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Electron emission from excited states of E' centers in SiO_2

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Abstract

The applicability of the non-stationary optically stimulated electron emission (OSEE) to the spectroscopy of E' centers in different SiO_2 modifications was demonstrated. Spectral dependences of the OSEE from E' centers in samples of silica glass, crystalline α-quartz, SiO_2 films and nanoceramics exposed to fast electrons and ions were obtained. A model of the energy structure of E' centers accounting for the absence of luminescence and taking into account the presence of two non-radiative relaxation channels (intracenter and ionization) is discussed. This model was used to substantiate the mechanism of the photothermal decay of E' centers and to determine the quantum yields of OSEE for different types of E' centers.

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1. Introduction

The E' center belongs to the best studied defects in silicon dioxide, however the excited states properties of these centers still cannot be considered as reliably established [1,2]. The main problem encountered in describing electronic properties of the E' center family lies in the lack of information about processes involved in their optical excitation, relaxation, and decay. This situation may be accounted for partially by the fact that E' centers belong to the class of defects that do not produce luminescence. This problem can be reasonably solved if one uses special experimental approaches that are sensitive to processes of the non-radiative relaxation of electronic excitations. The method of thermally stimulated electron emission (TSEE) was used earlier for analysis of electronic processes involving E' centers [3,4]. The optically stimulated electron emission (OSEE) consists essentially in the release of electrons from defect centers under the action of light and the escape of the electrons from the surface of solids. The OSEE method is used increasingly in studies of photosensitive defects and properties of the surface layer of materials. The theory and hardware of the OSEE method have been well developed and it has shown itself useful in studies of color centers (including E') in surface layers of oxide crystals and glasses [4–6].

In this work properties of excited states of radiation-induced E' centers were studied in different silica matrices using the optically stimulated electron emission (OSEE).

2. Objects and experimental procedures

The objects of study were samples of KV silica glass, α-quartz crystals with optical-grade polished surfaces, SiO_2 films (100 nm) on silicon substrates, and a nanostructured SiO_2 ceramic. To produce defect centers, the samples under study were irradiated by electrons (10 MeV) or Fe^+ ions (30–100 keV).

OSEE measurements were made in a vacuum of 10^{-4} Pa with a VEU-6 secondary-electron multiplier. The experimental setup made it possible to measure the OSEE spectral response over the temperature interval of 80–750 K under thermostating. Information about the excited

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states properties of different species of E' centers was obtained by a special method for processing and analysis of OSEE spectrum curves [5]. This method included the following steps: (1) selection of the contribution of point defects from initial non-selective spectral emission dependences, (2) inclusion of the transient pattern of the emission process, and (3) the determination of spectral-kinetic parameters and the concentration of E' centers.

The spectral-response treatment procedure is based on the assumption that the OSEE spectrum of an irradiated sample can be presented as a superposition of an exponential described by the Urbach rule and a set of Gaussians corresponding to various species of point defects [5]. The OSEE data thus obtained were used to determine spectral parameters and the concentration of photosensitive defects in the emission-active layer of materials.

3. Results

Our experiments and subsequent processing of the emission curves produced OSEE excitation spectra with selective bands of radiation point defects (Figs. 1 and 2). The dominant defects in crystalline and glassy samples were found to be bulk E' centers (the emission band at 5.78 eV). The OSEE spectra also included NBOHC (4.75 eV) and ODC (5.05 eV) bands, which we analyzed in an earlier study [6]. Spectral characteristics of all the detected centers agree fairly well with optical absorption data [1]. Surface E'_s centers with the emission bands at 6.0–6.3 eV were detected additionally in the glasses, films and nano-SiO_2 (Fig. 2). This implied that surface E'_s centers were localized in a thin surface layer and could be detected only by the surface-sensitive OSEE method.

Since intracenter optical transitions were realized at the stage of the optical excitation of E' centers, the obtained OSEE spectra represented emission analogs of optical absorption spectra. This analogy allowed determining the concentration of bulk and surface emission-active E' centers in the samples under study using the well-known Smakula relation in a form modified for the OSEE case [5]. For instance, the calculated two-dimensional concentrations ($\sim 10^{12}$ cm^{-2}) of surface E'_s centers in the irradiated silica glass and nanostructured SiO_2 ceramics were in good agreement with the analogous concentrations on the

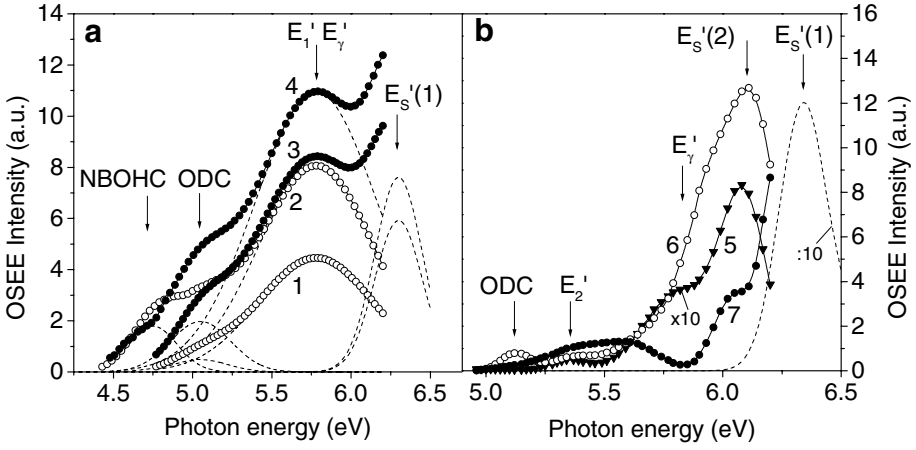

Fig. 1. OSEE spectra: (a) electron irradiated SiO_2 crystal (1, 2) and glass (3, 4) measured at different temperatures (1, 3 – 298 K, 2, 4 – 473 K); (b) X-rayed nanostructured SiO_2 ceramics. The nanostructured sample was annealed: 5 – 48 h at 600 °C; 6 – 6 h at 1200 °C; 7 – 6 h at 1400 °C.

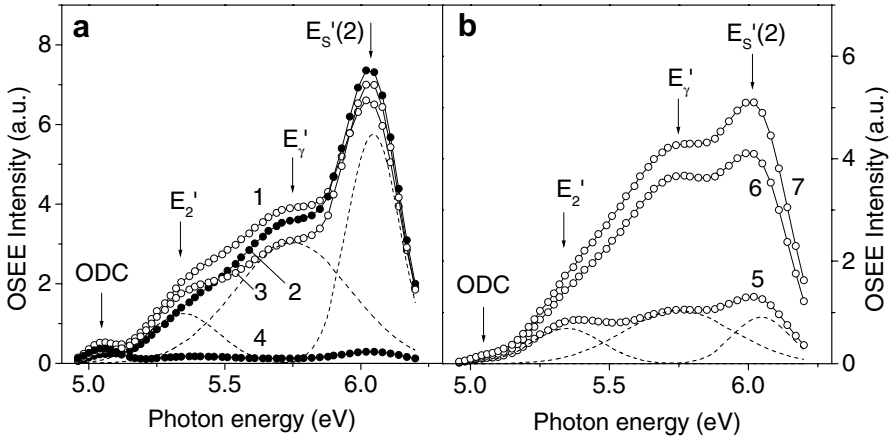

Fig. 2. OSEE spectra of SiO_2 glass (a) and films (b) implanted with Fe^+ ions (1, 2, 5–7 – irradiated surface, 3, 4 – back surface): energy 1, 3, 5–7 – 30 keV (pulsed), 2, 4 – 100 keV (steady); fluence 5 – 10^{15} cm^{-2}, 6 – 10^{16} cm^{-2}, 1–4, 7 – 2×10^{17} cm^{-2}.