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The Production and the Evolution of A-Centers and Divacancies in Silicon

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The production and evolution of A-centers and divacancies in p-type Si irradiated at 80 K is studied. The emergence and development of A-centers advocates the notion that part of them at low temperature have an electrically neutral structure which converts to the normal active configuration gradually, at higher temperatures. Small yet characteristic variations of the V_2 and (O–V) concentrations around room temperature are explained by considering the reaction processes occurring in this temperature range leading to the liberation of Si_i and V.

Die Bildung und Entwicklung von A-Zentren und Doppelleerstellen in bei 80 K bestrahltem p-Si wird bei Raumtemperatur untersucht. Ein Teil der A-Zentren hat eine elektrisch neutrale Struktur, die allmählich bei höheren Temperaturen in die normale, aktive Konfiguration übergeht. Kleine, aber chrakteristische Änderungen der V_2- und (O–V)-Konzentrationen bei Raumtemperatur werden erklärt, indem die Prozesse, die in diesem Temperaturbereich zur Freisetzung von Si_i und V führen, berücksichtigt werden.

1. Introduction

The main practical reason of the study of defects in semiconductors is to examine in depth their properties and behavior in order to enable technology to control their effects, mostly degradating, on the electronic devices.

A lot of papers have been published so far about V_2 and (V–O) in Si. These defects have been studied extensively both experimentally and theoretically. The atomic configuration of V_2 is simply two vacant lattice sites at nearest neighbor positions. It is electrically active introducting three levels [1] in the forbidden gap located at $E_v + 0.23$ eV (0/+), $E_c - 0.23$ eV (=/−), and $E_c - 0.41$ eV (−/0). The atomic configuration of the A-center is essentially substitutional oxygen. However, oxygen is displaced from the high symmetry tetrahedral (T_d) site, resided "off center" in the ⟨100⟩ direction thereby reducing the symmetry to C_{2v}. Electrical measurements have shown that the A-center is a single acceptor (−/0) whose level position [1] lies at $E_c - 0.17$ eV. Furthermore, it is well-known that the levels of V_2 and A-centers affect the carrier lifetime and the effective carrier concentration via generation–recombination and carrier trapping.

Both centers are produced by irradiation (electrons, protons, γ-rays, neutrons, etc.). V_2 can be created directly by the primary collision process but mainly by single vacancy pairing [2]. The A-center is created when highly mobile vacancies interact with interstitial oxygen atoms. It is commonly used as a monitor of the vacancy concentration in silicon [3]. Modern silicon processing technology (like ion implantation, plasma etching, electron beam lithography, neutron transmutation doping) involves particle irradiation leading to

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the creation of divacancies and A-centers. Therefore the technological interest about these two defects is obvious moreover if one thinks that both are stable above room temperature.

The present study aims at examining the production and evolution of V_2 and (O–V) created by irradiation at liquid nitrogen temperature. The role and the contribution of the various reaction mechanisms and processes involved are discussed.

2. Experimental Details

In our investigation Cz-grown Si ($[O_i] \approx 10^{18}\,cm^{-3}$, $[C_s] < 10^{16}\,cm^{-3}$) and Fz-Si ($[O]) \approx 10^{16}\,cm^{-3}$, $[C_s] < 10^{16}\,cm^{-3}$) boron-doped material was used with nominal resistivities 3 to 5 Ω cm for the first and 0.5 to 1.15, 1.45, 6.4 to 7.4, and 9 Ω cm for the latter. The defects were introduced by electron irradiation ($E = 1.5$ MeV, dose $\approx 4 \times 10^{16}$ electrons/cm^2) in-situ at 80 K. The concentration of the defects was measured using the DLTS (deep level transient spectroscopy) technique for the majority traps, like the V_2 (0/+) level and the MCTS (minority carriers trap spectroscopy) technique for the minority traps, like A-center (−/0) level, in p-type Si. The isochronal annealing of the defects was studied over the temperature range from 120 to 350 K ($t = 30$ min, $\Delta T = 20$ K).

3. Experimental Results and Discussion

The variation of the concentrations of V_2 ($E_v + 0.19$ eV) and A-center ($E_c - 0.17$ eV) is shown in Fig. 1. Experimental errors are smaller than the dimensions of the dots.

3.1 Divacancy

In the case of V_2 one could distinguish three stages. Stage (I) refers to observations below the onset of the vacancy migration ($T < 160$ K). It indicates that a certain number of divacancies is created during the direct collision process where the electrons knock out two Si atoms from adjacent lattice sites. The percentage of these V_2 depends on the oxygen and

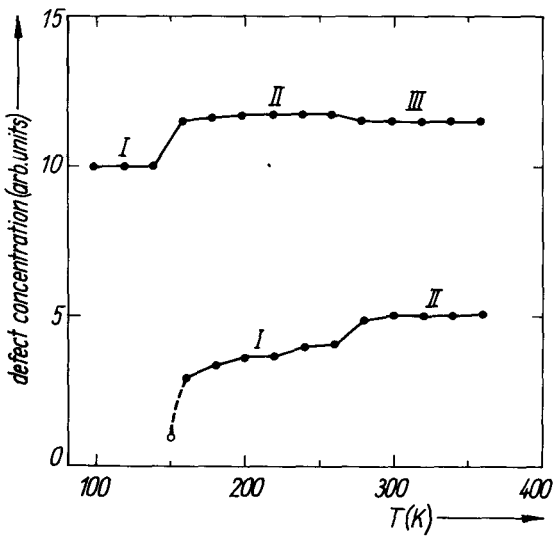

Fig. 1. The evolution of A-centers (lower curve) and V_2 (upper curve) after irradiation at 80 K

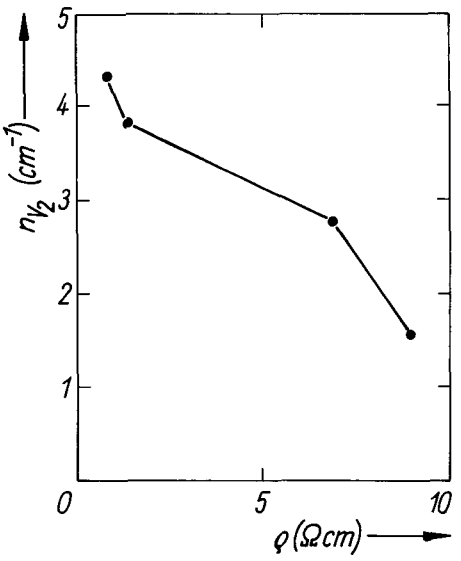

Fig. 2. The introduction rate of V_2 created during irradiation in the primary collision process as a function of specific resistivity

boron content of the material. It is larger in Cz-Si than in Fz-Si. It can be suggested that oxygen captures Si self-interstitials ($O_i + Si_i \rightarrow O_iSi_i$) thus reducing V_2 annihilation ($V_2 + Si_i \rightarrow V$). A decay in the introduction efficiency of these divacancies with the increase of the specific resistivity ϱ is characteristic in our spectra. The phenomenon was studied in Fz-Si (Fig. 2). Since ϱ could be taken as approximately inversely proportional to the doping impurity concentration [4] we conclude that the introduction rate for divacancies increases with the increase of the boron content of the material. The role of boron in this stage is similar to that of oxygen. Boron competes with V_2 in capturing Si_i($B_s + Si_i \rightarrow Bi$) therefore reducing the number of the directly formed V_2 which are annihilated by Si_i ([5]).

The large increase of V_2 concentration around 160 K is due to the formation of new divacancies by vacancy pairing ($V + V \rightarrow V_2$) as vacancies begin to migrate. During this process, also oxygen and boron compete with vacancies, trying to combine with other vacancies to form O–V and B–V pairs. The observed increase in V_2 concentration is again larger in Cz-Si than in Fz-Si. At first sight, this seems irrational since B and mainly O are expected to trap vacancies leading to the reduction of divacancies. However, another mechanism seems to prevail where oxygen and boron atoms prevent vacancy annihilation ($V + Si_i \rightarrow 0$) by capturing the Si self-interstitials ultimately leading to the enhancement of the V_2 concentration [6]. It was found that the step between stages (I) and (II) varies between less than 10% for the 9 Ω cm sample to $\approx$ 20% of the V_2 concentration for the 0.85 to 1.15 Ω cm sample, a fact indicating a significant role for boron. With the completion of this process the concentration of V_2 remains more or less steady, stage (II) in contrast with that of A-centers which has a tendency to increase. We shall comment on this point later.

The variations in stage (III) will be discussed together with the corresponding variations appearing in A-center evolution since, as we believe, they are the result of the same series of involved defect reactions.

Finally, it is worth noting that the energy position of V_2 in the gap ($E_v + 0.19$ eV) after 80 K irradiation is always found lower than that after room temperature irradiation ($E_v + 0.21$ eV). It might indicate that V_2 created after low-T irradiation have a slightly

different geometry or that these V_2 are perturbed by Si_i trapping nearby, thus modifying its structure. Similar aspects have been put forward previously in the literature [7]. The second assumption is corroborated by our data which show an increase in V_2 activation energy as the sample temperature reaches room temperature. Additionally, it is known in n-type Si that V_2 with trapped Si_i form transient metastable structures which dissociate below room temperature liberating Si_i.

3.2 A-center

In the case of the A-center two stages (I and II, Fig. 1) could be distinguished. Prior to discussing these stages we wish to concentrate our interest on the point (○) in Fig. 1 which we believe has the merit of particular attention. This point corresponds to a faint DLTS peak at $E_c - 0.17$ eV appearing in the spectra before the migration of vacancies begins. Interestingly, this peak does not appear in the spectra immediately after the irradiation. The energy position of the level is small enough to be detected when scanning with slow rate windows below 120 K. However, traces of the peak begin to appear in the spectra when the temperature of the sample has been cycled for some times in the range 80 to 150 K although the corresponding signal from the V remains stable [8].

One could think about a direct creation of close vacancy–oxygen pairs during the irradiation at 80 K. Since V are immobile we have to consider that limited vacancy migration may take place under the irradiation conditions [9]. In other words, the irradiation provides adequate energy so that some vacancies are enabled to jump and meet O_i forming A-centers. The fact that the signal from the latter defect emerge in the spectra after annealing at ≈ 150 K tends, at first sight, to militate against a direct formation of (O–V) during the 80 K *in-situ* irradiation. It might be argued, however, that the low temperature irradiation creates some kind of elastic stress field which locks these A-centers to an electrically inactive configuration. The existence of alternative structures of A-centers has been previously suggested in the literature [10]. Metastable configurations of the $(V–O)^-$ pair have also been observed which are low temperature precursors to the formation of the final defect configuration [9, 11]. It is tempting to think that the increase of temperature relieves the stresses and the center restores its normal configuration with the corresponding electrical properties. A more extensive presentation of this aspect about the existence of neutral configurations of defects which convert to active ones at higher temperatures will be discussed later.

Alternative explanations for the above phenomenon could also be put forward. The release of lattice strain induced by irradiation could occur via the formation of impurity–vacancy pairs. In this line of thinking the creation of O–V pairs in Cz-Si is favored irrespective of the vacancy migration. It is also possible, however, that the signal at $E_c - 0.17$ eV below 160 K comes from the contribution of different types of defects [12].

At about 160 K vacancies begin to migrate. The amplitude of the $E_c - 0.17$ eV peak increases sharply due to vacancy capturing by oxygen atoms. Interestingly, as the temperature increases the height of this peak gradually increases indicating additional formation of A-centers. We distinguish two stages (I) and (II). The former is extended up to ≈ 270 K where a small but characteristic increase of the peak amplitude indicates further formation of A-centers presumably by other reaction processes. The variation of the concentration in the range 270 to 340 K is denoted in Fig. 1 as stage (II) and it is probably correlated to the stage (III) of divacancies. Increases in the A-center concentration in the

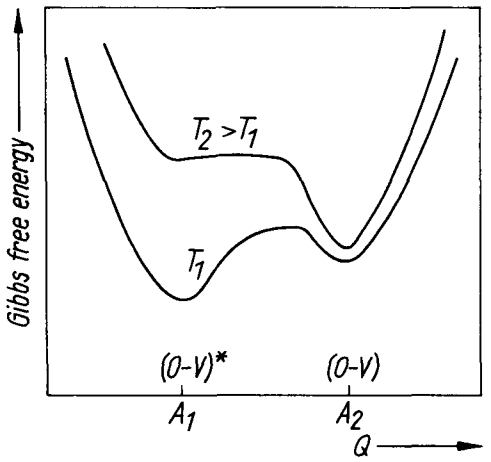

Fig. 3. A rough schematic diagram of the Gibbs free energy as a function of a general coordinate Q, suggested for the A-center

range 20 to 300 K have been previously reported for n-type material [6]. A simple explanation would be to consider the phenomenon as an indication of a long annealing stage of the monovacancies which might be due to the weak trapping of the migrating V by some impurity atoms. As temperature increases these liberating vacancies react with O_i atoms leading to the formation of additional (O–V) pairs. Similarly, one could think about liberation of vacancies from unknown, electrically neutral centers which are trapped by stationary interstitial oxygen. The existence of such centers could be conjectured by the fact that the initial vacancy concentration is larger than the sum of the concentrations of the V-related defects created after the V migration [13].

The increase of A-centers is, however, much larger than that of V_2 which is almost stable, pointing out that other mechanisms and processes also contribute to the phenomenon. We invoke again the idea that a fraction of (O–V) pairs formed at low temperature have a distorted structure which does not introduce levels in the energy gap. As temperature increases these modified centers transform to the normal ones therefore justifying the observed enhancement of the amplitude of the $E_c - 0.17$ eV peak. The whole picture could be understood through the schematic diagram of the Gibbs free energy as a function of a generalized coordinate Q (Fig. 3).

Suppose a defect possessing two configurations A_1 and A_2 separated by an energy barrier. At a low temperature T_1, only configuration A_1 could be populated and, if it is neutral, no signal on the spectra would be traced. As T increases the defect constituents are able to move more easily. Defect bonds to the lattice are also subjected to some changes. All these changes could induce changes to the local minima of the Gibbs free energy of the configurations and/or lower the dynamical barrier. At sufficiently high temperatures the defects manage to overcome the barrier and convert to configuration A_2 which is now more stable. As temperature increases more defects transform from A_1 to A_2. Since configuration A_2 is electrically active, the corresponding signal in the spectra increases. In the case of the A-center one component of which (oxygen) is neutral, one could envisage the following procedure. As is well-known V has various charge states. At the temperature of irradiation some of the V are captured by O_i in a charge state that leads to a neutral defect structure (O–V)*. However, the Fermi level moves with temperature. As temperature increases a change in the charge state of these vacancies could occur. Thus a tendency for

internal rearrangement appears which together with (or not) some kind of lattice relaxation helps the defect to stabilize in the normal geometry of (O–V). Fig. 3 does not represent a configurational coordinate diagram in the sense of those for bistable defects. Its qualitative shape with two minima indicates that the defects could stabilize at a different geometry (O–V)* at low T, but at high T it transforms to the normal configuration (O–V). The reverse transformation (O–V) → (O–V)* could not take place when T becomes low again. The conversion (O–V)* → (O–V) does not occur automatically but proceeds to completion as the temperature increases. One could think of an equation like $N_{(O-V)^*}/N_{(O-V)} = c \exp(E_b(T)/kT)$ where N denotes concentration, E_b the energy barrier between the two configurations, and c a constant, although a more complex relationship between electrical activity and defect structure could exist. Speculations about different kinds of (O–V) centers [14] or that the A-center could exist in an alternative configuration [15] have been previously appeared in the literature. At this point an idea is worth noticing about a possible metastability of A-centers postulating that the defect gives rise also to a donor level deeply in the valence band [16].

An alternative explanation, which is however in the same line of argumentation as above, is the electrical passivation of A-centers at low T, through the capturing of an unknown impurity X,

$$(A + X) \rightleftarrows A + X,$$
$$X \rightarrow \text{sinks}.$$

The capture of X by an A-center pushes its level position outside the energy gap. As temperature is raised the equilibrium in the first equation is shifted to the right according to the law of mass action to induce further dissociation of the (A + X) complex. This explains the gradual increase observed in the A-center concentration. It is reasonable to think that X may be a primary defect, more specifically a Si_i. Thus the capture of very mobile Si_i at low T leads to a modified A-center geometry which is neutral. The release of Si_i at higher temperatures restores the normal defect structure. Notably, if these mechanisms have an essential contribution to the formation of A-centers, then the evolution of the latter defect could not be considered as a means of monitoring the production and motion of vacancies in this temperature range.

Stages (II) of A-center evolution and (III) of V_2 are, in our opinion, the manifestations of the same series of reaction processes which take place in the region of room temperature. On the one hand, Si_i liberated by dissociation of O_iSi_i pairs [17] and presumably V_2Si_i structures, destroy (O + V) pairs and, on the other hand, help in the creation of new ones. One could write down the following scheme of reactions:

$$(O_iSi_i) \rightarrow O_i + Si_i, \tag{1}$$

$$(V_2Si_i) \rightarrow V_2 + Si_i, \tag{2}$$

$$(V + O) + Si_i \rightarrow O_i, \tag{3}$$

$$V_2 + Si_i \rightarrow V, \tag{4}$$

$$O_i + V \rightarrow (V + O), \tag{5}$$

$$V + V \rightarrow V_2. \tag{6}$$

In the case of A-centers it can be argued that the prevailing reaction would be (3) since it has a large geometrical capture cross-section and the energy of Si_i migration is much lower than that of V. Thus a reduction of the concentration of (O–V) pairs would be expected. This point of view however seems to be misleading since it neglects the participation of Si_i in other possible reactions (e.g. $C_s + Si_i \rightarrow C_i$, $B_s + Si_i \rightarrow B_i$, $Si_i + Si_i \rightarrow Si_iSi_i$, $Si_i + V \rightarrow 0$, etc.) which weaken the impact of reaction (3). In other words, the overall result as expressed by reactions (3) and (5) is a slight increase in the number of A-centers.

The observed increase of C_i during an inverse annealing stage at this temperature range [18] is consistent with the above observations. In fact, it indicates that the annihilation of (O + V) pairs by Si_i is suppressed due to the competition of other defects in capturing Si self-interstitials. Furthermore, the impact of the reaction $C_i + (O + V) \rightarrow C–O–V$ seems to be negligible for the final result.

The dynamic equation concerning A-center evolution at this stage could be written

$$\frac{dN_A}{dt} = K_{VO}.N_V.N_O - K_{ASii}N_A.N_{Si_i},$$

where N stands for concentration and K_{VO}, K_{ASi_i} are the vacancy capture coefficient of oxygen and Si_i capture coefficient of the A-center, respectively. A mathematical analysis of the problem requires the exact knowledge of the number of Si_i contributing in the above equation which is impossible due to the participation of Si_i in a plethora of reactions. We should add that similar arguments could be advanced for the case of V_2 evolution where the final result as described mainly by (2), (4), and (6) is a slight decrease of V_2 in the above temperature range.

4. Conclusions

We have proposed that the increase of A-centers in the range 160 to 270 K could be partially ascribed to the conversion of a portion of the created defects from neutral configurations to active ones. Such neutral structures could arise from distorted A-centers or from A-centers modified by the attachment of unknown defects, presumably Si_i. A schematic representation of the Gibbs free energy as a function of a generalized coordinate is suggested to explain the results. However, configurational coordinate diagrams could only provide a phenomenological description of the phenomenon. Obviously, such a consideration is still incomplete and further theoretical investigations are necessary for a thermodynamic description of the point defect formation process under irradiation. It is concluded that, in the temperature range 160 to 270 K, the evolution of A-centers cannot be used as a monitor of the evolution of vacancy in p-type Si. Around room temperature a series of processes occurs leading to the liberation of primary defects which in turn participate in various reactions resulting in the production and/or destruction of A-centers and V_2.

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