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БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ
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МАТЕРИАЛЫ И СТРУКТУРЫ СОВРЕМЕННОЙ ЭЛЕКТРОНИКИ

OPTICALLY ACTIVE DEFECTS FORMED UPON THERMAL DOUBLE DONOR ANNIHILATION IN SILICON

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1. INTRODUCTION

Heat-treatment of Czochralski-grown (Cz) Si crystals in the temperature range 350–550 °C results in generation of several families of oxygen-related thermal donors. Among them the thermal double donors (TDDs) are the most known [1, 2]. TDDs comprise a series of species with a helium-like excitation spectrum. They are formed sequentially upon heating and are distinguished by their increasingly shallow levels. The electronic transitions of 17 neutral (TDD0-TDD16)] and ten positively charged TDDs (TDD0-TDD9) were observed in infrared absorption spectra [1-4]. According to present models of TDDs they are oxygen clusters (chains) involving different numbers of interstitial oxygen atoms (O_i) [5]. It is argued that the sequential formation of the TDD family occurs mainly via a migration of the oxygen chains (dimers, trimers and TDD species) and their interaction with single O atoms.

TDDs are not stable at temperatures above 550 °C and annihilate rather rapidly. The kinetics of TDD annihilation has been studied in a number of works (e.g., see [6, 7] and references therein). It has been established that the main mechanism of the TDD elimination is their dissociation as a substantial recovery of interstitial oxygen has been normally observed in carbon-lean Cz-Si crystals. However, as a rule this recovery has not been complete and the transformation of a part of TDDs into other centres has been suggested. Besides, it was noted that in such samples an enhanced generation of the new thermal donors (NTDs) and oxygen precipitate nuclei occurred upon following heat-treatments in the range 600–700 °C, but a microscopic mechanism of this phenomenon was not established.

Local Vibrational Mode (LVM) spectroscopy has recently appeared to be a very powerful tool in the studies of small oxygen-related clusters in Si [8 – 11]. In this work, LVM spectroscopy is used to explore a possible origin of oxygen-related defects formed upon TDD annihilation at 650 °C.

2. EXPERIMENTAL DETAILS

The samples used in this investigation were prepared from n-type commercial Cz-Si crystals (ρ = 50 Ω·cm, [O_i] = 1,3·10^{18} cm^{-3}) with low content of carbon ([C_s] ≤ 1·10^{15} cm^{-3}). To generate TDDs the samples were annealed at 450 °C for 60, 120 and 240 h. The thermal donor killing treatments were performed at 650 °C in air for different durations up to 40 h. A few as-grown samples were irradiated with fast electrons or neutrons at room temperature and then annealed isochronally up to 700 °C.

IR absorption analysis was carried out using a Bruker IFS 113v spectrometer. A spectral resolution of 0.5–1.0 cm^{-1} was used and the samples were measured at 20 and 300 K in the range 400–4000 cm^{-1}. Electrical properties of the samples were controlled by four-probe resistivity measurements at room temperature (RT).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. TDD generation at 450 °C

Figure 1 shows fragments of infrared absorption spectra of Cz-Si samples in as-grown state (spectrum 1) and after treatments at 450 °C for 60, 120 and 240 h (spectra 2, 3 and 4 respectively). In the spectrum of as-grown sample, the well-known vibrational bands related to single interstitial oxygen atoms as well as to oxygen pairs [11] can be seen. The treatment at 450 °C resulted in the growth of an overall absorption due to the increase in free electron concentration (the sample resistivities were 0.31, 0.23 and 0.21 Ω·cm after anneals for 60, 120 and 240 h respectively) and appearance of the LVM bands at about 580, 730 and 1000 cm^{-1} related to TDDs [5,8]. The broad band centred at about 900–950 cm^{-1} is also related to TDDs but originates from electronic transitions in TDDs being in a positive charge state. Due to high concentration of introduced donors an essential part of thermal donors is not ionized at room temperature.

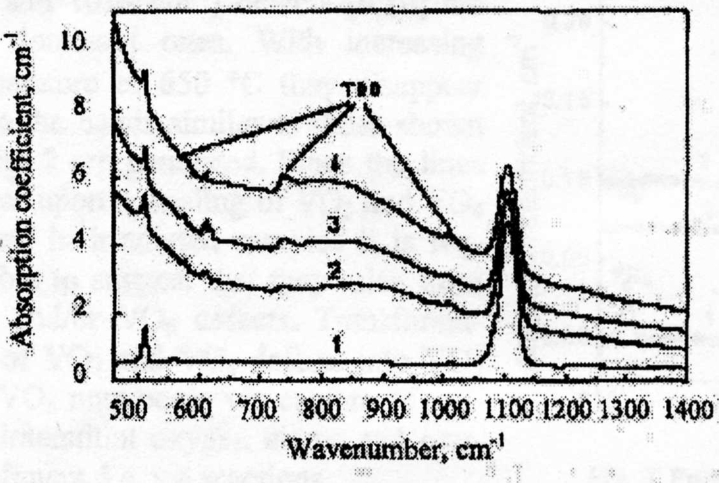

Fig. 1. Fragments of absorption spectra at 300 K of Cz-Si samples in as-grown state (*1*) and after treatments at 450 °C for 60 h (*2*), 120 h (*3*) and 240 h (*4*)

It should be pointed out that a noticeable decrease in the intensity of the O_i related bands with increasing heat-treatment time at 450 °C is observed while the integrated intensity of the TDD bands increases and their peak positions are shifted to higher energies probably due to increase in the number of oxygen atoms involved in the TDD chains [5].

3.2. TDD annihilation at 650 °C

Infrared absorption studies of the TDD containing samples annealed at 650 °C for 1 h have shown that such treatment results in disappearance of all the features related to TDDs and a recovery of O_i. However, the recovery is not complete and a significant part of O_i should be present in other forms. Careful analysis of the absorption spectra has shown that a number of new LVM bands are appearing upon TDD annihilation (see Fig. 2). The most intense of them are positioned at about 1040, 1056 and 1107 cm^{-1} at 20 K.

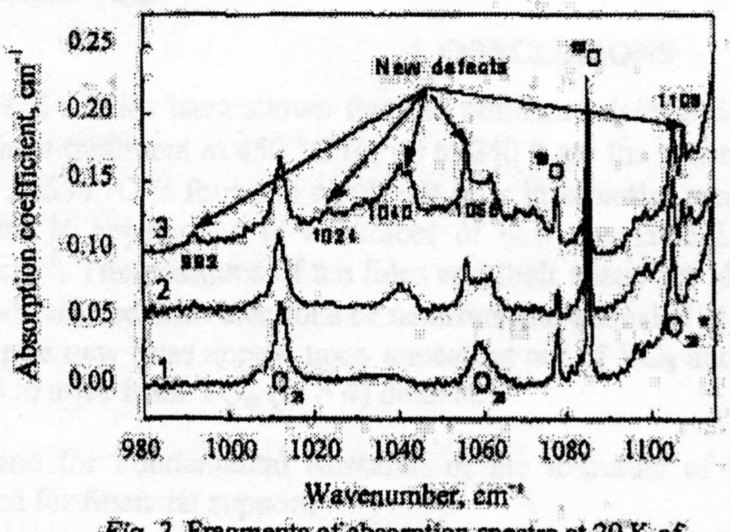

Fig. 2. Fragments of absorption spectra at 20 K of Cz-Si samples in as-grown state (1) and after treatments at: 650 C for 1 h after 450 C for 120 h (2) and 240 h (3)

Evidently, some oxygen-related defects should give rise to these bands. When seeking for a possible origin of such defects we found a very useful hint from the annealing studies of radiation-induced defects (RDs) in Cz-Si. Figure 3 shows fragments of infrared absorption spectra of Cz-Si sample irradiated with 10 MeV electrons at room temperature and then isochronally (30 min) annealed up to 700 °C. For simplicity only the spectra after anneals at 600, 650 and 700 °C are presented. After anneal at 600 °C the bands related to VO_3 (at 910, 975and 1005 cm^{-1}) and VO_4 (at 991 and 1014 cm^{-1}) defects [9,10] are still dominant ones. With increasing temperature to 650 °C they disappear while the bands similar to those shown in Fig. 2 are generated. Since the lines appear upon annealing of VO_3 and VO_4 defects in irradiated samples it is reasonable to suggest that they arise from VO_5 and/or VO_6 defects. Transformation of VO_3 and VO_4 defects into VO_5 and VO_6 may occur via capture of mobile interstitial oxygen atoms and oxygen dimers, i.e. via reactions

$$VO_3 + O_{2I} \rightarrow VO_5$$
$$VO_4 + O_I \rightarrow VO_5$$
$$VO_4 + O_{2I} \rightarrow VO_6$$

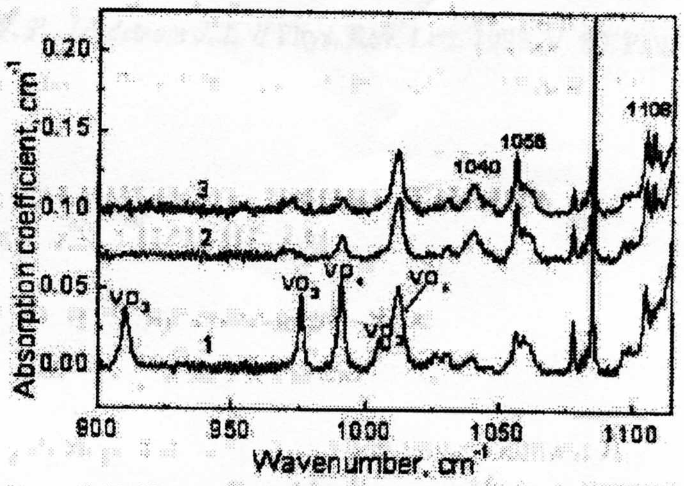

Fig. 3. Fragments of absorption spectra at 20 K of Cz-Si sample irradiated with 10 MeV electrons ($F = 3\times10^{17}$ cm^{-2}) at RT and annealed for 30 min at: *1* – 600 °C: *2* – 650 °C: *3* – 700 °C

Formation of the latter defects in pre-annealed crystals can occur most likely via injection of Si self-interstitial by O_{im} (m > 4) defects, i.e. via the reaction

$$O_{IM} \rightarrow VO_M + I_{Si}.$$

pparently, there are two parallel ways of the TDD annihilation: dissociation and transformation into VO_m.

4. CONCLUSIONS

LVM studies have shown that the dominant defects developing in carbon-lean Cz Si upon heat-treatment at 450 °C for up to 240 h are the thermal double donors. Their annihilation at 650 °C is found to result not only in a partial recovery of the interstitial oxygen, but also in appearance of a number of new O-related LVM bands in the range 990–1110 cm^{-1}. The positions of the lines and their shape are identical to those observed in Cz Si pre-irradiated with electrons or neutrons and annealed at 600–700 °C. In irradiated samples these new lines appear upon annealing out of VO_3 and VO_4 defects and they are suggested to arise from VO_m (m > 4) defects.

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