ANNALES
UNIVERSITATIS MARIAE CURIE - SKŁODOWSKA
LUBLIN — POLONIA
VOL. XLIII/XLIV, 27 SECTIO AAA 1988/1989

Instytut Chemii Nuklearnej i Technologii

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Oxygen Related Defects in Silicon

INTRODUCTION

For more than 30 years the effects of oxygen impurity presence in silicon have been investigated /a comprehensive literature is given in ref. 1 and 2/. Depending on the oxygen content in a silicon crystal (CZ or FZ) and the treatment applied (heat, particle and laser beams) a wide variety of oxygen-related defects have been reported /3,4,5,6/.

Early experiments revealed that heat treatment to higher temperatures above 300°C can produce transformation from p- to n-type of electrical conductivity as a result of some donor centers creation /1/.

Experiments performed with the use of energetic radiation (γ,e^-, ions) at room temperature or below showed a number of simple defects related to the presence of oxygen impurities /2/.

In the first part of this short overview a survay of

simple, oxygen related defects will be given. The second part will be concerned with the extended defects produced under high temperature treatment. Particular emphasis is placed on recent progress in the understanding of the most interesting ones, the so called thermal donors (TD).

SIMPLE DEFECTS

Radiation damage studies in semiconductors have more than 30 years history and have contributed significantly to our understanding of defect creation and interactions /2/.

There are many techniques by which defects can be produced in a crystal, as for example by diffusion, precipitation, quenching, plastic deformation or irradiation with energetic beams (particle, laser). Among them irradiation has an important feature of producing damage (defects) in a "cold" lattice and, simple defects perhaps not present in other experiments involving high temperature treatment, can be frozen-in for further studies.

In order to study the simple defects in a silicon crystal, it is necessary to irradiate the sample at low temperatures (LN_2 LHe). At temperature much higher than this the isolated vacancies become mobile and dissapear being trapped by other defects to form more stable defect-vacancy pairs or aggregates.

A great deal of information has been obtained due to the electrical, optical and magnetic measurements which have provided microscopic data. In the last years transient capacitance techniques were introduced by Sah et al /7/ and by Lang /8/, which proved to be a powerful tool for defect studies in semiconductors directly associating energy levels and capture cross section of defects.

Infrared absorption /9/, photoluminescence /10/ and DLTS /6/ measurements, made before and after 90K electron irradiations of silicon crystals containing oxygen, carbon or carbon plus oxygen impurities, indicated formation of a wide variety of centers such as O_i, V-O, C-O-V, C_sO_i and a series of multivacancy-multioxygen complexes V_2-O, V_3-O, V_2-O_2, V_3-O_2, V_3-O_3 /2/.

In Fig. 1 schematically is shown a typical IR absorption spectrum for CZ silicon before and after electron irradiation /11/. The very well pronounced band at 9µm arises from a localized vibrational mode of the oxygen impurity in its normal interstitial position /12/. It is absent in high-purity (low

oxygen content) FZ silicon.

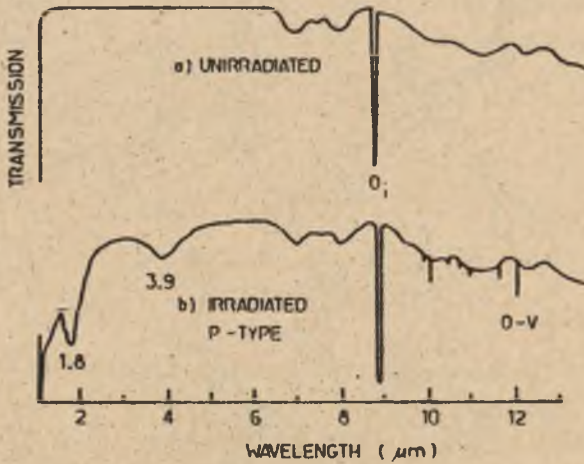

Fig. 1 Schematic diagram of infrared absorption bands produced by high energy electrons or fast neutron irradiation in p-type silicon /11/.

The sharp bands from 9-13 μm arise from localized vibrations of oxygen ion in various kinds of new complexes created by irradiation. They are known to involve O because of their general dependence upon the original Oxygen concentration /4, 13-17/.

The band at 12 μm arises from the simple V-O pair, the identification coming largely from a detailed correlation with EPR results /4/.

Fig. 2a demonstrates the bond-centered configuration in which the oxygen impurity is between the two neighbouring silicon atoms on interstitial sites /9/. The model has been proposed relating interstitial properties to a set of criteria involving the minimisation of dangling-bond energy. As a matter of fact, the oxygen atom does not occupy exactly the position along the <111> direction but the angle between its two bonds equals to about 140°C /9/. The estimated migration energy of interstitial oxygen amounts to 2.5 eV /18/.

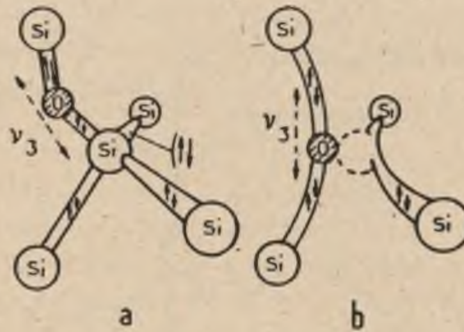

Fig. 2 The bond-centered interstitial configuration of oxygen atom (a) and a vacancy-oxygen pair (A-center) (b) - in silicon /9/.

Fig. 3 shows schematically annealing properies for impurity interstitials in silicon including oxygen /2/. The recovery temperature for oxygen interstitial was estimated from diffusion data.

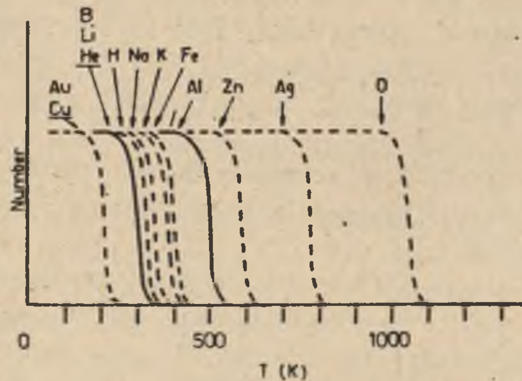

Fig. 3 Schematic annealing information of impurity interstitials in silicon. The curves are estimated from diffusion data /2/.

The proposed model for a major defect in p-type silicon, the K-center comprising carbon-oxygen-vacancy components (C-O-V) is shown in Fig. 4 /2/. Jaworowski et al. /19/ have measured the energy position for an acceptor level of this centre - E_v+0.39eV.

There are a lot of identified multivacancy-oxygen defects. One of the best known in n-type silicon is the A-center - a vacancy-oxygen pair shown in Fig. 2b /9/.

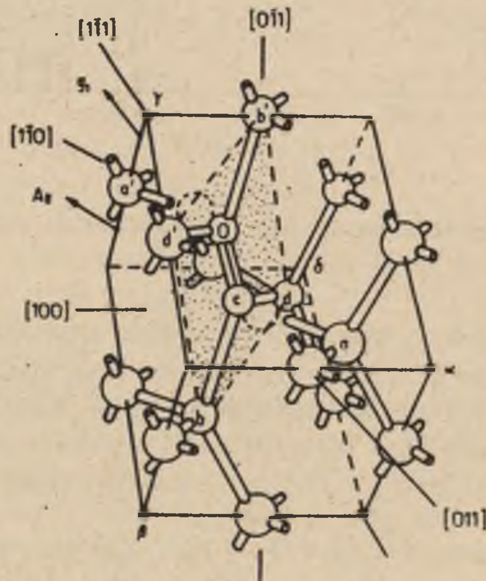

Fig. 4 The proposed model for the K-centre (V-O-C) /2/.

In this case, the energy level position E_c - 0.18 eV, the electronic capture cross section 10^{-14} cm^{-2} and the annealing kinetics E_a = 1.3 eV measured by DLTS /6/ support correlation with the A-centre /3,4/.

Fig. 5 demonstrates a schematic annealing information on vacancy-oxygen complexes in silicon from a simple V-O pair to V_3-O_3 centres /2/. The energy levels and capture cross sections for V_2-O and V_3-O complexes based on a tentative identification have been reported. For V_2-O centre: E_c-0.30 eV /6/, E_v+(from 0.44 to 0.48) eV /20,21,24/, and for V_3-O centre: E_c-0.20 eV /6/

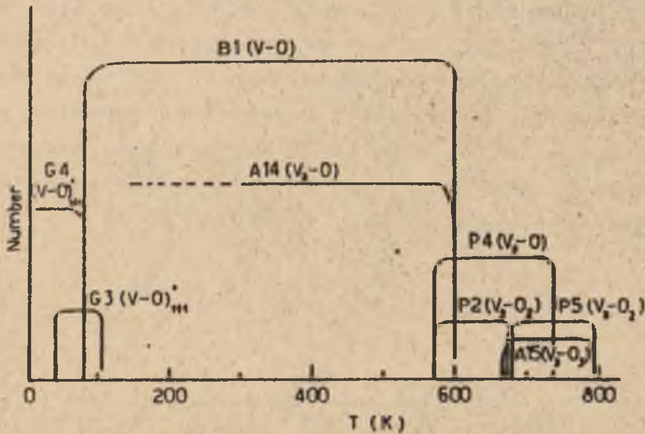

Fig. 5 Schematic annealing information on vacancy-oxygen defects in silicon /2/

In the paper by Konoplev et al /10/ the nature of luminescence centres in silicon irradiated by fast electrons has been studied. The observed band 0.49 eV in CZ-grown silicon crystals leads to the conclusion that the centre comprises as a "basis" a pair of impurities C_sO_i always present in small quantities in silicon containing oxygen and carbon.

After a careful analysis of the experimental data (the piezospectroscopic splitting of a Zero-phonon line 0.49 eV and an estimate of the energy-level structure of the suggested centre) they come to the conclusion that an additional carbon interstitial atom C_i takes part in the formation of a final form of the 0.45 eV centre, thus producing a split interstitial $\{C_iC_i \langle 111 \rangle\}$ located near the oxygen atom.

EXTENDED DEFECTS

CZ-silicon crystals contain a large amount ~$10^{18}cm^{-3}$ of oxygen atoms as the dominant impurity. In device technology this oxygen concentration shows many beneficial aspects as for instance results in the increase of mechanical strengh and the decrease of metal contaminants in a silicon substrate.

Oxygen atoms normally occupy interestitial positions (bond-centred) and themselves are electrically neutral. However, thermal treatment produces a wide variety of oxygen-related extended defects, some of them being electrically active.

One of the most interesting of these is a so called Thermal Donor (TD) formed at the lowest annealing temperature 350-500°C, and introducing two relatively shellow donor states as a result of heat treatment.

Following an interesting paper by Bergholz et al /25/ we will present a short survay of oxygen-related extended defects with particular emphasis given to the thermal donors.

Various oxide precipitate morphologies in CZ-silicon have been observed after heat treatment in the temperature range 400-1300°C. Although recent high resolution transmission electron microscopy revealed the nature and sizes of oxide precipitates formed during various thermal annealing stages, the accurate knowledge at the respective stages of nucleation and growth of oxygen precipitates remain a focus for current investigations.

a) T = 400 - 600°C

It is generally believed that at this early annealing stage thermal donors are produced in the form of aggregates of small number of oxygen atoms. However, prolonged annealing at 485°C for 300 - 900 h leads to the formation of coesites /26/, one of the high pressure modification of SiO_2, typical form of oxygen precipitates at higher temperature annealing.

b) T = 600 - 700°C

Most of the oxygen atoms precipitate in the form of amorphous SiO_2 and a new crystalline SiO_2 phase identified as the coesite emerges with thermal treatment.

c) 700 - 950 °C

Although the oxygen impurities precipitate amorphously a plate-like geometry ({100} with edges ⟨110⟩) of these precipitates dominates. The strain produced around the precipitates relieved by the emission of silicon self-interstitials and the formation of dislocation loops.

d) 950 - 1300 °C

At this high temperature annealing stage the oxygen precipitates of amorphous SiO_2 assume a polyhedral forms of 15-20 nm diameters. The emission of self-interstitials to minimize the strain energy condense into the stacking faults.

At these various annealing stages the oxygen precipitation is accompanied by a large volume expansion of about 250% /26/ and the emission of self-interstitials to relieve the resulting strain. The formation of SiO_2 precipitates assumes various modifications and geometries.

THERMAL DONORS

The microscopic structure and the formation kinetics for thermal donors still remain an interesting problem to be solved. The experimental studies initiated in 1954 by the observation that n-type electrical conductivity can be produced in CZ-silicon crystals by 450°C heat treatment showed that the process of donor centres formation is related to the presence of oxygen atoms in a crystal.
Many experimental techniques and theoretical analyses have been employed to solve the nature of these centres /27/.

Spectroscopic investigations employing near-infrared absorption revealed the presence of thermal donors in CZ silicon /29,30/.

Benton et al /28/, using DLTS measurements in CZ silicon, identified two oxygen-related donor states E_c-0.07 eV and E_c-0.15 eV introduced during 450°C heat treatment. They observed that the production of these states is not enhanced by point defects (vacancies and self-interstitials) introduced by 1 MeV electron irradiation.

From the oxygen diffusion measurements (the recovery kinetics of a stress induced dichroism in the 9 μm oxygen infrared absorption band) they conclude that the observations are

consistent with the formation of oxygen donors structure by an aggregation process.

Magnetic resonance studies (EPR, ENDOR) have firmly established the presence of oxygen in the core of thermal donor centers, but the oxygen aggregation process upon heat treatment during which the thermal donors are formed presents still an open question.

The kinetics of TD formation /31/ differs heavily from known oxygen migration rates /32/ and suggest the necessity of taking into accountthe possibility of oxygen containing, fast diffusing species at that low annealing temperatures 300-500°C.

Table 1 and Table 2 summerize the main characteristics and the models for thermal donors, respectively /25/.

Table 1. Experimental facts about thermal donors (TD)

No.	Feature	Method	Ref.
1	Double donor, levels within 200meV of CB edge.	DLTS, IR	/28/./29/ /30/./33/
2	Related TD, population varies with annealing time. Progressively shallower levels.	IR	/30/./34/
3	Initial formation rate $[TD] \propto [O]^4$ (t=0), $[TD]_{max} \propto [O]^3$ ($[TD]$ = sum of all TD conc.)	Hall effect	/35/
4	All donor species give rise to a single broad ESR line, mm2 symmetry, no hyperfine interaction with O^{17}, Si^{29}	ESR, "NL8"	/29/./36/. /37/
5	$\bar{4}$2m symmetry from piezospectroscopy	DLTS	/38/
6	TD destroyed by annealing above 500°C, Si_i emission.	IR	/39/

The last two models given in Table 2 are the most comprehensive ones and are presented in Fig. 6.

Recent magnetic resonance studies (EPR, ENDOR, FSt-ENDOR) have shown the possibility of other structures of TD. The NL 10 centre incorporating one aluminium and two oxygen atoms is given in Fig. 7 /45/. The other model proposed involving 4 oxygen atoms and a vacancy in the core is shown in Fig. 8 /46/.

Table 2. Models for thermal donors (TD)

Name(s)	Structure	Ref.	*)
Kaiser, Frisch and Reiss	SiO_4 cluster	/40/	2,4,5,6
Helmreich and Sirtl	V + O_i --- O_s (V fast-diffusing)	/41/	2,4,5,6
Gösele and Tan	O_4 molecule, O_2+O_2 ---O_4 (O_2 fast diffusing)	/43/	2,4,5
Keller	O_s + $3O_i$	/44/	2,4,5
Henry, Farmer and Meese	Weakly bound O_2 + O_2 molecules	/38/	2,4
Pajot, Compain, Lerouille and Clerjaud	Si $(O_i)_n$, n variable	/29/	4,5
Newman, Oates and Livingston	Si $(O_i)_n$, fast-diffusing S_iO_i	/39/	4,5
Stavola and Snyder	YLID (Fig.6)	/42/	4
Ourmazd, Bourret and Schröter	Divalent Si, bound to two O_i, chain of O_i (see also Fig.6)	/31/	ref. /34/

*) features of Table 1 not accounted for

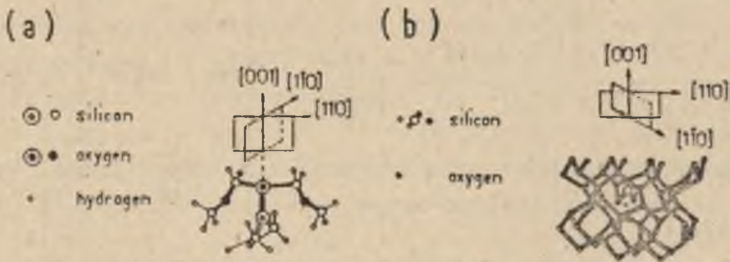

Fig. 6 (a) YLID model for TD /43/; Trivalent Si-atom and split-interstitial oxygen atom are ringed.
(b) OBS model for TD /31/; Displaced divalent Si-atom is ringed and its original lattice position indicated.

In spite of many suggestions put forward on the formation and properties of thermal donors no satisfactory atomic structure of TD has been produced. There are some important aspects which remain for further verification.

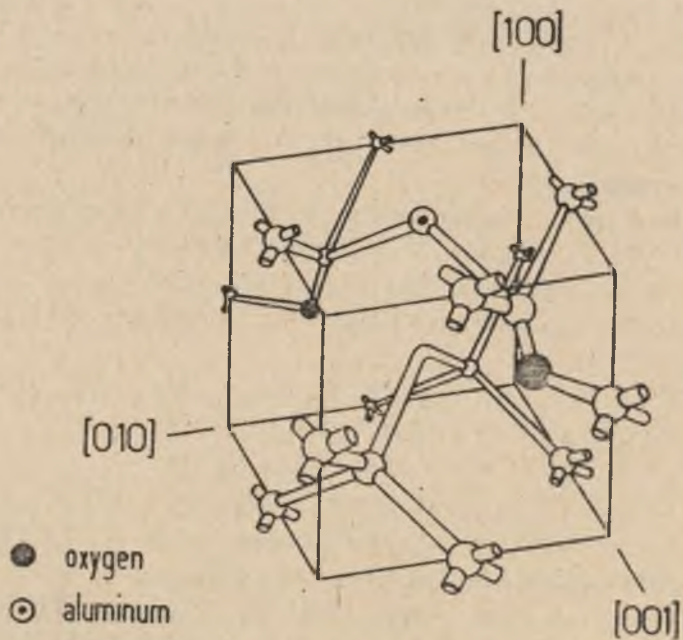

Fig. 7 A structural model for an NL 10 center - one aluminium and two oxygen atoms /45/.

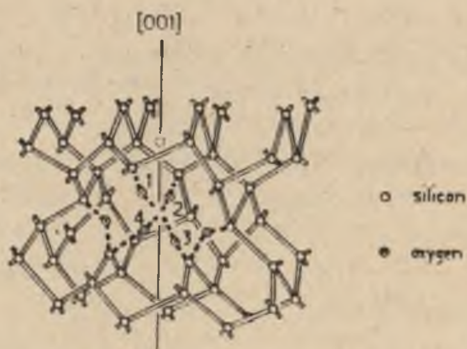

Fig. 8 A proposed TD model incorporating 4 oxygen atoms and a vacancy /46/.

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