The Peculiarities of Charge Carriers Trapping Processes and Mechanisms in Anion-defective α-Al_2O_3 Single Crystals

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Abstract – The main peculiarities of influence of deep trapping centers on luminescent properties of anion-defective aluminum oxide single crystals are established. The model of interactive interaction of traps is proposed for explanation of the observed phenomena mechanism.

1. Introduction

Main types of structural disturbances, which are induced in nominally pure wide-gap oxides by thermochemical or radiation effects, are oxygen vacancies in different charge states (F- and F^+-centers). These defects cause considerable changes in many radiation-optical properties of materials modified by these means.

One of effects, when the changes are most vivid, is thermoluminescence (TL) of single crystals of aluminum oxide grown or thermally treated under reducing conditions or exposed to high-energy electrons. A series of TL peaks is recorded over the temperature interval of 300 to 900 K. The peak at 450 K, which is called the main peak, is most convenient for the use in practical thermoluminescence dosimetry [1]. Moreover the high temperature TL peaks associated with deep trapping centers are present. It is known that competitive processes in charge carriers capture between different types of traps can play an important role in the TL mechanism of materials. These competitive processes cause appearance of the anomalous TL features which are not explained in terms of simple two-level kinetic model [2].

This work deals with experimental and theoretical investigation of the charge carriers capture mechanisms and processes with participation of the traps with different thermal depth in anion-defective aluminum oxide single crystals.

2. Samples and experimental technique

The basic objects of investigation were the samples of nominally pure anion-defective aluminum oxide single crystals which were grown by the method of oriented crystallization under reducing conditions. Nominally pure α-Al_2O_3 samples, grown under neutral conditions and exposed to an electron fluence of 1.5×10^{18} el·cm^{-2} with an energy of 9 MeV at room temperature in a Microtron MT-20 accelerator (Ural State Technical University), also investigated. Optical absorption (OA) spectra of the samples were recorded using a spectrophotometer type "Specord" M-40. Excitation spectra of the exoelectron emission were measured in a vacuum of ~10^{-5} Pa using a secondary electron multiplier. A deuterium lamp and a monochromator provided the required spectral interval of the quanta energy (4.1 to 6.2 eV). The deep traps were filled by the full radiation spectrum of a mercury lamp type DRT-240 at different temperatures. To empty deep traps, the crystals were treated at a temperature of 1170 K for 10 min. TL of the main peak was excited using a beta-radiation source based on the $^{90}Sr/^{90}Y$ isotope. The light stimulated migration of charge carriers from the deep traps to the main trap was realized using an optical radiation source at the wavelength of 470 nm. The source included an assembly of light-emitting diodes type SDK-S469-5-10 with a high spectral luminosity and an objective having the focal length of about 2 cm, which concentrated the light flux in an area of about 2 cm^2. TL during linear heating and fractional glow technique and the phototransferred thermoluminescence (PTTL) were measured using a standard method. Interference filters served for resolving the luminescence spectral bands.

3. Results and discussion

Deep traps in anion-defective aluminum oxide single crystals, grown under reducing conditions, were founded by the direct observation of high temperature TL peaks at 730 and 880 K [3]. Our investigations show the deep connection between the main peak parameters and the degree of deep traps occupancy. One of the anomalous features in these crystals is the drop of TL output in the main peak with growing heating rate [1]. It was founded that the relative value of this drop is determined by the state of deep traps occupancy. After filling the deep traps the decrease of TL output becomes less essential. The other anomalous feature of the main peak is the drop of mean activation energy value during fractional glow technique [4]. The experimental data testify that this dependence is associated with the occupancy of deep traps too.

The correlation between aforementioned TL features of the main peak and the thermal quenching of F-center luminescence was noted in other work [5]. If this correlation exists it is to be expected that luminescence quenching curves will depend on the state of deep trapping centers too. The temperature dependences of the radioluminescence output in the band of F-centers emission during the excitation of samples by the beta-radiation source are presented in the Fig. 1. It was founded that the shape of quenching curves depends on the state of deep traps too.

Besides aforementioned features, the state of occupancy of deep traps influences on the TL intensity

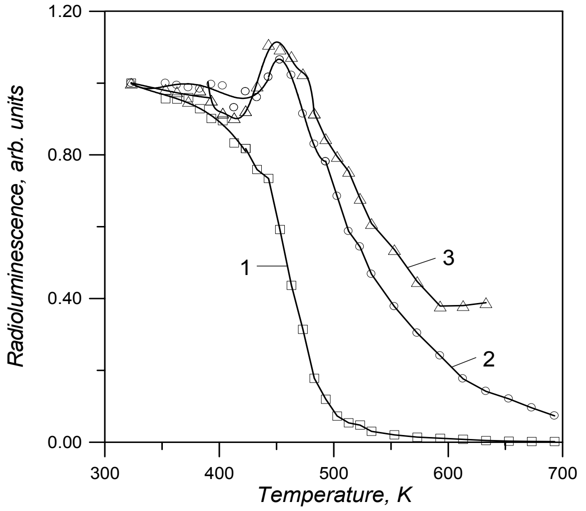

Fig. 1. Quenching curves of radioluminescence of F-centers for different states of deep traps: 1 – deep traps were not filled deliberately; 2 – the deepest trap is filled at 775 K; 3 – both deep traps are filled at 620 K.

in the peak at 450 K (TL sensitivity), peak shape evaluated as full width, nonlinearity value of dose dependence. TL sensitivity grew during filling deep traps. Moreover, the sensitivity variance of samples decreased. It was founded that the full width of the peak decreased as the degree of occupancy grew. The nonlinearity value of dose dependence in such conditions diminished too. The filling of deep traps resulted in change TL spectrum of the main peak. The TL intensity ratios measured in the luminescence bands of F- and F^+-centers (420 and 330 nm respectively) before and after the deep traps have been filled show that the 420-nm luminescence band dominates in the initial crystals. After the deep traps have been filled, the intensities of the 420-nm and 330-nm bands become comparable. The obtained results show that the deep traps effect essentially on the TL parameters in the main peak.

The similar TL features were founded in radiation-colored aluminum oxide single crystals. The TL output of the main peak of these crystals also decrease as the heating rate grows. The temperature dependence of the mean activation energy value experiences a drop over the peak. The principal observation is that these TL features correlated analogously with the state of deep traps occupancy. The presence of deep trapping centers in radiation-colored crystals is also confirmed by the availability of the high temperature TL peaks. Among other common features of TL process for both types of crystals it is ought to note that during filling of deep trapping centers the sensitivity of the crystals to X- and gamma-rays increases in several times. The TL spectrum in the main peak changes. The obtained results show that the anion-defective aluminum oxide single crystals display general features of the deep traps influence on TL properties. These features do not depend on the way of receipt of oxygen vacancies.

For explanation of whole totality of experimental data the kinetic model was designed. The base of the model is a performance about the system of interactive main and deep traps and the competitive capture of charge carriers, which are released during main TL peak registration, by deep traps. The principal difference of the model proposed in this work is the consideration of the temperature dependence of the probability of charge carriers capture on deep traps. This dependence is observed experimentally. The calculations, which were carried out in terms of this model, allowed to describe the dependences of TL features in the crystals under study on the degree of deep traps occupancy: the shape and the position of the peak, the heating rate influence on the TL output, the nonlinearity of dose dependence, the change of TL sensitivity [3].

However, the fundamental assumption of the proposed model that deep traps can capture carriers released from traps responsible for the main peak at 450 K during TL measurements and the temperature dependence of the efficiency of this capture was made on the basis of indirect observations when deep traps were pre-filled artificially rather than filled during recording of TL in the main peak. For this reason, the interactive relationship between the main and deep traps in crystals of anion-defective α-Al_2O_3 should be confirmed more comprehensively in experiments. In this connection, a serious support to the proposed model would be a direct observation of the migration of charges during reading of TL in the main peak to deep traps and from the deep traps to the trap responsible for the main peak.

The samples with pre-filled deep traps and emptied main traps were used for evidence of the possibility of the charge migration between deep and main traps, and PTTL was registered. It was established that the optical stimulation results in migration of the charge from the deep traps to the main traps, which are responsible for peak at 450 K. The very fact of PTTL excitation in the peak at 450 K is a direct proof of the interaction between the deep and main traps.

The dependence of the TL yield on the heating rate (curve 1 in Fig. 2) was explained in terms of the model of the interactive trap system by the capture of some charge carriers, which were released during heating, in the deep trap and, consequently, by the decrease in the number of charge carriers participating in recombination processes responsible for the luminescence. If this explanation is true, the PTTL yield in the main peak should, oppositely, increase with growing heating rate of the irradiated sample. Later PTTL measurements confirmed this supposition (Fig. 2). The comparison of the trends of the curves 1 and 2 in Fig. 2 demonstrated their good correspondence to these assumptions and allowed stating that the drop of the TL yield with increasing heating rate is due to the capture of some charge carriers in the deep trap during TL reading in the main peak.

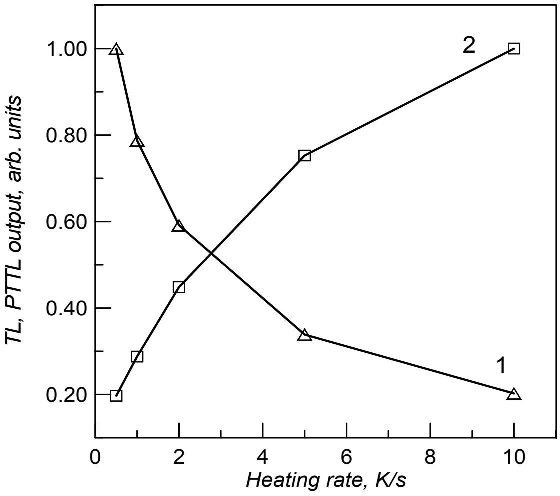

Fig. 2. TL (1) and PTTL yields (2) in the peak at 450 K vs. the heating rate.

All other factors being equal, the concentration of charge carriers in the deep trap could be increased by repeated "irradiation – TL measurement" cycles. The analysis of the dependence of PTTL yield in the peak at 450 K at different heating rates versus the number of the cycles performed for accumulation of carriers in the deep trap shows that the charge is accumulated more efficiently in the deep trap as the number of "irradiation – TL measurement" cycles grows and, also, the heating rate of the irradiated samples increases.

Thus, in our opinion, the interactive relationship between aforementioned traps is confirmed by direct experiments by means of PTTL features investigation.

Other important results, which confirm the interactive trap system model, were got during study the dose dependence of TL output in the main peak. During measurements of the dose dependence in the irradiation–heating cycles, the dosimetric trap is repeatedly depleted and charges are accumulated in the deep trap. The filling of the deep trap leads to an increase in the number of charge carriers involved in the recombination processes and to an increase in the sensitivity of the samples to radiation. As a consequence, the dose dependence of the thermoluminescence output becomes nonlinear and exhibits superlinear behavior. If the model proposed in this work is valid then it is ought to expect the dependence of the dose characteristic nonlinearity both on heating rate and number of cycles "irradiation-heating" during it's receipt. These factors would affect together on the degree of the deep traps occupancy. The results of experimental confirmation of these features are presented in Fig. 3 and 4. In these figures the dose dependences of one and the same sample, which are obtained during TL measurement with different heating rates and the irradiation step 32 and 64 mGy, are offered. The analysis of these figures shows that range of nonlinearity area and it's value grow as the heating rate and the number of cycles "irradiation-heating" increase.

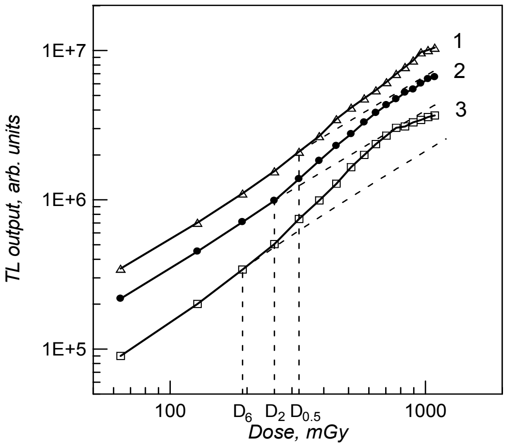

Fig. 3. Dose dependences of the TL output measured for anion-defective α-Al_2O_3 crystals at heating rates of: 1 – 0.5 K/s; 2 – 2 K/s and 3 – 6 K/s.

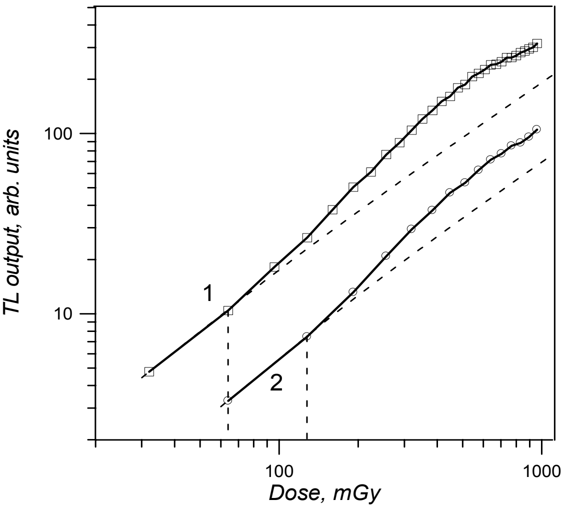

Fig. 4. Dose dependence of the TL output measured for different step of dose variation (heating rate is 6 K/s). 1 – the step of dose variation is 32 mGy; 2 – 64 mGy.

Although the effect of deep traps on luminescent and dosimetric properties of the crystals at hand has been a reliably established fact, many details of the deep trap filling are still unclear. To determine the source of charge carriers during filling of deep traps we analyzed the optical absorption of anion-defective corundum crystals containing deep traps in different states. It was founded that when the deep traps are filled, the intensity of the OA band at 205 nm, which is due to F-centers, diminishes, while the intensity of the bands at 230 and 259 nm, which are caused by F^+-centers, is enhanced. The bands regain their initial intensity after the high-temperature thermal treatment. These results suggest that electrons fill deep traps during the photoionization of F-centers and the concentration of F^+-centers grows during the filling process. The elucidation of the nature of the deep trapping centers in the crystals under study demands a further investigation. The latest results show that the energy spectra of deep traps can change from one sample to another and can have a complicated character. Now we can only propose that one part of deep traps are electron centers, and another part are hole centers.

The conversion of $F \rightarrow F^+$ centers in the absorption band of F-centers in the crystals at hand is clearly pronounced for excitation spectra of exoelectron emission thanks to a high density of the optical excitation of a thin surface layer (100 nm). The spectrum has a maximum in the region of the optical absorption of the F-center at 205 nm. This fact suggests that the registered electrons are formed thanks to the photoionization of F-centers. The excitation spectrum is shifted when the samples are exposed for several minutes to light with the wavelength of 205 nm. The spectrum maximum is registered at 230 nm, which corresponds to the position of the absorption peak of an F^+-center. These data illustrate immediately the conversion of $F \rightarrow F^+$ centers.

The model discussed in this work explains the most part of features observed experimentally. However it is in a difficulty in comparison of the heating rate dependences of the output of TL, thermally stimulated conductivity and thermally stimulated exoelectron emission. Unlike TL the heating rate does not affect on the output of last two processes [6]. The preliminary investigations show that these difficulties can be partially got over by means of consideration of the thermal ionization of excited states of F-centers process [7].

4. Conclusions

It is showed experimentally that in anion-defective α-Al_2O_3 single crystals the heating rate dependence of TL output, the drop of mean activation energy, thermal quenching of luminescence, TL sensitivity are associated with the occupancy state of deep traps.

The model of interactive relationship between the main and deep trapping centers, which describe experimentally observed TL features, is designed.

The practical important result of studied features is the establishment of the reasons of the superlinearity of dose characteristic and the dependence of superlinear area range and its value on the measurements regimes.

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