



Symmetry and structure of N–O shallow donor complexes in silicon

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ABSTRACT

Shallow donors in silicon related to nitrogen–oxygen complexes have been investigated by piezo-spectroscopy of their hydrogenic transitions in the far infrared. Complete stress dependences up to 0.25 GPa were obtained for the $1s \rightarrow 2p_0$ and $1s \rightarrow 2p_{\pm}$ transitions of the most prominent members of the (N, O)-family, N–O-3 and N–O-5. Very unusual for shallow donors in silicon, the symmetry of the ground state wave function is T_2 -like. The lifting of orientational degeneracy for stress in the $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions is compatible with a C_{2v} defect symmetry. Data from the other species of the (N, O)-family are indicative for the same symmetry. The microscopic structure of these centers, in part contradictory to present theoretical models, is discussed.

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1. Introduction

Nitrogen-related centers in silicon crystals are of particular interest because of their impact on intrinsic point defects and defect agglomerates. Intentional nitrogen doping is considered as a favorable tool for the improvement of crystal quality after typical high-temperature processing steps. Nitrogen–oxygen complexes occur in nitrogen-doped Czochralski (Cz) silicon crystals. Among these, the family of electrically active shallow donor complexes is of special importance as a considerable fraction of the total nitrogen content in the crystal can be bound therein.

Systematic investigations of the thermal equilibrium concentrations of (N, O)-centers in Cz crystals with varying nitrogen and oxygen concentrations by measuring the strength of the FIR transitions showed that the major members of the (N, O)-shallow donor family all contain one nitrogen atom but different numbers of oxygen atoms [1]. More important, species with both even and odd numbers of oxygen atoms must exist. The chemical composition of all shallow donor centers with respect to the number of oxygen atoms incorporated could finally be derived by an extension of these studies on a crystal with a large axial gradient of the O_i concentration, grown by a special oxygen-doping technology [2]. The result was that the center with the highest donor binding energy is chemically NO, the center with the highest concentration after annealing between 600 and 650 °C is NO_2 .

2. Experimental

Samples investigated were cut from a float-zone silicon crystal doped with nitrogen and oxygen by a special growth technique [3].

Nitrogen and oxygen concentrations were about 3×10^{14} and $6 \times 10^{17} \text{ cm}^{-3}$, respectively. The samples were thermally annealed at 600 °C for 7 h under nitrogen atmosphere to generate (N, O)-centers at high concentrations [4]. The total concentration of these centers was estimated to be around 10^{14} cm^{-3} . Uniaxial stress experiments up to 0.25 GPa at a sample temperature of 10 K were performed in the $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ crystallographic directions using a home-made push-rod apparatus similar to the construction of Tekippe et al. [5]. Fourier transform infrared (FTIR) measurements were carried out with a vacuum instrument (Bruker IFS 113v) equipped with a global IR light source and a Si bolometer detector. The spectral resolution used was between 0.3 and 0.5 cm^{-1} .

3. Results and discussion

Normally eight different species of (N, O)-centers can be observed by FIR absorption spectroscopy in nitrogen-doped Czochralski silicon. Following the original work of Suezawa et al. [6,7], these are referred to as N–O-1 to N–O-6, furthermore N–O-6' and N–O-8 [2]. After long-term annealing between 550 and 750 °C, N–O-5 and N–O-3 have the strongest absorption bands, i.e. are the complexes with the highest concentration. Their chemical composition is NO and NO_2 , respectively [1,2]. We investigated in detail the hydrogenic-like transitions $1s \rightarrow 2p_0$, $1s \rightarrow 2p_{\pm}$, and $1s \rightarrow 3p_{\pm}$ in the range between 180 and 280 cm^{-1} .

As an example, spectra of the $1s \rightarrow 2p_{\pm}$ transitions at different stresses σ parallel to the $\langle 001 \rangle$ direction are shown in Fig. 1. In contrast to usual donors in silicon, such as phosphorous or arsenic with a $1s(A_1)$ ground state, the shift of the transitions of about 1 cm^{-1} per 0.1 GPa is very small. This can occur if the donor ground state belongs to the T_2 representation of the tetrahedral group. In this case initial and final states of the

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observable transitions move identically under stress, such that the transition energy remains the same [8]. Shifts and splittings shown in Fig. 1 are due to a higher-order effect, the removal of orientational degeneracy under stress. There is only one comparable case reported in literature: the oxygen-related thermal double donors in Cz silicon. They also have a T_2 ground state as revealed by piezospectroscopy [9].

For N–O–3 and N–O–5, the complete stress dependences of the $1s \rightarrow 2p_0$ and the $1s \rightarrow 2p_{\pm}$ transitions are shown in Fig. 2. Some of

the stress-split branches obviously exhibit a nonlinear shift with stress. This behavior is unusual and will be discussed later. Aside from this peculiarity, the interpretation of the stress splitting is straightforward for the $1s \rightarrow 2p_0$ transition: 2 branches for stress in the $\langle 100 \rangle$ direction, 2 in the $\langle 111 \rangle$ direction, and 3 in the $\langle 110 \rangle$ direction are indicative for a center with C_{2v} symmetry (rhombic I according to Kaplyanskii's tabulation) [10].

The situation is more difficult for the $1s \rightarrow 2p_{\pm}$ transitions where 4 branches are observed in the $\langle 111 \rangle$ direction and at least 5 branches in the $\langle 110 \rangle$ direction. According to Kaplyanskii's tabulation these numbers are compatible only with triclinic symmetry. This would mean that the $2p_{\pm}$ final states feel lower defect symmetry than the $2p_0$ states. However, fitting of a unique set of piezospectroscopic parameters (6 in this case) to the splitting in all 3 crystallographic directions is not possible. Careful analysis, in particular in conjunction with the observed band intensities under polarized light (see below), led to the conclusion that the $2p_{\pm}$ states split under stress in the $\langle 111 \rangle$ and $\langle 110 \rangle$ directions. These states are degenerate for a center with T_d symmetry. However, there is no reason to assume that this degeneracy should persist for lower symmetry. Indeed, for the oxygen thermal double donors, Stavola et al. [9] observed a splitting of $2p_{\pm}$ states even at zero pressure. In this case, a very satisfying fit of our data on the basis of C_{2v} symmetry is possible. The conclusion is that the $1s$ ground state as well as the $2p$ excited states are subjected to a perturbative defect potential of C_{2v} symmetry.

Extremely helpful is the analysis of the absorption intensities under polarized light. It turns out that both centers investigated in detail, N–O–3 and N–O–5, have transition dipole moments that are closely related to the C_2 symmetry axis of the defect. For example, a center oriented along the $\langle 110 \rangle$ direction has a transition dipole

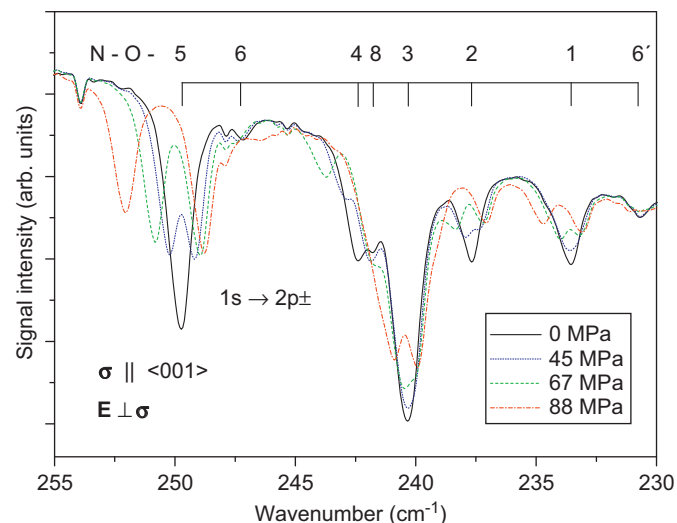


Fig. 1. Hydrogenic $1s \rightarrow 2p_{\pm}$ transitions of (N, O)-donor complexes as a function of uniaxial stress in a $\langle 100 \rangle$ direction.

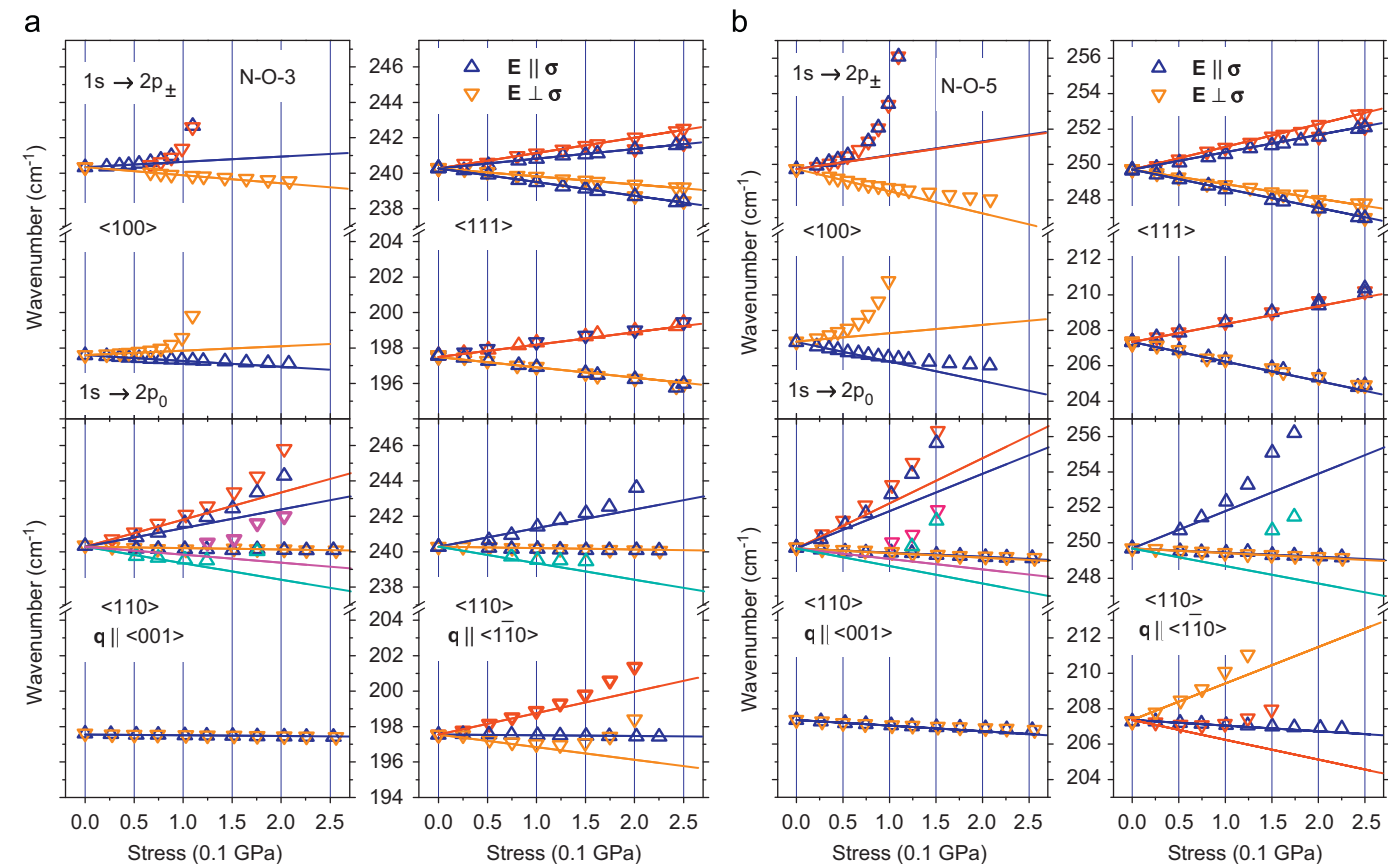


Fig. 2. Complete stress splitting of N–O–3 and N–O–5: $1s \rightarrow 2p_0$ and $1s \rightarrow 2p_{\pm}$ transitions at 10 K. From Ref. [11].

moment for the $1s \rightarrow 2p_0$ transition parallel to the C_2 -axis, whereas for the $1s \rightarrow 2p_{\pm}$ transition it is oriented perpendicular to this axis. This is shown schematically in Fig. 3. The reduction of the ground state of the donor wave function (T_2 representation of the tetrahedral group) from T_d to C_{2v} leads to two wavefunctions of A_1 symmetry that fulfill the requested polarization behavior. They consist of a single pair of Bloch states coming from the two conduction band minima in k -space being parallel to the C_2 -axis. These minima are also plotted in Fig. 3. The resulting transition intensities are calculated and compared with the experimental results (Table 1). The close agreement supports strongly the proposed microscopic model for the dominating (N, O)-centers N–O-3 and N–O-5.

We also investigated the transitions arising from other members of the (N, O)-shallow donor family (see Fig. 1). Due to the weakness of some of the bands and due to the effect of overlapping during application of uniaxial stress it is not possible to record complete stress dependences for all crystallographic directions. In Fig. 4 some of the more complete data sets for the $\langle 100 \rangle$ and $\langle 111 \rangle$ crystallographic directions are shown. Generally, the behavior of these complexes is qualitatively similar to N–O-3 and N–O-5: for stress in the $\langle 100 \rangle$ direction a splitting into 2 branches occurs, for stress in the $\langle 111 \rangle$ direction a splitting into 2 branches for each of the both $1s \rightarrow 2p_{\pm}$ transitions occurs. Also the polarization behavior is the same, with the exception of N–O-6'. We speculate that this complex does not belong to the (N, O)-shallow donor family. Altogether, these data provide strong evidence that all proper (N, O)-shallow donor complexes have C_{2v} symmetry. The FTIR results are in agreement with earlier spin resonance data of Hara et al. [12] where also C_{2v} symmetry was found. However, spin resonance cannot resolve

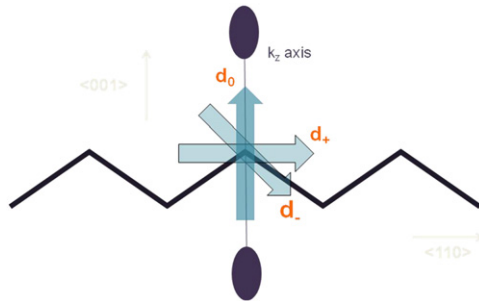


Fig. 3. Schematic view of the observed dipole orientation for a particular complex aligned along the $\langle 110 \rangle$ direction. Associated Bloch states are also shown.

Table 1

Splittings, shifts, and relative intensities for $1s \rightarrow 2p_0$ transitions of N–O-3 and N–O-5 under uniaxial stress in the $\langle 100 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$ directions. Notation is according to Kaplyanskii [10]. A more complete compilation is given in Ref. [11].

Direction of stress σ	Frequency shift, Δ	Multiplicity	intensity		
			Calculation	N–O-3	N–O-5
$\langle 100 \rangle$	$A_2 \sigma$	4	$I_{ }:I_{\perp}$	0:2	0:1.9
	$A_1 \sigma$	2		2:0	1.9:0
$\langle 111 \rangle$	$1/3$	3	1:1	1.1:1.1	1.4:1.4
	$(A_1+2A_2+2A_3) \sigma$				
	$1/3$	3	1:1	1.0:1.0	1.2:1.1
	$(A_1+2A_2-2A_3) \sigma$				
$\langle 110 \rangle$			$I_{110}:I_{001}:I_{110}$		
	$(A_2+A_3) \sigma$	1	0:1:0	0:1.2:0	0:0.9:0
	$1/2 (A_1+A_2) \sigma$	4	2:0:2	1.9:0:1.7	1.7:0:1.5
	$(A_2-A_3) \sigma$	1	0:1:0	0:1.1:0	0:0.7:0

the different species of (N, O)-shallow donors and, therefore, average over the properties of the ensemble.

A separate discussion is needed for the nonlinear stress dependences of some of the bands. It is observed that all observable transitions with this property of a specific donor have the same curvature. Different donors behave differently. Furthermore, only transitions originating from the lowest level of the stress-split $1s(T_2)$ ground state are affected. This means that this effect is due to a nonlinear shift of this lowest level to lower energy. We speculate that this behavior is caused by the quantum mechanical repulsion from another state coming energetically closer with increasing stress. Higher-lying $1s$ states would be candidates for such a state.

From the theoretical point of view, so far two structural models have been presented for (N, O)-shallow donor complexes. Considering only the lowest-energy configuration, Ewels et al. [13] presented a symmetrical model for NO_2 (C_{2v} symmetry) where a three-fold coordinated nitrogen atom is complexed with two interstitial oxygen atoms in an (110) in-plane geometry. A square-like structure for a NO complex, again in a (110) plane very similar to the N–N pair defect [14], was proposed by Gali et al. [15].

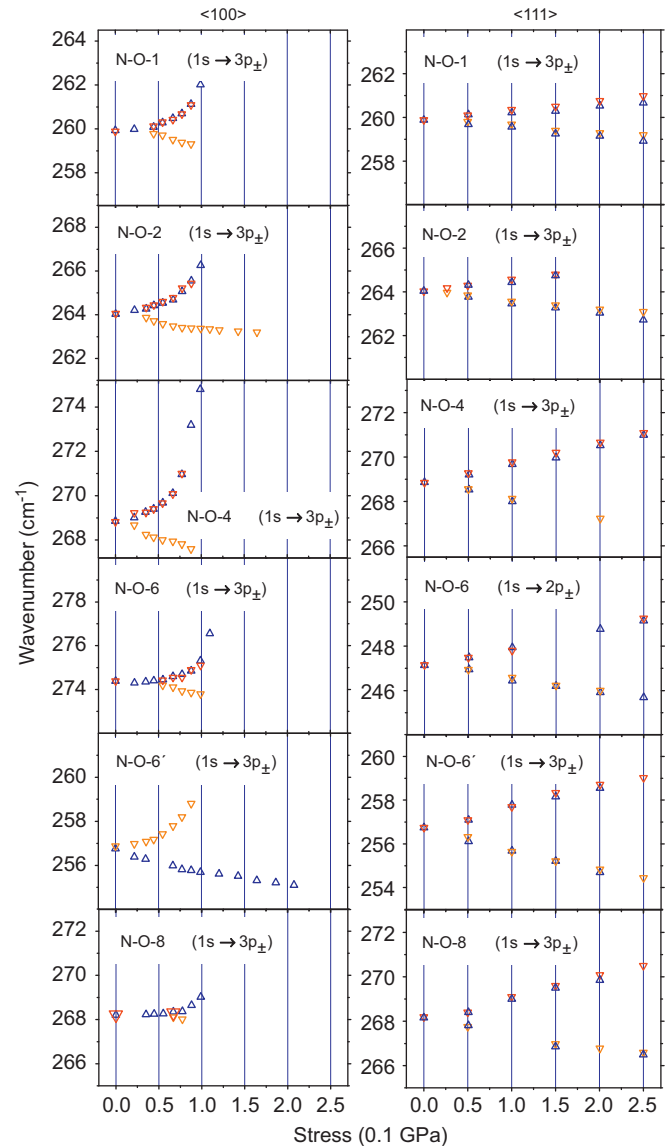


Fig. 4. Stress splitting of the other (N, O)-centers (see Fig. 1) in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. Those $1s \rightarrow np_{\pm}$ transitions are shown that give the most complete set of data.

This structure has the lower C_s symmetry. Very recently, this latter configuration has been confirmed by Fujita et al. [16].

None of these proposals is consistent with the experimental results. Either the chemical composition or the defect symmetry is in conflict with our data. Putting the focus only to N–O–5, there are in principle three possibilities to overcome this:

- (i) N–O–5 (NO) as the donor with the highest binding energy has indeed C_{2v} symmetry. This requires that the N–O axis is oriented along the C_2 -axis.
- (ii) The lower symmetry of N–O–5 (C_s) is not felt by the wave function of the donor electron. This seems unlikely as the 1s ground state as well as the excited states at least up to $4p_{\pm}$ are obviously influenced by the core structure of the defect.
- (iii) The chemical composition of N–O–5 is not NO but NO_2 . At first, this is in conflict with our data on the equilibrium concentration as a function of the O_i concentration [2]. However, it is not impossible that a different model for the formation kinetics [4] might offer a solution.

4. Conclusions

We used Fourier transform spectroscopy to investigate the electronic $1s \rightarrow 2p_0$ and $1s \rightarrow 2p_{\pm}$ transitions of (N, O)-complexes in the far infrared under uniaxial stress to get further information about the microscopic structure. Rather unusual for shallow donors in silicon, the influence of stress on the transition energies is numerically very small. However, we observe a splitting of the bands in the $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ crystallographic directions, being typical for lifting of orientational degeneracy.

The behavior under uniaxial stress is basically described by ground and excited state wave functions belonging to the T_2 representation of the tetrahedral group. The lifting of orientational degeneracy is treated as a small perturbation on the basis of Kaplyanskii's tabulations. The result of the full analysis of the two most prominent shallow donors N–O–3 and N–O–5, in terms of selection rules and line intensities under polarized light, is that the electronic states are perturbed by a defect potential of apparent C_{2v} symmetry. The donor wave function itself can be

constructed from Bloch states derived from a single pair of conduction band minima. The observation of nonlinear stress responses of some of the transitions is not covered by this analysis and is tentatively attributed to interactions with higher-lying 1s states.

It is concluded that present theoretical proposals for the microstructure of these complexes must be reconsidered.

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