Identification of Dominant Nitrogen-Oxygen Defects in Silicon using First Principles Calculations

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The kinetics of defect nucleation and growth in nitrogen doped Czochralski Si (N-CZ), can be clarified by studying the atomic structure, the formation energies and the infrared absorption of nitrogen-oxygen defects. These have been investigated using quantum mechanics density functional theory (DFT) and semi-empirical Hartree-Fock MNDO-AM1 methods. The electrically inactive NNO_n (n=1,2) are the dominant complexes since 80% of nitrogen atoms in silicon are paired, sitting either in interstitial [1] or in substitutional sites [2]. Calculations have been performed for N_2, VN_2 and V_2N_2 with a single or two oxygen atoms bridging the Si-Si dilated bond next to the N-N core, along <111> directions [3], forming then N_2O, N_2O_2, VN_2O, VN_2O_2, V_2N_2O, and $V_2N_2O_2$. These complexes were obtained by reactions of N pairs with one or two O atoms. Periodic systems and molecules have been used to model the defect and its crystalline environment. In the relaxed structures, oxygen atoms set off the Si-Si bond center, forming angles that vary from 137.7 to 174.7° depending on the defect structure. This is in agreement with the 164° average angle given by Bosomworth et al [4]. To accommodate the O atom, the Si-Si equilibrium distance increases up to 3.20 Å, this is in good agreement with the observed 36 % Si-Si bond dilation. DFT calculations showed that N_2O_2 and $V_2N_2O_2$ can form spontaneously, and so does N_2O and V_2N_2O to a less extent, as it appears from their heat of formation in Table I. The reactions forming VN_2O and VN_2O_2 are less energetically favorable, while previous ab-initio calculations showed the ability of VN_2 to react spontaneously with a vacancy forming very stable V_2N_2 complexes [5, 6]. Because of strong Si-N and Si-O bonds the N_2O_n and $V_2N_2O_n$ do not dissolve easily even at high temperature and could act as nucleation sites for oxygen precipitation. This may explain the enhancement of O precipitation observed in N-CZ Si as well as the strong change in the kinetics of void formation.

The IR absorption of the N-O complexes occur at 806, 815, 1000, 1021, and 1031 cm^{-1} [7]. The ab-initio harmonic vibrational frequencies are typically larger than the fundamentals observed experimentally. When using the scaling factor of 0.9532 for semi-empirical AM1 method established by Scott and Radom [8] we obtained a good correlation between the degree of stability of the complexes, their respective LVMs and effective charges. The effective charge computed from the change in the dipole moment, is directly proportional to the absorption intensity of the mode. Three classes of points are remarkable in the effective charge-frequency chart, see Fig.2; each class is related to a base N-pair defect, i.e, N_2, V_2N_2 , or VN_2. The frequency population with higher infrared intensity is concentrated around the known 1000 cm^{-1} band for N-O defects and pertains to N_2O, N_2O_2 and $V_2N_2O_2$ which were found stable. The calculated lines for N_2O, N_2O_2 $V_2N_2O_2$ are within or close to the observed 1000, 1021 and 1031 cm^{-1} frequencies. The measured 1000 cm^{-1} line can be assigned to N_2O_2 as well as $V_2N_2O_2$. Likewise, the 1021 cm^{-1} line is attributed to N_2O and 1031 cm^{-1} to N_2O_2 and N_2O. It can be safely stated that the measured 806 and 815 cm^{-1} line are signatures for N_2O and N_2O_2 respectively. Since VN_2O_n defects were found instable we did not consider them for the observed N-O lines in as grown material. However, this does not exclude them from existing in annealed wafers, since the more intense calculated LVM for VN_2O_n defects is very close to the observed 1031 cm^{-1} line.

References:
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Table I. Formation energies (eV) of the NNO_n complexes as calculated from DFT-LDA.

N_2O	N_2O_2	V_2N_2O	$V_2N_2O_2$	VN_2O	VN_2O_2
-0.8	-1.35	-0.64	-1.14	0.08	0.5

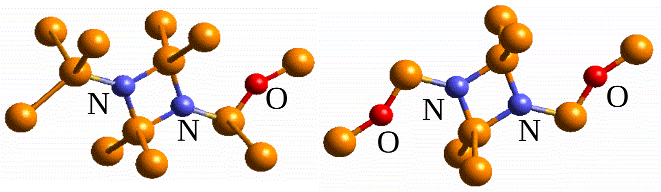

Fig.1: N_2O and N_2O_2 complexes and immediate surrounding.

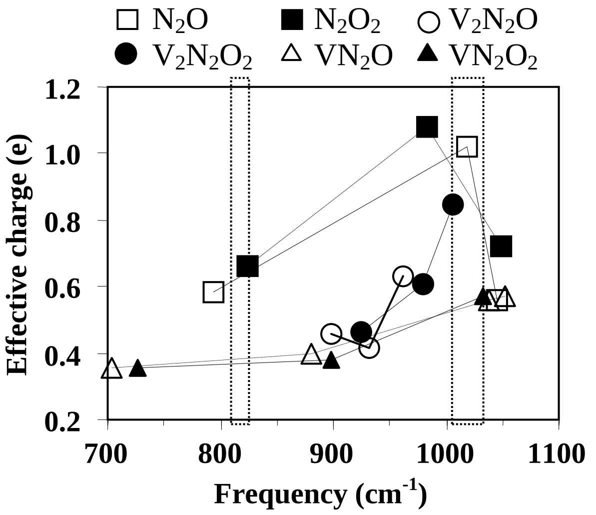

Fig. 2: Calculated effective-charges and frequencies for N-V-O complexes. The bars represent the experimentally observed N-O bands.