Complexing of Nitrogen with Carbon and Oxygen in Silicon: Photoluminescence Studies

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We study interactions of nitrogen with carbon and oxygen in crystalline silicon by photoluminescence spectroscopy. Such processes manifest themselves in five photoluminescence lines in the spectral region around 1.6 µm emerging after nitrogen and carbon implantations and furnace annealing with 550°C optimum temperature. Nitrogen and carbon isotope shifts of the lines confirm the incorporation of these atomic species in the optical defects. Nitrogen-oxygen interactions are demonstrated by differences in the lines' appearance between oxygen-lean float-zone and oxygen-rich pulled silicon starting materials. The data suggests similar basic nitrogen-carbon units in all five defects.

Key words: Nitrogen-Carbon Complexing, Silicon, Photoluminescence.

INTRODUCTION

Technical use and potential applications of nitrogen in silicon, such as in silicon nitride dielectric layers and diffusion barriers or for mechanical strengthening of oxygen-lean wafers has stimulated studies on the incorporation and bonding of nitrogen in the silicon lattice reviving earlier academic investigations. Incorporation of nitrogen in point-like defects in silicon was demonstrated by electron-spin-resonance, deep-level transient spectroscopy, infrared absorption, and photoluminescence. Recent infrared absorption spectroscopy showed that almost all nitrogen is melted or implanted silicon preferentially bonds into pairs for a wide range of processing conditions. In contrast, most of the defects mentioned above need rather specific treatments to appear in undoped as-grown silicon, nitrogen melt-doped crystals, or nitrogen ion implanted samples, and possible reaction partners in the formation of the defects remained often unidentified. However, interaction of nitrogen with carbon was positively established in recent photoluminescence work and with oxygen in infrared measurements. Likewise, preliminary photoluminescence data seemed to indicate nitrogen-oxygen complexing.

In the present paper we extend our earlier preliminary study of five photoluminescence (PL) lines, N1–N5. We show that the optical defects are preferentially formed upon sequential nitrogen and carbon implantation with overlapping depth profiles and annealing at 550°C. Nitrogen and/or carbon isotope line shifts confirm nitrogen-carbon pairing in all five defects. A summary of the optical data suggests that defects incorporate the same basic N-C unit. Additional interactions in three of the defects with oxygen are demonstrated by apparent differences in the defect formation between oxygen-lean float-zone (FZ) and oxygen-rich pulled Czochralski (CZ) silicon.

EXPERIMENTAL

The experiments were performed on many samples cut from the four following starting materials:
1. Si:P 240 Ωcm, floating zone (FZ)
2. Si:P 10 Ωcm, FZ
3. Si:B 20 Ωcm, Czochralski grown (CZ)
4. Si:B 0.3 Ωcm, CZ

The samples were implanted either with nitrogen or carbon alone at equal doses of 5 × 10¹⁴ cm⁻² at an energy of 200 keV or with both species sequentially with overlapping depth profiles. Following literature data the profiles are approximately 0.8 µm deep with maxima at ~0.5 µm. Other implantations were made with Ar and Si ions at the same conditions to cross-check the results. In addition to the incorporation of nitrogen by ion implantation, melt-doped crystals were employed and subjected to C, Ar, and Si ion implantation. Following damage these crystals were furnace annealed, ruby pulse laser annealed at 2.8 Jcm⁻² with 20 nsec pulse length, or thermal-pulse annealed at 900°C for 20 sec.

Photoluminescence spectra were taken with the samples immersed in liquid helium at 4.2K or 2K.
They were excited by 647.1 nm Kr or 514.5 nm Ar ion laser lines with PL light dispersion by a single-pass grating monochromator of 1 m focal length. Using conventional lock-in technique the spectra were detected by cooled Ge or PbS detectors. Isotope effects observed on all of the lines are only small and require scanning accuracy and resettability of the spectrometer enhanced over the specified values by the following method: The monochromator is set at the specific PL line position and the spectrum is scanned rotating an electrically driven quartz plate in the optical beam inside the instrument.

Red or green laser light used to excite the luminescence penetrates into the crystals 1–2 μm. Assuming that the defect formation occurs in the implanted region within the ~0.8 μm deep profiles of nitrogen and carbon it is inferred that all of the optical defects created by nitrogen-carbon interactions are excited.

RESULTS: BASIC PHOTOLUMINESCENCE DATA

The signature of the nitrogen-related defects discussed here are five photoluminescence no-phonon transitions in the spectral region around 1.6 μm (Fig. 1). The exact line positions are

- N1 1.6624 μm—745.6 meV
- N2 1.6352 μm—758.0 meV
- N3 1.6277 μm—761.5 meV
- N4 1.6152 μm—757.4 meV
- N5 1.6047 μm—772.4 meV

Table I. Production of the Nitrogen-Related Defects. In all Cases, Sequential N and C Implantation Yields by Far the Highest Photoluminescence Intensities of the Defect Lines. The data Refer to Furnace Anneal (cf also Figs. 3 and 4). N1 was also Observed after Ruby Pulse Laser Annealing and Thermal Pulse Annealing (no Corresponding Experiments were Performed for N2–N5). Damage of the Crystals Prior to Anneal is Needed to Produce the Defects.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Implantation</th>
<th>Remarks</th>
<th>Isotope Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>N plus C</td>
<td>sequentially with overlapping depth profiles</td>
<td>14N, 15N, 12C, 13C</td>
</tr>
<tr>
<td></td>
<td>N or C</td>
<td>other species in sufficient concentration in starting material</td>
<td></td>
</tr>
<tr>
<td></td>
<td>“arbitrary”</td>
<td>N doped in the melt, C in sufficient concentration in starting material</td>
<td></td>
</tr>
<tr>
<td></td>
<td>N alone</td>
<td>C in sufficient concentration in starting material</td>
<td></td>
</tr>
<tr>
<td>N2</td>
<td>N plus C</td>
<td>sequentially with overlapping profiles</td>
<td>14N, 15N, 12C, 13C</td>
</tr>
<tr>
<td></td>
<td>N alone</td>
<td>C in sufficient concentration in starting material</td>
<td></td>
</tr>
<tr>
<td>N3</td>
<td>N plus C</td>
<td>sequentially with overlapping profiles</td>
<td>12C, 13C</td>
</tr>
<tr>
<td></td>
<td>N alone</td>
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<tr>
<td>N4</td>
<td>N plus C</td>
<td>sequentially with overlapping profiles</td>
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</tr>
<tr>
<td></td>
<td>N alone</td>
<td>C in sufficient concentration in starting material</td>
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The maximum energy difference between the line positions is 26.8 meV, small compared to the shift of the lines from the silicon band edge at 1.1695 eV, of order 400 meV. Given the similar production conditions of the defects this close proximity of the line positions is an indication of similar electronic energy levels in the forbidden gap and hence, similar electronic structure of the defects which is in fact confirmed by experiments to be discussed below. A previous study of the N1 transition showed that the optical emission of this defect is due to the recombination of a loosely bound electron (binding energy $E_e \sim 50$ meV) with a tightly bound hole ($E_h \sim 375$ meV). The similarity of all data taken for N1–N5 including the line positions suggests that all of the defects represent deep hole traps with binding energies in the 300–400 meV range.

DEFECT PRODUCTION

The production conditions of the five defects are listed in Table I. In all cases, the largest emission intensities are observed for sequential N and C implantations followed by thermal annealing. When the defect lines were detected after N or C implantation alone (cf Table I) the presence of the respective other species in the starting material could be inferred from sample data or independent experiments: Carbon has always high enough concentration in FZ or CZ silicon to account for the formation...