USE OF ELECTRON IRRADIATION IN STUDYING THERMAL DONORS IN SILICON BY THE EPR METHOD

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The bistable thermal donors in Czochralski-grown silicon crystals were investigated by EPR spectroscopy and IR-absorption techniques. It is shown that using heat treatment at a temperature \( \leq 400 \)°C and appropriate conductivity compensation by irradiation with 3.5 MeV electrons, one can select from the total signal the EPR-signal associated with only one type, namely TDD2, of the thermal donors. Based on the model of a two-center core structure of the given complexes, an explanation of the EPR-spectroscopy data on the oxygen thermal donors in silicon is suggested.

Keywords: crystalline silicon, thermal defects, EPR spectroscopy.

A study of the behavior of oxygen impurity in silicon is of particular importance in modern microelectronics. Oxygen enters the silicon from a quartz crucible when crystals are grown by the Czochralski method. During the process of production at lower temperatures, the solid solution of oxygen in silicon decomposes with the formation of a variety of structure defects. According to current concepts, the decay occurs in several steps [1, 2]. First, small oxygen complexes are formed, which act as donor centers, i.e., thermal donors (TDD). They represent a set of bivalent oxygen complexes successively formed at 350-500°C that are labelled TDD\( n \), where \( n \) is the number of the center (\( n \geq 11 \)) [3]. Although the studies have been conducted for more than 40 years and a wealth of data has been accumulated, the structure of the TDDs and the mechanism of their formation have not been clarified as yet. This is the reason for the continued activity in studying the TDD [4]. Recently a number of new important results on the structure of TDD have been obtained by EPR spectroscopy. First is evidence of the existence of nonisotropic internal lattice stresses in the region of the defect [5] and, second is the discovery of the deviation from \( C_2 \)-symmetry that varies nonmonotonically with increase in the number of the TDD complex [6].

However, a significant drawback of the aforementioned studies is the ambiguity in the comparison of the results of EPR measurements with the data obtained by other experimental techniques (IR-absorption, Hall’s measurements, etc.). Above all, this is due to the fact that the observed EPR spectrum of TDD represents a superposition of signals caused simultaneously by several types of TDD. For this reason, in studying TDD properties by the EPR technique it is often impossible to determine specifically the number of the center to which the results obtained are related, and this limits the possibilities of using this technique for determining the structural features of the defects under study. The goal of this work is to show the manner in which electron irradiation allows one to increase the efficiency of the EPR technique in the TDD structure investigation.

A necessary condition for the study of TDD by the EPR technique is their sufficiently high concentration in a singly ionized state (TDD\(^+\)). Since each subsequent member of the series under study is formed from the previous one, one should expect that at small heat treatment times the centers with initial numbers will

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prevail. The time dependence of the ratio of their concentrations is determined by their formation reaction constants, which are temperature dependent. Consequently, to realize the aforementioned conditions it is necessary first of all to choose an optimum heat treatment temperature. To do this, we have studied the kinetics of the formation of TDD at 400 and 475°C.

The most informative technique for studying TDD formation kinetics is the IR-spectroscopy method. The TDDs give a series of absorption bands in the regions ~300-550 and ~550-1200 cm⁻¹ associated with the excitation of electrons from the ground state (1s) to different excited states of the neutral (TDD₀) and singly ionized centers. The most intense absorption lines are associated with the transitions to the 2p₀ and 2p₊ states. If the measurements are carried out at constant temperature, then at not-too-long heat treatment times each line intensity may be considered as proportional to the individual defect concentration [7].

Figure 1 shows the dependences of the intensities of the absorption bands, associated with the 1s → 2p₊ transitions for TDDⁿ (n = 1-5), on the time of heat treatment at 400 and 475°C. The samples were cut out from the same wafer with specific resistance 20 Ω·cm and oxygen concentration 9·10¹⁶ cm⁻³. All the spectra were measured at 12 K. To ensure the measurement of the total concentration of TDD₁ and TDD₂, cooling of the samples to the measurement temperature was carried out with constant illumination.

As is seen from the plots presented, the TDD₁ and TDD₂ dominate at the initial times of heat treatment. Moreover, the lower the temperature (400°C), the more distinct the predominance. The lower temperature also ensures higher maximum concentrations of TDD₁ and TDD₂, which agrees with the data of other researchers [3]. However, the maximum concentration of TDD₁ is still small. Therefore, one must seek conditions under which the fraction of the other bistable center, i.e., TDD₂, will be maximum. Figure 2 shows the dependence of the ratio of the TDD₂ concentration to the total concentration of all types of TDD (the relative fraction of TDD₂) for two materials with different contents of oxygen. It is seen that the maximum fraction of TDD₂ is virtually independent of the initial concentration of oxygen, but when this concentration increases, the greatest possible concentration of the centers under study increases. Thus, from the data presented it follows that for EPR measurements materials with a higher oxygen concentration should be used and the TDD should be introduced at the temperature ≤400°C.

The TDD₂ have one more property that allows one to detect their presence without resorting to laborious studies of IR-absorption spectra. These centers are bistable and responsible for long-term conductivity relaxations at the temperatures close to 300 K [8]. Using the bistability, it is possible to determine the concentration of defects by measuring the ratio of two values of the Hall coefficient (the dark one and that obtained with low external illumination) or by measuring the conductivity at a fixed temperature. The ratio of these two