Technical Papers

The Effect of Neutron Bombardment on the Low Temperature Atomic Heat of Silicon

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Experiments at Purdue with 10 mev deuterons and at Oak Ridge with fast neutrons have indicated that irradiation produces both electron and hole traps in silicon, since both *N*- and *P*-type materials become very poorly conducting (resistivities as high as 250,000 ohm-cm have been reached in this way). Thus a result of the lattice disorder (vacant sites and interstitial atoms) produced by elastic collisions is the removal of free carriers (*1, 2*). Since annealing at 450° C restores the initial conductivity, it appears to remove the electron and hole traps and to release the trapped carriers; hence, any electronic (or hole) contribution to the atomic heat at very low temperatures should be decreased by bombardment and then restored by annealing at elevated temperatures.

The lattice contribution to the atomic heat at very low temperatures should also be sensitive to bombardment because of the dependence of the thermal vibrations on the interatomic forces, which in turn are affected by the disordering of the lattice (*3–5*). This has been known for some time from the investigation of the specific heat of the so-called metamict crystals (*6*), in which the bombardment is produced by radioactive inclusions in the lattice.

In order to see whether such changes could be observed experimentally, the atomic heat of a silicon ingot[4] was measured before and after exposure to about $5 \times 10^{18}/\text{cm}^3$ neutrons in the nuclear reactor at Oak Ridge. The sample was then annealed at several temperatures up to 780° C (Table 1), being held at each temperature for the time indicated, and then cooled at about 10° C/hr. Its heat capacity below 5° K was measured after each heat treatment.

The experimental method was similar to that of Nernst and Eucken (*7*) and has been described in detail elsewhere (*8*). At very low temperatures, the contribution of the lattice to the atomic heat will be given by (*9*)

$$1944(T/\theta)^3 = \alpha T^3 \text{ J/mole degree,} \quad (1)$$

where θ is the Debye temperature. The contribution of the carriers can be written (*10*)

$$1.62 \times 10^{-12} V n^{1/3} \mu T = \gamma T \text{ J/mole degree,} \quad (2)$$

where V is the atomic volume, n is the carrier concentration per cm^3, and μ is the ratio of carrier mass to electron mass. Other evidence indicates that this ratio is about unity for carriers in silicon (*11*); hence, the total atomic heat should have the form

$$C_v = \alpha T^3 + \gamma T \quad (3)$$

at very low temperatures. We verified this form of temperature-dependence for our data by plotting C_v/T vs. T^2 and observed that the points scattered about a straight line for each run. The slope α and intercept γ were calculated by least squares, and θ (calculated from α using Eq. [1]) and γ are listed in Table 1.

TABLE 1

LATTICE AND CARRIER CONTRIBUTIONS TO ATOMIC HEAT OF SILICON AS A FUNCTION OF BOMBARDMENT AND HEAT TREATMENT

	Run	N	θ (°K)	γ-J/mole degree^2
1	Si II—before bombardment	18	645	13.03×10^{-6}
2	" " " "	33	659	22.51
3	" " " "	35	661	22.51
	Runs 1, 2, and 3 combined	86	658	21.02
4	Si IIB—after bombardment	18	633	1.11
5	" " " "	20	640	1.96
	Runs 4 and 5 combined	38	637	1.55
6	Si IIB(A1)—anneal at 135° C (24 hr)	15	628	−0.91
7	Si IIB(A2)—anneal at 253° C (24 hr)	17	632	0.43
8	Si IIB(A3)—anneal at 472° C (24 hr)	16	628	−2.08
9	Si IIB(A4)—anneal at 455° C (48 hr)	13	637	1.74
	Runs 6, 7, 8, and 9 combined	61	632	−0.03
10	Si IIB(A5)—anneal at 780° C (24 hr)	14	642	13.69

The number of heat capacity measurements made during each run is given in the third column of the table.

The electronic term became very small after bombardment and remained small after the first four anneals. There would appear to be no significant change in the electronic term after any of these treatments, whereas the last anneal restores the original linear term, within the accuracy of our measurements. We attempted to determine n, the carrier concentration, independently from measurements of the Hall constant, but the agreement found with n determined from Eq. (2) (about 10^{18}cm^{-3} before bombardment) is inconclusive, since probe measurements of the large ingot showed it to be very inhomogeneous, with both *N*- and *P*-type regions of high and low conductivity.

The effect on the Debye temperature is not as clear, although it also appears to decrease after bombardment and to rise after the last heat treatment. The initial decrease would imply that the decrease of elastic constants attributable to vacancies predominates over the increase due to interstitial atoms. Dienes' calcula-

[1] Assisted by Signal Corps contract.

[2] Assisted by AEC contract.

[3] We would like to thank D. Finlayson for his measurements of the Hall constant, and L. Roth for the probe measurements and heat treatments.

[4] The ingot weighed about 260 g, and was kindly supplied by G. L. Pearson, of the Bell Telephone Laboratories. Its impurity concentration was not known.

tions for copper and sodium (*3–5*) show that this situation would be favored in an open lattice, such as the diamond structure in which silicon crystallizes.

Our results thus lend further support to the idea that lattice disorder produced by neutron bombardment results in carrier traps in silicon which can be healed out by suitable heat treatment. It also confirms the division of the total atomic heat into two parts, as indicated by Eq. (3), and the identification of the linear term with the contribution of the carriers.

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Note added in proof: Another more homogeneous B.T.L. Si sample (Si V) has been investigated, and the results obtained agree with the results given above: $\theta_{orig} = 658°$ K, $\theta_{bomb} = 636°$ K; $\gamma_{orig} = 34.6 \times 10^{-6}$, $\gamma_{bomb} = 9.26 \times 10^{-6}$. Heat treatment again restores the electronic specific heat.

Insecticidal Effect of Inert Solid Diluents

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It has been known for many years that the inert diluents in insecticide dust mixtures have an influence on the toxicity of these mixtures. Many attempts have been made to determine the governing factors of this phenomenon (*1–3*). The answer is not only of scientific interest, but it is of great importance for insecticide manufacturers too, because it will help to select the most effective diluents.

The killing effect of the inert diluents is more likely to be related to the physical than to the chemical properties of the material.

The first step in this investigation was to locate the diluent particles when dusted onto the insect. It was thought that the smallest particles would enter the body of the insect through the mouth or spiracles and might cause fatal injuries to internal organs or interfere with their function (*4*). The second well-founded alternative, as advocated by Wigglesworth (*5*), claimed that the killing effect was due to an abrasive action on the exocuticle, with subsequent dehydration of the insect.

The diluent was coated with a fluorescent compound, Aesculin, for easier tracing of the small particles.

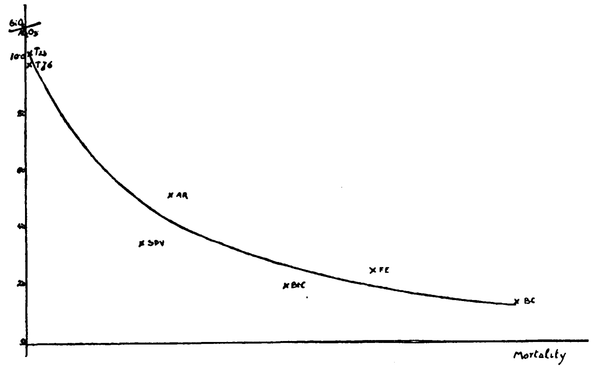

FIG. 1.

After the death of the insects they were examined externally and internally with the ultraviolet microscope, but no evidence could be found for the diluent particles having entered the body of the insects.

It was observed that the death of the larvae treated with coated silicates was retarded somewhat, as compared with insects treated with the same, but not coated diluent. This shows the harmlessness of the fluorescent compound, but no proper explanation could be given for the prolonged survival of the larvae. An agglomeration of smaller, microscopic particles as a result of the coating process is possible, since the diluent treated with distilled water gave similar delaying effect.

It was considered that the shape of the diluent particles or their crystal structure might bear a relation to the mortality of the larvae. Therefore the experiments were extended in this direction. Mexican bean beetle larvae were again used, since the effect of various diluents on the same insect had been already in-

FIG. 2. EMTCO 23 T (T 23). No mortality.