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DEFECT-RELATED RELAXATION PROCESSES IN IRRADIATED RARE GAS SOLIDS

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Electronic and atomic relaxation processes in preirradiated solid Ar doped with N_2 were studied with a focus on the role of radiative electronic transitions in relaxation cascades. Combining methods of activation spectroscopy – thermally stimulated and photon-stimulated exoelectron emission, a new channel of relaxation induced by photon emission from metastable N atoms was detected. It was shown that in insulating materials with a wide conduction band photons of visible range can release electrons from both kinds of traps – shallow (lattice defects) and deep thermally disconnected ones. Correlation in the charge recombination reaction yield and the yield of low temperature desorption – important relaxation channel in a preirradiated solid – clearly demonstrates interconnection between atomic and electronic processes of relaxation.

Keywords: Rare gas solids; Activation spectroscopy; Recombination; Electron emission; Desorption

1. INTRODUCTION

Defects play an important role in a course of relaxation processes in irradiated materials. Interaction of ionizing radiation with insulators changes a set of defects and creates new metastable centers – charge carriers self-trapped or localized at defects and products of radiation-induced reactions involving dopants (atoms, molecules, radicals). An impact of heating or photon flux on preirradiated solids can release the energy stored by these centers, and thus strongly influences the transport and conversion processes involving both electronic and atomic subsystems. Understanding of the underlying basic processes and elementary stages of relaxation in irradiated solids is of considerable interest both from the point of view of fundamental solid state physics, and a number of important applications in material science, dosimetry, radiation and chemical physics. Rare gas solids (RGS) – the simplest model insulating materials – are traditionally used for unveiling mechanisms of a diversity of physical and chemical phenomena common to condensed media. And indeed, individual relaxation

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processes were studied, so thermally stimulated mobility of guests in RGS is a well-known phenomena, which is actively used in cryochemistry [1, 2]. Reactions of these species and their recombination are very often followed by an intense chemiluminescence (see *e.g.* [3, 4] and Refs. therein). Another process induced by heating of preirradiated matrices is thermally stimulated recombination of charge carriers resulting also in luminescence [5–7].

Recently we observed another phenomenon – thermally stimulated exoelectron emission (TSEE) from preirradiated solid Ar [8]. Due to combination of luminescent spectroscopy with methods of activation spectroscopy – thermally stimulated luminescence (TSL), including spectrally resolved TSL, thermally and photon-stimulated exoelectron emission (TSEE and PSEE), interesting interconnection between thermally driven chemical reactions of neutral species and charge carrier dynamics [9–11] was found. A new radiative mechanism of electronic relaxation in metastable cryomatrices containing different dopants was suggested – induced by chemiluminescence release of electrons from traps in the lattice followed by their emission and recombination with positively charged intrinsic (self-trapped holes) and extrinsic centers. For the first time we observed desorption from preirradiated matrices [10], which stems from recombination events.

In this paper, the role of radiative electronic transitions in the relaxation cascades is explored as an extention of our recent studies. We present new results of TSEE and PSEE experiments as well as desorption study performed with N_2 doped solid Ar preirradiated with an electron beam. The study enabled us to follow relaxation processes and to demonstrate an additional channel of relaxation induced by radiative decay of metastable N atoms in the lattice.

2. EXPERIMENTAL SECTION

A detailed description of the experimental techniques is given elsewhere [8–10]. In brief, the samples of nominally pure solid Ar and Ar doped with N_2 were grown from the gas phase by pulsed deposition on a silver-coated metal substrate cooled by a closed-cycle 2-stage Leybold RGD 580 cryostat. High-purity Ar (99.999%) gas was used. Experiments were performed with nominally pure Ar and Ar doped with N_2. The dopant to the Ar gas ratio was varied between 10^{-5} and 10^{-3}. A mixture was prepared in a gas-handling system by a standard procedure. Samples were deposited with a concurrent irradiation by a low energy (150 eV) electron beam. A typical thickness of Ar films was 50–100 μm. The sample thickness and the deposition rate were determined by measuring the pressure decrease in a known volume of the balloon for mixture preparation. A typical deposition rate was kept at about $10^{-2}\,\mu m s^{-1}$. The samples of high optical quality were prepared by condensation on the substrate gradually cooled down from 60 to 7 K. The temperature was measured with a calibrated silicon diode sensor, mounted at the substrate. The programmable temperature controller permitted to keep the maintained temperature during sample preparation and irradiation, as well as to control the desirable heating rate. In the TSEE experiments samples were heated with a constant rate of $3.2\,K min^{-1}$. The measurements were performed in the temperature range of 7–45 K. The pressure in chamber, which characterizes desorption yield, was measured as a function of temperature simultaneously with current detection.

The emission of electrons from preirradiated samples was detected with a movable Au-coated Faraday plate kept at a small positive potential +9 V. During measurements it was positioned at a distance of 5 mm in front of the sample grown on a grounded substrate. The current from the Faraday plate was amplified by a FEMTO DLPCA 100 current

amplifier. The signal was reversed in the polarity by an invertor and digitized in a PC. A current as low as 100 fA can be easily detected.

In the PSEE experiments the samples were held at a temperature (7 K) that is lower than the threshold temperature of TSEE [8] and TSL [6] in solid Ar (10 K). The laser light was introduced into the sample chamber with optical fiber. A Coherent CR-599-01 standing wave dye laser operating with Rhodamine and pumped with a Coherent Ar ion laser (Innova 70) was used. The power did not exceed 20 mW. The emission of electrons was measured with another electrode connected to the same system of current detection.

3. RESULTS AND DISCUSSION

Nitrogen-containing solids represent especially attractive systems for elucidating the role of radiative transitions in relaxation cascades because of an intense afterglow, indicating the formation of N atoms – the well-known forbidden $^2D \rightarrow {}^4S$ transition. N atoms are efficiently formed under electron bombardment of rare-gas matrices [12] and one can also expect an appearance of recombination emission due to N_2 formation under heating of the matrix, when diffusion of the N atoms becomes significant. We measured the emission of electrons from solid Ar doped with N_2. Measurements were performed immediately after sample preparation under electron beam at $T = 7$ K. Figure 1 shows the typical curve of "afteremission" taken from the sample with the dopant to the Ar gas ratio of 10^{-3}. Similar curves were obtained from the samples with the ratio 5×10^{-3} and 10^{-2}. All these current decay curves can be fitted by a second order exponential decay function with characterisitic times $\tau_1 = 33$ s and $\tau_2 = 170$ s (estimated error is about $\pm 15\%$). Simultaneously with "afteremission" we observed a discernible green afterglow. One can suggest that this afterglow stimulates the yield of electrons released from the lattice traps. In solid Ar because of its negative electron affinity $E_a = -0.4$ eV [13] only such kind of defects like vacancies, vacancy clusters or pores may be efficient traps for electrons. Note that N atom in the ground state has negative electron affinity $E_a = -0.1$ eV [14] and seems not to serve as a trap for electrons.

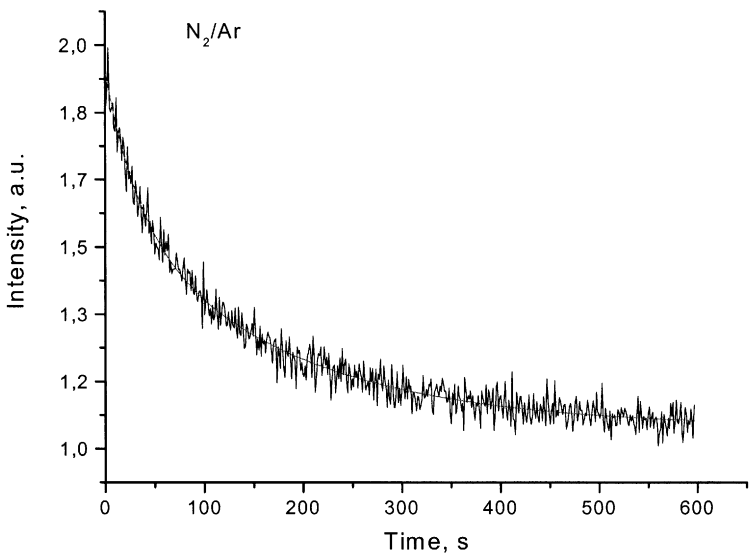

FIGURE 1 Yield of electron "afteremission" from N_2 doped solid Ar at the dopant to the Ar gas ratio of 10^{-3}.

However, if one takes into account the polarization energy of the Ar matrix $E_p = -1.15$ eV [15] it appears that the binding energy E_b of electrons is of about 1 eV and N atoms can be considered as deep thermally disconnected electron traps. The energy of the $^2D \rightarrow {}^4S$ transition of 2.37 eV is sufficient to excite the trapped electrons into the conduction band stimulating electron transport followed by the exoelectron emission. The decay curves in the range not too far away from the starting point can be treated as for the case of no retrapping and the free-carrier density N_c can be described by the simple expression [16]:

$$N_c = g\tau_c N_0 \exp(-gt), \tag{1}$$

where g is the product of the density of photons irradiating the sample and effective interaction cross-section of the photons and the electrons in the traps, τ_c is the effective lifetime of the electrons in the conduction band, N_0 – the initial concentration of electrons in the traps. So, the current-time transient decay (1) is a function of the excitation intensity. In the special case when the density of photons follows an exponential decay of afterglow $g = g_0\exp(-t/\tau)$. Then the density of free electrons N_c can be expressed by:

$$N_c' = g_0 \exp\left(\frac{-t}{\tau}\right)\tau_c N_0 \exp\left[-tg_0 \exp\left(\frac{-t}{\tau}\right)\right]. \tag{2}$$

Analyzing the current decay curve one should keep in mind that the characteristic time τ estimated from the experimental data on the electron emission induced by the decaying photon flux is in fact some effective time, which should be corrected taking into account that $g \neq \text{const}$. In the range $t \sim \tau$, the characteristic time for second exponent in (2) will be $\sim (g_0)^{-1}$ and for the case of low intensity photon flux, N_c' decay will be described mainly by first exponent $g_0\exp(-t/\tau)$. If we suppose that τ is the lifetime of the metastable N atom, one can expect that τ_1 extracted from the current decay curve will differ not so much from the radiative lifetime of the ^2D state. Indeed, $\tau_1 = 33 \pm 7$ s estimated from our experiments is quite close to the recently measured lifetime τ of the ^2D state of N atom in the Ar matrix $\tau = 43 \pm 1$ s [4]. The slow decay stage is, possibly, caused by retrapping of electrons.

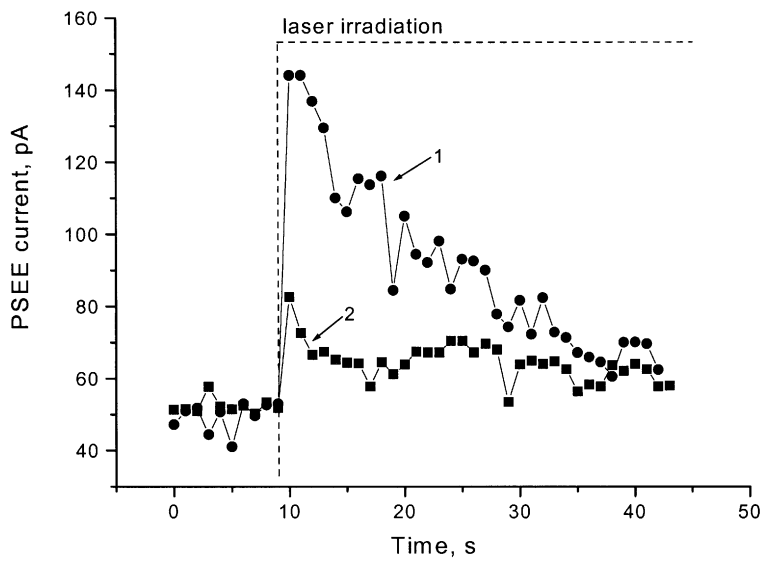

FIGURE 2 Yield of PSEE from solid Ar under irradiation by laser light at $T = 7$ K (curve 1); the yield taken from the sample annealed at $T = 16$ K (curve 2).

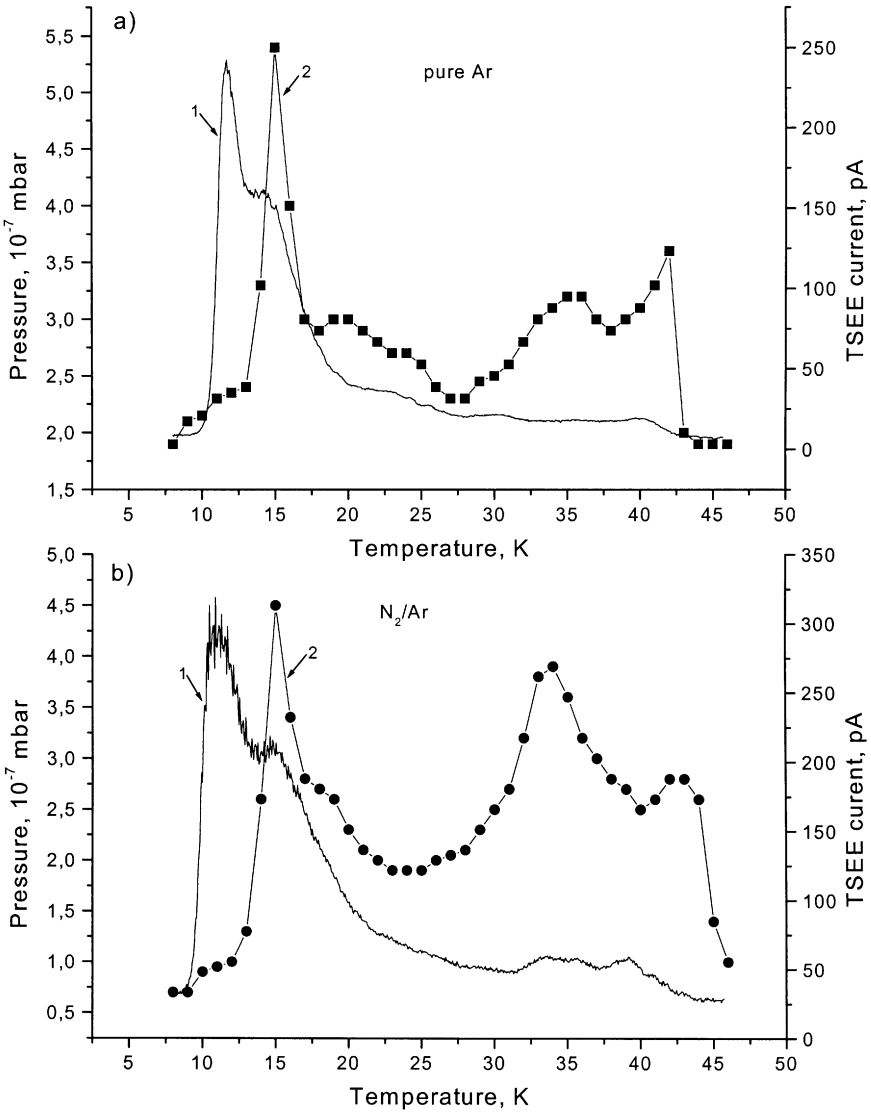

FIGURE 3 Temperature dependence of TSEE current (1) from nominally pure Ar (a) and Ar doped with N_2 at the dopant/matrix gas ratio 10^{-3} (b) and measured simultaneously pressure (2) in the sample chamber.

In nominally pure Ar electrons can escape from a depth of about 500 nm [17]. In the presence of electron scavengers electron escape depth will be considerably smaller. Note that the "after-emission" was not observed from the Ar samples doped with O_2 (efficient electron scavenger) at the ratio 10^{-3} in the absence of perceptible amount of N_2.

In order to support the suggested scenario and directly check the radiative mechanism of low temperature exoelectron emission from preirradiated solid Ar, experiments by PSEE were performed. We used photons of energy close to the energy of the $^2D \rightarrow {}^4S$ transition. Figure 2 demonstrates the influence of laser light on the electron yield (curve 1). Because of the wide conduction band of solid Ar (several eV) the current-time transient curve contains contributions from both kinds of electron traps in the matrix – shallow traps (lattice defects) and deep traps (impurities with positive E_a). To distinguish between these two the PSEE yield

was measured from the sample which was annealed at $T = 16\,\mathrm{K}$ after second cycle of low temperature irradiation. The contribution from deep thermally disconnected electron traps is seen in Figure 2 (curve 2). In TSEE experiments it has also been found that the increase in the time of exposure to visible light prior to the heating of sample results in more pronounced suppression of the low temperature peaks of TSEE.

An effect of doping with N_2 on TSEE and desorption yields (pressure curves) is shown in Figure 3. The first two peaks of TSEE at 11 and 15 K are matrix-specific and no change by doping was observed. The first peak is related to surface defects, the second one – to the defects in the bulk induced by electronic excitation [8]. At higher temperatures doping with N_2 (10^{-3}) resulted in an emerging broad band around 35 K (Fig. 3b). Interesting correlation in peak position in TSEE and desorption yields was found indicating close connection between these two processes. Indeed, the relative intensities of the peaks differ significantly. Note that because of negative E_a there is no barrier for electrons to escape. The energy needed for an Ar atom to desorb is around the sublimation energy 78 meV [13]. As a source of energy for the neutral atom desorption from preirradiated solid Ar we considered the recombination reaction of the intrinsic charge carriers [10]:

$$\mathrm{Ar}_2^+ + \mathrm{e} \rightarrow \mathrm{Ar}_2^* \rightarrow \mathrm{Ar} + \mathrm{Ar} + \Delta E_k,$$

which is the background for TSL phenomenon. The recombination mechanism of desorption during excitation was discussed in [18] and explored by different groups [13, 19–21]. The excess energy ΔE_k of order 1 eV is converted into kinetic energy of the lattice atoms by dissociative deexcitation of Ar_2^*. The energy can be transferred over 10 and even 100 lattice constants along the close packed directions (preferentially [1 1 0]), as it was found in a molecular dynamics study of energy transfer in solid Ar [22]. Pronounced enhancement of the desorption yield around 35 K, which was observed for the doped solid Ar, may be related to activation of N atom diffusion in Ar matrix followed by N_2^* formation and emission of photons capable of releasing electrons from deep traps. Further experiments, which are in a progress, can verify this assumption.

3. SUMMARY

Methods of activation spectroscopy – thermally stimulated and photo-stimulated exoelectron emission (TSEE and PSEE) were applied to investigate relaxation processes in N_2 doped solid Ar preirradiated with an electron beam. It enables us to find a new channel of relaxation induced by the emission of metastable N atoms. An influence of nitrogen impurity on low temperature desorption from preirradiated samples was demonstrated. The desorption observed is obviously an important relaxation process in preirradiated solids.

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