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Gettering and Defect Engineering in Semiconductor Technology
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THE INFLUENCE OF OXYGEN ON THE MIGRATION OF THE CARBON INTERSTITIAL DEFECT IN SILICON.

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1. Introduction

Oxygen and carbon are the principal residual impurities invariably present in silicon crystals. The broad outline of their behaviour in silicon were established mainly through infrared absorption studies /1, 2/. Carbon is an isoelectronic impurity in Si at concentrations in the vicinity of $10^{16}cm^{-3}$. It occupies substitutional sites (C_s) and is electrically inactive. Oxygen atoms on the other hand, are incorporated in the lattice as bonded interstitials (O_i) bridging two neighbour silicon atoms. O_i is electrically inert. Its typical concentrations are $10^{16}cm^{-3}$ for the float-zone and $10^{18}cm^{-3}$ for the Czochralski-grown material.

Irradiation of Si with high energy electrons causes lattice atoms to be displaced into interstitial sites. These self-interstitials are selectively trapped by carbon atoms which are knocked out to interstitial positions. EPR measurements have shown that the carbon is bonded to a silicon atom forming a mixed dumbbell structure the 100 C - Si interstitialcy /3/. From molecular cluster calculations it has also be concluded that in the diamond lattice C_i prefers an interstitialcy configuration as against the hexagonal or tetrahedral interstitial sites /4/.

Carbon interstitial remains locked in the lattice up to nearly room temperature. Then it begins to migrate. The annealling kinetics is first order yielding an activation energy $E_a \simeq 0.80$ eV /3,5/. The moving carbon atom can be captured by 1) another C_s atom to form a structure recently indentified as C_s-Si_i-C_s /6/. 2) an oxygen atom to form a C_i-O_i pair 7 and 3) an oxygen complex like O+V to form the C+O+V structure /8/.

2. Experimental

The experiments reported here were carried out on Al-p-type Si Schottky barriers. We were confined on boron doped silicon samples of float-zone and pulled material with nominal resistivities of (6.4-7.4)Ωcm and (3-5) Ωcm respectively. The specimens were cut from highly-pure, one-side prepolished wafers, purchased by Walker. The etching procedure was made in a solution of acids HNO_3 : CH_3COOH : HF in the ratio 5:3:3 respectively.

The specimens were irradiated with 1.5MeV electrons from a Van der Graaf accelerator to doses around $(1.5\text{-}4)\times10^{16}e^-/cm^2$ and current densities in the range $(0.1\text{-}0.3)\mu A/cm^2$. Irradiations were performed in situ in a liquid Nitrogen flown cryostat at 80K.

For our measurements we used a DLTS system similar to that described by Lang /9/. The DLTS technique has been proven very fruitful in studying the annealing behaviour of defects.

3. Results and Discussion

After the electron bombardment at 80K the specimens in the present experiment were subjected a thermal treatment at 320K for 3 hours. Figures 1 and 2 summazize the obtained results for the float-zone and the pulled material respectively. Peak H_1 in both figures is probably the divacancy which is out of the interest of the present work. Peak H_2 also in both figures arises from the carbon interstitial. Peak H_3 grows simultaneously with the decay of H_2. The striking difference between the two figures is the persistence of the C_i signal in the float-zone material as compared with the pulled. In the latter material the C_i peak has been almost entirely (90%) converted to the H_3 peak after the 3 hours anneal at 320K. However, this is not the case for the float-zone material were the conversion from H_2 to H_3 amounts only to 50% of H_2 after the same thermal treatment.

We incline to believe that this behaviour manifests a certain underlying reality. We have attributed the phenomenon to the influence of the oxygen content which is different

between the two materials. This argument is

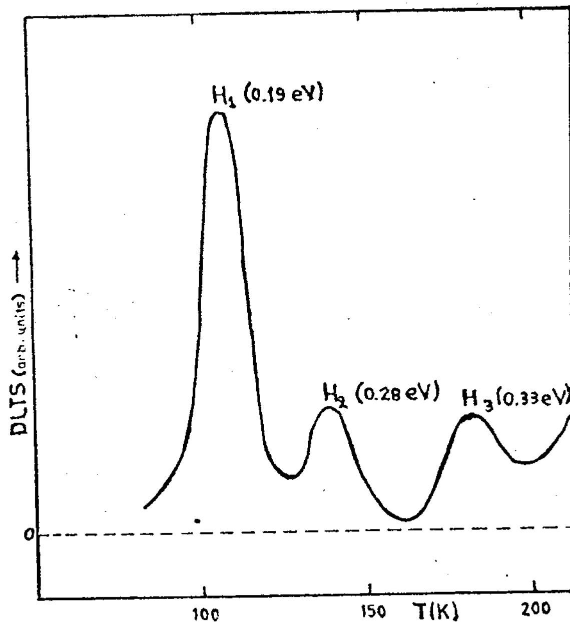


Fig.1: The DLTS spectrum of float-zone silicon, ρ= (6.4-7.4)Ωcm, 1.5MeV electron irradiated at 80K, after a thermal treatment at 320K for 3 hours.

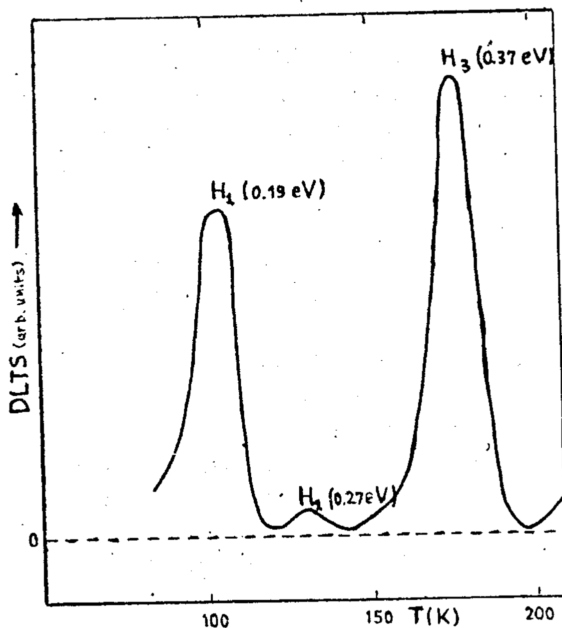


Fig.2: The DLTS spectrum of pulled silicon, ρ= (3-5)Ωcm, 1.5MeV electron irradiated at 80K, after a thermal treatment at 320K for 3 hours.

based on the facts that oxygen can affect the migration of the carbon atoms in the following ways:

a. Oxygen distorts the S_i lattice: It is well-established that the interstitially incorporated oxygen bridges two silicon atoms. As a result the two atoms are pushed apart and thus the lattice is locally deformed. Obviously, any local expansion of the lattice is accompanied by a corresponding local contraction. Energetically thinking, this means that there are regions inside the crystal with an energy density larger than the average and other regions with smaller than the average energy. The number of both kind of such regions is obviously larger in the pulled material. As a result of this situation carbon atoms having the physical tendency to move to the more stable regions, are prone to travel more easily through the lattice. This is equivalent to say that the average height of the barrier for diffusion is smaller in the pulled material.

It is understood that the jump of a defect in a crystal is an activated process and consequently the frequency of jumps is an exponential function of temperature.

$$w = x\nu \exp\left(-\frac{\Delta G}{KT}\right) = x\nu \exp\left(\frac{\Delta S}{K}\right)\exp\left(-\frac{\Delta H}{KT}\right)$$

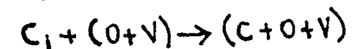
$$\text{or} \quad w = \nu_0 \exp\left(-\frac{\Delta H}{KT}\right), \quad \nu_0 = x\nu \exp\left(\frac{\Delta S}{K}\right) \quad (1)$$

Where x is the transmission coefficient determining the probability that an atom, having sufficient energy will jump to another position; ν is the frequency factor which in the first approximation is equal to the frequency of vibrations of atoms in the lattice sites (the Debye frequency). ΔG is the change of the free energy of the system during the jumps and ΔS and ΔH are the entropy and enthalpy changes of this process. ΔH is equal to the activation energy for diffusion, namely to the barrier height that the defect must pass. We believe that the excess oxygen content in the pulled material cause a dropping of the barrier height, namely $\Delta H_{f.z.} > \Delta H_{pulled}$ However we do not know if this decrease of the barrier could account for the observed phenomenon.

b. Provision by oxygen of trapping sites for C_i: It is well-known that apart from C_s, O_i and (O+V) pairs are also active traps for the C_i:

$$C_i + C_s \longrightarrow (C_i + C_s)$$

$$C_i + O_i \longrightarrow (C_i + O_i)$$



$$C_i + (O+V) \longrightarrow (C+O+V)$$

Since the concentrations of O_i and O+V are larger in the pulled material carbon atoms have a larger possibility to be captured in this material. The rate of a particular process could be expressed as

$$w_{react} = \nu_{react} \exp\left(-\frac{\Delta H_{react}}{KT}\right) \quad (2)$$

where ΔH_{react} is the barrier which characterizes the reaction process. Due to the existence of more primary reaction channels for the C_i in the pulled material we expect that $\Delta H_{react,f.z.} > \Delta H_{react,pulled}$.

Considering now the relations (1) and (2) and supposing that the possibilities of the two events to occur are statistically independent we may write the final formula for the diffusion process /10/ as following:

$$w = \nu_0 \cdot \nu_{react} \cdot \exp\left(-\frac{\Delta H + \Delta H_{react}}{KT}\right)$$

It is obvious that $W_{f.z.} < W_{pulled}$.

c. Oxygen may transfer energy to the carbon atoms: We know that around room temperature the S_i-O-S_i molecules behave as almost free rotators jumping from one orientation to another between six equivalent positions /11/. Given the natural tendency of carbon and oxygen to combine forming CO molecules it is very reasonable to invoke the possibility that an oxygen atom may meet a carbon atom and transfer some energy to the latter helping it to displace more easily through the lattice.

It is the author belief that some of the above processes could occur in parallel giving rise to the observed discrepancy in the annealing behaviour of the carbon interstitial between the high-oxygen and the low-oxygen material.

4. Acknowledgements

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