Oxygen-driven relaxation processes in pre-irradiated Ar cryocrystals

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Relaxation processes in oxygen-containing Ar cryocrystals pre-irradiated by low-energy electrons are studied with the focus on the role of diffusion controlled atom-atom recombination reaction of oxygen in the relaxation cascades. The results of correlated in real time measurements of thermally stimulated phenomena are presented. The experiments have been performed using activation spectroscopy methods — thermally stimulated exoelectron emission and spectrally resolved thermally stimulated luminescence. Solid evidence of the radiative mechanism of electron detrapping triggering the relaxation cascades is obtained.

Introduction

Oxygen is one of the most abundant elements in the universe that exhibits in many respects unique properties attracting considerable interest of scientists over many years. A.F. Prikhot'ko studied extensively elementary excitation of solid oxygen [1] and a lot of the credit must go to her research group which discovered a number of novel phenomena in solid oxygen. The brilliant findings of A.F. Prikhot'ko inspired us when we went to the heart of the matter on the role of oxygen in the relaxation pattern of pre-excited cryocrystals. Exposure of insulating materials to ionizing radiation results in formation of electron-hole pairs, defects of structure, molecule fragments. Relaxation channels following the primary electronic excitation involve such processes as electron-hole recombination, trapping or self-trapping of charge carriers, emission of electrons and photons etc. Some fraction of energy absorbed by solids under irradiation is then stored by charged and neutral centers formed in the lattice.

After the irradiation is completed a further relaxation can be stimulated by heating the samples or optically — by photons. Both factors can induce relaxation processes in electronic and atomic subsystems. Clear understanding of the radiation effects changing the solid properties is of great importance for material and surface sciences as well as for radiation chemistry. Very often electronic and atomic relaxation processes occurring in pre-irradiated solids are considered separately ignoring the interconnection between these channels of relaxation. Our recent studies demonstrated the fundamental importance of the interconnection between atomic and electronic processes in the formation and branching of relaxation paths [2].

Ar cryocrystals were chosen as matrices for several reasons: (i) because of a small atomic radius of oxygen (0.12 nm) it can be easily stabilized at low temperatures in Ar solids without any significant distortion of the lattice; (ii) solid Ar and O_2 have close sublimation temperatures (about 30 K); (iii) a high mobility and

free-like behavior of electrons in solid Ar [3] together with a large electron escape depth of about 500 nm [4] enables one to gain information about relaxation processes in the bulk and at the surface; (iv) a negative electron affinity of solid Ar (−0.3 eV [3]) facilitates escaping the electrons from the surface. Moreover, the first successful experiments on thermally stimulated exoelectron emission (TSEE) [5] offered the prospect for developing of low-temperature comprehensive activation spectroscopy technique as applied to cryocrystals.

We combined TSEE studies with measurements of the total and spectrally resolved yields of thermally stimulated luminescence (TSL). Partial yields in the visible and in the vacuum ultraviolet (VUV) ranges were detected. In addition, the experiments on photon-stimulated exoelectron emission (PSEE) were performed. Since both TSL and TSEE are quite sensitive to sample structure and concentration of guest centers there is a clear need to make synchronous measurements of TSL, TSEE on the same sample. We present the results of «correlated activation spectroscopy» studies of relaxation processes in pre-irradiated Ar solids doped with oxygen. The studies are aimed to elucidating in detail the role of oxygen in the relaxation cascades.

Experimental

In this study we used the low-temperature modification of activation spectroscopy technique developed recently by our group, namely the real time-correlated measurements of relaxation processes in cryogenic solids with simultaneous measurements of TSEE, spectrally resolved TSL or partial TSL yields in a chosen wavelength range. The samples were grown from the gas phase by deposition on a metal substrate coated with a thin layer of MgF_2. The substrate was cooled by a closed-cycle 2-stage Leybold RGD 580 cryostat. The high-purity (99.999%) Ar gas was used. A base pressure in the vacuum chamber was 10^{-8} mbar. The samples were doped with minute amounts of O_2 (10^{-4}). The deposition was performed with a concurrent irradiation by 500 eV electrons to generate charge centers throughout the layer. The current density was kept at 30 $\mu A/cm^2$. A typical deposition rate was 10^{-1} $\mu m/s$. We deposited the Ar films of 50−100 μm thickness. The sample thickness and the deposition rate were determined by measuring the pressure decrease in a known volume of the gas-handling system. The temperature was measured with a calibrated silicon diode sensor, mounted on the substrate. The relaxation processes in the Ar samples were studied in the temperature range from 7 to 42 K. The programmable temperature controller LTC 60 allowed us to maintain desired temperatures of deposition, irradiation and heating regimes. Two heating modes were used: linear

heating at a constant rate of 3.2 K/min and step-wise heating of the samples with a step of 2 K and a 5 min interval between successive steps. After the sample preparation the substrate was turned to the position for measurements. We measured simultaneously the yields of thermally TSEE from the samples and spectrally-resolved TSL in the visible range or the yield of TSL in the VUV range. The exoelectron yield was measured with an Au-coated Faraday plate kept at a small positive potential +9 V and connected to a current amplifier FEMTO DLPCA 100. A centrally located hole in the Faraday plate permitted us to detect spectra from the sample through an optical window. The spectra were recorded by a spectrometer (Multichannel S2000 Spectrometer Ocean Optics based on CCD detectors) operating in the range 170−1100 nm with a resolution not worse than 1.3 nm in the millisecond time window. This spectrometer allows monitoring the temporal evolution of the spectra in the operating range. The program developed permitted us to detect synchronously spectra over the entire operating range, TSEE current, temperature and pressure in the chamber.

Results and discussion

Figure 1 shows typical curves of the yields of thermally stimulated exoelectron emission and recombination thermally stimulated luminescence in the VUV range stemmed from the reaction

$$Ar_2^+ + e \rightarrow Ar_2^* \rightarrow Ar + Ar + \Delta E + h\nu \ (9.7 \ eV). \quad (1)$$

The measurements were performed simultaneously on the same sample in the temperature range 7−42 K using heating at a constant rate of 3.2 K/min. The clearly seen structure of the curves reasonably agrees
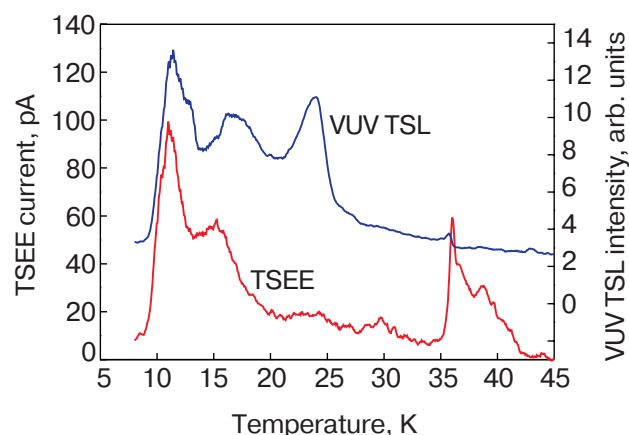

Fig. 1. Yields of TSL in the VUV range and TSEE taken from the sample of Ar which was annealed at 25 K and then irradiated at 7 K.

with the previously measured yield of TSL detected in the M-band [6,7] and the yield of TSEE [5] with the only difference that the curves in Fig. 1 show more distinct features. The low-temperature peak at 11.5 K is related to the electron traps in a subsurface layer or at inner interfaces of the sample. The peak at about 15 K exhibiting the pronounce dose dependence was assigned to radiation-induced defects [5,6,8,9]. A rather strong TSEE maximum observed between 37 and 41 K is presumably due to electrons trapped too deep in the sample to be promoted to the conduction band, which are however released on the sample evaporation. The corresponding maximum in the VUV TSL turned out to be quite weak.

The origin of the broad 23 K peak in thermally stimulated phenomena was under discussion over 10 years. This peak was detected in the total yield of TSL [5,8] and in intrinsic recombination emission — spectrally resolved TSL in the M-band [6] taken from Ar pre-irradiated by a 1 keV electron beam as well as from Ar pre-irradiated by x-rays [7]. Note, that the peak at 23 K was also registered in the thermally stimulated conductivity [9] and in thermally stimulated exoelectron emission [5]. On the other hand, the intensity of this peak showed a clear connection with the presence of oxygen in the samples enhancing TSL and TSEE peaks at 23 K with increasing oxygen content. Monitoring of spectrally resolved TSL in the visible range taken from pre-irradiated Ar solids revealed the emergence of O_2^* emission near 23 K in oxygen-containing samples. Different mechanisms of the 23 K peak formation were suggested to explain this puzzling behavior of this peak in the yields of thermally stimulated phenomena in Ar solids. For instance it has been suggested in [9] that this peak is caused by recombination of O^- ions with neutral O atoms. Another scenario was discussed in [10,11]. It was supposed that neutral O atoms on heating started to diffuse through the Ar lattice forming oxygen molecules O_2^*. The radiative transition of O_2^* into the ground state was considered as a stimulating factor to electron detrapping which is the primary step of branching relaxation channels.

To verify the discussed above [9–11] mechanisms of triggering relaxation cascades by recombination reactions we performed the experiments with synchronous measurements of thermally stimulated chemiluminescence of O_2^* stemmed from the diffusion-controlled atom-atom recombination reaction and TSEE yield as well as yields of TSEE and TSL in the VUV range originated from the intrinsic charge recombination reaction (1). The samples were doped with O_2 (10^{-4}) and the generation of O atoms under irradiation was monitored spectroscopically. Figure 2 shows a part of
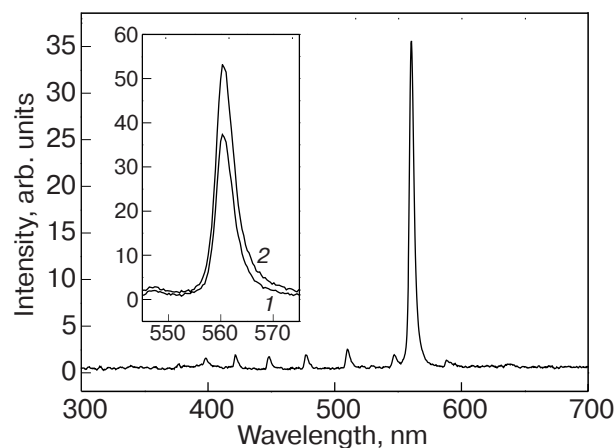

Fig. 2. Luminescence spectrum of the Ar sample doped with O_2 (10^{-4}) recorded in the range of O_2 and O emissions. The spectrum was detected during deposition under electron beam. The O line detected after 10 (*1*) and 20 (*2*) min exposure is shown in the insert.

the luminescence spectrum in the visible range recorded under electron beam at low temperature (7 K). The molecular bands of oxygen (the $C^3\Delta_u \rightarrow X^3\Sigma_g^-$ transition) became relatively weak just after 10 min irradiation. The strongest feature in the spectrum belongs to the O atoms effectively formed in the sample under electron beam. An increase of the O line intensity with exposure time is illustrated in the insert.

In order to study the origin of the 23 K peak we «removed» all the peaks at temperatures lower than the temperature of emerging the peak under study. For the purpose we used the so-called «cleaning technique» [12] and irradiated oxygen containing samples at 18 K. On completing the irradiation we recorded the yield of TSEE and the TSL yield in the VUV range shown in Fig. 3. Both curves exhibit a maximum near 23 K thus demonstrating the correlation of the exoelectron emission and the emission of the VUV photons of the intrinsic charge recombination reaction (1). The VUV TSL curve turn out to be much broader than the TSEE curve which is to say that some additional electron traps are involved in the bulk recombination channel. The corresponding VUV TSL curve taken from the sample annealed at 25 K (Fig. 1) exhibits a more narrow peak which correlates with the 23 K peak in TSEE. At the same time the correlated in real time measurements of the TSEE yield and spectrally resolved TSL in the operating range of the spectrometer demonstrated in a conclusive way the correlation in the TSEE yield of the sample irradiated at 18 K and the observed simultaneously photon emission
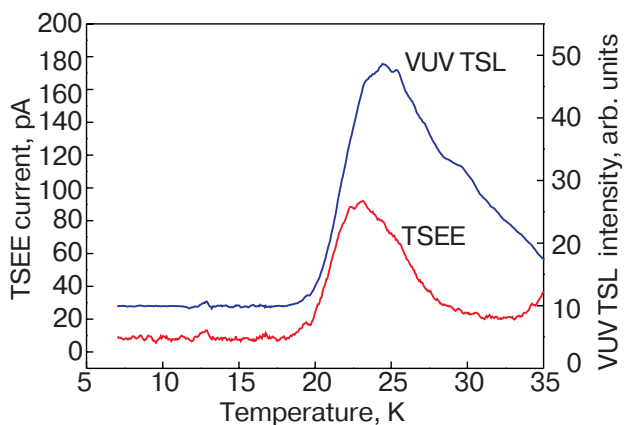
Fig. 3. Yields of TSL in the VUV range and TSEE taken from the oxygen-containing sample pre-irradiated at 18 K.

Fig. 5. Yields of O_2 emission in TSL and TSEE taken from the oxygen-containing sample pre-irradiated at 18 K.

of O_2^* (the $C^3\Delta_u \to X^3\Sigma_g^-$ transition). Two cycles of the experiments were performed to check carefully the correlation (with liner and step-wise heating). Figure 4,*a* displays the oxygen molecule progression in TSL mea-
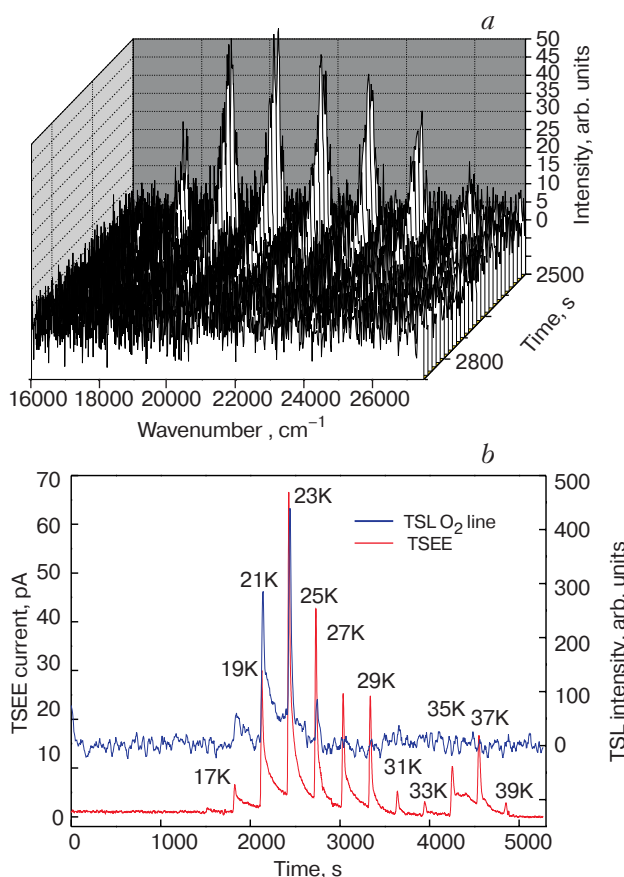

Fig. 4. TSL yield in the visible range and TSEE yield measured at step-wise heating of the Ar sample doped with O_2 (10^{-4}). The sample was pre-irradiated at 18 K. The TSL spectrum measured at the 23 K step is shown in (*a*); (*b*) displays the temperature behavior of the 0–10 molecular band of the $C^3\Delta_u \to X^3\Sigma_g^-$ transition.
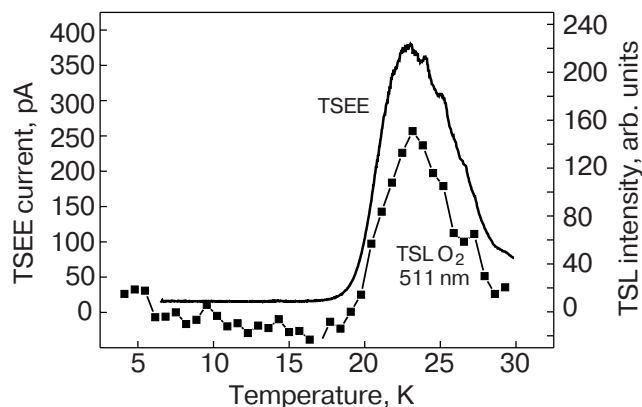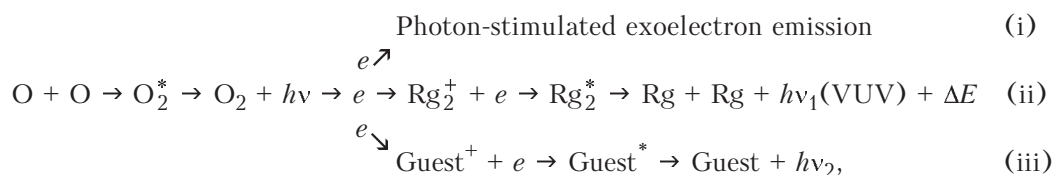
sured in step at 23 K. The simultaneously detected TSEE current is depicted in Fig. 4,*b* together with the behavior of the chosen band of the progression ($v' = 0$, $v'' = 10$). The experiment with the linear heating (Fig. 5) confirmed the correlation between the molecular oxygen emission and the yield of the TSEE current near 23 K.

Our experimental data on relaxation processes in pre-irradiated Ar solids doped with oxygen enable us to restore the following scenario to explain the pattern puzzling at first sight.

The charge recombination reactions in pre-irradiated rare-gas atomic cryocrystals are controlled by the mobility of electrons. The weakest bound in the traps electrons are mobilized at the lowest temperatures and escape the crystal or neutralize positive intrinsic (self-trapped holes) ions. These charge recombination reactions result in the appearance of the VUV emission. At a definite, higher temperature, the O atoms present also start to diffuse, and a complex sequence of events may take place. Recombination of neutral O atoms results in the formation of molecular O_2^* in bound excited electronic states. This is followed by a rapid relaxation, and eventually by radiative transition into the ground state. The emitted visible range photons, in turn, can be absorbed and provide the energy needed to detrap electrons from deeper traps promoting them to the conduction band. This is some kind of «internal photoeffect» followed by (i) ejection of exoelectrons from the surface, (ii) conversion of visible light into VUV photons via recombination of electrons with self-trapped holes by the reaction (1), or (iii) conversion of visible light into photons of other range via recombination of electrons with some extrinsic positively charged centers. All these electron-driven processes, which are outlined in the scheme below, were detected in our experiments.

$$\text{Photon-stimulated exoelectron emission} \qquad \text{(i)}$$

$$\text{O} + \text{O} \rightarrow \text{O}_2^* \rightarrow \text{O}_2 + h\nu \rightarrow e \rightarrow \text{Rg}_2^+ + e \rightarrow \text{Rg}_2^* \rightarrow \text{Rg} + \text{Rg} + h\nu_1(\text{VUV}) + \Delta E \quad \text{(ii)}$$

$$e \searrow \text{Guest}^+ + e \rightarrow \text{Guest}^* \rightarrow \text{Guest} + h\nu_2, \qquad \text{(iii)}$$

where Rg is a rare-gas atom.

The results obtained provide solid evidence for the electronic relaxation stimulation via chemiluminescent reactions. It is worthy of note that in contrast to the local energy release under nonradiative radical recombination the revealed radiative mechanism provides a long-range energy transfer for hundreds of lattice constants. Based on these results other radiative mechanisms of relaxation cascades triggering in pre-irradiated solids can be predicted, e.g., stimulation of relaxation by radiative transitions of metastable atoms or molecules. The first results demonstrating reliability of this mechanism are presented in [14]. The experiments on stimulation of relaxation processes by laser light [2,15] provide an additional proof of the mechanisms discussed.

Summary

The combination of correlated in real time measurements of spectrally-resolved thermally stimulated luminescence and exoelectron emission from pre-irradiated Ar solids doped with O_2 has given conclusive evidence in favour of relaxation cascades stimulation via chemiluminescent reactions. The verified mechanism provides a long-range energy transfer and demonstrates the existence of a new relaxation channel (triggering of electronic relaxation processes by diffusion controlled atom-atom recombination reaction followed by light emission).

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