Stimulated by laser light exoelectron emission from solid Ar pre-irradiated by an electron beam

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Spatially separated stable charge centers, self-trapped holes and trapped electrons, were generated in Ar cryocrystals by a low-energy electron beam. A combination of the cathodoluminescence (CL) and photon-stimulated exoelectron emission (PSEE) methods was used to monitor center formation and selected relaxation channel – exoelectron emission. It was found that photon-promoted electron current decreased exponentially under irradiation with the laser operating in the visible range. Influence of the laser parameters (power and wavelength) on the characteristic lifetime of exoelectron emission is discussed. Effective bleaching of the low-temperature peaks of thermally stimulated exoelectron emission by the laser light in a visible range was observed.

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\textbf{Introduction}

Irradiation of solid insulators with vacuum ultraviolet (VUV) light above the band gap energy $E_g$ or with fast particles results in changing properties of solids via excitation of the electronic and atomic subsystems, defects creation and following relaxation. These changes and especially last stage — relaxation cascade — are of high interest for radiation physics and chemistry as well as for materials science. A variety of relaxation processes have been under extensive investigation in various classes of materials [1–4]. Atomic cryocrystals — model insulating materials — offer the best opportunity to study radiation effects and various relaxation channels because of their simple structure, weak interatomic forces, and strong electron-phonon interaction. The final relaxation stage, i.e., the processes occurring on completion of the irradiation, is of special interest for understanding the radiation effects, the dynamics of charge carriers, and stability of radiation-induced defects. The primary states of the relaxation cascades in this case are states of self-trapped or trapped holes and trapped electrons, as well as metastable levels of the guests. A stimulating factor for these relaxation processes could be the heating of the sample or irradiation by visible light.

The methods of activation spectroscopy are especially powerful tools for the investigation of relaxation in solids, and the method of thermally stimulated luminescence (TSL) is the most common in use [5]. Indeed, TSL of atomic cryocrystals has been studied in several publications — irradiation by x-rays [6,7], electron beams [8–11], and synchrotron radiation [12]. The total and spectrally resolved yields [6–13] of TSL were measured and the activation energies of various electron traps were estimated. Analysis of the thermally stimulated intrinsic recombination luminescence in the VUV range, the well-known M-band [1], was performed for solid Ar in the range 15–30 K [7] and in a wider range 5–30 K [9,13,14]. Relaxation processes involve not only charged species but also neutral ones and that is why we combined the methods of optical and current activation spectroscopy. Thermally stimulated exoelectron emission (TSEE)
was recently detected from solid Ne [15,16] and Ar [13, 14]. The later studies demonstrated a correlation in the yields of exoelectrons and VUV photons in the intrinsic recombination emission from pre-irradiated solid Ar. It was suggested [17] and then proved [10,11,14] that the thermally stimulated recombination of neutral guest oxygen atoms in the Ar matrix followed by $O_2^+$ formation and radiative decay of the oxygen molecule resulted in the emission of exoelectrons from solid Ar. These findings posed the question concerning the influence of visible light on the relaxation paths in the atomic cryocrystals.

Up to very recently there was only an additional study related to photon-stimulated processes in atomic cryocrystals [18]. In those experiments the samples were irradiated by pulsed synchrotron radiation. Between synchrotron pulses the samples were exposed to laser pulses. Photoelectrons and photon-stimulated luminescence in the M-band of Xe and Kr were registered in those experiments. It was found that the characteristic times of photon-stimulated luminescence from solid Xe and Kr (1700 ns and 190 ns, respectively) are very close to those in the spontaneous luminescence from Rg$_2^+$ dimers in the well-known M-bands [1]. The excitation spectra after laser irradiation were found to be identical with those for the spontaneous luminescence from atomic cryocrystals [1].

To investigate the role of stable lattice defects and the effect of visible light on the relaxation paths, other experiments on photon-stimulated spectrally resolved recombination luminescence were performed. Solid Ar pre-irradiated with a low-energy electron beam was exposed to the irradiation of a He–Ne laser operated in the continuous mode. Stimulated by photons in the visible range, spectrally resolved luminescence in the M-band was registered [19]. In this case we used laser light as the external source to trigger the relaxation channels in pre-irradiated solid Ar. The experiments were performed at low temperatures to exclude a possible contribution from thermally stimulated processes. The characteristic decay time of photon-induced intrinsic recombination luminescence observed under continuous laser emission was found to be around 200 s in contrast to the very short lifetime of the radiative transition $3\Sigma_g^+ \rightarrow 1\Sigma_u^+$ (1200 ns) for the spontaneous luminescence of solid Ar [1].

Additional information on photon-stimulated processes was obtained in the experiments [20,24] with some kind of an «internal light source». For that purpose, solid Ar was doped with nitrogen and xenon to form not only intrinsic but also extrinsic charged centers and metastable ones. The sample was deposited under electron beam on a cooled substrate. Under electron bombardment, N$_2$ molecules were fragmented and metastable nitrogen atoms were efficiently formed. The green afterglow from atomic nitrogen due to the well-known forbidden transition $^2D \rightarrow ^4S$, indicating the formation of N atoms, was used as the «internal light source» to stimulate the relaxation. Photon-stimulated exoelectron emission as well as spectrally resolved VUV recombination luminescence of intrinsic Ar$_2^+$ and extrinsic Xe$_2^+$ centers with electrons (indicated by the radiative transition of neutralized centers Ar$_2^+$ and Xe$_2^+$ to the ground state) were registered. Simultaneously with exoelectron emission an afterglow in the visible range from the doped solid Ar was observed. It was found that the characteristic lifetimes of the exoelectron emission and recombination luminescence from intrinsic and extrinsic charged centers were around 20 s, which characterized the duration of afterglow from atomic nitrogen in Ar matrix [20].

Analysis of the data obtained shows that the photon-stimulated relaxation processes are branched into the several paths: (i) radiative recombination of intrinsic ionic centers (self-trapped holes) of the dimer Ar$_2^+$ with electrons released from the traps by visible light; (ii) radiative recombination of ionic guests with electrons, and (iii) exoelectron emission.

Here we present new results on the effect of the parameters of external source (laser light) on the characteristics of the relaxation channel — exoelectron emission. Influence of the laser power and wavelength on the lifetime of photon-stimulated exoelectron emission (PSEE) was investigated.

**Experimental**

In view of the fact that the relaxation can be triggered by photon irradiation or heating we combined the thermal and optical activation spectroscopy methods in order to investigate the whole set of relaxation paths and their interrelations. The general sequence of experimental procedures was as follows: (1) sample preparation under electron bombardment, (2) irradiation with a laser light and measurement of the photon-stimulated exoelectron yield, (3) upon completion of the laser irradiation the samples were heated at a constant rate and thermally stimulated exoelectron emission was recorded. Details of the experiments are given below.

The samples of nominally pure solid argon (99.999 %) were grown from the gas phase by depositing on a metal substrate coated by a thin MgF$_2$ layer, which was cooled to 6 K by a two stage, close-cycle Leybold RGD 580 cryostat. The base pressure in the vacuum chamber (about $10^{-9}$ mbar) was monitored with a Compact BA Pressure Gauge PBR 260. The content of impurities such as O$_2$, N$_2$, CO$_2$ and H$_2$O did not exceed 100 ppm. The sample thickness (of about 100 µm) was determined by measuring the pressure decrease in a known volume of the bulb in the gas inlet system. The typical deposition rate was kept at about $10^{-7}$ µm/s.

For the creation of neutral and charged defects in the films via excitation of the electronic and atomic subsys-
To initiate the relaxation of a pre-irradiated matrix, we used laser light as the source of photons. To cover the whole visible range, a coherent Ar Ion Laser (Innova 70) and a Coherent CR–599 Dye Laser operating with Rhodamine 6G and pumped with Ar Ion Laser were used. The laser light was introduced into the sample chamber via an optical fiber. The laser power was varied in the range 10–75 mW, as measured in front of the sample, and laser beam was defocused to the diameter of about 3 cm to cover the whole the sample. The overheat did not exceed 0.2 K under excitation by the most powerful (75 mW) laser light.

The temperature was measured with a calibrated silicon diode sensor, mounted at the substrate. The programmable temperature controller LTC 60 permitted us to keep the temperature fixed during sample preparation, as well as to control the desirable heating rate. During deposition the temperature was kept at 6 K to minimize possible thermally stimulated processes. Note that the threshold temperature for thermally stimulated processes in solid Ar is about 10 K. During measurements of the photon-stimulated exoelectron emission, the temperature was kept at 6 K. For the experiments on the influence of laser light on the ensuing TSEE we used continuous heating with a constant rate of 3 K/min. The TSEE yield was measured in a range 6–45 K.

The emission of electrons from pre-irradiated samples was detected with an Au-coated Faraday plate kept at a small positive potential +9 V positioned at 5 mm in front of the sample. The Faraday plate current was amplified by a low-noise current amplifier FEMTO DLPCA-200, converted into voltage, and the inverted voltage digitized in a PC. Currents of about 100 fA can be easily measured in our experiments.

To investigate the influence of sample structure on the lifetime of the relaxation processes we performed experiments with annealed samples. To this end, the Ar samples were prepared as was described above. After laser light irradiation each sample was annealed at 25 K during 5 min and then cooled down to 6 K. After cooling the sample was irradiated once again with the electron beam. The laser was switched on again and exoelectron emission from the annealed sample was measured. Then we repeated the cycle of annealing and laser irradiation and measurements of the exoelectron emission.

Results and discussion

Electron-hole pairs are created quite efficiently in atomic cryocrystals under electron bombardment. Holes are self-trapped in the lattice within 10–12 s [1] due to the electron-phonon coupling, become immobile at low temperatures. As suggested theoretically [1] and proved experimentally [21,22], self-trapped holes (STH) have the configuration of a dimer ion and can be considered as Rg2+ centers in their own matrix. Frenkel pairs, interstitials and vacancies, can be created in atomic cryocrystals via excitation of the electronic subsystem by a low-energy electron beam [9]. Electrons are not self-trapped in Ar matrix and characterized by free-like behavior [1]. Because of a negative electron affinity $E_a = -0.4$ eV [1], with repulsive forces prevailing the electron can be trapped in solid Ar only by such lattice defects as vacancies, vacancy clusters, or pores. Although these traps are thought to be relatively shallow, the trapped electrons remain nevertheless stable at low temperatures at least up to 10 K. The activation energy needed to release electrons from traps can be transferred by heating or photon irradiation. STH are less mobile than electrons (by a factor of $10^{-4} -10^{-5}$) and bound more tightly therefore, they cannot be released in the same way [1]. Solid Ar is a wideband material with the conduction bandwidth of about 2.3–3.7 eV [23]. The depth of the most shallow trap was estimated to be about 12 meV [8]. The strongest peak at 15 K in the thermally stimulated luminescence (TSL) of nominally pure Ar related to the exciton-induced defects is characterized by an activation energy of 15 meV, according to [8], or 36 meV, according to [12]. The deep thermally disconnected trap could be a guest atom or molecule with positive electron affinity. The typical example of the so-called «electron scavenger» is oxygen. The oxygen atom has a binding energy of 2.61 eV and for molecular oxygen this value is 1.59 eV, as one can estimate by taking into account the polarization energy of the Ar matrix [10]. In fact, photons of energies above 3-10$^{-7}$ eV can be used to release electrons from shallow traps and promote their passage to the conduction band.

When an electron starts to move through the lattice, there are at least two possibilities for further relaxation:

(i) to reach the surface and escape the sample directly as was observed in [10,11,14,17] for nominally pure and doped solid Ar;

(ii) to recombine radiatively with positively charged intrinsic Ar$_2^+$ and extrinsic (for example Xe$_2^+$) centers via the following reactions [19,20]:

$$\text{Ar}_2^+ + e \rightarrow \text{Ar}_2 \rightarrow \text{Ar} + \text{Ar} + h\nu_1(9.8 \text{ eV}), \quad (1)$$

$$\text{Xe}_2^+ + e \rightarrow \text{Xe}_2 \rightarrow \text{Xe} + \text{Xe} + h\nu_1(7.2 \text{ eV}). \quad (2)$$

To check the influence of visible-range photons on the direct escape of electrons from the sample (channel i), we...
performed experiments on photon-stimulated exoelectron emission. The yield of exoelectrons stimulated by a laser of wavelength \( \lambda = 514 \text{ nm} \) and power \( W = 25 \text{ mW} \) is shown in Fig. 1. Switching on the laser light resulted in a sharp signal rise with a subsequent slow decay. As was shown in [20,25], the decay can be described in a no-retrapping case by the expression:

\[
N_c = N_0 g(t) \tau_c \exp(-gt), \tag{3}
\]

where \( g(t) \) is the product of the density of photons irradiating the sample and the effective interaction cross section of the photons and the electrons in the traps; \( \tau_c \) is the effective lifetime of electrons in the conduction band; \( N_0 \) is the initial concentration of electrons in the traps. Note that the current is proportional to the concentration of electrons in the conduction band. Since the rate of exoelectron emission and the recombination luminescence in the M-band depend on the concentration of electrons in the conduction band, the same expression (3) can be applied to describe the decay of photon-stimulated recombination luminescence (1), (2) [20]. The characteristic lifetime for this recombination luminescence (several tens of seconds) exceeds the «intrinsic» M-band lifetime (1.8 ns for singlet and 1200 ns for triplet in Ar matrix [1]) by many orders of value [19,20]. When we use the laser light as a source of photons, \( g(t) \) can be described as a product of the power \( P \) and the effective interaction cross section \( \sigma \) of photons and electrons in the traps. In that case, \( g(t) \) is a constant: \( g(t) = g = Pa \). The decay shown in Fig. 1 can be described by (3) with \( \tau = g^{-1} \), which characterizes the time scale needed for electrons to pass the conduction band and to escape the sample without any barrier because of the negative electron affinity of Ar (–0.4 eV).

Using a laser as the source of photons we can easily vary the laser power \( P \) at fixed wavelength in order to understand how the laser light power influences the lifetime \( \tau \). For this purpose we performed a series of experiments on PSEE with varying laser power. The results are depicted in Fig. 2. At a laser power of 15 mW the decay curve lifetime \( \tau \) is about 42 s. With increasing laser power the lifetime clearly decreases. At 75 mW the lifetime is about 23 s. Note that the overheating during irradiation at the highest laser power does not exceed 0.2 K, so we can be sure that no additional thermal stimulation processes occurred. We can suppose that substantial error can be caused by differences in sample structure. We found that the lifetime determination experiment is quite sensitive to sample quality. In Fig. 3 one can see the results of the PSEE experiment performed with 2 cycles of annealing. After completing the electron-beam irradiation the laser was switched on and the exoelectron emission from the sample was measured. In that case we used the laser at 20 mW power and a wavelength of 514 nm. After a cycle of laser irradiation the sample was annealed at 25 K during 5 min and then was cooled down to 6 K and irradiated once again by electron beam. The laser was switched on again. The lifetime extracted from the exoelectron emission curve is about 13 s after the first annealing cycle and 8 s after the second cycle. The annealing procedure improves sample structure and effects of electron scattering on structure defects become less pronounced, which results in a shorter time the electrons needs to escape the sample. And, indeed, \( \tau \) shortens with each next annealing cycle.
The lifetime \(\tau\) depends on two factors: (i) \(\tau\) is inversely proportional to the density irradiation of photons (laser power), (ii) the effective interaction cross section of photons and electrons in the traps. This is why we can expect the lifetime the photon-stimulated exoelectron emission to depend on laser wavelength. To check this assumption, we performed PSEE experiments with a tunable laser. In this case, a Coherent Ar Ion Laser (Innova 70) and a Coherent CR–599 Dye Laser operating with Rhodamine 6G and pumped with Ar ion laser were used to cover the range from 450 to 640 nm. In Fig. 4, we show decay curves for the current from pre-irradiated samples stimulated by laser light of wavelengths 622, 514 and 476 nm. The laser power in all these experiments was fixed and in front of the sample it was 25 mW. The lifetimes extracted from these curves are: \(36\) s for the exoelectron emission stimulated with the red laser, \(24\) s for the green laser, and \(10\) s, for the blue laser. Figure 4, shows the PSEE lifetime versus the laser wavelength at fixed laser power. The lifetime increases with laser wavelength. Thus we can say that laser light with a shorter wavelength shortens the lifetime of the relaxation process. Changing the laser wavelength can result in some changing of the effective interaction cross sections and, hence, the lifetime \(\tau\) of the relaxation processes. Moreover, the photons of higher energy create «hotter» electrons in the conduction band and ensure preference for the PSEE with respect to the charge recombination processes.

An interesting question is the interrelation between thermally and optically stimulated relaxation processes. In this aspect we performed experiments on the laser stimulated exoelectron emission with subsequent heating. The samples were exposed to the laser light of variable power. After \(600–700\) s, when the PSEE current goes down to a noise level, laser irradiation was completed. After that the samples were heated at a constant rate of \(3.2\) K/min from \(7\) up to \(45\) K. A thermally stimulated exoelectron emission was observed and the behavior of the peaks was similar to that in our previous study [10,13,14]. Since the origin of the peaks on this curve was discussed in those papers, we outlined below it briefly. The first peak at \(12\) K is caused by the release of electrons from traps in the subsurface layer or from grain boundaries [13], the peak at \(15\) K belongs to radiation-stimulated defects. The shoulder at \(23\) K has a rather nontrivial origin [11,26]. It was shown that at this temperature, residual neutral oxygen atoms embedded in the matrix become mobile. Their diffusion results in a recombination of neutral O atoms, creating \(O_2^*\) molecules. Their formation is followed by a luminescence in the range of the well-known Herzberg progression. This light was treated as an «internal» source of photons to help release electrons from traps. In our experiments it was found (see Fig. 5) that the intensities of these low-temperature thermally stimulated peaks (LT TSEE) depend on the laser power at fixed wavelength, which was used before heating. The heating after laser irradiation using a more powerful laser leads to an effective bleaching of the LT TSEE peaks. It means that laser light of \(75\) mW power at \(514\) nm, for example, releases electrons from all kinds of shallow traps more effectively than laser light with a power of \(15\) mW at the same wavelength, which results in a decreasing of the LT TSEE
Ar which was pre-irradiated by a low-energy electron beam. Influence of the laser power and wavelength on the characteristic lifetime $\tau$ of PSEE was investigated. To avoid the contribution of thermally stimulated processes, the experiments were performed at low (6 K) temperatures. The characteristic lifetime $\tau$ proved to be quite sensitive to the sample structure: $\tau$ is shorter for more perfect samples.

The study of the bleaching of the TSEE peaks has shown that the laser light ensures an effective release of electrons not only from deep but also from shallow traps in pre-irradiated solid Ar. From PSEE experiments it is concluded that increasing the photon flux shortens the characteristic relaxation time $\tau$ and bleaches more effectively the LT TSEE peaks. With increasing laser wavelength the time $\tau$ increases. These results are in good agreement with the model of photon-stimulated processes [25] which assumes the lifetime $\tau$ to be inversely proportional to the product of the density of irradiating photons and the effective interaction cross section of photons and electrons in the traps.

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**Summary**

Using the current activation spectroscopy method in combination with cathodoluminescence spectroscopy, we investigated photon-induced relaxation processes in solid Ar which was pre-irradiated by a low-energy electron beam. Influence of the laser power and wavelength on the characteristic lifetime $\tau$ of PSEE was investigated. To avoid the contribution of thermally stimulated processes, the experiments were performed at low (6 K) temperatures. The characteristic lifetime $\tau$ proved to be quite sensitive to the sample structure: $\tau$ is shorter for more perfect samples.

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