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Correlation of Solubilities of Various Elements in Silicon

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Si is a basic material in modern electronic technology. The performance of Si devices is largely influenced by the properties, the characteristics, and the behaviour in general of the various impurities present unintentionally or on purpose in the Si lattice. On the other hand, the behaviour for example of the metallic impurities in Si depends on their diffusivity and solubility variations as a function of temperature. In this light the study of the solubilities of various elements in Si acquires significant technological interest. From our point of view it is also important for basic knowledge of solid state physics.

It has been argued recently /1/ that for a given process in solids involving defects (for example defect formation, diffusion, solution of impurities, etc.) the corresponding enthalpy h^i and entropy s^i have to be interconnected through the relation

$$\frac{s^i}{h^i} = \frac{\beta B + dB/dT|_p}{B - T\beta B - T(dB/dT)|_p} \equiv F \quad , \tag{1}$$

where β denotes the thermal volume expansion coefficient and B the isothermal bulk modulus of the host material. Thus the microscopic parameters characterizing a certain process are connected to a macroscopic quantity F characterizing the material itself. More specifically, the quantity s^i/h^i depends solely on the bulk properties of the host crystal and it is independent of the various elements which participate in the process.

In the present note relation (1) has been checked for the solubility process of various foreign atoms in silicon. Fortunately enough, because of the importance of this material a large volume of experimental work has been gathered which provides a wide sampling system for the purpose of this note.

The temperature dependence of the solubility of an impurity in a crystal is given by the relation

$$S = S_o \exp(s^i/k - h^i/kT) \text{ cm}^{-3} \quad , \tag{2}$$

where S_o is the density of lattice sites of the host material which for Si is $S_o = 5\times10^{22}$ cm^{-3}. Relation (2) does not hold at temperatures close to the melting point of the crystal. In Table 1 we have collected the solubility parameters published by

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Table 1

Solubility data of various elements in Si

element	h^i (eV)	s^i/k	reference
Ti	3.05	4.2	/2/
Cr^a	2.79	4.7	/3/
Cr^b	2.95	5.4	/4/
Mn^a	2.81	7.3	/3/
Mn^b	2.70	5.9	/4/
Mn^c	2.78	6.9	/5/
Fe^a	2.94	8.2	/6/
Fe^b	2.87	7.3	/6/
Fe^c	3.1	7.9	/7/
Fe^d	3.0	5.53	/8/
Fe^e	2.55	5.7	/5/
Co^a	2.83	7.6	/3/
Co^b	2.99	7.5	/9/
Co^c	2.95	7.2	/5/
Ni^a	1.68	3.4	/3/
Ni^b	3.1	7.6	/10/
Cu^a	1.49	2.4	/4/
Cu^b	1.14	1.87	/5/
C	2.3	4.38	/11/
O^a	1.52	0.59	/12/
O^b	2.3	5.39	/13/
Si	4.5	1.1	/14/, /15/
V	3.6	6.8	/16/
B	0.73	0.62	/17/

various authors /2 to 17/. We should notice at this point that some workers /18, 19/ prefer to report the experimental curve of S = S(T) than (2). It seems imprudent to us to extract s^i and h^i from such curves because of the large errors which might be involved in the values of the seeking parameters in this process. The data have been worked out as cited in the literature without taking into

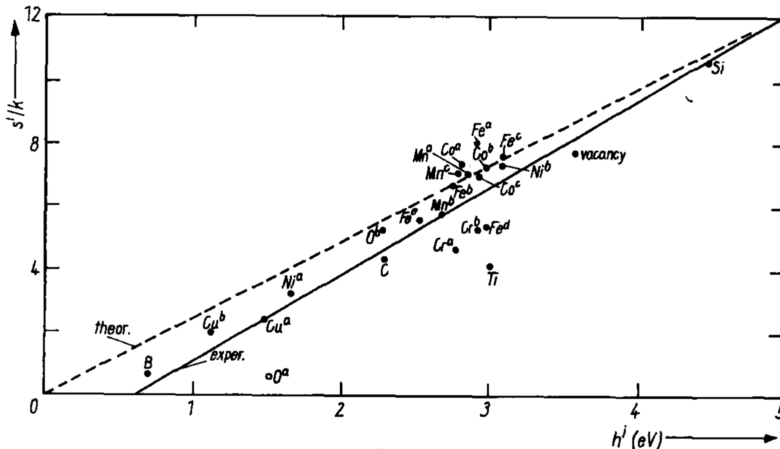

Fig. 1. Plot of s^i/k versus h^i for various impurities in silicon. Letters a, b, c, ... attached as exponents on the symbol of an element indicate in general the experimental results reported by various authors for that element as cited in Table 1

account that the foreign atom may solute interstitially or substitutionally in the host lattice. We have also not considered the effect of the shallow dopant impurity on the solubility of the solute element. In order to improve the quality of our calculations we used in general the most recent results since the improvement of the experimental techniques allows more accurate values to be determined.

A least-squares fitting of s^i/k versus h^i gave a straight line (Fig. 1) with a slope 2.76 eV^{-1}. This value deviates less than 20% from the value of F/k, estimated to about 2.44 eV^{-1} /20/. At present it is not understood why the experimental curve does not cross the 0, 0 point. However, in view of the large scatter of the parameters s^i and h^i reported in literature we regard that the experimental data in general follow remarkably well the predictions of (1). The result acquires special interest since Si is a semiconductor. It shows the wider validity of (1) which could be extended to different classes of solids.

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