Electron-paramagnetic-resonance study of heat-treatment centers in *n*-type silicon

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Donor formation in heat-treated phosphorus-doped Czochralski-grown silicon has been studied by electron paramagnetic resonance and resistivity measurements. Both "thermal-donor-" and "new-donor"-formation temperature regions (470 and 650 °C, respectively) have been investigated. The results allow one to identify the spectra in both regions as arising from the Si-NL10 defect.

I. INTRODUCTION

It is a well-established phenomenon that oxygen-rich silicon develops electrically active centers on annealing at different temperatures. The centers, known as thermal donors, are thought to be oxygen clusters. Various sizes and structure models have been proposed for those clusters, but no final agreement has been reached thus far.[1]

Many experimental techniques have already been applied in studies on thermal donors —among them electron paramagnetic resonance. Early investigations by Muller *et al.*[2,3] revealed that a variety of heat-treatment centers of 2-mm symmetry were formed, depending on heat-treatment conditions and parameters of the starting material. Recently, one of those heat-treatment centers has been identified with one of the thermal donor energy levels observed in infrared absorption.[4]

Following the study by Muller and co-workers, other papers on electron-paramagnetic-resonance investigations of heat-treatment centers appeared. One of them, by Suezawa, Sumino, and Iwaizumi,[5] presented extended work on heat-treatment centers produced at different temperatures in *n*-type crucible-grown silicon. Among other results, they claimed to observe spectra significantly different from those reported by Muller, Sieverts, and Ammerlaan.[3] It is the purpose of this paper to clarify the situation.

II. EXPERIMENT

Following the purpose of the experiment, materials similar to those used by Suezawa and co-workers were chosen. The samples were cut from high-grade dislocation-free *n*-type crucible-grown silicon. The initial phosphorus concentration was determined to be 5×10^{13} cm^{-3}, and the initial interstitial oxygen concentration was 1.5×10^{18} cm^{-3}. The samples were given an initial oxygen dispersion heat treatment and then annealed in an argon atmosphere at 470 and 650 °C. The heat treatment at 650 °C followed only after 48 h/470 °C preanneal. Thus, the thermal-donor- and new-donor-formation regions have been considered. The so-called "deformation donors" were not investigated. The specimens subjected to the above treatments were then studied by electron-paramagnetic-resonance and resistivity measurements. The electron-paramagnetic-resonance measurements were performed in the 23-GHz microwave band with the spectrometer tuned to dispersion. The sample temperature was 4.2 K. Resistivity measurements were performed at room temperature by the conventional four-point probe technique.

III. RESULTS

A. Thermal donor: 470 °C annealing temperature region

Electron-paramagnetic-resonance studies revealed the presence of heat-treatment centers that could be identified as the Si-NL10 family.[6] No new heat-treatment centers were found. Figure 1 presents the concentration of the Si-NL10 centers as a function of annealing time. Thermal donor concentration has also been depicted in Fig. 1. It has been calculated from room-temperature resistivity measurements under the assumption that each thermal donor supplies one electron to the conduction band. Figure 2 presents the transformation of the observed centers as a function of annealing time. The ΔB separation of two resonance lines observed in the [111] crystallographic direction (scaled down to 23.0-GHz microwave frequency) was chosen as a measure of this transformation.[6] ΔB is directly proportional to the off-diagonal element of the g tensor g_{yz} and was shown to exhibit the most pronounced shift on prolonged heat treatment.[3,6] The data in Fig. 2 are presented for measurements with and without white-light illumination of the sample. In both cases the

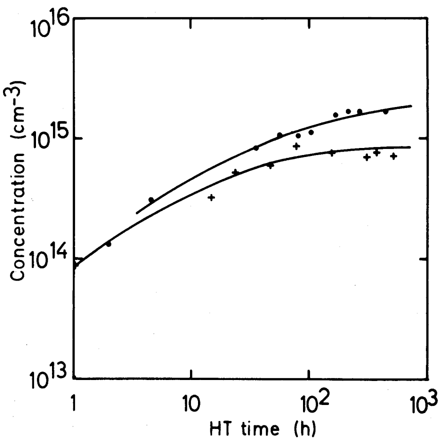

FIG. 1. Concentration of thermal donors (●) as calculated from room-temperature resistivity measurements under the assumption that each thermal donor supplies one electron to the conduction band and centers responsible for the Si-NL10 electron-paramagnetic-resonance spectrum (+) as a function of 470 °C heat-treatment time.

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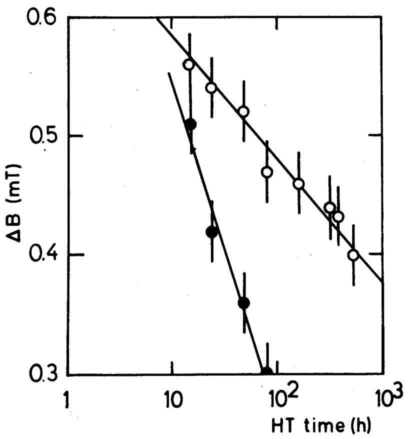

FIG. 2. Annealing time dependence of g shifting for the Si-NL10 spectrum as observed with (open symbols) and without (closed symbols) white-light illumination. ΔB values have been scaled to 23-GHz microwave frequency.

observed spectra transform toward smaller anisotropy, which agrees with the behavior of the Si-NL10 spectrum for p-type material.[6]

B. New donor: 650 °C annealing temperature region

To verify the results of Suezawa and co-workers[5] reported for the new-donor-formation region, the samples were studied following 48-h heat treatment at 650 °C. Additionally, those samples were given the 48-h initial heat treatment at 470 °C. The electron-paramagnetic-resonance studies revealed again centers of the Si-NL10 family. In addition, a broad, weaker, unidentified resonance could be seen.

IV. DISCUSSION

The results presented show that, similar to our recently reported studies on p-type oxygen-rich silicon,[6] in n-type material, centers responsible for the Si-NL10 spectrum also constitute the main thermal donor species for both thermal-donor- and new-donor-formation regions. The Si-NL10 spectrum itself undergoes constant transformation from an anisotropic pattern to an almost isotropic one. The transformation, as depicted in Fig. 2, is influenced by illumination of the sample. It is therefore most probable that the almost isotropic resonance reported by Suezawa and co-workers[5] with $g_1 = 1.9985$, $g_2 = 1.9989$, and $g_3 = 1.9983$, and confirmed in a recent paper of Wörner and Schirmer[7] for the new-donor-formation temperature region, is the Si-NL10 spectrum in the late stage of its transformation. It is not completely clear from the paper of Suezawa and co-workers to what duration of the annealing time the quoted g values should correspond. There are, however, some indications that annealing times exceeding 100 h were used. In that case the corresponding value of ΔB would be approximately 0.3 mT, since the reported measurements were performed without illumination. This value is close to the resonance linewidth of heat-treatment centers as observed in X band, and therefore the anisotropy of the spectrum was beyond available resolving power. Similar remarks apply also to the work of Wörner and Schirmer,[7] since that study has also been performed in X band. Because of its low resolution, the 9-GHz microwave band is not really appropriate for studies of heat-treatment centers with small anisotropy of their g tensors.

For the spectrum observed in the new-donor-formation region Suezawa *et al.* give a similar g tensor as for the thermal donor range. This is confirmed in the present study. Our electron-paramagnetic-resonance studies revealed also for that annealing temperature region the presence of the Si-NL10 family spectrum. Here again, because of insufficient resolving power, neither Suezawa and co-workers nor Wörner and Schirmer could identify the spectrum, whose angular dependence could only be observed as "breathing behavior." Contrary to Wörner and Schirmer, we did not observe any other resolved resonance spectra for the new-donor-formation temperature region. It should be noted that our results for p-type oxygen-rich silicon also revealed only Si-NL10 family spectra to be present for the new-donor annealing temperature region.[6] The above observations agree with the results of Gaworzewski, Hild, and Schmalz[8] from infrared absorption measurements on oxygen-rich silicon heat treated at 600–800 °C, who found that centers similar to those observed after 470 °C heat treatment could also be formed in that temperature region.

V. CONCLUSIONS

The "almost isotropic" resonance reported recently by Suezawa and co-workers[5] and Wörner and Schirmer[7] for heat-treated n-type Czochralski silicon has been identified to be a member of the Si-NL10 family.[6] Therefore, the role of the heat-treatment center with the associated Si-NL10 electron-paramagnetic-resonance spectrum as a dominant thermal donor species has been confirmed for both thermal-donor ($\sim$470 °C) and new-donor ($\sim$650 °C) annealing temperature regions. Moreover, contrary to the observation by Wörner and Schirmer, Si-NL10 was the only resolved electron-paramagnetic-resonance spectrum found for both temperature regions.

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