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LATTICE DEFECTS IN SEMICONDUCTORS

N. Urli

"Rudjer Bošković" Institute, Zagreb

Abstract: A review has been given on the present status of understanding of the radiation effects in semiconductors. The emphasis has been placed on defect creation mechanisms, discussing the elastic displacement threshold values and ionization effects. Vacancy and interstitial formation and migration processes are also discussed as well as more complex defects created by ion-implantation.

1. Introduction

This review paper is not intended to give a complete catalogized inventory of all known defects in all elemental or compound semiconductors but would rather stress some common features and basic problems in that field. The emphasis will be given to the present status of understanding of defect creation in semiconductors by irradiation, discussing the displacement threshold values and surveying the various mechanisms of defect generation, migration of primary intrinsic defects and formation of various complexes. Ion-implantation damage as well as the thermal stability of some more important identified defects will be also discussed. Extended imperfections such as dislocations or plane defects will not be considered here.

2. Displacement Energy Threshold

The simplest approach to the problem of displacement of atoms from regular lattice sites by irradiation is a model of an isotropic square-well potential of the depth T_d, corresponding to a minimum displacement energy, independent of the mutual orientation of the crystal axis and the direction of the flux of the incoming energetic particles. The high energy particle strikes an atomic nucleus causing that atom to recoil; if the recoil energy T is greater than a threshold

energy T_d then a vacancy-interstitial pair (Frenkel pair) will be created.

The reported threshold energies in the literature are not very consistent. That follows from the fact that in realitj T_d often depends on the number of different parameters such as the relative orientation of the electron beam and the crystallographic axes [1], the sample temperature during irradiation, charge-state of the nascent Frenkel pair [2], ionization effects and various sensitivity of the specific experimental measurements. The situation is even more complicated in the case of binary semiconductors where two different atoms exist with different threshold energies. The two experimental threshold values are often assigned to displacements in each of the sublattices.

Theoretical approaches to the problem of displacement energies have been based on semiempiric models. Here, we will present Van Vechten's method [3] based on the thermodynamics arguments, dielectric-two-band model [4] and macroscopic lattice distortion measurements [5].

The displacement threshold energy T_d consists of three terms

$$T_d\,(A) = \Delta H_f\,(V_A) + \Delta H_f\,(A_i) + E_L \qquad (1)$$

where the first one denotes the energy of formation of the vacancy, the second, the energy of formation of the interstitial, A_i, and the last, the lattice distortion energy as the atom is driven away from its lattice site.

The first term was calculated by Philips and Van Vecthen [6] for diamond type semiconductors (Ge, Si, Sn, C), where, because of the high electron density, the vacancy was treated as a macroscopic cavity. Both experimental and theoretical values for $\Delta H_f(V)$ are in the range from 2 to 3 eV. The same has been even true for the majority of III-V and II-VI semiconducting compounds, as was shown later [7] for zinc-blende and wurtzite type semiconductors.

The lattice distortion energy is given by

$$E_L = k_\Theta R^2 \quad (2)$$

where k_Θ is the bond bending force constant and R the normal nearest neighbour distance. Because of the very open lattice structure of semiconductors, the lattice strain term E_L can not be substantially larger than the first term. Taking into account the experimentally determined values of T_d (Ge) = 15 eV[8] or even T_d (O) = 57 eV[9] in ZnO, it follows that $\Delta H_f(A_i)$ must be of order 10 eV in Ge, and even 50 eV for O_i in ZnO. How to explain such a big difference between the energies of formation of vacancies and interstitials by radiation ? Van Vechten has shown[3] that in the case of the simple interstitial C_i, as an extra atom in the lattice which does not make any bonds to the host atoms and introduces a minimal distortion of the lattice, its energy of formation may be represented by

$$\Delta H_f (C_i^x) = Z (C_i) E_g / 2 \quad (3)$$

where $Z (C_i^x)$ is the number of its valence electrons, and E_g the dielectrically defined average gap. (Note that it is greater than the usually defined energy gap E_{CV}; E_g (Si) = 4.8 eV $>$ E_{CV}(Si) = 1.2 eV).

The calculated values of T_d, by use of Eqs. (1 to 3) for various semiconductors are within the limits of experimental errors of the empirical values of T_d.

In addition, the relation (3) implies an asymmetry between anion and cation displacement energies because of the factor $Z (C_i)$, as the second term in the right side of Eq. (1) is dominant. That means that it is easier to produce a cation Frenkel pair than an anion Frenkel pair by radiation.

It is instructive to represent the displacement threshold values as a function of the lattice parameter a_o, following the idea of Corbett and Bourgoin[10]. Fig. 1 shows the mean value of the displacement energy of crystals which are tetrahedrally coordinated plotted versus the reciprocal of the lattice parameter. Curve 4 shows

the original interpretation of the experimental data, supposing that both elemental and compound semiconductors follow the same $\bar{T}_d \sim a_o^{-4.363}$ relation[10].

Curves 1 to 3 represent our calculations[11] for group IV elements, III-V and II-VI semiconductors, respectively, based upon Van Vechten's theory. It is important to note that all three curves have the same slope, i.e. the same $a_o^{-5/2}$ dependence. On the other hand, the most reliable experimental points, such as those of the elemental semiconductors (full circles in Fig. 1) may be also represented by

$$\bar{T}_d = 3.9 \left(\frac{10}{a_o}\right)^{5/2} \qquad (4)$$

where $\bar{T}_d$ is expressed in eV and a_o in Å, showing that the theoretical curves are basically correct. Thus, one may conclude that the measured experimental values of T_d for the compound semiconductors are too low, or, better to say, they do not represent the pure "elastic" displacement process, but involve the so-called "ionization-enhanced damage", caused by the presence of ionizing radiation.

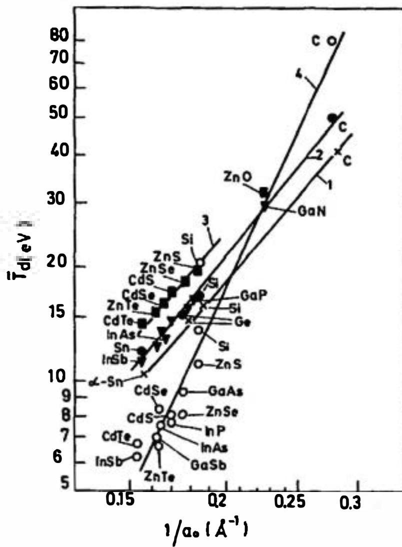

Fig. 1. Correlation of the mean threshold energy with the lattice parameter; (1) group IV elements, (2) III-V semiconductors, (3) II-VI semiconductors; (4) Cheng-Corbett's interpretation of experimental data; ●, o experimental points, X, ■, ▼ calculated points.

3. Vacancies and Interstitials, Their Migration and Formation of Complexes

The radiation created interstitial and vacancy in semiconductors at low temperature will in times of 10^{-13} sec or greater recombine with each other, stay where they are or migrate away. Their behaviour will depend upon temperature, defect structure and their charge states. In the process of correlated recovery, a fraction of induced Frenkel pairs will annihilate, as interstitials find their own vacancies. Those which succeeded to escape have been of interest in radiation damage studies because they are precursors of a great variety of complex defects, created by pairing of vacancies or interstitials with impurities already present in the lattice. For the so-called uncorrelated recovery, probability of an impurity capturing a mobile defect is proportional to the impurity concentration.

In germanium and silicon interstitials are mobile at very low temperature (even less than 4 K). Their long range migration may be explained by the athermal Bourgoin mechanism(12) involving a successive change in the charge state of a migrating defect or by energy release mechanisms(13). The Si-interstitial may have 3 charged states: I^-, I^0, and I^+, and the Ge-interstitials $I^=$ state, in addition. The Si--interstitial created in p-type material after electron irradiation at 4 K can displace a substitutional impurity of the group III (Al, B, Ge etc.) into an interstitial site(14).

The vacancy in silicon has 4 charged states: $V^=$, V^-, V^0 and V^+. It can be treated theoretically as a defect molecule with dangling bonds, exhibiting a large Jahn-Teller distortion. At present, only one localized electronic level at $E_v + 0.13$ eV is positively identified by TSC and DLTS methods to be associated with vacancy(15). Its introduction rate is $0.1\ cm^{-1}$ independent of doping.

The electrical properties of n-type silicon of a lower doping level after irradiation are dominated by formation of vacancy-impurity pairs; however, in p-type material the divacancy dominates the electrical properties.

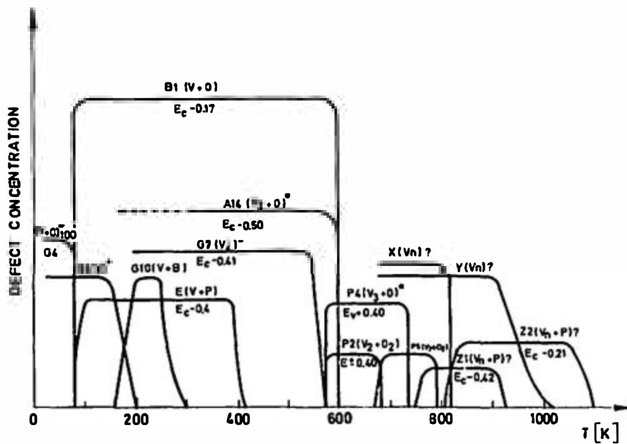

Fig. 2. The annealing data of some more important defects in silicon.

The EPR measurements in silicon have been especially fruitful in the identification of various vacancy-substitutional impurity complexes in silicon. Some of them are V + P, V + As, V + Sb, V + B, V + Al, V + Ga, V + C, V + Ge, and V + Sn.

Figure 2. shows growth and annealing of some more important complexes in silicon(16) in a large temperature interval. The energy levels of some of them were determined recently by photo-EPR experiments.

Beside multiple charge states of a single vacancy and divacancy multivacancies such as V_3, V_4 (planar), V_4 (non-planar), and V_5 have been also identified(16).

The situation with defect formation in germanium(17) is somewhat different from that in silicon. In n-type Ge interactions of primary defects and group V impurities result in neutralization of electrical activity of those shallow donors, as opposed to Si where vacancy-impurity pairs act as acceptors. Vacancy-oxygen pairs anneal near room temperature and they are not important in defect transformation as in silicon. In addition, group III impurities do not interact with point defects in germanium in contrast to silicon.

In compound semiconductors such as the II-VI compounds the radiation damage picture is even more complicated. As there are two sublattices, there are also two kinds of vacancies, two kinds of interstitials with several configurations, possibility of antisite defects, and as impurities are always present in significant concentrations, they can make pairs with the intrinsic defects.

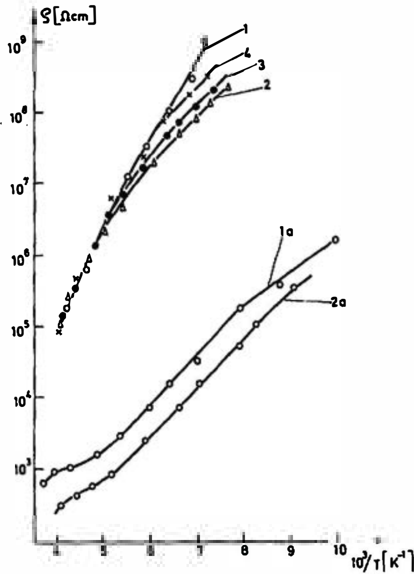

Fig. 3. The changes in resistivity of CdTe lithium diffused samples prior and after Co^{60}-irradiation (taken from Ref. 18)

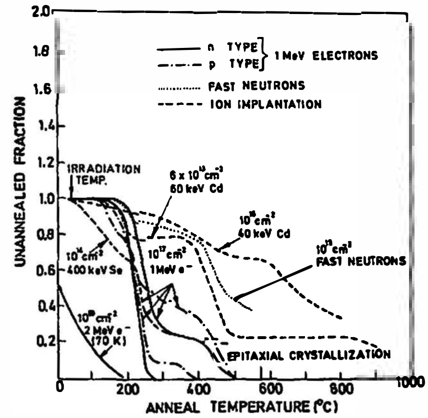

Fig. 4. Annealing stages in ion implanted silicon

As an example of radiation-induced defects in II-VI compounds, following our systematic research on the behaviour of the lithium-dopant in various semiconductor materials, Fig. 3 shows the changes in resistivity of p-type Li-doped CdTe samples before and after gamma--irradiation and after room temperature annealing. Radiation-induced Li-V_{Cd}-Cu complex was proposed[18] after analysis of isothermal--annealing and Li-diffusion data.

In the III-V semiconductors, as compound semiconductors, it is

expected that defects are more stable than in elemental semiconductors because of greater complexity in moving in two sublattices. Indeed, it was found that the wider band gap III-V's have stable intrinsic defects above room temperature, and that the dominant radiation effects in GaAs and GaP at room temperature are independent of impurities[19]. An analysis of the experimental data shows that some of the annealing above room temperature in those semiconductors is due to isolated vacancies.

Another characteristic feature of III-V compounds is the strong orientation dependence in the defect production rates which offers some advantages in defect identification as well as in research of the damage creation mechanisms.

4. Ion - Implantation Damage

In distinction to other kinds of bombarding particles an implanted ion slows down in a crystal by making many violent collisions with lattice atoms, producing a highly disordered region around its path, and finally may act as a doping impurity in the target material. At sufficiently high doses a disordered amorphous layer is formed.

The parameters which influence the defect production are: the nature and energy of implanted ions, the dose and intensity of irradiation, the nature of target material, the temperature, the type and the concentration of the impurities and the free carriers and the lifetime of minority carriers.

For low-fluence implantation there is a predominant annealing stage at about 200°C which correlates in temperature with divacancy annealing (Fig. 4). The amorphous layer anneals at higher temperatures (between 550 and 600°C), as shown by Curve $X(V_n)$ in Fig. 2. It is interesting to point out that n-type Si irradiated with 10^{18} 1 MeV electrons/cm^2 shows the same annealing stage . They are also three even higher temperature annealing stages shown in Fig. 2. Curve

$Y(V_n)$ corresponds to high fluence neutron irradiation and Curves Z1 and Z2 to channeled low energy phosphorus ion damage (presumably multiple vacancy-phosphorus complexes) with well defined localized electronic energy levels[20].

5. General Comments

Summarizing this review article, we wish to point out the importance of using various experimental techniques on the same material under research in order to get a more complete picture and knowledge of defects, that is, of their atomic and electronic configurations, their electronic levels, formation mechanisms, diffusion, interaction with impurities and other defects and annealing stages.

The present understanding of defect creation and motion mechanisms is greatly influenced by notion of importance of several enhancement effects such as ionization, electrical fields, charge state of defects, carrier recombination, recoils and strain-energy-release mechanisms.

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