Observation of thermal double donors in the energy spectrum of new donors in silicon

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Thermal double donors have been observed among the high-temperature ($T \gtrsim 600$ °C) "new donors" in silicon by Fourier transform spectroscopy. The energy spectrum of these double donors is the same as that of low-temperature ($T = 320$–500 °C) thermal double donors, but there are differences in formation kinetics and in the stability of the atomic configuration. The results are evidence of a high thermal stability of double donor centers in silicon.

The use of oxygen precipitation in silicon grown by The Czochralski method to produce internal getters in microelectronics elements has sparked an active research program on the nature and properties of the thermal defects generated by these precipitation processes. Of particular research interest among the thermal defects are thermal double donors (TDDs), which exhibit a number of interesting physical properties: a complex energy spectrum of the donor states, distinctive features in the wave functions of electrons localized at donor centers, and a bistability of the atomic configuration, among others.[1] These donors form during heat treatment of silicon in the temperature range 320–500 °C. They are generated at a maximum rate at $T \approx 450$ °C; at higher temperatures, the formation rate falls of extremely fast, as can be seen from literature. At $T \gtrsim 600$ °C, processes leading to the formation of TDDs have not been studied at all.

For this reason, the thermal donors with a broad energy spectrum, 20–180 meV, which arise during oxygen precipitation at $T \gtrsim 600$ °C have been termed "new donors" (NDs; Refs. 1–4, for example). A recent study of the temperature dependence of the electron density $n(T)$ (through the use of γ-ray bombardment, to cause a progressive compensation for thermal donors by radiation-induced acceptors)[5] has shown that the energy spectrum of the NDs is actually a composite spectrum. In particular, it contains donor states whose properties are extremely similar to those of TDDs. However, no reliable conclusion about the identity of these centers can be drawn until spectroscopic methods are brought to bear on the problem.

The experimental data which we are reporting here show without question that the thermal stability of TDDs is indeed significantly higher than has heretofore been assumed. Since the TDD family contains at least 11 types of centers,[1] the question of

the contribution of "old" thermal donors, in particular, TDDs, to the overall energy spectrum of the NDs requires a more careful analysis.

Samples were cut from high-resistivity p-type silicon (the residual concentrations of acceptors and donors satisfied N_a, $N_d \lesssim 5\times10^{13}$ cm^{-3}). The oxygen content and the carbon content were $\approx 6\times10^{17}$ cm^{-3} and $\lesssim 5\times10^{16}$ cm^{-3}, respectively, according to IR spectroscopy. The samples were heat treated in dry nitrogen at 600 °C for 50 or 100–120 h. For a comparative study, several control samples were heat treated at 450 °C for 1–16 h. The IR photoconductivity spectra at low temperatures (4–20 K) were recorded by a contactless method[6] over the range 200–800 cm^{-1} on a Bruker IFS-113V Fourier transform spectrometer.

1. Figure 1 illustrates the results with part of the photoconductivity spectrum of silicon heat treated at 600 °C. The lines observed here are a consequence of a photothermal ionization and a simultaneous optical absorption of donors.[7] At low tempera-

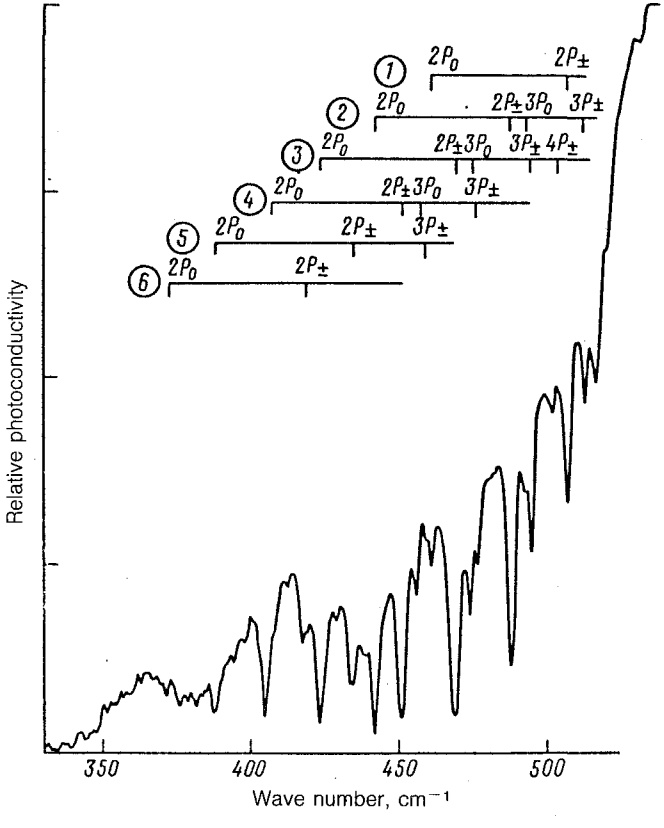

FIG. 1. Photoconductivity spectrum of a Cz-Si sample which had been heat treated at $T = 600$ °C for 120 h. The sample was subjected to interband illumination during cooling. The spectrum was recorded at $T = 7$ K at a resolution of 1 cm^{-1}.

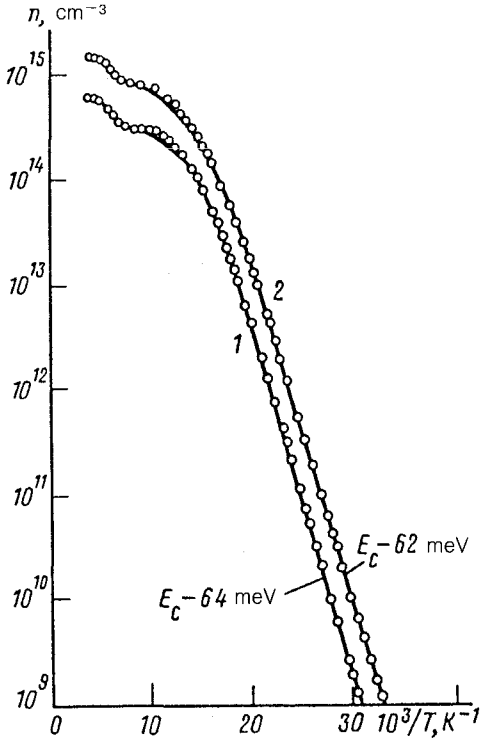

FIG. 2. Temperature dependence of the electron density for silicon subjected to heat treatment at $T = 600$ °C for (1) 50 h or (2) 120 h. Points—Experimental; curves—calculated with allowance for the relative distribution of double donors with respect to ionization energy (on the basis of data from optical measurements).

tures, $T \lesssim 8$ K, the optical absorption is predominant, and we see gaps in the continuum which correspond to absorption lines of impurity centers. At a higher temperature, $T \gtrsim 14$ K, the observed spectrum corresponds to the spectrum of photothermal ionization from the ground state.

The spectral lines for neutral donors, TDD^0, can be identified on the basis of the data of Ref. 1. This analysis reveals that at least 6 of the 11 types of TDDs are present (Fig. 1). The donors $(TDD2)^+$ and $(TDD3)^+$ were also detected in standard IR transmission spectra. This result alone indicates that the content of these centers is by no means low (see also Sec. 3 below). Furthermore, the manifestations of two donor states of these centers can be seen clearly on the plot of $n(T)$ for the ionization events $TDD^0 \rightarrow TDD^+$ ($\approx E_c - 0.06$ eV) and $TDD^+ \rightarrow TDD^{++}$ ($\approx E_c - 0.15$ eV) (Fig. 2).

2. Among the double donors which form in silicon at 450 °C, the TDD1 and TDD2 centers have a bistable atomic configuration: In one configuration, these centers have donor levels in the usual order of appearance for a helium-like donor center, $E(0/1) < E(+/++)$. In the other configuration, the order of donor states is inverted, and there is a negative effective correlation energy (Ref. 1, for example). A transition from the second configuration to the first can be induced by interband illumination of the sample during cooling. Using this procedure, we tested the donor centers which form at $T = 600$ °C for a bistability. We found that the center TDD1 is again bistable, while TDD2 has lost its ability to undergo a transition between two atomic configurations. We believe that the explanation for the latter result is the

presence of an internal stress, since at a higher heat-treatment temperature there is a substantial increase in the rate of growth of oxygen-containing precipitates and of accompanying large structural defects (Ref. 8, for example). As a result, the TDD2 donors, which "relax with the greatest difficulty," are "configuration-frozen."

3. A comparative study of the formation kinetics of the TDDs at 450 °C and 600 °C showed that the processes by which they form at these two temperatures are greatly different. In the first place, at the higher heat-treatment temperature the total rate of TDD formation is lower by about an order of magnitude (it has dropped from $\approx 6\times 10^{13}$ cm^{-3}/h to $\approx 6\times 10^{12}$ cm^{-3} /h; here we are allowing for the "incubation period" for the formation of TDDs, which is about 20 h for heat treatment at $T = 600$ °C). Second, the higher heat-treatment temperature changes the nature of the distribution of thermal donors with respect to ionization energy: After heat treatment at $T = 600$ °C for 50 and 120 h, the distribution is dominated by the donors TDD2–TDD4, while an increase in the duration of the heat treatment at 450 °C, from 4 to 120 h, shifts the center of gravity of the distribution from TDD2–TDD4 to TDD4–TDD6 (this shift was also noted in Ref. 1). That the TDD distribution remains essentially unchanged as the heat-treatment temperature is raised is confirmed by data from electrical measurements (Fig. 2): With the increase in the duration of the heat treatment, the increase in the concentration of thermal donors results primarily from the formation of TDDs with small numbers (TDD2–TDD4). As a result, the effective ionization energy, which is determined by the shallowest donor centers, remains basically unchanged. This conclusion is also confirmed by data found in an analysis of the $n(T)$ curves during a sequential compensation for the thermal donors by acceptors induced by radiation (specifically, by γ-ray bombardment of the heat-treated samples).

In summary, the results of joint optical and energy measurements lead to the conclusion that the thermal stability of thermal double donors is far higher than one would be led to believe by the current literature. Since the concentration of these centers in silicon heat treated at $T = 600$ °C is by no means low (it ranges up to $\approx 7\times 10^{14}$ cm^{-3}; Fig. 2), these centers should be taken into consideration in an analysis of the energy spectrum and formation processes of the new donors.

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[1]P. Wagner and J. Hage, J. Appl. Phys. A **49**, 123 (1989).
[2]W. Cazcarra and P. Zunino, J. Appl. Phys. **51**, 4206 (1980).
[3]V. M. Babych, N. P. Baran, A. A. Bugay *et al.*, Phys. Status Solidi A **109**, 537 (1988).
[4]G. Pensl, M. Schulz, K. Hölzlein *et al.*, J. Appl. Phys. A **48**, 49 (1989).
[5]Yn. N. Daluda, V. V. Emtsev, and K. Schmatz, Radiat. Eff. **107**, 93 (1989).
[6]B. A. Andreev, V. B. Ikonnikov, G. A. Maksimov, and V. B. Shmagin, Vysokochistye Veshch. **1**, 138 (1987).
[7]G. Bambakidis and G. J. Brown, Phys. Rev. B **33**, 8180 (1986).
[8]K. Schmalz, F.-G. Kirscht, and K. Tittelbach-Helmrich, Phys. Status Solidi A **109**, 279 (1988).

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