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Electronic mechanism of thermal destruction of radiation-induced E'-centers in crystalline and glassy SiO_2

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ABSTRACT

The thermal decay regularities for radiation-induced E'-centers in crystalline and glassy SiO_2 were investigated. The results obtained point out that the destruction of E'-centers can be described as ionization process of deep centers in electric field. In terms of used model, the electric field and electron–vibration coupling parameters are sensitive to structural disorder. The most weak electron–phonon coupling in E'-centers is observed for amorphous systems.

1. Introduction

The E'-center is a well known defect which determines many important properties of SiO_2 and silica-based devices. However, the criteria for formation and destruction mechanisms are still not fully understood. There are several different schemes of E'-centers formation (bond breaking, oxygen vacancy creation, recharging of precursors, etc), which may depend on impurities and their contents [1–3]. These reasons result in the different interpretations of defect charged states and destruction mechanism. Today it is not clear what actually happens during E'-center thermal destruction: hole release, electron release, some ionic process or just broken bonds recovery.

In this paper we consider an alternative electronic mechanism of radiation-induced E'-center destruction taking into account the structural state of irradiated crystalline and glassy SiO_2.

2. Samples and experimental techniques

Three types of SiO_2 samples were studied in this work: silica glass KV, synthetic quartz and natural black quartz crystals (morion). The quartz crystals and glass samples were flat polished slices, 0.5 mm thick. In order to create radiation defects the synthetic samples were irradiated by fast neutrons (10^{15}–10^{19} cm^{-2}) and X-rays (Fe anode). Morion crystals were taken from the Zhelannoe quartz deposit, Northern Region, Prepolar Ural, Russia. They have the biographical radiation defects created during geological history and were investigated with naturally grown surface. Finally the samples were cut to several pieces in order to be measured independently with different experimental techniques.

Identification of radiation defects in the samples was performed by means of electron spin resonance (ESR) and optical absorption (OA). Dynamic effects accompanying the E'-centers destruction were studied using simultaneously registered thermally stimulated electron emission (TSEE) and thermally stimulated luminescence (TSL). The TSEE measurements were carried out in vacuum at a pressure of 10^{-4} Pa with a VEU-6 secondary electron multiplier with an entrance grid biased to 500 V from sample substrate. The experimental setup made it possible to measure the emission response in the temperature interval of 80–750 K under linear heating. Charging effects during E'-centers formation and their destruction were studied using electron energy spectra measurements and computer treatment. The experimental setup allowed measuring the changes of electron energy spectrum within the narrow temperature intervals.

3. Thermally stimulated effects

The thermal destruction of neutron-induced E'-centers in the samples under study is accompanied by the effects of TSEE, TSL and also ESR signal relaxation. In principle TSL and TSEE curves give the same information concerning the localized carriers release from traps. As a rule, the coincidence of both TSEE and TSL signals provides an evidence of bulk centers of electronic localization. Contrary to luminescence, the electron emission is sensitive to surface and

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adsorption-related defects as well. In our investigations the behavior of 653 K TSL peak [1,4] (2.21 eV activation energy) is similar to that of 660 K TSEE peak by its energy and kinetic parameters. Both of them are related to ionization of E'-type traps while the recombination in quartz occurs with oxygen hole centers located at defected AlO_4 and SiO_4 tetrahedra [5].

Experimental investigations (Fig. 1a) show that TSEE dependencies for X-ray irradiated crystalline quartz in 300 ÷ 600 K interval contain multiple maxima of adsorption and biographical nature [6]. Shallow traps (adsorption- and treatment-related centers) become almost completely passivated after fast neutron irradiation while the intensity of 650–670 K TSEE peak considerably increases. Such behavior allows to assume that this TSEE peak is related to the neutron-induced structural defects of crystalline quartz.

Experimentally observed TSEE dependencies of silica glass (Fig. 1b) are similar to those for crystalline samples. One can see the adsorption TSEE peaks that have lower intensity than their analogues in crystal. However they are completely vanished after neutron irradiation and the 650 K maximum rises significantly. It is interesting that the thermal annealing of E'-centers observed in ESR spectra of both crystal and glass takes place in the same temperature range of 650–670 K TSEE peak (Fig.1). This fact allow us to suggest that 650–670 K TSEE maxima are related to radiation-induced E'-centers.

The investigation of E'-centers concentration dose dependencies for quartz crystals and glasses by means of optical absorption (5.75 eV band) and ESR techniques shows that they coincide with analogous dependency for 650–670 K TSEE peak intensity (Fig. 2). It should be noted that defect concentration dose dependencies for silica glass have an extremum at ~3×10^{18} cm^{-2} neutron fluence. It is obvious that the noted dose is the threshold value for neutron fluence under which the "radiation annealing" of E'-centers suppresses the process of their creation. Thus the correlation of TSEE and ESR temperature dependencies (Fig. 1), on the one hand, and their concentration dependencies (Fig. 2), on the other hand, confirms that the observed neutron-induced TSEE peaks are directly connected to E'-centers thermal destruction both in crystals and glasses.

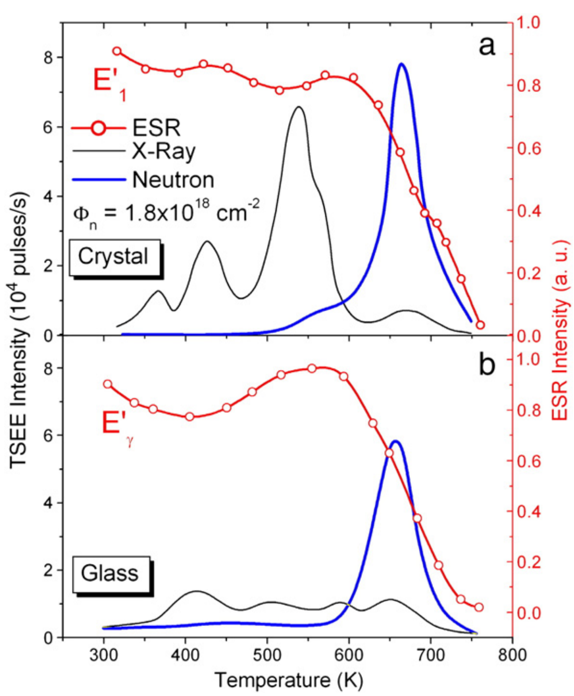

Fig. 1. TSEE of crystalline and glassy SiO_2 after X-ray (thin line) and neutron (bold line) irradiation along with ESR isochronal annealing of paramagnetic E'-centers.

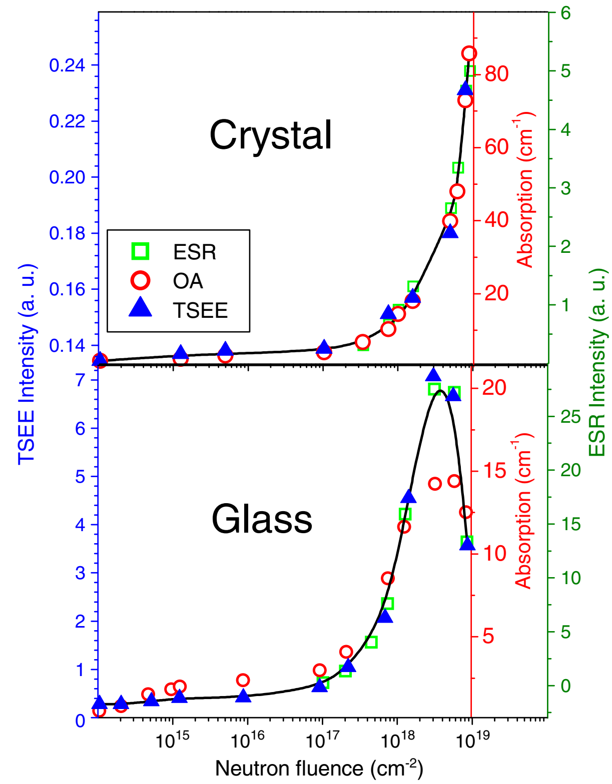

Fig. 2. Normalized TSEE, ESR and OA dose dependencies for neutron-irradiated crystalline and glassy SiO_2. Absorption coefficient was measured for radiation-induced band (5.75 eV).

TSEE analysis was performed using special software based on the formal kinetics equation:

$$I(T) = -\frac{dc}{dt} = p_0 c^l \exp[-(\varepsilon_T + \chi)/kT], \quad (1)$$

where I—emission intensity; c—active centers concentration; p_0—frequency factor; ϵ_T—thermal binding energy; χ—electron affinity; l—kinetics order. The results obtained are presented in the Table 1. It is worthy of note that E'-centers destruction TSEE curves have second order kinetics that assumes not only ionization but the possibility of repeated electron trapping [7]. Elementary peak shape suggests that all trapping and retrapping represented by Eq. (1) must occur at E' center precursor sites, all of which must be of the same nature. All the results presented point out the thermal ionization of E'-centers taking place in different investigated SiO_2 matrices. So we can see that these neutron-induced defects, such as E'-centers, may play a role of *electron donors*. At the same time repeated X-ray irradiation completely recovers the E'-centers precursors population leading to occurrence of the same characteristic TSEE maxima.

The analysis of the thermally stimulated effects (TSEE, TSL and ESR annealing) and dose dependencies shows that E'-centers energy depth is about 2.1–2.3 eV and surface electron affinity changes from 0.4 to 0.9 eV. Their precise values depend on matrix structural

Table 1
Kinetic parameters of E'-center thermal destruction for SiO_2.

Materials	Irradiation	T_{max} (K), TSEE	ε_T (eV)	Kinetics order	Electron affinity, eV
α-Quartz	Neutron	665–675	2.25–2.35	2	0.50 ± 0.04
Morion	Natural	670	2.25	2	0.90 ± 0.06
SiO_2 glass	Neutron	660–665	2.1–2.2	2	0.40 ± 0.04