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An insight in the formation of thermal double donors in Cz-silicon

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Sixteen neutral species of thermal double donors (TDD1-TDD16) and nine positively charged species (TDD1-TDD9) have been detected and confirmed through IR absorption spectra. However, the existence of TDD0 based on photoconductive and Hall measurement is still under debate. Though the strength of the donors is reasonably good totalling to twenty six, the formation kinetics still carries a mark of interrogation. Average number of oxygen atoms involved in a single TD is also not certain. One of the authors has earlier reported on an average, the involvement of seven oxygen atoms. This point very much relevant to the understanding of formation kinetics is to be looked into. There are similar many questions still unanswered which may be explained based on the concept of dimers and trimers. However, there is a likelihood of dimer-trimer pairing via defect states. TDD0 does not seem to be a stable configuration as more and more oxygen atoms may further add to TDD0 converting into other configurations. A further insight into the TDD problem can be gained on the basis of dimers, trimers and their consequent pairing. The purpose of the present article is to highlight its vibrant character still not fully understood.

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1. Introduction

Oxygen impurities in silicon are one of the most puzzling and challenging phenomena. Crystalline silicon typically contains nearly 10^{18} atoms/cm^3 of oxygen impurities in electrically inactive twofold coordinated interstitial sites [1, 2]. Although single oxygen atoms in silicon are electrically inactive, they can form electrically active clusters. Most oxygen atoms and vacancies are incorporated into the crystal as a VO complex from the solid-liquid interface. The concentration of VO is approximately equal to that of self interstitials near the interface.

When the temperature rapidly goes down, VO dissociates in V and SiO_2 according to following reversible reaction:

$$2VO + Si \rightleftharpoons SiO_2 + V \tag{1}$$

For the slow cooling process

$$VO \rightleftharpoons V + O \tag{2}$$

Reaction (1) occurs violently according to the rapid temperature decrease and Anomalous Oxygen Precipitation (AOP) [3] is formed by the nucleus of SiO_2. The AOP appearance region becomes vacancy rich and reverse reaction indicates AOP disappears between high temperatures. According to eq (2) VO becomes a source and sink of vacancies and oxygen atoms.

1.1 Thermal Double Donor family

Thermal Double Donor (TDD) family consists up to 17 different electrically active defects forming in a sequential way [4]. They are assumed to have a common electrical core with added O atoms which gradually shift the donor state towards the conduction band edge (E_c) [5]. Trivalent oxygen forms a donor in covalent crystals [6]. Chadi [2] suggested that three oxygen atoms form first donor. Based on O_i loss upon generation of thermal donors, Dubey & Singh [7] have suggested on an average, the involvement of seven oxygen atoms but the accompanying O_i loss upon generation of TDDs by heat treatment at 650 °C gives an average of $\approx$ 10 oxygen atoms per TDD [8]. Each species of TDD_n sequentially appears with increasing the annealing time. TDD3 is smaller than TDD1 and TDD2 in concentration [9]. It was assumed that only O_2 acts as the fast diffusing species but extremely high values of O_2 diffusivity are required to account for the successive transformations of the first TDDs [10]. Aberg et al [11] concluded that O_3 formation rate would be three orders of magnitude longer than any other reaction rate of O_2 and exclude this possibility in their kinetic model. The existence of TDD0 has been under debate for a long time and is still under debate. TDD0 is located at the depth of 0.45 ± 0.01 eV below the lower edge of the conduction band [12]. Murin et al also reported that TDD0 is hardly four oxygen atom complexes as well. He further suggested the likely involvement of at least five oxygen atoms in the formation of TDD0. We feel presence of three oxygen atoms may help in the formation of TDD0. Interstitial oxygen, oxygen dimer and trimers play a significant role as briefly discussed below:

1.2 Interstitial oxygen

It is known to lie near a bond-centred site with equal Si-O bonds with C_1, C_{1h}, C_2 or D_{3d} symmetry. The activation energy for an oxygen atom hopping between neighbouring bond centres in Si has been measured by stress-induced dichroism to be 2.56 eV. The energy of the y-lid was calculated to be 2.1 to 2.2 eV [13].

1.3 Oxygen dimers

The molecule was less stable than an oxygen dimer where both oxygen atoms are tilted along the [110] direction with respect to each other. The oxygen atoms were found to be bound by 1 eV [14]. The oxygen atoms are found in silicon as staggered, skewed and double-y-lid. The binding energy of the oxygen atoms in the staggered dimer is found to be about 0.5 eV and in double-y-lid is 1.2 eV [15]. The oxygen dimer in silicon is stable in the staggered form with modes calculated to be in good agreement with experiment.

1.4 Oxygen Trimers

Since O_i is the most common impurity in Cz-Si it seems likely that O_i will complex with this.

This also suggests that it must be one of the earlier complexes to form, with a trimer being the next simplest structure after the dimer. C. P. Ewels suggested that the trimer may be the linear O_i structure [16].

$$O_i + O_{2i} \rightarrow O_{3i}$$

A recent study on LVMs of the oxygen trimers in Si has shown LVM appearing at 1006 cm^{-1} [17].

2. Core structure model

2.1 Oxygen-only complexes

- Y-lid configuration: One oxygen is bonded to three silicon atoms to form the threefold coordinate known as y-lid.
- $(O_i)_2$: O_i occupies a puckered bond-center position between two neighboring silicon atoms.
- $(O_r)_2$: The four-member ring structure in which two threefold-coordinated oxygen atoms and two silicon atoms.
- $(O_Y)_2$
- Interstitial O_2 molecule, two oxygens intercepting parallel Si-Si bonds in a (111) plane and also bonded to each other.
- Two O_3 complexes, one is (O_Y) stabilized by O_i atoms on both sides, the other is that two oxygen atoms intervene at the nearby bond-centered sites, and the silicon atom bonded both sides with these two oxygens is repelled upward and the broken two bonds with other silicon atoms repaired by addition of one more oxygen atom [18-22].

(a) Oxygen + vacancy complexes: *V*O, one vacancy and one O_i

VO_2, one vacancy and two O_i's

VO_4, one vacancy and two bond-centered O_2 molecule

(b) Oxygen + self-interstitial complex: IO_2, one self-interstitial and two threefold coordinated oxygens [23, 24].

3. Experimental

Boron-doped CZ-silicon of resistivity 5 Ω-cm and thickness 500 μm with oxygen concentration of 5×10^{17} atoms/cm^3, having orientation <111>, were cut into small pieces of 1×2 cm^2. The samples were annealed at 450 °C for 5, 10, 15 hrs repectively. FTIR analysis was performed. The fragment of the spectra is shown in Fig. 1.

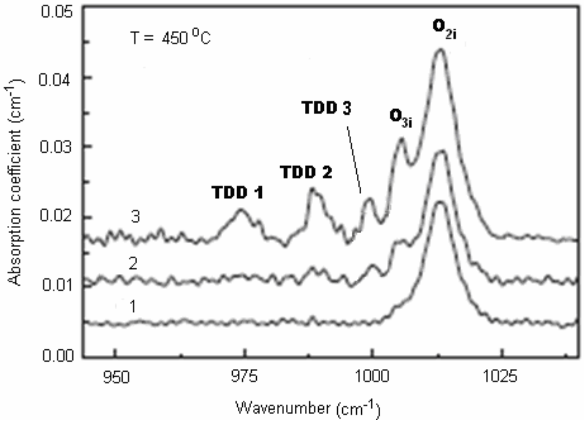


Fig. 1. Fragment of absorption spectra at 450 °C for CZ-Si.

4. Results and analysis

4.1 LVM of TDDs

Fig. 1 clearly depicts five distinct peaks at 1012, 1006, 1000, 988, 975 cm^{-1}. These are due to oxygen dimers, trimers, TDD0, TDD1 and TDD2 respectively. Addition of more oxygen atoms may generate TDD3, TDD4 and so on.

Physico-chemical equations representing the behavior of formation of TDD0 and onward are given below:

$$VO_i \rightarrow V + O_i \qquad \text{[From eq (2)]}$$

$$O_i + O_i \rightarrow O_{2i}$$

and

$$O_i + O_{2r} \Rightarrow \left(O_i.O_{2r}\right)$$

This complex of oxygen is TDD0. Next generation of TDD is formed to the subsequent adding and pairing of oxygen atoms in this complex as given below:

$$O_{2i} + O_{2r} \Rightarrow \left(O_{2i}.O_{2r}\right) \qquad \text{[TDD1]}$$

$$\left(O_i.O_{2r}\right) + O_i \Rightarrow \left(O_i.O_{2r}.O_i\right) \qquad \text{[TDD2]}$$

$$\left(O_i.O_{2r}.O_i\right) + O_r \Rightarrow \left(O_i.O_{3r}.O_i\right) \qquad \text{[TDD3]}$$

and

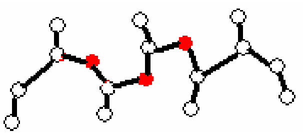
$$\left(O_i.O_{2r}.O_i\right) + O_{2r} \Rightarrow \left(O_i.O_{4r}.O_i\right) \qquad \text{[TDD4]}$$

$$\left(O_i.O_{2r}\right) + O_n \Rightarrow \left(O_i.O_{xr}.O_i\right) \qquad \text{[TDDn]}$$

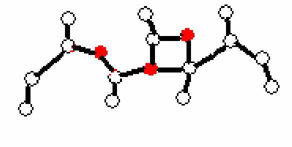
where $x = n + 2$, n = 1, 2, 3,. ......,7 for linear structure. However, involvement of more oxygen atoms is quite possible for di-y-lid configuration.

4.2 The structural models of the formation kinetics of TDD

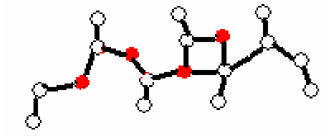
These are given below in Fig. 2.



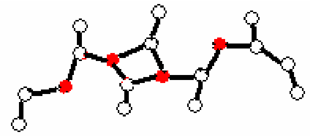
O_{3i}



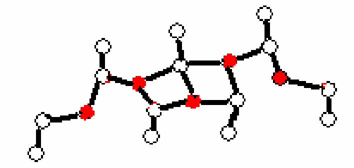
$O_i.O_{2r}$ or TDD 0



TDD 1



TDD 2



TDD 3

Fig. 2. Structural models of O_{3i}, TDD0, TDD1, TDD2, TDD3 correspond to equations given above. Positions of the atoms are not to the scale. White circles are for Si atoms and red circles are oxygen atoms.

5. Summary

TDD0 and TDD1 are sequentially formed and are fast diffusing species. However, TDD0 acts as a nucleus for further growth of TDDs. TDD1 and TDD2 both have same oxygen content but differ only in the position of oxygen atom. Further interaction with dimers/trimers may yield higher TDD species, irrespective of the order of TDD.

Cz-silicon is a core material for electronic industry. As such, scientists all over the globe are striving hard to understand and analyse its multiple character in order to harness its maximum potential for optimum industrial use. But the issue of TDD is still surrounded by an air of uncertainty and needs consistent efforts to demystify its exact kinetics.

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