Self-Diffusion in Tellurium. I. Anisotropy and Impurity Effect

R. N. Ghoshtagore*

Xerox Research Laboratories, Webster, New York

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Volume self-diffusion in high-purity (<1 ppm absolute total impurities) single-crystal tellurium has been determined between 300 and 400°C using Te^{127m} as the tracer. Along [0001], the data can be represented by $D=1.30\times10^2 \exp[(-1.75\pm0.05 \text{ eV})/kT]$ cm^2/sec, whereas $D=3.91\times10^4 \exp[(-2.03\pm0.10 \text{ eV})/kT]$ cm^2/sec represents the data along all the atomically equivalent directions perpendicular to [0001]. Above (300 ± 7)°C, the self-diffusivity is higher perpendicular to the c axis than along [0001]. At lower temperatures, aluminum has been shown to increase, and iodine to decrease, the self-diffusion coefficient of tellurium along both the principal crystallographic directions. The vacancy-formation energy is estimated to be about 1 eV.

I. INTRODUCTION

THE influence of heterovalent substitutional impurities on point-defect equilibria, and hence diffusivities, of elements is fairly well understood in ionic solids.[1] Similar information is sparse and qualitative in covalent semiconductors[2–5] even though general principles are well elucidated.[6–8] From studies of self-diffusivities in p- and n-type Ge[2] and Si[4] a lattice vacancy has been inferred to be an electron acceptor whereas a carbon vacancy in SiC has been found to be a hole acceptor (virtual donor).[3] For a better understanding of diffusion processes such information is invaluable in all elemental and compound semiconductors.

Little attention has been paid to an understanding of point-defect equilibria in the elemental semiconductors of Group VI of the periodic table,[9–11] partly because of their relative unimportance in the semiconductor technology and partly because of the unavailability of well-defined single crystals of these elements. Self-diffusivity studies of the nature performed in Si,[4] Ge,[2] and SiC[3] should be particularly significant for Se and Te, especially because no one has ever been able to change their conductivity types by doping and consequently no information is available on the possible modes of impurity interaction with these host lattices. Again, because of the major difference of the principal crystal structures of these elements (discussed later)

compared to the major cubic semiconductors (Si, Ge, and III-V's), it is difficult to extrapolate the available information on point-defect type in other semiconductors to this group of elements. Some data on the self-diffusivity in doped and undoped single-crystal tellurium samples are presented here as a contribution to an understanding of diffusion processes in this group of elements.

Tellurium crystallizes in hexagonal lattice (trigonal system[12]) with atoms covalently held in spiral chains around the [0001] direction (c axis). Every fourth atom is directly above another atom in the same chain, so that a chain appears triangular on looking along the c axis. The chains are assumed to be bonded to one another by van der Waals–type forces. The distance between the nearest neighbors in any chain (two per atom) is 2.86 Å and that of the adjacent chains (four per atom) is 3.46 Å. This material is also known to respond very easily to mechanical forces and is characterized by a pure edge-dislocation system along [0001] and two pure screw-dislocation systems perpendicular to the c axis crossing at 60° or 30° to each other (along $\langle 11\bar{2}0\rangle$ and $\langle 2\bar{1}\bar{1}0\rangle$).[13]

II. EXPERIMENTAL

Single crystals of pure tellurium (0.3 in.×3 in.) used in this work were Czochralski-grown by R. C. Keezer (now in this laboratory) and one $\frac{1}{3}$ in.×6 in. single crystal was procured from Atomergic Chemetals Company of New York City. All of these single crystals were characterized by 0.65-Ω cm room-temperature resistivity and 2×10^{14} hole concentration at 77°K. But the latter crystal contained about 1100 ppm absolute (ppma) carbon impurity whereas the other two crystals contained <1 ppma total impurities (by spectrographic analysis). The crystals were cut by a wire saw using

* Present address: Fairchild Semiconductor Research and Development Laboratories, Palo Alto, California 94304.

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FIG. 1(a) Concentration profiles of Te^{127m} in single-crystal pure tellurium along [0001]. (b) Concentration profiles of Te^{127m} in single-crystal pure tellurium along $\langle 10\bar{1}0 \rangle$ and $\langle 11\bar{2}0 \rangle$.
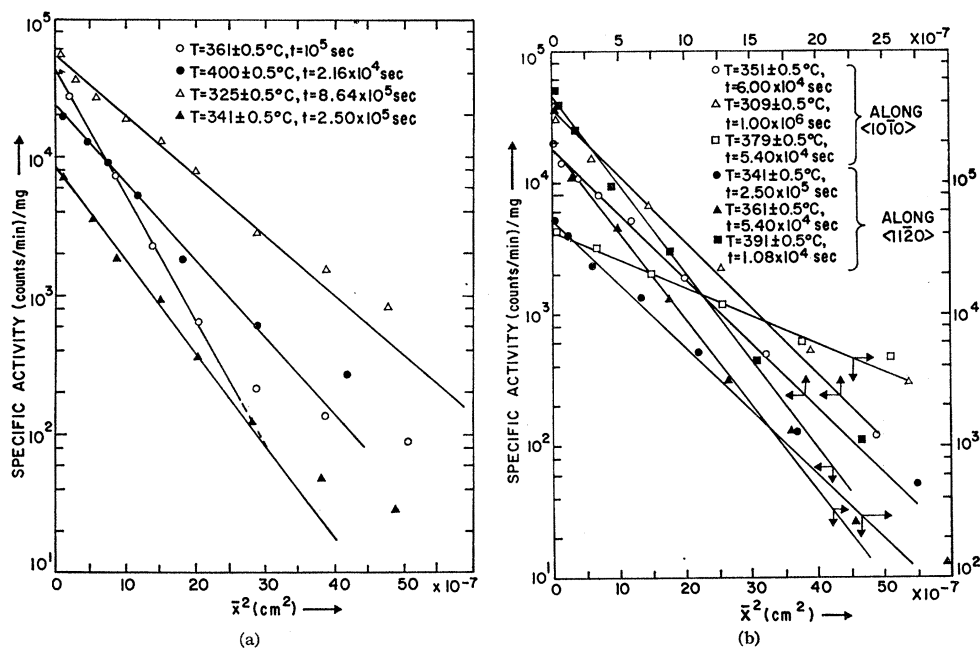
600-mesh SiC abrasive slurry, smoothed on 600-mesh SiC paper, and finished to 2–3-mm-thick wafers (flat and parallel sides) with 0.05-μ Linde semiconductor-grade alumina abrasive. The crystal orientations were determined (to $\pm 1°$) by Laue back-reflection x-ray photographs, their surface area by low-power ($\simeq 12\times$) photomicrography.

The samples were chemically polished at room temperature in chromic acid (1:1:3 = CrO_3:concentrated HCl:H_2O, by weight) at a rate of about 4 μ/min. to remove about 300-μ–deep deformed region formed by the mechanical finishing procedure. An alternative procedure of anodic dissolution in hot concentrated H_2SO_4 (150°C) between platinum electrodes at 1.5 V gave a faster polish and flatter surface. The final dislocation density of the samples determined by etch pit counting[13] was about 10^3 cm/cm^3 for both edge and screw dislocations. A thin film of Te^{127m} ($T_{1/2} \simeq 105$ days) was then electroplated[14] on one surface of the sample from $3N$ HCl solution to about 0.02-μ thickness. The uniformity of the thin film was checked microscopically (500$\times$) and its thickness determined from the change in weight of the sample (to $\pm 10^{-6}$ g). The samples were set face-to-face in a $\frac{7}{8}$-in. diam quartz furnace tube (on a flat quartz plate) and diffusion annealed in a pure argon atmosphere (static). The resistance furnace temperature was controlled to better than $\pm 0.5°C$ by a West stepless digital set-point controller and the temperature measured by Pt–10% Rh thermocouple in conjunction with a Leeds and Northrop potentiometer.

After diffusion anneal each sample was weighed, counted for surface activity, and ground on all sides other than the coated side. The thickness removed was

about 50–100 times the anticipated penetration [$2(Dt)^{1/2}$]. This operation on the edges also helped to remove the rounded area along the edges (produced by chemical etching and polishing). Each sample was then sectioned manually on 2-in.-diam. preflattened stainless-steel planchets (obtained from Tracerlab, Inc.) using measured amounts of Linde 0.05-μ semiconductor-grade alumina slurry (in water). The thickness of each section was determined from the difference in sample weight before and after sectioning. The average thickness removed (2–4 μ) was determined to an accuracy of ± 0.002 μ. The grindings were then uniformly spread on the entire planchet, dried at 60°C and counted (to a maximum accuracy of ± 1.0 count/min) in a flow counter provided with anticoincidence arrangement. Background was maintained below 1 count/min and no self-absorption was observed in controlled experiments.

The same procedure was used with the doped samples. The doping was performed in sealed quartz (G. E. "copper-free") ampules (at 10^{-6} Torr) using 2–3 mm-thick sample wafers at 440°C for 100 days. The dopant concentration was determined by spectrographic analysis. BDH Al_2Te_3 (analytical grade) was used for Al doping whereas 99.9999% iodine (from Atomergic Chemetals Company, New York) was used for iodine doping. No gradient of dopant concentration was detected from the surface to the interior of doped samples (by spectrographic analysis).

III. RESULTS

Some of the concentration profiles of Te^{127m} in pure (<1-ppma total impurities) single crystal along [0001] are shown in Fig. 1(a). Diffusion coefficients calculated from the slopes of these linear profiles using a thin-film

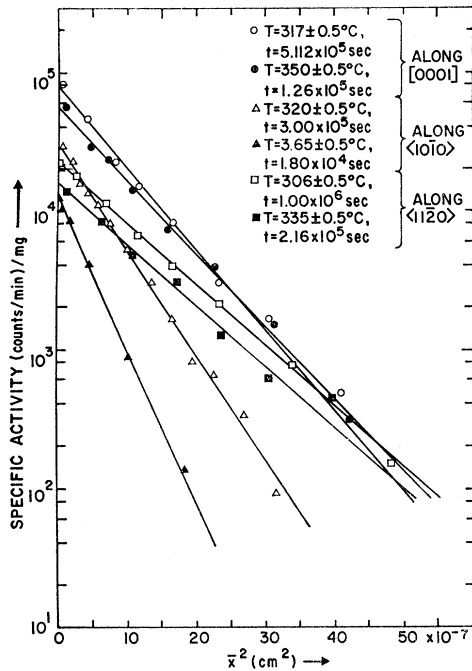[14] A. J. Panson, J. Phys. Chem. **68**, 1721 (1964).

FIG. 2. Concentration profiles of Te^{127m} in 35-ppma Al-doped tellurium single crystals.

boundary-condition solution of Fick's second law (diffusion from an infinitesimally thin layer into a semi-infinite body with a reflecting boundary):

$$C(x,t) = [\alpha/(\pi Dt)^{1/2}] \exp(-x^2/4Dt), \qquad (1)$$

are shown in Fig. 4 as a function of inverse temperature. These data (between 305 and 400°C) along [0001] can be represented by the equation

$$D = 1.30 \times 10^2 \exp\{[(-1.75\pm0.05)eV]/kT\} \text{ cm}^2/\text{sec. (2)}$$

Similar representative concentration profiles of Te^{127m} in the same material along $\langle 10\bar{1}0\rangle$ and $\langle 11\bar{2}0\rangle$ are shown in Fig. 1(b) and the diffusion coefficients calculated from the slopes of these straight lines using Eq. (1) are shown in Fig. 4 as a function of inverse temperature. Between 306 and 390°C they can be described by the equation

$$D = 3.91 \times 10^4$$
$$\times \exp\{[(-2.03\pm0.10) eV]/kT\} \text{ cm}^2/\text{sec. (3)}$$

The representative concentration profile data of Te^{127m} in the 35-ppma Al-doped single crystals along the same two principal crystallographic directions are shown in Fig. 2. Along [0001] the data between 290 and 350°C can be represented by the equation

$$D = 0.81 \exp\{[(-1.44\pm0.02)eV]/kT\} \text{ cm}^2/\text{sec}, \qquad (4)$$

whereas those (between 305 and 380°C) along $\langle 10\bar{1}0\rangle$

and $\langle 11\bar{2}0\rangle$ can be described by the equation

$$D = 3.22 \times 10^2$$
$$\times \exp\{[(-1.74\pm0.08) eV]/kT\} \text{ cm}^2/\text{sec. (5)}$$

The diffusion coefficients described by the Eqs. (4) and (5) are shown in Fig. 4.

Diffusivity of Te^{127m} (between 335 and 415°C) in 16-ppma iodine-doped single crystals along [0001] can be represented by the equation

$$D = 2.94 \times 10^7$$
$$\exp\{[(-2.45\pm0.05) eV]/kT\} \text{ cm}^2/\text{sec}, \qquad (6)$$

whereas the same (between 330 and 400°C) along $\langle 10\bar{1}0\rangle$ and $\langle 11\bar{2}0\rangle$ are described by the equation

$$D = 8.92 \times 10^9$$
$$\times \exp\{[(-2.73\pm0.10) eV]/kT\} \text{ cm}^2/\text{sec. (7)}$$

The representative concentration profiles in these iodine-doped specimens are shown in Fig. 3 and the diffusion coefficients calculated therefrom using Eq. (1) are shown in Fig. 4.

The data in Figs. 1(a) and 1(b) show some tailing at deep penetrations. This effect has been found to be due to the high diffusivity along dislocation cores (even at 10^3 cm/cm^3 concentration).[15] The absence of these tails in Figs. 2 and 3 is presumably due to annealing out of the dislocations during the 100-day diffusion doping at 440°C.

The effects of Al and I impurities at 333°C on the determined diffusion coefficients are shown in Fig. 5 as a function of the impurity concentration (by spectro-
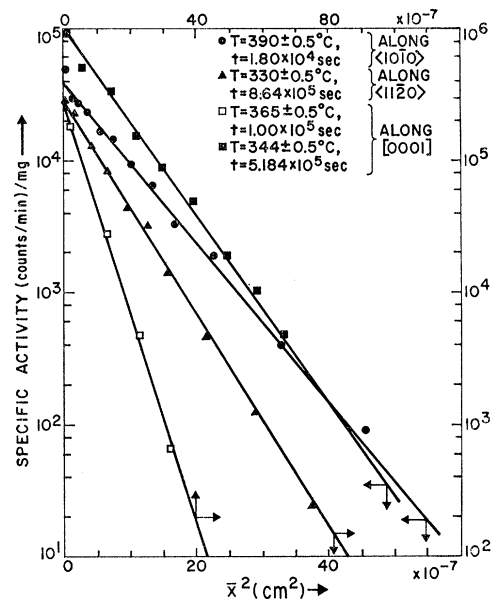

FIG. 3. Concentration profiles of Te^{127m} in 16-ppma I-doped tellurium single crystals.

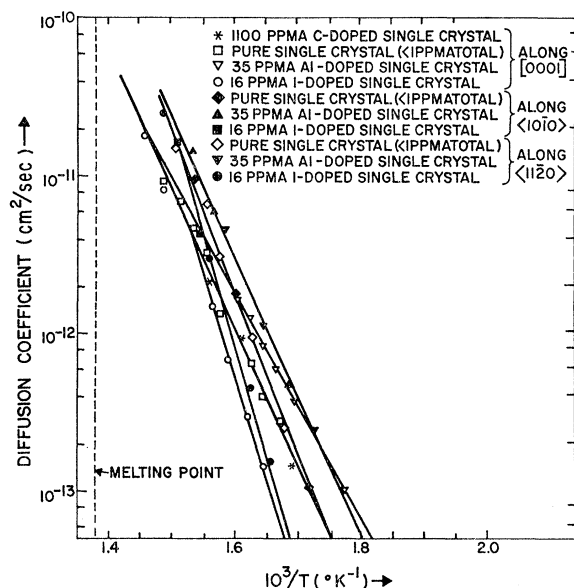[15] R. N. Ghoshtagore, Phys. Rev. 155, 603 (1967).

FIG. 4. Self-diffusion coefficients in single-crystal tellurium as a function of temperature.

graphic analysis). Above about 5-ppma (I) and 18-ppma (Al) impurity concentration the diffusion coefficient is directly (Al) or inversely (I) proportional to the first power of the impurity concentration.

Figure 6 shows the effect of surface oxidation on two concentration profiles. Here the samples were annealed in air (static) instead of in argon. The calculated diffusion coefficients from their slopes fit the data shown in Fig. 4, contrary to the findings of Dyson, *et al.*[16] in a different system.

IV. DISCUSSION

Volume self-diffusivity (at a fixed temperature) in single-crystal tellurium has been found to be higher in lightly Al-doped material and lower in lightly I-doped material than in pure crystals (Fig. 4) along both [0001] and ⟨10ī0⟩ or ⟨11ī0⟩ directions. This can be explained by arguments analogous to those used for Ge[2] even though no change in the conductivity type is known to happen with either Al or I doping. Thus both Al and I seem to go substitutionally into Te lattice sites producing either an excess electron (Al) or an excess hole (I) which in turn changes the concentration of point defects responsible for self-diffusion.[6-8] These observations along with the fact that tellurium lattice vacancies are known to be acceptors[17-19] seem to indicate that self-

diffusion in tellurium occurs by a vacancy mechanism. Consequently, a carbon impurity (probably being in an interstitial position) does not affect the vacancy concentration and hence the diffusion coefficient (Fig. 4).

In any fixed impurity-type and level-controlled (or in the pure) material the difference in the activation energy for volume self-diffusion along the two principal directions [0001] and ⟨10ī0⟩ or ⟨11ī0⟩ in tellurium is found to be (0.30 ± 0.10) eV. Since the impurity effects on the self-diffusivity in Te are identical (both qualitatively and quantitatively) along both of these principal directions (Figs. 4 and 5) this is presumed to represent the difference in the activation energy for the motion of point defects (probably vacancies) along these two directions, i.e., the activation energy for the motion of vacancies is higher by (0.30 ± 0.10) eV along ⟨10ī0⟩ or ⟨11ī0⟩ compared to that along [0001]. This contention is qualitatively supported by the fact that the nearest-neighbor distances are greater along ⟨10ī0⟩ or ⟨11ī0⟩ by about 21% (3.45 Å versus 2.86 Å)[12] and there is no chemical bonding between the atoms of the adjacent chains.

For a useful estimate of point-defect formation energy in tellurium the following facts are relevant: (a) At high temperatures the activation energy of formation of acceptors in tellurium (from quenching studies) is about 0.95 eV.[18] (b) From a detailed study of dislocation and grain boundary self-diffusivities (both in pure and doped samples), it has been concluded that the activation energy for the atomic mobility is in the neighborhood of 0.7 eV along the *c* axis and 1 eV perpendicular to it.[15] (c) The ratio of total bond strength
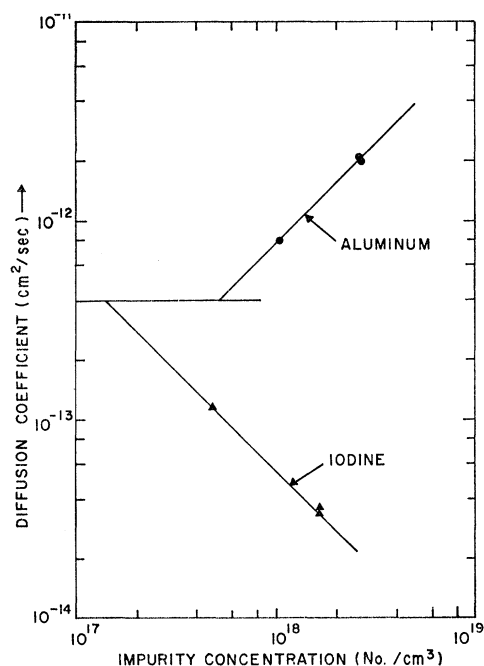

FIG. 5. Self-diffusion coefficients in tellurium as a function of Al or I dopant concentration at 333°C and along [0001].

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● T=380±0.5°C, t=5.40×10⁴sec
Dcal= 4.21×10⁻¹²cm²/sec
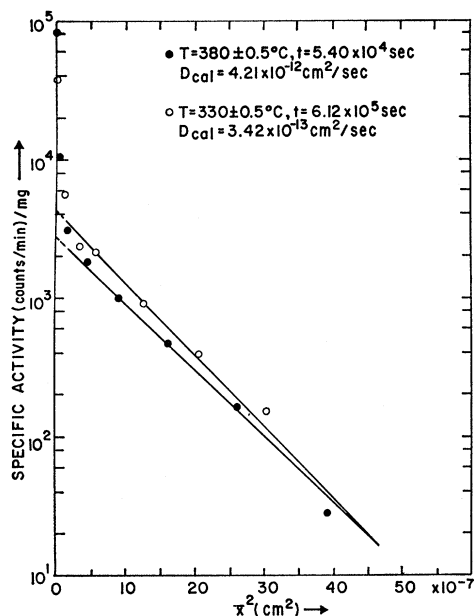
○ T=330±0.5°C, t= 6.12×10⁵sec
Dcal= 3.42×10⁻¹³cm²/sec

FIG. 6. Concentration profiles of Te^{127m} in pure single-crystal tellurium annealed in air along [0001].

and energy of formation of a vacancy in Ge is 3.06 whereas single-bond strength in tellurium is 33 kcal/mole.[20] (d) It is assumed that the same mechanism of self-diffusion is operative in all crystallographic directions in tellurium. The impurities in dilute solution only change the activation energy of formation of point defects whereas the activation energy for the motion of these defects is fixed by the host lattice (i.e., interatomic distance, crystal structure, bond strength, etc.) (e) From the present work the activation energy of self-diffusion in single crystals is 1.75 eV along [0001] and 2.03 eV along ⟨11$\bar{2}$0⟩ or ⟨10$\bar{1}$0⟩. It seems reasonable therefore to estimate that the activation energy of formation of lattice-point defects (vacancies) is about 1 eV in tellurium.

In contrast to the usual form of anisotropy of diffusion in other solids self-diffusion coefficients in two perpendicular directions in tellurium get further and further apart at higher and higher temperatures [above $(300\pm7)°C$]. This can, however, be visualized by looking at the change in lattice parameters in Te as a function of temperature.[21,22] The jump distance perpendicular to the c axis (proportional to the a parameter) increases with temperature whereas the reverse is true for the jump distance along the c axis (proportional to the c parameter). This temperature of $(300\pm7)°C$ is also considered to be the cross-over temperature for the vacancy mobilities along the two principal per-

pendicular crystallographic directions. This has also been observed for Tl diffusion in pure Te.[23]

Among the pre-exponential factors (D_0) expressed by Eqs. (2) to (7), those in Eqs. (4) to (7) describe extrinsic processes and consequently, so far as is known at present, do not have any fundamental significance. Moreover, as shown in Fig. 4 these extrinsic processes do change at higher temperatures to either of the intrinsic processes described by the Eqs. (2) and (3). Wert and Zener's[24] theory of D_0 extended to vacancy diffusion[25] gives

$$D_0 = d^2\nu \exp(\Delta S/R), \quad \nu = k\Theta/h, \qquad (8)$$

where d is the lattice parameter, ν is the vibration frequency of the diffusing atom, ΔS is the activation entropy of diffusion, Θ is the Debye temperature, k is Boltzmann's constant, and h is Planck's constant. In the absence of suitable values of the required parameters necessary for the independent calculation of ΔS, the experimental values of D_0 will be used to calculate ΔS for self-diffusion in tellurium. For tellurium, d (c axis) $= 4.4565$ Å, d (a or b axis) $= 5.9268$ Å[26] and $\Theta = 129°K$.[27] Thus, for diffusion along [0001] $\Delta S/R = 6.06$ and for diffusion along ⟨10$\bar{1}$0⟩ or ⟨11$\bar{2}$0⟩ $\Delta S/R = 10.63$. These values of $\Delta S/R$ for self-diffusion in tellurium are much higher than those observed in pure metals. But, as expected, they are positive.

V. CONCLUSIONS

Volume self-diffusivity in tellurium appears to proceed by a vacancy mechanism in much the same manner as in germanium.[2] The effects of impurities like Al and I are also as predicted from general principles[6-8] and as has been observed in Ge[2] and Si.[4] The anisotropy of diffusion along the two principal crystallographic directions (parallel and perpendicular to the c axis) has been shown to result in higher entropy of activation along ⟨10$\bar{1}$0⟩ and ⟨11$\bar{2}$0⟩. Above $(300\pm7)°C$ the D values are higher along ⟨10$\bar{1}$0⟩ and ⟨11$\bar{2}$0⟩ than along the c axis. This is presumed to be due to higher activation energy for mobility of point defects perpendicular to the c axis. At 333°C the self-diffusion coefficient along the c axis is increased by Al and decreased by I proportionally to the impurity concentration (above about 5 ppma with I and 18 ppma with Al). The energy of vacancy formation in tellurium is estimated to be about 1 eV.

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