Monatshefte für Chemie 136, 1877–1883 (2005)
DOI 10.1007/s00706-005-0381-0

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Thermodynamic Aspects of the Increased Thermal Stability of Silicon by Doping with Transition or Rare-earth Metals

Alexander Ya. Potemkin[1], **Vladimir B. Koltsov**[2,*],
and **Maria G. Vahrameeva**[2]

[1] Moscow State Institute of Aviation (Technical University), 125993 Moscow, Russia
[2] Moscow Institute of Electronic Engineering (Technical University),
124498 Zelenograd, Russia

Received September 12, 2004; accepted March 10, 2005

Summary. The main reason of the degradation of silicon monocrystals at heating is a structural transformation connected with a partial transition of the diamond-like structure into the structure of white tin. The reason for this transformation being observed under high pressures is the appearance of stress zones at the boundaries of variously oriented crystal microvolumes due to heat expansion anisotropy. The high stress concentration in the microvolumes provides sufficient pressure for the indicated phase transformation which results in the observed degradation of the electrophysical properties of silicon. The prevention of the structural transformation is considered to be possible by doping of Si by transition or rare-earth metals which increases the interatomic energy and decreases the thermal expansion coefficient. The choice of the doping additions is based on the bonding energy and the charge density calculated for a system of non-polarised ionic radii. The technology to increase the thermal stability of silicon has been patented[#].

Keywords. Structural transformation; Silicon monocrystals; Thermal stability; Doping; Transition metals; Rare-earth metals.

Introduction

The effort to increase the thermal stability of the electrophysical properties of silicon (electrical conductivity, life time of minority carriers, *Hall* coefficient) exists in practice from the beginning of its use as the basic material of semiconductor electronics [1]. For the elimination of the material's degradation effect after its heating and cooling a special heat treatment – *i.e.*, annealing at a definite temperature followed by slow cooling – is given to the material. Such a heat

---

[*] Corresponding author. E-mail: Koltsov_V_B@mail.ru
[#] Patent of Russia, No 2094904, 13/10/1995

treatment decreases the degradation of silicon, but is insufficient to prevent it completely. Therefore, it is attempted to solve this problem by doping silicon with selected alloying additions. In this work we examine the basic principles of selecting the adequate doping additions in order to increase the thermal stability of silicon.

Theory

The obvious approach for the selection of suitable doping additions is based on the consideration of the reasons which are responsible for the changes in the electrophysical properties of silicon after heating and cooling. The main cause of the degradation at heating is a recently discovered structural transformation [2]. It is known, that at high pressure silicon undergoes polymorphous transformations [3]. *Pirous* [4–6] observed tape-like precipitations of hexagonal Si at the microindentation of diamond-like silicon at temperatures of 400–500°C which were explained by the process of the martensite transformation. Therefore, on heating the centres of strain concentration appear at the boundaries of differently oriented parts of the monocrystal (subgrains, blocks) because of the anisotropy of heat expansion. The high pressures formed in these local parts of the monocrystal induce the precipitation of silicon with white tin structure (high pressure phase). These considerations are confirmed by studies of stressed monocrystals of silicon before and after heat treatment [7]. The formation of the high pressure phase in local parts of the crystal led to the relaxation of stress and it stopped the further growth of precipitations. However, the perfection of the monocrystals after heating and cooling according to the steps of the technological process is found to be strongly disrupted because of the formation of numerous defects in the lattice and the thermodonors [1] which are responsible for the degradation of the electrophysical properties of silicon.

This work is an attempt to solve this problem by doping silicon with selected alloying additions which are supposed to suppress the indicated transformations and, as a result, are believed to increase the thermal stability of silicon. The dissolution of such additions increases the strength of interatomic bonds and thus of the lattice itself. Alloying with such additions results in a decrease of the thermal expansion coefficient and, therefore, lowers the probability of the formation of the high pressure centres which are responsible for the phase transformation. With the help of the non-polarised ionic radii method [8] we examine the basic principles how to select the doping additions which increase the thermal stability of silicon.

Methods

According to the classical theory of chemical structure the electron structure of a compound can be regarded as a result of individual pair interactions superimposed on one another. The combination of such interactions defines a molecular or crystalline compound as a chemical or structural entity. The development of methods to calculate effective charges, z, and the radii, R_i, of the interacting atoms (A, B) as functions of the distance, d, between them is crucial for such studies. Accordingly, a metal-chemistry model of pairwise interatomic interactions was developed. In this model, z_A and z_B are related to the direction of interaction consisting of a spherical ($z_{i\ \mathrm{min}}$) and directional ($\Delta e/2$) component according to $z_A = z_{A\ \mathrm{min}} +$

$\Delta e/2$ and $z_B = z_{B\ \min} + \Delta e/2$ [8]. In order to identify such values, the following system of Eqs. (1)–(3) has to be solved for an assigned d where $R_i^{z_i}$ is the radius of ion i with charge z_i, R_i^0 and tgα are constants typical of the type of atom, and they are tabulated in literature [8].

$$R_A^{z_A} + R_B^{z_B} = d \tag{1}$$

$$\lg R_A^{z_A} = \lg R_A^0 - (z_{A\min} + \Delta e/2)\mathrm{tg}\alpha_A \tag{2}$$

$$\lg R_B^{z_B} = \lg R_B^0 - (z_{B\min} + \Delta e/2)\mathrm{tg}\alpha_B \tag{3}$$

$z_{A\ \min}$ and $z_{B\ \min}$ refer to as individual pair of atoms and can be calculated *a priori* from such tabulated values under the assumption that the interaction is purely ionic (*i.e.*, assuming that $z_A = -z_B$ and the contact is a point contact between spherical ions). The system of Eqs. (1)–(3) is solved using the method of step-by-step approximation, *i.e.*, by fitting Δe so as to satisfy condition (1).

The interpretation of chemical bonding rests on three ideas which are common to classical and quantum chemistry. Their simultaneous fulfilment is the aim of solving the system of Eqs. (1)–(3).

1. It is possible to calculate z_i and $R_i^{z_i}$ separately for every direction of the interatomic interaction in a molecule or a crystal. This permits, in particular, the assessment of the anisotropy of the atom's electron cloud in view of the interaction with the neighbours in the first and second coordination spheres of the compound.
2. The quantities z_i and $R_i^{z_i}$ vary in accordance with d, but they are unique for the fixed interatomic distance defined by the size of bonding atoms (R_i^0). The ionic component of the chemical bond, $z_{i\ \min}$, is a constant for a certain pair of atoms whereas the directional component, Δe, varies. Positive Δe are (in the first approximation) a sign of metallization (a donor bond), whereas negative Δe are a sign of covalency (an acceptor bond). Thus, an important general preassumption of the theory of chemical bonding is used: there are no charges and ion radii in general, but there are their values of z_i and $R_i^{z_i}$ with respect to their actual bonding partners [8].
3. The method of calculating Δe, z_A, and z_B is based on the assumption that interatomic interaction can be interpreted in accordance with the diagram shown in Fig. 1. The condition required for any type of chemical bonding is a smooth joining of the electron densities of the ionic shells of the bonding partners and the transition of a part of their valence electrons from atomic to bonding orbitals (into the shaded zone in Fig. 1). The position of point $\rho_{l\ \min}$ divides d into sections corresponding to the radii of the ions (R_A, R_B) which possess the charges z_A and z_B. The condition $\rho_{l\ A} = \rho_{l\ B}$ is the metal chemistry analogue of the assumption that electrical negativity of interacting ions evens out and of the quantum-mechanical method of "sewing-up" the electron clouds of the reactants.

In the model, $\rho_{l\ i}$ characterizes the "directional" charge density at a distance of $R_i^{z_i}$ from the nucleus and can be identified from Eq. (4) [8].

$$\rho_{l_{\lim R_i^{z+\Delta z} \to R_i^z}} = \frac{\Delta z}{R_i^{z+\Delta z} - R_i^z} = \frac{0.434}{R_i^z \cdot \mathrm{tg}\alpha} \tag{4}$$

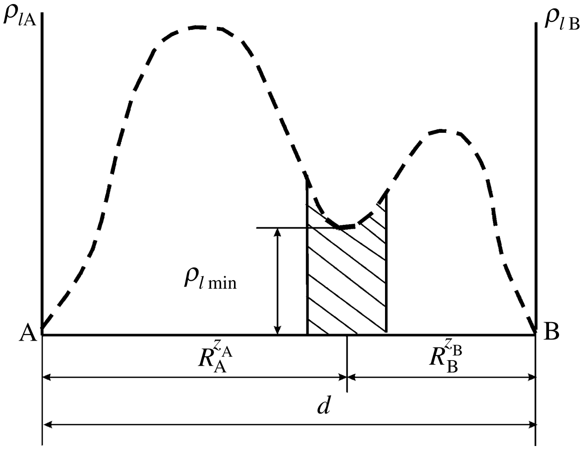

Fig. 1. Diagram of directional interatomic interaction

Distribution of Impurities in Semiconductors

It is known that the properties of semiconductors are highly sensitive to impurities. Moreover, the influence of impurity atoms is not limited to local region, but it is propagated on the entire lattice of semiconductor. For understanding the nature of this sensitivity it is important to establish the factors, which influence the arrangement of impurity atoms in the lattice. From the difference in the mechanism of dissolution (formation of interstitial, substitutional, or substractional solutions), it can be expected that the influence of an impurity on the properties will change. In some cases the entry of atoms into the vacant sites of the lattice destroys donor levels and, by this way, decreases the electric conductivity. However, with the introduction of impurity atoms into the interstices of the lattice the number of donor levels grows which leads to an increase of the electric conductivity. The distinction of the impurities into donor or acceptor type impurities is – from a theoretical point or view – of limited significance because in the majority of cases acceptors have donor behaviour and *vice versa* [9].

The possibility to determine z and R_i in accordance with d, $R_i{}^0$, and $tg\alpha$ allows to analyze the changes introduced by an impurity atom into the electron structure of the matrix. For this, it is necessary to know the position of the impurity in the lattice of matrix and to determine its neighbours. As basic parameter for the improvement in the thermal stability of silicon we have selected the bonding energy between the atoms of the matrix and the alloying element. In first approximation, our purpose was to explain which atoms when dissolved in silicon strengthen the lattice, *i.e.*, which elements have maximal bonding energies in interaction with the silicon atoms of the lattice. The authors take into account that the analysis of this single parameter is only the first step for the solution of the problem of thermal stability of silicon. The calculations were performed only for those donor and acceptor type alloying elements which are the most important ones for obtaining silicon with the required electrophysical properties.

Results and Discussion

For the determination of the alloying elements which possess a maximal bonding energy in the lattice of silicon, we have calculated the model parameters ($z_{\min}$, d, and ρ_l at $z_{\min}$) for the 40 most important elements of the periodic system. The model parameters for some elements are listed in the Table 1.

Experimental data on the bonding energies were taken from Ref. [10]. The relationship between the experimental bonding energies of a given pair of atoms (in kcal/mol) and the directed charge density (in Coulomb/Å) was found to be linear (Eq. (5), correlation coefficient $r = 0.93$).

$$D = 85 \cdot \rho_l - 310 \qquad (5)$$

Using the charge density calculated from Eq. (4), Eq. (5) allows to estimate the bonding energy of the pair of atoms located at the specific distance. Calculations

Table 1. Model parameters of electronic configuration of the bonds in doped silicon

Alloying element	$z_{\min}$	d (Å)	ρ_l at $z_{\min}$ (C/Å)
W	0.354	2.341	5.523
Mo	0.292	2.322	5.432
Au	0.178	2.406	5.312
Ta	−0.117	2.399	5.001
Cr	0.005	2.21	5.133
P	−0.361	1.964	4.754
Al	−1.75	2.125	3.549
Na	−2.15	1.925	3.303

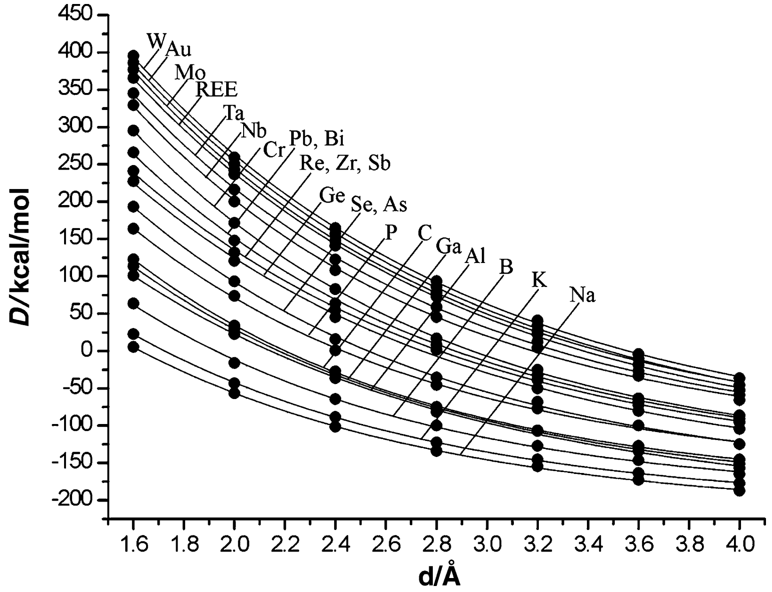

Fig. 2. Bonding energy D *versus* interatomic distance d between the interacting parts in binary dilute alloys of silicon with some elements of periodic table

were carried out for interatomic distances of 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, and 4.0 Å for the most important alloying elements. Figure 2 shows that bonding energy between silicon and the alloying element depends on the physicochemical nature of the interacting atoms and decreases exponentially with the increase of the distance between the interacting atoms. For the selection of the appropriate alloying addition it is necessary to consider the interrelation between bonding energy D and charge density ρ_l at the distance which corresponds to the interatomic distance in the lattice of silicon ($d \sim 1.5$ Å). The shortest interatomic distance in the lattice of silicon between planes {100} is 1.3577 Å, but due to the dissolution of doping additions it changes. Therefore, we have taken an approximate value of the interatomic distance in Si lattice.

The dependence of bonding energy *versus* charge density is linear (Fig. 3). The part of the line in the region of high bonding energy corresponds to data from Ref. [10]. It indicates the reliability of the predictions. Values of the effective charges of the atoms z and the charge densities ρ_l at $d = 1.5$ Å are represented in Table 2 for some elements.

The analysis of the computed bonding energies in the lattice of silicon makes it possible to select the substances, which increase the strength of the interatomic bonds, strengthen the lattice, and rise the thermal stability of the physical properties of silicon. These are the substances which have bonding energies with silicon higher than that in unalloyed silicon. As can be seen from Fig. 3 these substances are transitional and rare-earth metals. On the contrary, alloying with substances

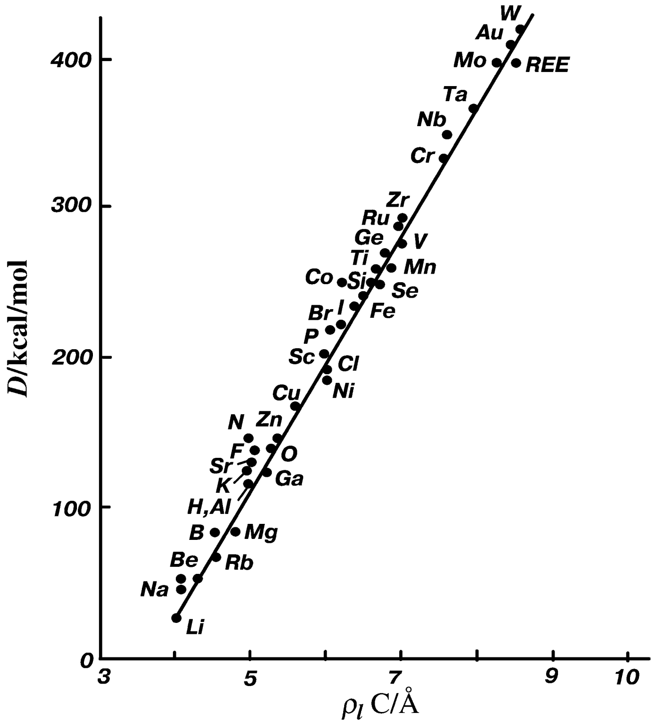

Fig. 3. Interrelation between the bonding energy D and the charge density ρ_l at the interatomic distance of $d = 1.5$ Å

Table 2. Model parameters of electronic configuration of the bonds in doped silicon at $d = 1.5\,\text{Å}$

Alloying element	z	ρ_l (C/Å)	D (kcal/mol)
W	3.312	8.639	424.3
Mo	3.188	8.440	407.4
Au	3.639	8.538	415.7
Ta	3.519	8.002	370.2
Cr	2.545	7.563	332.9
P	1.594	6.225	219.1
Al	2.724	5.034	117.9
Na	2.514	4.195	46.6
Si	1.027	6.359	230.5

with bonding energies lower than that of pure silicon will lead to a weakening of lattice and, consequently, to a decrease in the thermal stability of its electrophysical properties.

Analogous conclusions about the influence of different alloying elements on silicon monocrystals can be found in the widely known monograph of *Milnes* [9] which generalizes the experimental data, obtained by different authors during the last 50 years. The presented procedure of calculation is very promising because, by analyzing the known data of bonding energy and performing simple calculations, we have obtained the same conclusions as in Ref. [9].

Conclusion

The calculations based on the concept of non-polarized ionic radii facilitate the selection of the alloying elements which increase the thermal stability of silicon. Such elements are transitional or rare-earth metals which strengthen the crystal lattice of silicon and lower its thermal expansion coefficient. They suppress the formation of centres of high pressure during heating and, therefore, also the structural transformation.

References

[1] Glazov VM, Zemskov VS (1967) Physical–Chemistry Foundation of Semiconductors Alloying. Science, Moscow, p 503
[2] Glazov VM, Koltsov VB, Cutsova VZ, Regel AR, Taran YN, Timoshina GG, Uzlov KI, Falkevitch ES (1991) Fiz Tekn Poluprov **25**: 588
[3] Tonkov YY (1979) Phase Diagram of Elements at High Pressure. Science, Moscow, p 286
[4] Pirous P, Chaim R, Dahmen U, Westmacott KH (1990) Acta Metall Mater **38**(2): 313
[5] Pirous P, Chaim R, Dahmen U, Westmacott KH (1990) Acta Metall Mater **38**(2): 323
[6] Dahmen U, Westmacott KH, Pirous P, Chaim R (1990) Acta Metall Mater **38**(2): 329
[7] Taran YN, Cutcova VZ, Uzlov KI (1987) Dokl Akad Nauk USSR Phys-Mat and Tech Sci **6**: 74
[8] Prihod'ko EV (1995) Metallochemistry of Multicomponent Systems. Metallurgiya, Moscow, p 320
[9] Milnes AG (1974) Deep Impurities in Semiconductors. Carnegie-Mellon University Wiley, New York London Sydney Toronto, p 562
[10] Handbook of Chemistry and Physics (1989–1990). CRC Press, Boca Raton, Florida, p F197