

Ab-initio Calculations of Infra-Red Absorption in Nitrogen Doped Czochralski Silicon

F. Sahtout Karoui¹, A. Karoui¹, G. A. Rozgonyi¹
N. Inoue², H. Harada²

¹: Materials Science and Engineering Dept.
North Carolina State University, Raleigh, NC
27695-7916

²:Japan Electronics & Information Technology
Association,
RIAST, Osaka Prefecture University

The ground state and the frequencies of vibration normal modes of N related complexes in CZ Si have been investigated using a semi-empirical quantum mechanics Hartree-Fock method [1] in order to address the issue of N measurement in N-CZ Si. The calculations have been carried out for N₂ interstitial (N_{2int}), N₂O, N₂O₂, VN₂, and V₂N₂ complexes. The N complex defect is placed in the center of a H terminated molecule (Si₇H₇). As shown in Table I, both N and O atoms have very short bonds with their neighboring Si atoms and lie between 1.65 and 1.75 Å, which is much smaller than the Si-Si bond (2.35 Å). This is due in part to the large electronegativities of both N and O atoms. The calculated Si-O bond lengths lie between those published for interstitial (1.6 Å) and substitutional oxygen (1.75 Å) [2]. After relaxation O atoms in N₂O and N₂O₂ stand off the bond centered sites, with a Si-O-Si angle of ~ 155°.

The main features of the ab-initio calculated IR absorption spectra, see Tab. II and Fig 1 are described below:

1. The 783 cm⁻¹ line in the IR spectra of N_{2int}, due to N vibrations in [110], is close to the experimental value 766 cm⁻¹ [3]. A stretching mode in [110] with a frequency of 1042 cm⁻¹ has been assigned to the measured 963 cm⁻¹ line [3]. Both lines result from high absorption and in-phase N-N vibrations.

2. Calculated frequencies for VN₂ are 749, 923 and 931 cm⁻¹, which can be correlated to the measured 766 and 963 cm⁻¹ lines. All these lines denote a strong IR absorption. Line 749 cm⁻¹ involves in phase vibrations of the two N atoms, while the 923 and 931 lines involve independent vibration.

3. Six frequencies were obtained for V₂N₂, two weak lines at 608 and 640 cm⁻¹, and four strong lines peaking at 953, 961, 976 and 984 cm⁻¹ which all fall around the measured 963 cm⁻¹ line. The weak lines are due to in-phase vibrations, while the strong ones originate via independent vibrations of N atoms.

4. Three strong modes appear for N₂O, two due mainly to N-N stretching with IR lines at 857, and 1053 cm⁻¹, while one mode which peaks at 1083cm⁻¹ is due to Si-O stretching. The former pair of frequencies are best matched to the measured frequencies 801, 996 cm⁻¹ [4, 5], and the latter (i.e., 1083 cm⁻¹) to line 1026 cm⁻¹ [6].

5. N₂O₂ has four vibration modes with frequencies 848, 1088, 1098, 1108 cm⁻¹. The latter three lines involve mainly Si-O stretching with

different amplitudes which are close to the measured 1107 cm⁻¹ absorption line of the O interstitial. The 848 cm⁻¹ line corresponds exclusively to the N-N stretching mode.

Our calculations show that: (i) lines 766 cm⁻¹ and 963 cm⁻¹ constitute a fingerprint of N_{2int} and VN₂, whereas only line 963 cm⁻¹ might be associated to V₂N₂. These confirm Stein's proposal that N atoms are paired and bonded to Si atoms [3], (ii) the calculated N₂O and N₂O₂ absorption lines correspond, in fact, to a shift of N_{2int} lines toward higher frequencies (blue shift) by adding O atoms to N_{2int}, (iii) the measured- frequency at 801 cm⁻¹ is a fingerprint frequency for both for N₂O and N₂O₂ defects, since they have identical N-N vibrations (lines: 857 and 848 cm⁻¹) and identical N-Si bond lengths (1.66-1.75 Å), iv) the reversible conversion of N_{2int} into N₂O, observed in Q_i [4] and Wagner [5] might also produce the N₂O₂ complex.

References:

- [1] MNDO-AM1: Modified Neglect of Diatomic Overlap - Austin Model 1 Hamiltonian.
- [2] C. Ewels, Mater. Sci. Forum, **196-201**, 1297, 1995.
- [3] H.J.Stein, Mat. Res. Soc. Symp. Proc., Vol. **59**, p.523 (1986).
- [4] M.W.Qi, S.S.Tan, B.Zhu, P.X.Cai, W.F.Gu, X.M. Xu, and T.S.Shi, D.L.Que and L.B.Li, J. Appl. Phys., **69**, (6), 3775 (1991).
- [5] P. Wagner, R. Oeder, W. Zulehner, Appl. Phys. A, **46**, 73-76 (1988).
- [6] Y.Yamanaka, H.Harada, K.Tanahashi,T.Mikayama and N. Inoue, Sol. State. Phen., **82-84**, 63 (2002).

TABLE I. Calculated bond lengths (Å) in CZ Si.

	N _{2int}	VN ₂	V ₂ N ₂	N ₂ O	N ₂ O ₂
Si-N	1.70-1.77	1.75	1.71-1.75	1.66-1.75	1.66-1.75
N-N	2.40	1.33	3.20	2.38	2.35
Si-Si*	2.38	2.38	2.39-2.42		
Si-O				1.71	1.70

*: Nearest neighbor Si atoms

TABLE II. Calculated/Experimental frequencies (cm⁻¹).

	N _{2int}	VN ₂	V ₂ N ₂	N ₂ O	N ₂ O ₂
Calculated	742	749	608, 640	857	848
	1042	923	953, 961	1053	1088
		931	976, 984	1083	1098
Measured	963 [3]			801 [4, 5]	1018
	766 [3]			996 [4, 5]	[5, 6]
				1026 [4, 5]	801*

*: Attributed to N₂O in [4,5], and to N₂O₂ in this work.

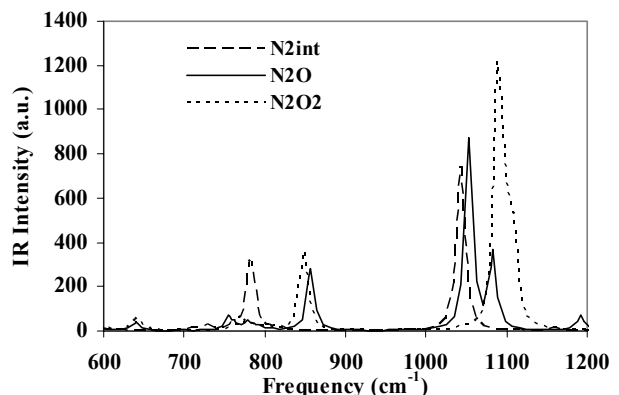


Fig. 1: Calculated IR absorption spectra of N_{2int}, N₂O and N₂O₂ in Si.