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Short Notes

Photon-stimulated recombination of self-trapped holes with electrons in pre-irradiated solid Ar

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Spatially separated stable charge centers – trapped electrons and self-trapped holes – are generated in Ar cryocrystals by a low-energy electron beam. A combination of the cathodoluminescence and photon-stimulated luminescence methods has been used to probe recombination reactions. Photon-stimulated vacuum ultraviolet intrinsic recombination luminescence from pre-irradiated solid Ar was detected for the first time. The 1.96 eV laser light has been demonstrated to release electrons from their traps that gives rise to the well-known M-band at 9.8 eV. Additional information on the photostability of charge centers at low temperatures has been obtained.

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Introduction

Irradiation of solid insulators with vacuum ultraviolet (VUV) light above band gap energy E_g or with fast particles results in the excitation of the electronic subsystem and the generation of electron–hole pairs, the creation of lattice defects, and the formation of metastable centers of guests. The subsequent relaxation represents a complex chain of branched processes and involves not only the electronic subsystem but the nuclear one as well. A variety of relaxation processes have been under extensive investigation in different classes of materials [1–4]. Atomic cryocrystals with their well-known electronic structure and simple crystal lattice are perfect model solids for studying relaxation paths. The final stage of relaxation, i.e., the processes occurring on completion of the irradiation, is of special interest for understanding the radiation effects, dynamics of charge carriers, and stability of radiation-induced centers. The primary states of the relaxation cascades in this case are states of self-trapped or trapped holes and electrons, as well as metastable levels of guests. A stimulating factor for these relaxation processes could be the heating of the sample or irradiation by visible light.

Charge recombination is one of the most important relaxation channels determining the carrier concentration and local electric fields in irradiated solids, which influence a number of processes such as emission of photons and electrons, energy conversion, desorption, etc. The methods of activation spectroscopy are especially powerful tools for investigation of relaxation in solids, and the method of thermally stimulated luminescence (TSL) is most common in use [5]. Indeed TSL from atomic cryocrystals has been studied in several publications — after irradiation with 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 different electron traps were estimated. Analysis of the thermally stimulated intrinsic recombination luminescence in VUV range – the well-known M-band [1], was performed for solid argon in the range 15–30 K [7] and in a wider range 5–30 K [9,13,14]. Recent experiments revealed thermally stimulated exoelectron emission (TSEE) from solid Ne [15] and Ar [13,14]. The latter studies clearly demonstrated the correlation in the yields of exoelectrons and VUV photons of the intrinsic recombination emission from pre-irradiated solid Ar. An interesting interconnection between atomic and electronic relaxation processes was found. It was suggested [16] and then demonstrated [10,11,14] that the thermally stimulated recombination of neutral guest oxygen atoms in the Ar

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matrix followed by O_2^* formation and radiative decay of the oxygen molecule resulted in the emission of exoelectrons from solid Ar. This posed a question on the influence of visible light on relaxation paths in atomic cryocrystals.

This paper reports the first experimental results on the influence of visible-range photons on the intrinsic recombination in atomic cryocrystals pre-irradiated by an electron beam. The experiments were performed with solid argon using the cathodoluminescence spectroscopy method combined with the technique of photon-stimulated luminescence (PSL).

Experimental

Some details of the experimental techniques were described elsewhere [17]. Only the essential points and the modification details are mentioned here. Samples of nominally pure Ar (99.99 %) were grown from the gas phase by deposition on a Cu metal substrate, cooled by a He-flow cryostat. During the deposition the temperature was kept low enough (4.5 K) to prevent all thermally stimulated processes. The content of impurities such as O_2, N_2, CO_2, and H_2O did not exceed 10^{-2} %. The base pressure in the deposition chamber was about 10^{-7} mbar. The samples were deposited for 5 min and their thickness (of about 50–100 μm) was determined by measuring the pressure decrease in the known volume of a bulb in the gas inlet system. The temperature of the samples was measured by a calibrated GaAs diode fixed to the substrate. All the films were irradiated by a 1 keV electron beam after deposition. The irradiation time averaged 30 min, and 1 mA/cm^2 current density of electron beam was maintained. As was shown in [9], electrons of this energy efficiently create stable Frenkel pairs — interstitials and vacancies.

The luminescence spectra of solid Ar were recorded under irradiation using a normal-incidence VUV monochromator with a dispersion of 1.6 nm/mm. After irradiation we tuned the monochromator to the wavelength of the *M*-band of solid Ar to register the spectrally resolved intrinsic recombination luminescence from the samples under a laser beam. A He–Ne laser of low power (2 mW) in the CW mode was used with the neutral attenuator 1:4. The laser beam was unfocused to a diameter of 2.5 cm to cover the sample. The indicated temperature value did not change when the laser was switched on. All measurements were made at temperature (4.5 K) lower than the threshold temperature for thermally stimulated processes (10 K) to prevent thermally stimulated release of electrons from their traps.

Results and discussion

On exposure to an electron beam, electron–hole pairs are generated quite efficiently because the ionization cross section for electrons is several orders of magnitude larger than that for VUV photons. The holes generated under irradiation are self-trapped in the lattice within 10^{-12} s [1] due to electron–phonon interaction and become immobile. As has been suggested theoretically [1] and proved experimentally [18,19], the self-trapped holes (STH) have the configuration of a dimer ion and can be considered as Rg_2^+ centers in their own matrix. In contrast, the electrons are not self-trapped in solid Ar and characterized by free-like behavior [1]. Because of a negative electron affinity $E_a = -0.4$ eV [1] and hence prevailing repulsive forces the electron can be trapped only by such kinds of lattice defects as vacancies, vacancy clusters, or pores. Although these traps are thought to be relatively shallow, the trapped electrons nevertheless remain stable at low temperatures at least up to 10 K. An activation energy needed to mobilize electrons can be transferred by heating or photon irradiation. Solid Ar is a wide-band material with a conduction bandwidth of about 2.3–3.7 eV [20], and the long-wavelength cutoff of the photoexcitation curve is defined by the trap depth. The depth of the most shallow trap was estimated to be about 12 meV [8]. The strongest peak at 15 K in the TSL of nominally pure Ar related to the exciton-induced defects is characterized by an activation energy of 15 meV according to [8] and 36 meV according to [12]. In fact, the photons in the range $3\cdot10^{-2}$ eV can be used to release electrons from their traps and promote their passage to the conduction band. Note that the intense exoelectron emission from pre-irradiated solid Ar was observed under excitation by laser light of 2.76 eV energy [16].

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

to reach the surface and escape the sample (as was observed in [10,11,14,16] for nominally pure and doped solid Ar);

to recombine with positively charged intrinsic centers such as Ar_2^+.

This recombination process can be presented by the following reaction:

$$Ar_2^+ + e \rightarrow Ar_2^+ \rightarrow Ar + Ar + h\nu\ (9.8\ eV). \quad (1)$$

Figure 1 shows a typical spectrum of solid Ar recorded on irradiation by an electron beam. The main feature of the spectrum is the well-known *M*-band at 9.8 eV stemming from the radiative decay of the Ar_2^* center, i.e., the transition from the $^{1,3}\Sigma_u^+$ state to a re-

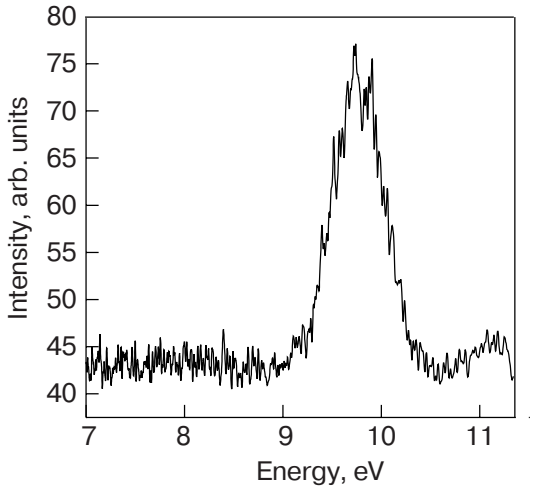

Fig. 1. Luminescence of solid argon, excited with an electron beam at 1 keV at 4.5 K. The main feature of the spectrum is the *M*-band at 9.8 eV.

pulsive part of the ground state $^1\Sigma_g^+$. Note that the radiative state can be populated via both process the exciton self-trapping and the recombination of the STH with an electron (1).

To check the influence of visible-range photons we performed an experiment on photon-stimulated luminescence. The pre-irradiated sample of solid Ar was exposed to laser light of energy 1.96 eV. The intensity of the intrinsic recombination emission due to reaction (1) was monitored during the exposure. To prevent thermally stimulated release of electrons from the traps the sample was kept at a temperature of 4.5 K.

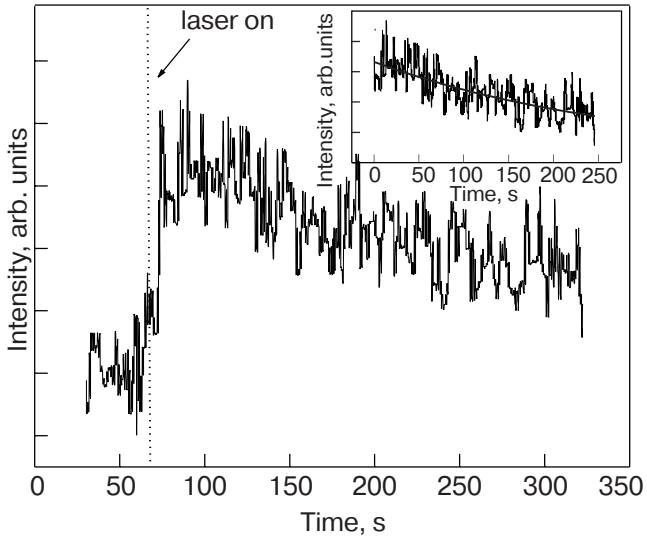

Fig 2. Spectrally resolved luminescence from pre-irradiated solid argon in the *M*-band, excited with laser light (hν = 1.96 eV). The decay part of the curve shown in the inset is approximated by a first-order exponential curve with a characteristic time of 280 ± 50 s.

The result is shown in Fig. 2. We observed an initial sharp rise in the VUV recombination intensity after switching the laser on, followed by a much slower decay with emptying of the traps. Blocking of the laser light resulted in disappearance of the signal. No such kind of effect was observed either from the substrate or from the samples not subjected to electron beam. The experiment clearly demonstrates a high efficiency of the VUV recombination-luminescence stimulation by low energy photons. The energy of these photons is sufficiently high to release electrons also from such a deep impurity trap as O_2^-, for example. The binding energy of electrons E_b at these centers is estimated to be $E_b = 1.6$ eV with a correction to the O_2 electron affinity $E_a = 0.44$ eV [21] due to the polarization energy of Ar taken into account. Formation of negative ionic centers is possible even in the case of low impurity concentration because of the large mean free path of electrons in solid Ar [22]. However, the contribution of this kind deep traps in the photon-stimulated processes discussed above is relatively small, as demonstrated in the experiments on photon-stimulated exoelectron emission [23].

After the electron has been released from the trap, it can stay in the conduction band until the recombination event or until it escapes the sample surface. According to [24], the decay of the free-carrier density N_c for the case of no retrapping can be given by the simple exponential expression:

$$N_c = N_{\text{eff}} g \tau_c \exp(-gt), \qquad (2)$$

where g is the product of the density of photons irradiating the sample, and the effective interaction cross section of photons and electrons in the traps, τ_c is the effective life time of the electrons in the conduction band. N_{eff} is the effective initial concentration of electrons in the traps. As one can see from Fig. 2, the decay of the recombination luminescence can be described by (2) with a time $\tau = g^{-1}$, which characterizes the interaction cross section of photons and electrons. The sharp rise and exponential decay of the laser-induced intrinsic recombination luminescence observed in our experiment is quite similar to that measured in the experiments [10,11,14,16] on photon-stimulated exoelectron emission from nominally pure and doped solid Ar. Taking into account these findings and the results of our experiments, one can see two channels of relaxation processes in pre-irradiated solid Ar films. Energy absorbed and stored in solids can be liberated by visible-range photons via direct release of electrons from the traps followed by the escape of electrons from the sample and by recombination with positively charged centers accompanied by VUV luminescence.

Summary

The relaxation process of charge recombination in solid Ar pre-irradiated by an electron beam was studied. We used the activation spectroscopy method — photon-stimulated luminescence in combination with cathodoluminescence spectroscopy. The experiments were performed at low temperatures to exclude a possible contribution from thermally stimulated processes. A spectrally resolved VUV luminescence in the *M*-band of Ar stemmed from the recombination of STHs and electrons was found under irradiation by laser light in the visible range. Thus we have obtained direct proof of the supposition that in pre-irradiated Ar cryocrystals the relaxation photon-stimulated processes include radiative recombination of STHs of dimer configuration Ar_2^+ with electrons. Additional information on the photo-bleaching of charged centers was obtained.

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1. K.S. Song and R.T. Williams, *Self-Trapped Excitons*, *Springer Series in Solid-State Sciences*, Springer Verlag, Berlin (1996), Vol. 105.
2. N. Itoh and A.M. Stoneham, *Radiation Effects & Defects in Solids* **155**, 277 (2001).
3. G. Zimmerer, *Nucl. Instrum. & Methods*, *Phys. Res*. **B91**, 601 (1994).
4. V.E. Bondybey, M. Räsänen, and A. Lammers, *Ann Rep. Prog. Chem*. **C95**, 331 (1999).
5. D.R. Vij, *Thermoluminescence*, in: D.R. Vij (Ed.) *Luminescence of Solids,* Plenum Press, New York, (1998).
6. M. Kirm and H. Niedrais, *J. Lumin.* **60**, 611 (1994).
7. M. Kink, R. Kink, V. Kisand, J. Maksimov, and M. Selg, *Nucl. Instr. & Meth*. **B122**, 668 (1997).
8. A.N. Ogurtsov, E.V. Savchenko, O.N. Grigorashchenko, S.A. Gubin, and I.Ya. Fugol', *Fiz. Nizk. Temp.* **22**, 1205 (1996) [*Low Temp. Phys.* **22**, 922 (1996)].
9. E.V. Savchenko, A.N. Ogurtsov, O.N. Grigorashchenko, and S.A. Gubin, *Fiz. Nizk. Temp.* **22**, 1210 (1996), [*Low Temp. Phys.* **22**, 926 (1996)].
10. E.V. Savchenko, O.N. Grigorashchenko, A.N. Ogurtsov, V.V. Rudenkov, G.B. Gumenchuk, M. Lorenz, M. Frankowski, A.M. Smith-Gicklhorn, and V.E. Bondybey, *Surf. Sci.* **507–510**, 754 (2002).
11. E.V. Savchenko, O.N. Grigorashchenko, G.B. Gumenchuk, A.G. Belov, E.M. Yurtaeva, M. Frankowski, A.M. Smith-Gicklhorn, and V.E. Bondybey, *Surf. Sci*. **528**, 266 (2003).
12. A. Schrimpf, C. Boekstiegel, H.-J. Stökmann, T. Bornemann, K. Ibbeken, J. Kraft, and B. Herkert, *J. Phys.: Condens. Matter* **8**, 3677 (1996).
13. E.V. Savchenko, O.N. Grigorashchenko, A.N. Ogurtsov, V.V. Rudenkov, G.B. Gumenchuk, M. Lorenz, A. Lammers, and V.E. Bondybey, *J. Low Temp. Phys*. **122**, 379 (2001).
14. E.V. Savchenko, O.N. Grigorashchenko, A.N. Ogurtsov, V.V. Rudenkov, G.B. Gumenchuk, M. Lorenz, A.M. Smith-Glicklhorn, M. Frankowski, and V.E. Bondybey, *Surf. Rev. Lett*. **9**, 353 (2002).
15. M. Frankowski, E.V. Savchenko, A.M. Smith-Gicklhorn, O.N. Grigorashchenko, G.B. Gumenchuk, and V.E. Bondybey, *J. Chem. Phys.* **121**, 147 (2004).
16. E.V. Savchenko, O.N. Grigorashchenko, A.N. Ogurtsov, V.V. Rudenkov. M. Lorenz, M. Frankowski, A.M. Smith-Glicklhorn, and V.E. Bondybey, *J. Lumin.* **94–95**, 473 (2001).
17. A.G. Belov, I.Ya. Fugol, E.M. Yurtaeva, and O.V. Bazhan, *J. Lumin.* **91**, 107 (2000).
18. E.V. Savchenko, N. Caspary, A. Lammers, and V.E. Bondybey, *J. Low Temp. Phys.* **111**, 693 (1998).
19. E.V. Savchenko, O.N. Grigorashchenko, O.M. Sokolov, J. Agreiter, N. Caspary, A. Lammers, and V.E. Bondybey, *J. Electron Spectrosc. Related Phenomena* **101**, 377 (1999).
20. I.Ya. Fugol' and E.V. Savchenko, *Excitons in Atomic Cryocrystals in Cryocrystals, B.I. Verkin and A.Ph. Prikhot'ko* (eds.), Naukova Dumka, Kiev (1983), p. 360.
21. D.R. Lide (Ed.) *Handbook of Chemistry and Physics,* CRC Press, Boca Raton, FL (1993).
22. N. Schwentner, E.-E. Koch, and J. Jortner, *Electronic Excitations in Condensed Rare Gases*, Springer Verlag, Berlin, (1985).
23. E.V. Savchenko, O.N. Grigorashchenko, G.B. Gumenchuk, A.N. Ogurtsov, M. Frankowski, and A.M. Smith-Gicklhorn, and V.E. Bondybey, *Radiation Effects & Defects in Solids* **157**, 729 (2002).
24. J.D. Brodribb, D. O'Colmain, and D.M. Hughes, *J. Phys. D: Appl. Phys.* **8**, 856 (1975).