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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 the diffusion-controlled atom-atom recombination reaction of oxygen in the relaxation cascades. The results of real-time-correlated 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 for the radiative mechanism of electron de-trapping triggering the relaxation cascades is obtained. © 2006 American Institute of Physics.

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INTRODUCTION

Oxygen, one of the most abundant elements in the universe, has properties that are in many respects unique and has attracted considerable interest of scientists over many years. A. F. Prikhot'ko studied the elementary excitation of solid oxygen extensively,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 to go 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 the energy absorbed by a solid under irradiation is then stored by charged and neutral centers formed in the lattice. After the irradiation is completed, 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 radiation effects on the properties of solids 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 have 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 the 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 O₂ have close sublimation temperatures (about 30 K); (iii) a high mobility and free-like behavior of electrons in solid Ar (Ref. 3) together with a large electron escape depth of about 500 nm (Ref. 4) enables one to gain information about relaxation processes in the bulk and at the surface; (iv) the negative electron affinity of solid Ar (−0.3 eV³) facilitates the escape of electrons from the surface. Moreover, the first successful experiments on thermally stimulated exoelectron emission (TSEE)⁵ offered the prospect for developing a low-temperature comprehensive activation spectroscopy technique for application 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, 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 and 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 the 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. High-purity (99.999%) Ar gas was used. The 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 $30 \mu\text{A}/\text{cm}^2$. A typical deposition rate was $10^{-1} \mu\text{m}/\text{s}$. We deposited the Ar films of thickness 50–100 μm . 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 in the 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 FEMTO DLPCA 100 current amplifier. 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 (Ocean Optics Multichannel S2000 Spectrometer 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 synchronous detection of the 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

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 agrees reasonably well 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 pronounced 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

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

electrons trapped too deep in the sample to be promoted to the conduction band, which are however released upon evaporation of the sample. 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 has been under discussion for 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 has also been registered in the thermally stimulated conductivity⁹ 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 has revealed the emergence of O_2^* emission near 23 K in oxygen-containing samples. Different mechanisms of the 23 K peak formation have been 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 Ref. 9 that this peak is caused by recombination of O^- ions with neutral O atoms. Another scenario was discussed in Refs. 10 and 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 the branching relaxation channels.

To verify the above-discussed^{9–11} mechanisms of triggering relaxation cascades by recombination reactions we performed experiments with synchronous measurements of thermally stimulated chemiluminescence of O_2^* stemming from the diffusion-controlled atom-atom recombination reaction and TSEE yield as well as yields of TSEE and TSL in the VUV range, originating 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 the luminescence spectrum in the visible range recorded under the electron beam at low temperature (7 K). The molecular bands of oxygen (the $\text{C}^3\Delta_u \rightarrow \text{X}^3\Sigma_g^-$ transition) became relatively weak after just 10 minutes of irradiation. The strongest

FIG. 2. Luminescence spectrum of an 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 an electron beam. The O line detected after 10 (1) and 20 (2) minutes of exposure is shown in the inset.

feature in the spectrum belongs to the O atoms efficiently formed in the sample under the 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 emergence of the peak under study. For this 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 yield of TSL 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 turns 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 real-time-correlated 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 simultaneously observed photon emission of O_2^* (the $C^3\Delta_u \rightarrow X^3\Sigma_g^-$ transition). Two cycles of experiments were performed to check carefully the correlation (with linear and

FIG. 3. Yields of TSL in the VUV range and TSEE taken from the oxygen-containing sample pre-irradiated at 18 K.

FIG. 4. TSL yield in the visible range and TSEE yield measured under step-wise heating of an 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 $C^3\Delta_u \rightarrow X^3\Sigma_g^-$ transition.

step-wise heating). Figure 4a displays the oxygen molecule progression in TSL measured in steps at 23 K. The simultaneously detected TSEE current is depicted in Fig. 4b together with the behavior of the chosen band of the progression ($\nu'=0$, $\nu''=10$). The experiment with 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 reconstruct the following scenario to explain the observed pattern, which is puzzling at first sight.

The charge recombination reactions in pre-irradiated rare-gas atomic cryocrystals are controlled by the mobility of electrons. The electrons most weakly bound in the traps are

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

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 rapid relaxation, and eventually by radiative transition into the ground state. The emitted visible-range photons can, in turn, be absorbed

and provide the energy needed to detrapp 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.

where Rg is a rare-gas atom.

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

SUMMARY

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

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