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A. Karoui, F. Sahtout Karoui, and G.A. Rozgonyi
North Carolina State University

T. Buonassisi and E.R. Weber
University of California at Berkeley

M. Michael
Lawrence Berkeley National Laboratory

T.F. Ciszek
National Renewable Energy Laboratory

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Stress-Induced Nitrogen and Oxygen Segregation and Complexing Investigated by High Resolution Synchrotron FTIR

A. Karoui¹, T. Buonassisi,² F. Sahtout Karoui,¹ G. A. Rozgonyi,¹
M. Michael,³ E. R. Weber,² T. Ciszek⁴

¹. *Dept. of Materials Science & Eng., North Carolina State University, NC*

². *Dept. of Materials Science & Eng., University of California at Berkeley, CA*

³. *ALS, Lawrence Berkeley National Laboratory, CA*

⁴. *National Renewable Energy Laboratory, CO*

Abstract: Nitrogen doped Czochralski (N-CZ) and Float Zone (N-FZ) silicon were measured by high resolution synchrotron Fourier Transform IR spectroscopy (HR-FTIR). The chemical complexes were analyzed in specific regions with known extended defects, i.e., denuded or precipitated regions of annealed N-CZ Si wafers, in N-FZ Si with ring defects and on “N-Skin” region. The absorption lines were assigned to chemical complexes previously studied by first principles calculations. In annealed N-CZ Si wafers, a strong correlation was observed between the absorption line intensity depth variations and the defect distributions revealed by an Oxygen Precipitate Profiler (OPP), and oxygen and nitrogen SIMS profiles. Transformation of chemical complexes from one type to another was observed. A defect band, visible as an OPP peak at the denuded zone-bulk interface was found to be related to vacancy defect enhancement of oxygen precipitation via production of mobile N₂. For the as grown N-FZ, the radial dependency of IR absorption line intensity is correlated to x-ray topography contrast.

I. Introduction

The large number of predicted IR absorption lines in N CZ silicon and the variations in experimental conditions (thermal history) complicate the assignment of these lines to chemical complexes. However, high spatial resolution Fourier Transform Infra-Red spectroscopy (HR-FTIR), supported by quantum mechanics calculations, is a powerful mean for analyzing complexes in special regions. In N-doped silicon we have investigated unique N and O related extended defects by various techniques including OPP/etching, HRTEM, Z-contrast and EELS, SIMS simultaneous profiling [1, 2] to depict the mechanisms of defect formation. The robustness of our complex identification method stems from detailed data on these extended defects and absorption line predictions by atomistic calculations. We also verify the viability of the identified N-O-V species (in as grown and annealed silicon) to their formation and stability thermodynamics. These interrelated studies on complexes benefit the continuum clustering modeling of extended defect growth in silicon [3, 4, 5].

The objective of this work is to use HR-FTIR depth profiling spectroscopy to detect chemical complexes produced in subsurface of annealed N-doped Czochralski (N-CZ) wafers [6, 7, 8]. To consolidate this analysis, a N-doped Float Zone (N-FZ) Si wafer is examined along its radius, where N defects vary. Assignment of detected IR optical lines, to previously proposed operative chemical complexes, relies on previously published results from first principles calculations. Among other N related issues, this study addresses the mechanisms of N and O co-segregation.

II. Experimental Methods

A state-of-the-art optical bench at the ALS [9] was used. It consists of a Nicolet IR microscope that produces a 5 to 10 μm spot size, a LN₂-refrigerated detector and an MCT (HgCdTe) He-refrigerated bolometer, and utilizes an IR light beam induced by a bending magnet in a synchrotron ring. The beam is highly collimated and more than 3 orders of magnitude brighter than a Globar source [10]. HR-FTIR line scans are necessary for precisely mapping the distribution of N and O species in N-CZ subsurface defects [1], and in N induced native extended defects (the N-FZ ‘N-Skin’ [11]). Line extraction is made possible by using a background spectrum from a defect free zone of the same sample acquired under identical conditions.

III. Results and discussions

1) N and O segregation in N-CZ heat treated wafers

We discuss in this section FTIR data on N-O complex nature and distributions, in N-CZ wafer Lo-Hi annealed at 650°C for 8 Hrs and 1050°C for 16 Hrs. Based on OPP and SIMS depth profiling, we previously reported [1] that three regions were identified [12]; Fig. 1(a) shows a typical OPP profile. The first region spreads over 2 μm and is saturated with N and O. Due to thermal stresses, up to $1 \times 10^{18} \text{ cm}^{-3}$ out-diffused nitrogen and $2 \times 10^{21} \text{ cm}^{-3}$ oxygen accumulated at the subsurface, which results in ultra shallow subsurface oxynitride layer. The latter is interesting for photovoltaic and optoelectronic devices [13, 14] but intriguing for IC technologies, because it contains a large density of small equilibrium precipitates [2]. The second region, referred to as Low Density defect Zone (LDZ), is basically an “oxygen

denuded zone” that was strongly modified by N [2] and is left (after annealing) with a low density of very small precipitates and nuclei comparable to the N-CZ as grown defects. The third is characterized by high density of precipitates and SF(s) that are formed by a significantly different mechanism than in N free CZ Si [2].

Figure 1(b) shows a 2D representation of the differential reflectance spectra and Fig. 1(c) the absorbance spectra as a function of depth. The intensity of the some absorbance lines are shown in Fig. 2(a); similar curves that are relevant to OPP profile features (in region III) are provided separately are provided in Fig. 2(b). The table in Fig. 2(c) gives an analysis of the absorption line positions in the three regions of the Lo-Hi beveled sample. These were obtained from the absorbance spectra given in Fig. 1(c). Lines are compared between themselves (within each of the three regions) and assigned to chemical complexes in connection to previously calculated absorption [6].

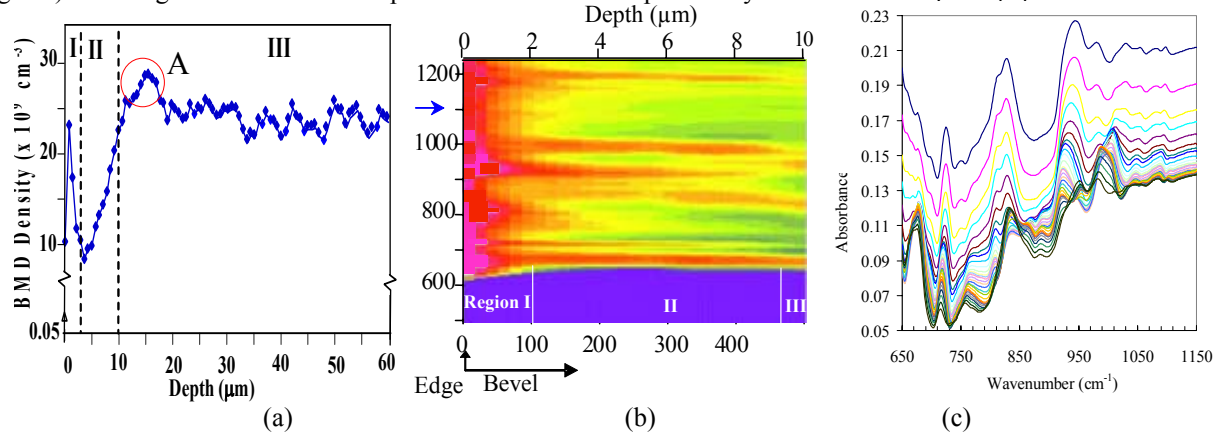


Fig. 1: (a) Defect depth distribution by OPP in Lo-Hi cycled wafer.
 (b) Differential reflectance spectra by HR-FTIR along bevel polished sample (magnification=50).
 (c) Differential absorbance spectra calculated from measured reflectance.

It is remarkable that in region I all lines show higher intensities and decay in the same fashion. More importantly, the decays have shape and the same depth range as the OPP defect density profile, in that region. Moreover, the shape of 984.1, 666.4, and 837.5 cm^{-1} and to less extent 681.3, 864.9, and 870.1, 890.1 cm^{-1} lines reproduce the OPP profile. This is especially visible on the peak at the beginning of region III, while 810.9 and 950.7 cm^{-1} lines show at that depth an opposite behavior to the OPP depth profiles. This data indicates the close relation of the identified complexes to the extended defects (detected by OPP, see Fig. 1(a)), as well as the interrelation between the complexes to which these IR lines belong. This represents a unique evidence of N-O species conversion into V-N. It occurs by loss of O from V-N-O complexes (i.e., reduction of N_2O , $\text{V}_2\text{N}_2\text{O}$, and $\text{V}_2\text{N}_2\text{O}_2$ concentrations) while increasing the concentration of V-N complexes (i.e., V_2N_2 and N_2). Note that the reflectance line at 1107 cm^{-1} (finger print of interstitial oxygen: O_i) varies smoothly, and increases in the subsurface towards the surface.

2) N complexes in as-grown N-FZ

We previously reported that the attempt of doping float zone silicon with high level of nitrogen using N_2 atmosphere gas during the zoning, leads to a non uniform distribution of the dopant [14]. As shown in the XRT image of a N-FZ 32 mm diam wafer, see Fig. 3(a), an external layer referred to as nitrogen-skin (N-Skin) is formed. In addition, there is a hallow of high density of pits (left in the central region after a long slurry polishing) that might be originated by voids in the central region, see micrograph in Fig. 3(a). Moreover, the XRT shows a series of co-centric rings (white contrast). The color coded map (see the strip superimposed to the XRT image) shows the correlation of chemical complex IR absorption and structural defects (rings). Because of the nitrogen and oxygen saturation in the ingot rim, the stresses during the FZ Si zoning, and the cooling rate, we expect a variety of N-V species. Therefore the “N-Skin” wafer is an excellent test-bed for delineating N-V complexes with HR-FTIR.

Figure 3(b) shows the differential absorbance spectra along the radius, excluding the central defected zone. In the differentiation we used the spectrum acquired 6mm away from the wafer center as reference. One must first note that the O_i line (1106 cm^{-1}) is not detected. Secondly, the N related band (between 650 and 720 cm^{-1}) is the most dominant, its intensity increases as we go from the center to the wafer edge and fluctuates at the same spacing as the XRT rings of Fig. 3(a). In fact, this band is formed of four N-related lines, among which three are found in N-CZ (666.4 and 681 cm^{-1} both assigned to V_2N_2), the third is 696.5 cm^{-1} (attributed to $\text{V}_2\text{N}_2\text{O}$). However, line V_2N_2 must be dominant. The smaller bands appearing between 720 and 890 cm^{-1} like in NCZ, see Fig. 2(c), are related to VNO and NO complexes. Although their intensity is limited, as expected from FZ material, to $\frac{1}{4}$ of similar ones in N-CZ, they show that N and O inevitably couple in float zone Si. This is in line with the very strong coupling of N and O found in

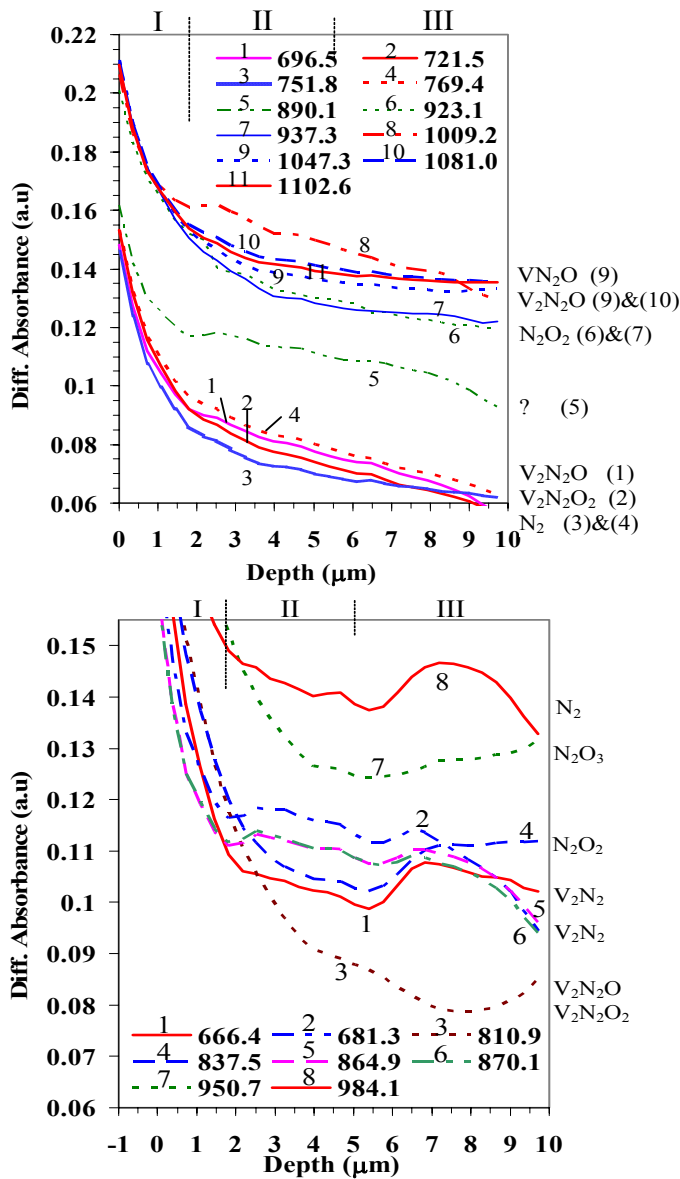


Fig. 2: (a) and (b) Intensity of absorption lines (measured from the base) of annealed N-CZ Si wafer. (c) Analysis of the absorption line intensity and assignment to chemical complexes.

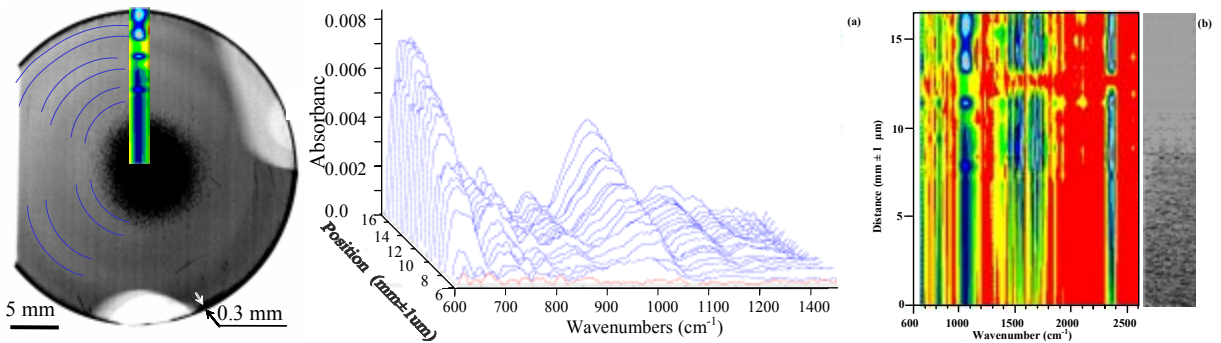


Fig. 3: (a) XRT of N-FZ wafer. Circles indicate defect rings. Color coded map shows variations of the intensity if IR absorption line (extracted from the FTIR spectra). (b) Differential absorbance spectra obtained along the radius of the same wafer, using HR-FTIR in transmission. (c) Space-wavenumber reflectance map acquired along the radius of wafer. Set of 24 micrographs taken by the video camera that is inline with the IR microscope used in the HR-FTIR system.

N-CZ Si [2]. The N and O interactions were discussed in Ref.2 based on O and N simultaneous profiling with HR-SIMS of the subsurface of N-CZ silicon. The stronger and broader band spreading from 920 to 1100 cm^{-1} is attributed to oxynitride phases within the silicon matrix. It denotes large variations in the concentrations of V-N species. It is remarkable that the V-N-O lines are detectable in this N-FZ wafer, and that their intensity increases as we go toward the wafer rim, where oxynitride skin is initiated. Moreover, the N appeared strong enough to drag a lot of oxygen and form oxynitride at the peripheral ring of the ingot as well as in the ring regions inside the wafer.

Conclusion

Detailed information relevant to chemical complex generation in N doped silicon were obtained using the HR-FTIR setup at the Advanced Light Source. The differential FTIR spectra (using background spectrum from the same line scan) reveal the smallest possible lines and increases the high resolution capabilities.

Using data from atomistic calculations, reported elsewhere, we have singled out the prominent FTIR lines. A variety of complexes in each of the three Lo-Hi annealed N-CZ wafer regions were identified. A strong correlation of the intensity depth profile of absorption lines with the OPP defect density was found for the three regions, in particular the subsurface region and at the LDZ-bulk interface. The surface effected the nature of these complexes by providing the necessary vacancies to form the most stable complexes at the surface and in the subsurface. In the N doped float zone we could detect the V-N species, as well as, N-O complexes.

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