocations. From the micrographs we estimate the density of dislocations in LID ^{73}As:Si to be 11(4) dislocations/μm^2. The lower micrograph is another part of the same ^{73}As:Si LID sample after an additional oven anneal at 1180 °C for 15 min. The density of dislocations is reduced by the oven anneal to 4(1) dislocations/μm^2. The density of dislocations is not homogeneous due to the overlapping of many laser-melted regions. The estimates quoted were made using areas believed to be typical.

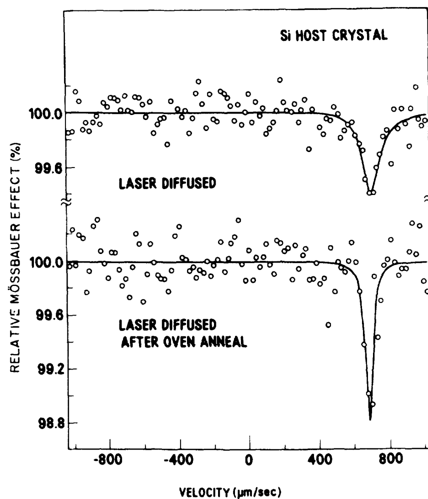

FIG. 3. Top curve: High-resolution ^{73}Ge Mössbauer spectrum of ^{73}As activity laser diffused at 8.0 J cm^{-2} into a Si(111) crystal as described in the text. This source was Mössbauer analyzed with the same enriched single crystal of ^{73}Ge used for the data of Fig. 2. Resonance linewidth 118(23) μm/sec FWHM, line position + 700(13) μm/sec. Bottom curve: Same source, absorber, and experimental conditions as in upper spectrum except laser-diffused ^{73}As:Si source subjected to subsequent oven anneal at 1180 °C in flowing Ar for 15 min. Resonance linewidth 49(11) μm/sec FWHM, line position 685(4) μm/sec.

IV. BAND-ORBITAL CALCULATION OF STRAIN-INDUCED EFG

We have proposed that the broadening observed in Figs. 2 and 3 is due to an EFG induced by a bulk strain arising during the rapid cooling following laser diffusion. The dislocations shown in Fig. 4 confirm that the laser-processed lattices are indeed strained. We now discuss a calculation that relates a strain and its induced EFG at a ^{73}Ge site. From the bond-orbital theory of Harrison[7] one can establish that the charge transfer between Ge and Si sp^3 orbitals at a Ge site is small to the extent that the electric field gradient $V_{zz}=eq$ at such a site results almost entirely from the Ge ligand orbital contribution, with any lattice contribution from neighbor Si sites being negligible. From Lines[8] we therefore expect the EFG at a Ge site to be

$$eq=\tfrac{1}{2}D(1+r)\langle 3\cos^2\theta_b-1\rangle e \ , \qquad (1)$$

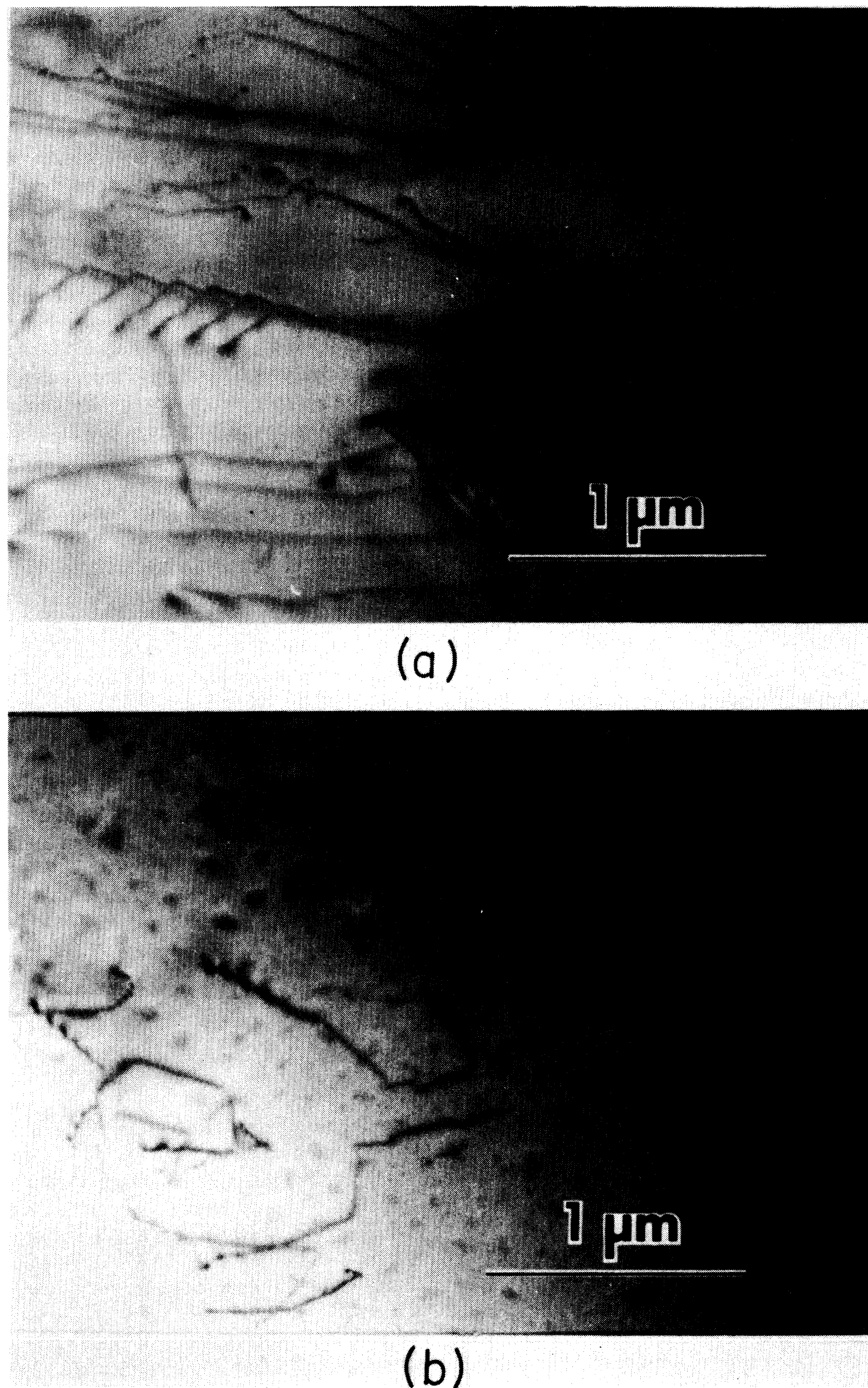

FIG. 4. Transmission electron micrographs of areas thinned to less than 2 μm of the same ^{73}As:Si LID sample used to take the RBS data of Fig. 1. (a) ^{73}As:Si sample directly after LID processing. (b) Another part of the ^{73}As:Si sample after LID processing with, in addition, a 15-min oven anneal at 1180 °C. These micrographs are intended to correspond to the samples used to obtain the upper and lower Mössbauer spectra of ^{73}As:Si in Fig. 3.

where $r=0$, θ_b is a ligand-bond angle, and D is a parameter which varies as $\langle 1/R^3 \rangle$ measured over sp^3 hybrids and is known to have values[8] 7.6 Å^{-3} for Cu and 13.2 Å^{-3} for Ga. Since $\langle 1/R^3 \rangle$ varies smoothly and monotonically[9] for equivalent orbitals as one progresses along row 4 of the Periodic Table, simple extrapolation suggests that $D \sim 16$ Å^{-3} for Ge.

Consider a strain $\delta = \Delta l / l$ uniform in the plane perpendicular to the (111) tetrahedral axis. When $\delta = 0$, taking (1,1,1) as the z=axis, the four bond angles are 0, θ_0, θ_0, and θ_0 where $3(3\cos^2\theta_0 - 1) + 2 = 0$ (by symmetry). This gives $\cos\theta_0 = -\frac{1}{3}$. If the Ge—Si bond length remains fixed during the strain δ, then the strained bond angles are 0, θ, θ, and θ where, (see Fig. 5) to first order in δ,

$$\cos^2\theta = \frac{1-16\delta}{9} \ .$$

It follows that

$$3\cos^2\theta_b - 1 = \frac{2+3(3\cos^2\theta - 1)}{4} = \frac{1}{4}\left[2+3\left[\frac{-2-16\delta}{3}\right]\right] = -4\delta \ , \quad (2)$$

from which we deduce, in units of Å^{-3} and cm^{-3}, respectively,

$$|eq| = 2D\delta e \text{ or } |eq| = 32\times 10^{24} |\delta e| \ . \quad (3)$$

For the ^{73}Ge ground state the quadrupole splitting is

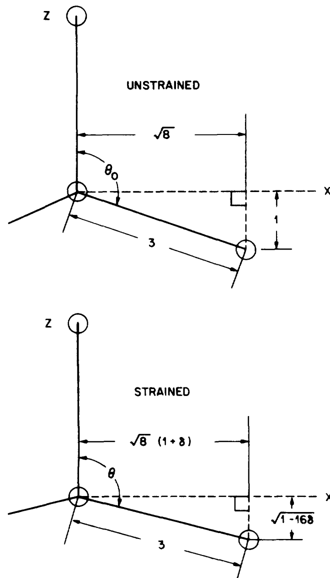

FIG. 5. Geometry used to relate a strain distortion of the Si lattice to an induced EFG at a substitutional ^{73}Ge site.

$$E_Q = \frac{60}{144} |e^2qQ| \ . \quad (4)$$

Noting that $e = 4.8\times 10^{-10}$ esu, 1 μm/sec $= 7.11 \times 10^{-23}$ erg for the 13.3-keV ^{73}Ge Mössbauer transition, and $Q_q = -0.173\times 10^{-24}$ cm^2 for the ^{73}Ge ground-state quadrupole moment[10] we obtain, using (3) and (4),

$$E_Q = 7500\delta \quad (5)$$

in units of μm/sec. Note that the maximum possible bulk strain that can be induced in a Si lattice by rapid cooling of a melt, from 1412 °C where the solid is formed to 20 °C, is just the total lattice contribution $\Delta l / l = 0.0056$. Using this value, we obtain $E_q = 42$ μm/sec for the calculated broadening due only to the ground-state nuclear quadrupole moment. This is of the same order but significantly smaller than the observed 106-μm/sec ^{73}As:Si LID broadening shown at the top of Fig. 3. This discrepancy can be resolved by assuming a nonzero value of the nuclear quadrupole moment Q_e of the 13.3-keV ^{73}Ge state (see Sec. VI). We will see later that this is justified by other data.

V. MODEL OF MAXIMAL STRAIN

The above calculation requires that large internal strains be introduced in the Si lattice during the laser melting to account for the Mössbauer line broadening of Figs. 2 and 3. Here we outline a physical model which makes this plausible. Consider a 125-nsec laser pulse at 532 nm focused to a 40-μm-diameter spot onto an As-coated Si(111) wafer 1 cm^2$\times$0.05 cm thick. For laser pulses of 8 J cm^{-2} energy density we know that the Si locally melts in a cylindrical region $\sim$40 μm across and 2—3 μm deep. We infer from Fig. 1 that the As coating rapidly diffuses throughout this melted region. Because of the speed and brevity of this melting, it is known that all Si several hundreds of microns away from the melted volume is at $\sim$20 °C. The unmelted Si in contact with the melt is of course hot, for instance, $\sim$1200 °C. This hot unmelted Si would expand to a lattice constant characteristic of $\sim$1200 °C, if it were not prevented from doing so by a great compressive stress from the cold crystal below. The brevity[11] of the heating and cooling prevents solid-state slip from relieving this stress in unmelted regions.

Now consider the recrystallization of the melted Si. The crystallization will proceed using the lattice spacing of the stressed solid as a template. Since this spacing is characteristic of the lattice at 20 °C, the resolidifying Si at 1412 °C undergoes a lattice mismatch (of about 0.56%) which it can relieve by introducing occasional missing planes. This is a probable explanation for the dislocations seen in Fig.

4, which would then be of edge character. Indeed, in Si samples which were similarly irradiated with little or no As, this network is very regular and resembles a network of misfit dislocations. Presumably this network is only seen after the extraordinarily high laser doses used in LID because of the long melt duration.

Assuming that the As or some other impurity keeps the dislocations from moving to the crystal surface, it is clear that the maximum strain that such a model would produce is given by the Si lattice contraction in cooling from 1412 °C to 20 °C. The minimal mean strain measured from TEM pictures taken after LID [such as Fig. 4(a)] is $\sim 0.1\%$. If the dislocations are all of the same type and sign as proposed above, we would obtain a value approaching 0.5%.

VI. ESTIMATION OF ^{73}Ge 13.3-keV NUCLEAR QUADRUPOLE MOMENT

The Mössbauer line broadening attributable to Si lattice strain observed in Fig. 3 is 106 μm/sec. The line broadening calculated in Sec. IV for this experiment is 42 μm/sec considering only broadening due to Q_g, the ground-state moment, and assuming the lattice strain is the maximal value due to thermal contraction from the melt. In this section we take the point of view that the strain calculations are correct and the maximal strain model at least provides an upper limit to the actual lattice strain. In this case the data of Fig. 3 allow an estimate of the unknown Q_e.

Figure 6 is a comparison of the data points near the Si resonance line from the upper spectrum of Fig. 3 with the calculated line shape obtained by adjusting the parameter Q_e as needed. The line shape shown gives $Q_e = -0.42 \times 10^{-24}$ cm^2 with $\chi^2/\nu = 65/49(10)$. Constraining the sign of Q_e to be positive gives $Q_e = +0.22 \times 10^{-24}$ cm^2 with a poorer fit $\chi^2/\nu = 78/49(10)$. These values assume the following: (i) Eq. (5) is correct; (ii) $Q_g = -0.17 \times 10^{-24}$ cm^2; and (iii) the Si lattice in the experiment sees a Gaussian distribution of strain of mean value $\Delta l/l = 0.56\%$ and FWHM$=0.28\%$. The error in our estimate is determined by the validity of these assumptions. Nuclear systematics suggest that Q_e is negative[12] and less than 1 b. Our experimental estimate is thus Q_e(13.3-keV ^{73}Ge) $= -0.4(3) \times 10^{-24}$ cm^{-2}.

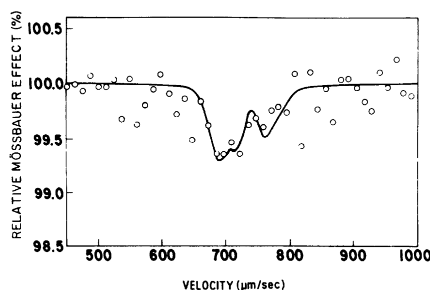

FIG. 6. Comparison of the data points near the ^{73}As:Si resonance line from the upper spectrum of Fig. 3 with the calculated strain EFG broadened line shape obtained by adjusting the unknown free parameter Q_e. The line shape shown requires $Q_e = -0.4 \times 10^{-24}$ cm^2 subject to the assumptions set forth in Sec. VI.

VII. COMPARISON WITH OTHER EXPERIMENTS AND CONCLUSIONS

By specifying the value $Q_e = -0.4 \times 10^{-24}$ cm^2 our strain model can be made to fit well the broadening observed in the upper ^{73}As:Si LID spectrum of Fig. 3 (see Fig. 6). We can extend the agreement to the lower ^{73}As:Si LID spectrum of Fig. 3 taken after the 1180 °C oven anneal by considering the micrographs of Fig. 4. These micrographs show the dislocation density on a ^{73}As:Si LID sample with and without the additional 1180 °C oven anneal. This sample of Fig. 4 was also used to obtain the RBS data of Fig. 1. We made and processed this sample to be as nearly identical as possible with the ^{73}As:Si Mössbauer source used in Fig. 3. Therefore, the upper and lower parts of Fig. 4 are intended to be in exact correspondence with the upper and lower spectra of Fig. 3. Observe that the strain as measured by the dislocation density is reduced from 11(4) dislocation/μm^2 to 4(1) dislocation/μm^2 by the oven anneal. This is in excellent accord with the reduction in strain broadening from 106 to 37 μm/sec found in the corresponding Mössbauer spectra of Fig. 3.

Comparable RBS and TEM data are not available for the ^{73}As:Ge LID experiment of Fig. 2. There is, however, evidence that dislocations move at lower temperatures[13] in Ge than Si, and that Ge cools more slowly[14] to the temperature where dislocations are pinned. Based on these qualitative trends it is not unreasonable that the strain seen in Fig. 2 is smaller than that of Fig. 3, and that the 850 °C oven anneal removes the residual strain.

There is another independent ^{73}Ge Mössbauer experiment in which strain is likely to be causing a large EFG quadrupolar broadening. Figure 7 is a reproduction of the first high-resolution ^{73}Ge Mössbauer spectrum published.[15] Subsequent work[2] has shown that the Mössbauer source used in that experiment was unbroadened, and that all of the resonance broadening observed is attributable to the Mössbauer absorber.

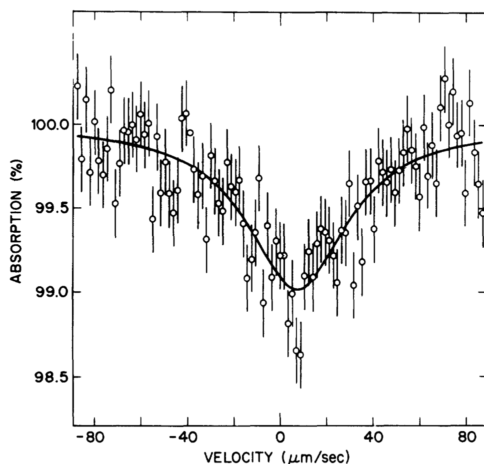

FIG. 7. First evidence for the Mössbauer effect from the 13.3-keV transition of ^{73}Ge. Figure is reproduced from Ref. 15. The Mössbauer absorber was a ^{73}Ge(111) single crystal grown epitaxially at 850 °C on a Si(111) substrate.

The absorber was made[1] by evaporating ^{73}Ge atoms onto a Si(111) crystal substrate held at 850 °C. The deposited ^{73}Ge film was cooled and found to be a Ge(111) crystal epitaxially grown on the Si substrate. The Si:Ge lattice mismatch during growth was probably accommodated by the interaction of edge dislocations at the interface, but upon cooling to 20 °C additional severe strain would be expected from the difference in lattice contraction between the Si and Ge crystals. On cooling from 850 °C to 20 °C, Si contacts by 0.32% and Ge contracts by 0.57%. The resultant 0.25% differential contraction is an upper limit to the bulk strain that could occur in the Ge epitaxial absorber from this mechanism.

The measured width of the Mössbauer resonance in Fig. 7 is 47(7) μm/sec FWHM. Of this about 35 μm/sec is attributable to strain-induced EFG's in the epitaxial absorber. Using the results of Secs. IV–VI to scale the strain effects from the ^{73}As:Si LID experiment allows us to translate this 35-μm/sec broadening into a proposed bulk strain of 0.18%. This is entirely consistent with the Si:Ge differential contraction picture discussed above and suggests that strains due to such differential contraction are frozen in only below about 625 °C.

Bulk strains of 0.18% are large enough to be seen in x-ray scattering experiments. The (3,3,3) diffraction peak from 8-keV Cu x rays on the Ge:Si epitaxial absorber indeed confirms a high strain level. We find an x-ray line broadening corresponding to a Gaussian distribution of strains of 0.23% FWHM. This is an upper limit for the strain because no account was taken of possible small grain size effects which also could produce a broadened diffraction peak. However, the x-ray diffraction results are clearly consistent with the models of lattice strain discussed in this work.

We wish to explicitly note again the ^{73}Ge Mössbauer resonances between a Si source host and a Ge absorber reported in Fig. 3. One is immediately struck by the surprisingly large + 685(4)-μm/sec isomer shift observed for the annealed ^{73}As:Si source compared to the Ge single-crystal absorber. This is by far the largest isomer shift thus far observed in ^{73}Ge Mössbauer spectroscopy. It is so large as to call into serious question our recent[16] calibration of the ^{73}Ge isomer shift. Fortunately, this new measurement itself makes possible an independent isomer-shift calibration. The new calibration will be reported and critically compared with our original calibration in a separate paper planned for future publication.

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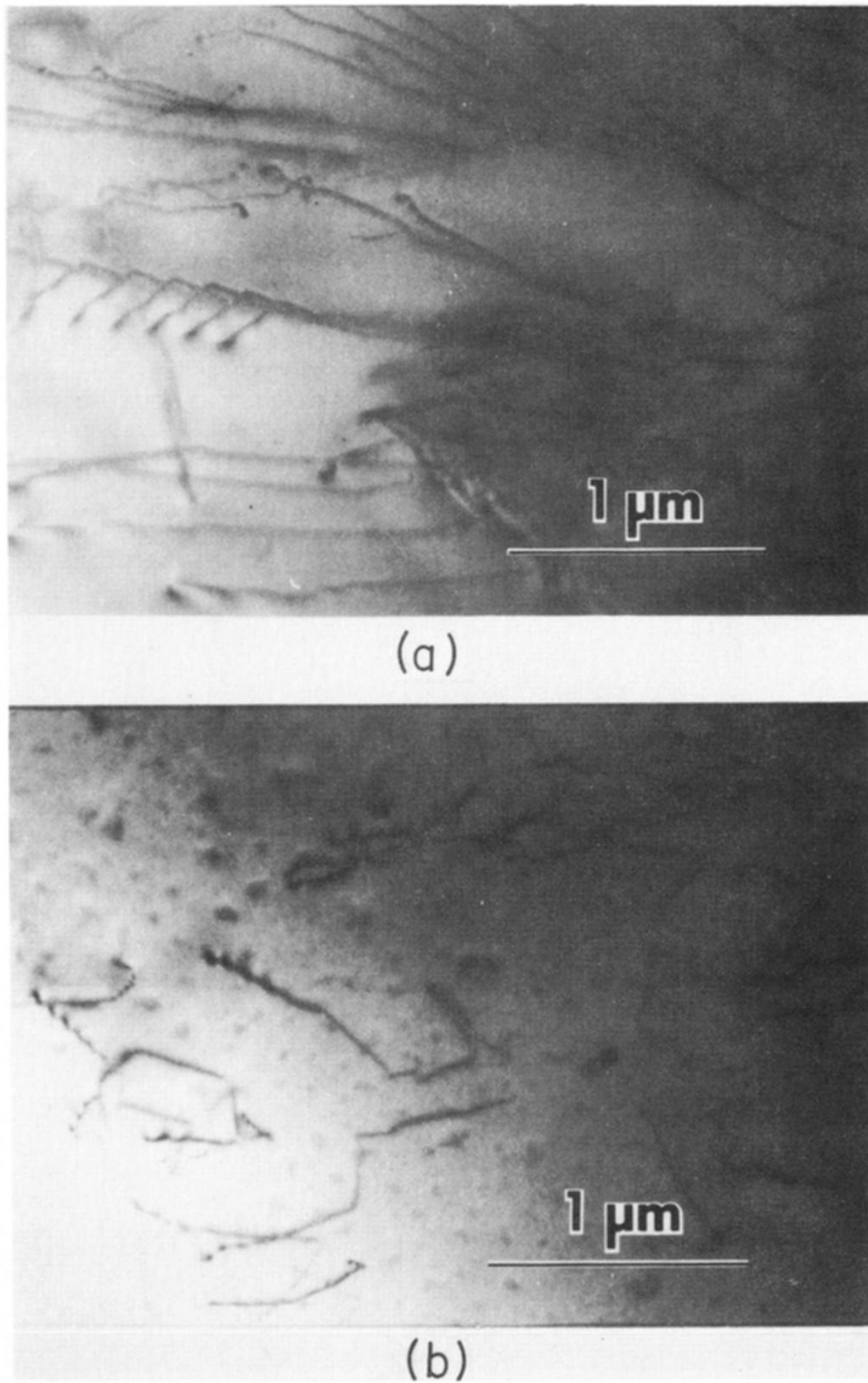

FIG. 4. Transmission electron micrographs of areas thinned to less than 2 μm of the same ^{73}As:Si LID sample used to take the RBS data of Fig. 1. (a) ^{73}As:Si sample directly after LID processing. (b) Another part of the ^{73}As:Si sample after LID processing with, in addition, a 15-min oven anneal at 1180 °C. These micrographs are intended to correspond to the samples used to obtain the upper and lower Mössbauer spectra of ^{73}As:Si in Fig. 3.