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Thermally stimulated exoelectron emission from rare gas solids in weak external electric fields

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Abstract

Charge carriers and neutral reactive intermediates were generated by ionizing radiation in model insulators—Ar solids doped with O_2, N_2 and CO. Combining methods of activation spectroscopy—thermally and photon-stimulated exoelectron emission (TSEE and PSEE) with thermally stimulated luminescence we studied electronic and atomic processes of relaxation in these metastable solids. This experimental approach enables us (i) to identify the charge of mobile charge carriers, (ii) to separate reactions of neutral and charged species and (iii) to find the interconnection between thermally driven chemical reactions and charge carrier dynamics in insulators.

Keywords: Activation spectroscopy; Charge carriers; Electronic relaxation

1. Introduction

Charge carriers formed in insulators subjected to ionizing radiation, their dynamics and relaxation, are of considerable interest both from the point of view of fundamental solid-state physics, and in a number of important applications in material science, photochemistry, and dosimetry. Part of the energy absorbed during the irradiation is accumulated in the lattice in the form of localized charge carriers and reactive neutral species. Recombination and relaxation of these metastable centers are characterized by a complex series of reactions and energy transfer processes. Methods of activation spectroscopy are very valuable tools for a study of relaxation processes in metastable solids and thermally simulated luminescence (TSL) is the most common in use [1]. However, analysis and interpretation of TSL data are hampered by a complex origin of stimulated emission—it can accompany not only recombination of charge carriers but also thermally stimulated chemical reactions [2,3]. In order to get reliable information on electronic relaxation processes in metastable solids, a study of stimulated luminescence may be complemented with measurements of stimulated currents.

Rare gas solids (RGS)—the widest band gap insulators, provide an attractive and fundamental model framework for exploring electronic

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processes of relaxation in irradiated insulators, elucidating the interconnection between electronic and atomic processes as well as studying the stability of charged centers and intermediates. Several studies of TSL from nominally pure [4–6] as well as doped [7–12] RGS were performed. However, activation current spectroscopy was rarely applied to RGS. To the best of our knowledge only few experiments were performed—thermally stimulated conductivity (TSC) of Ar solids doped with Au, Ag and O_2 was measured [10] and the method of thermally stimulated exoelectron emission (TSEE) was used for a study of thermal stability of charged centers in nominally pure solid Ar [13].

This paper reports the results of studies of relaxation processes in preirradiated solid Ar doped with CO, N_2 and O_2 by combining the TSL technique with a study of TSEE in weak external electric fields and photon-stimulated exoelectron emission (PSEE). The study enables us (i) to discriminate between reactions of neutral species and charge carriers, (ii) to find their interconnection, (iii) to identify the charge of mobile charge carriers and (iv) to differentiate between bulk and surface traps.

2. Experimental section

The samples were grown from the gas phase by pulsed deposition on a silver-coated metal substrate cooled by a closed-cycle 2stage Leybold RGD 580 refrigerator. The structure of samples and therefore the distribution of the charge carrier traps within the energy gap were varied by changing the conditions of deposition—condensation temperature and gas flow parameters (flow speed, pulse duration and frequency). A typical deposition rate was kept at about $10^{-2}\,\mu m\,s^{-1}$. The deposition rate and the sample thickness were determined by measuring the pressure decrease in a known volume. A typical sample thickness was 40 μm. The samples of high optical quality were prepared by condensation on a gradually cooled substrate. The first portions of gas were deposited at $T = 70\,K$ forming layers of more perfect structure. The next layers reproduced the structure to some extent. High-purity Ar (99.999%) gas was used. N_2, O_2 and CO were used as dopants. The dopant to the Ar gas ratio was varied between 10^{-5} and 10^{-2}. A mixture was prepared in a gas-handling system by a standard procedure. Before each experiment, the gas-handling system was degassed by heating under pumping. The pressure in the deposition chamber was 6×10^{-8} mbar. The presence of impurities and dopants was monitored by a mass-spectrometer and by the measurement of an infrared absorption spectrum. Analysis of the base line gave information on the content of structural defects. The mass spectrum of the residual gases showed lines of O_2, N_2, CO_2 and H_2O. The contamination was smaller than 10^{-5}. The following characteristic bands in the absorption were used for the control: CO—$2140.9\,cm^{-1}$, CO_2—$2338.7\,cm^{-1}$, H_2O—$1631\,cm^{-1}$.

In order to ionize the samples, we used an electron beam because the ionization cross section for electrons is by a factor of 10^2 greater than that at photoionization. A hot tungsten filament served as a source of electrons (Fig. 1a, top). To generate charged centers across the whole sample, we deposited the sample under an electron beam. The electrons were accelerated to the energy of 120 eV. The current density of the electron beam was kept at $30\,\mu A\,cm^{-2}$. In order to prevent recombination of charge carriers, the temperature during irradiation was maintained below the characteristic temperature of the first peak of TSL in solid Ar at $T = 12\,K$ [5]. The temperature was measured with a calibrated silicon diode sensor, mounted at the substrate. The programmable temperature controller permitted to keep the desired temperature during deposition and irradiation, as well as to control the heating rate.

In the TSEE and TSL experiments samples were heated with a constant rate of $3.2\,K\,min^{-1}$. The total yield of TSL was detected with a PMT. By introducing a convertor of vacuum ultraviolet radiation into visible light we were able to extend the available wavelength range and detect TSL from 800 up to 10 nm. In addition spectrally resolved measurements of the TSL were performed.

The emission of electrons from preirradiated samples was detected with a movable Au-coated

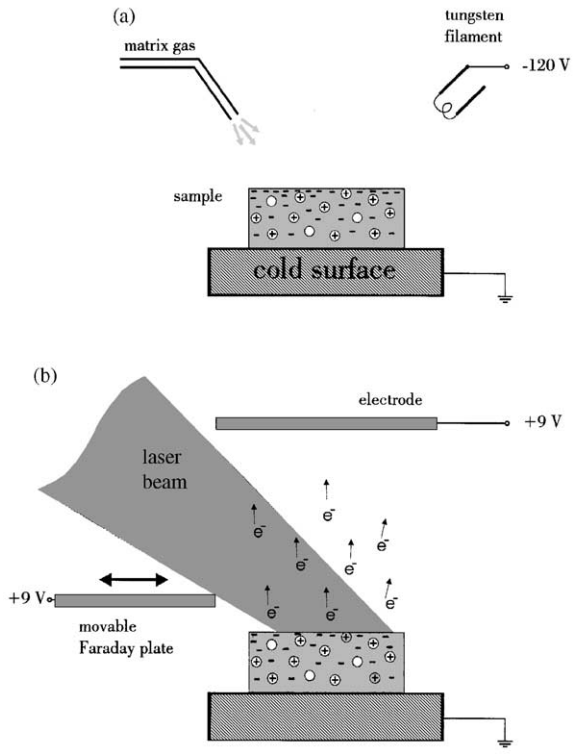

Fig. 1. Schematic drawing of the experiment: (a) sample preparation, (b) TSEE and PSEE measurements.

Faraday plate kept at a small positive potential + 9 V (Fig. 1b). 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 converted voltage was reversed in the polarity by an invertor and digitized in a PC. A current as low as 100 fA can be easily detected. The measurements were performed in the temperature range of 7–45 K.

We also investigated PSEE at a temperature (7.5 K) which is low enough to inhibit thermal release of charge from the traps (in solid Ar the threshold temperature of TSEE [13] and TSL [5] is 10 K). In the PSEE experiments (Fig. 1b) a Coherent 899-01 dye laser operating with Stilbene 3 and pumped with a Coherent Ar ion laser (Innova 200) was used. The laser light was introduced into the sample chamber with optical fiber. 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

Charge carriers in preirradiated solids are stable as long as carriers of opposite signs are spatially separated and immobile. The theoretical study of hole dynamics showed that holes are self-trapped in all RGS, which was confirmed by hole transport data [14]. It was found theoretically [14] as well as then in spectroscopic experiments [15–17] that the self-trapped holes are formed in the configuration of rare-gas dimer ions Rg_2^+. In contrast, electrons show free-like behavior and high mobility in all RGS heavier than Ne [14]. Therefore, one can expect high efficiency applying current activation spectroscopy methods based on emission of electrons into vacuum. Furthermore, electron affinity E_a in solid Ar is negative $E_a = -0.4$ eV and electrons will experience an increase of kinetic energy while exiting the surface. A large electron escape depth of about 500 nm [18] permits obtaining information about electron traps in the bulk as well as on the surface. It was found that the yield of electrons produced by MeV H^+ is extremely large—several orders of magnitude larger than that observed from metals and other insulators [19,20] and it is strongly affected by a weak external electric field. Due to the high ionization potential I of Ar ($I = 15.760$ eV), many guest ionic species can be generated in an Ar matrix. E.g. one can expect that CO^+ and CO_2^+ can be produced in an Ar matrix, because their ionization potentials are lower than that for Ar—the band gap E_g of solid Ar at Γ-point is 14.16 eV and exceeds I (CO_2) = 13,77 eV and I (CO) = 14.01 eV [21]. Besides ions, the irradiation of the doped matrices by electrons can also produce atomic species, e.g. N or O atoms, which are capable of diffusing through the matrix under heating. While O atoms in their ground state ^3P are effective deep traps for electrons because of the high $E_a = 1.461$ eV [21], atomic nitrogen in its ^4S ground state has negative electron affinity $E_a = -0.1$ eV [22] and cannot be seen as centers of trapping for electrons. The

electron irradiation initially produces nitrogen atoms also in the metastable ^2D state, which then decays radiatively with a lifetime τ of about 20 s in an Ar matrix [23]. Interestingly, that nitrogen-containing samples exhibit a green afterglow and "afteremission", which can be observed at low temperature 7 K right after sample irradiation. The decay curve can be fitted by a single exponential fall giving $\hat{o}$ close to the known time of the $^2D \rightarrow {}^4S$ transition of N atoms.

The thermally stimulated electron yields from preirradiated nominally pure Ar, Ar doped with N_2 and with CO are compared in Fig. 2. The electron emission current of all these samples shows intense maxima at about 11 and 15 K, which dominate in pure Ar. These coincide with the peaks observed in the total yield of TSL and yields of spectrally resolved TSL measured in the bands of intrinsic [24] and extrinsic [11] recombination luminescence by the reactions:

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

$$CO^+ + e \rightarrow CO^* \rightarrow CO + h\nu(5.65\,eV). \quad (2)$$

The former process is characterized by the well-known 9.7 eV M band of self-trapped excitons [25] related to the $^{1,3}\Sigma_u + \rightarrow {}^1\Sigma_g +$ transition of the molecular dimer Ar_2^*. The latter reaction produces the $X^1\Sigma^+ \rightarrow \Pi^1$ Cameron progression, which was monitored in the 5.65 eV (0–1) vibronic band. The correlation of low-temperature peaks in the TSEE and TSL curves is an important criterion to confirm the common origin of intrinsic relaxation processes involving charge transport by highly mobile electrons. The first peak at 11 K can be attributed to surface traps [13], the one at 15 K exhibits pronounced dose dependence and stems from radiation-induced defects, more likely Frenkel pairs. Formation of stable Frenkel pairs induced by excitation of an electronic subsystem was found theoretically [26] and observed experimentally [27] for Ar centers in Ne matrix. The broad peak at about 16 K was also detected in TSL and TSC of solid Ar doped with Au and Ag [10]. The positions of these peaks in our experiments were slightly influenced by the presence of uncompensated negative space charge in the samples. An increase in the space charge resulted in a shift of the peaks to a lower temperature.

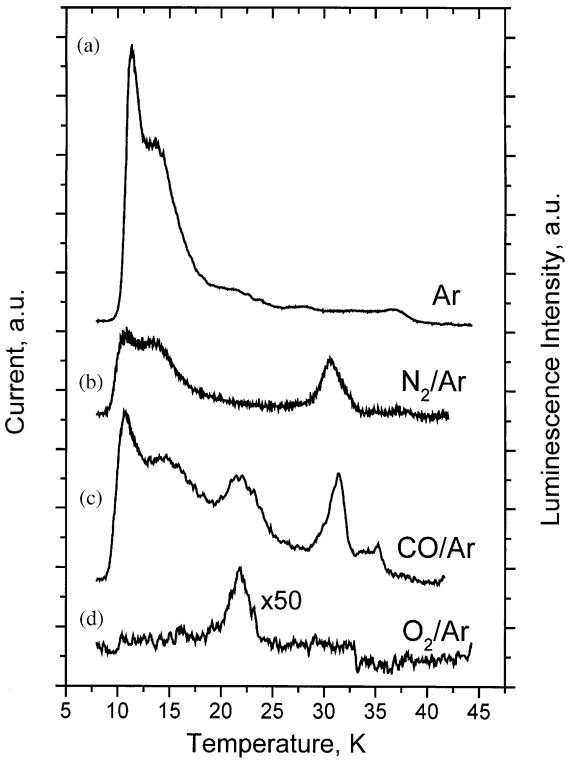

Fig. 2. Yields of TSEE from nominally pure Ar (a) [13], and Ar doped with 3×10^{-3} N_2 (b), 1×10^{-3} CO (c) TSL from Ar doped with O_2 (1×10^{-3}) is shown in (d).

Doping with small amounts of N_2 resulted in a rather strong TSEE peak around 30 K as shown in Fig. 2b. A similar peak at 30 K is observed in samples doped with CO (Fig. 2c), which contain also N atoms. The peak was detected as well in the TSL of Ar cryocrystals irradiated by X-rays [6]. An elucidation of the origin of this peak requires further experiments.

The peak under discussion is the peak at 22 K. This feature is very weak in yields measured from nominally pure Ar (Fig. 2a). Doping with small amounts of O_2 (10^{-4}–10^{-3}) resulted in an emergence of the peak at 22 K. It is seen in the TSEE curve measured from CO doped sample (Fig. 2c). The sample was annealed at 23 K and then photolyzed before the irradiation at 8 K. The sample contained O and N atoms. The TSEE yield

was recorded after the decay of the "afteremission". The content of neutral CO guests in the matrix monitored by the absorption measurement, increased during the heating. Subsequent cycles of irradiation (without photolysis) and heating showed no distinctive feature at 22 K in the TSEE yield. The TSL of O_2 doped solid Ar is shown for a comparison in Fig. 2d. A high sensitivity of this peak to the presence of O_2 and observation of the Herzberg bands $A^3\Sigma_u^+ \rightarrow X^3\Sigma_g^-$ at 23 K in the TSL from Ar doped with O_2 and Au [10] suggest that this peak may be caused by the thermally stimulated chemiluminescence of O_2.

While the 22 K peak in TSEE and TSL yields seems to be associated with the presence of oxygen, it clearly cannot be attributed to thermal detrapping of electrons from O^- or O_2^-. One can estimate for this peak an activation energy $E_t = 61$ meV [11], which is several orders of magnitude smaller than the electron binding energy E_b to O atoms in Ar matrix (that is the O atom electron affinity $E_a = 1.461$ eV [21] corrected for the polarization energy E_p of an Ar matrix, $E_p = -1.15$ eV [28]: $E_b = E_a - E_p = 2.61$ eV) whereas E_t appears to be close to the energy of vacancy formation near guest O atom in solid Ar (90 ± 30 meV). On the other hand, we observed also this peak under the recombination of electrons with self-trapped holes (Ar_2^+) and ionic guests (CO^+) by the reactions (1) and (2) correspondingly.

Although these data might at the first sight seem to be contradictory, they might be reconciled with the following scenario. The thermally stimulated diffusion and reactions of the O atoms can release the stored chemical energy, which can then detrap and mobilize electrons. The energy transfer can proceed nonradiatively, but more likely by the emission of light accompanying the recombination reaction. In order to provide support for the suggested mechanism of energy transfer and relaxation we carried out a control experiment to verify that irradiation of the sample by visible light can result in electron emission. In this PSEE experiment the ionized sample was held at a low temperature (7.5 K) to prevent the thermally stimulated release of electrons from shallow traps. It was then irradiated by laser light tuned to one of the O_2 Herzberg band at 2.76 eV, and the emission of electrons from the solid was monitored as a function of time. The schematic of the PSEE experiment is shown in Fig. 1b, the observed strong photoemission of electrons, its sudden rise as the irradiation is started, and its exponential decrease as the traps are depleted is shown in Fig. 3. Obviously no such emission of electrons is observed either from the substrate without deposited sample, or from the sample which was not irradiated to produce charged centers. The energy of photons used in the PSEE experiments was lower than the threshold energy of photoemission from the substrate (the work function of Ag is of 4.26–4.74 eV [21]). The photon-stimulated relaxation processes are illustrated in Fig. 4. An irradiation of the ionized sample with photons results in release of electrons to the conduction band CB. In oxygen-containing samples one can expect trapping of electrons by O and O_2 centers. Corresponding binding energies of electrons at these centers are $E_b = 2.61$ eV (O^-) and $E_b = 1.6$ eV (O_2^-). Note that because of the wide CB (several eV) electrons can be released from both kind of traps—deep and shallow ones. After the electrons have been photoreleased from the traps, they can move through the sample until they will escape from the surface in an external electric field or recombine with positively charged centers like self-trapped holes and guests. A possibility to release

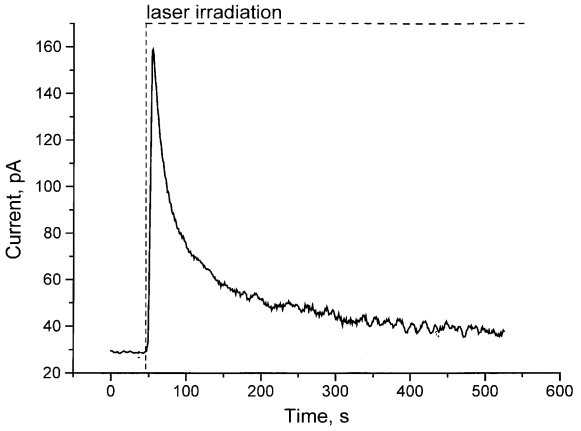

Fig. 3. Yield of PSEE from solid Ar under irradiation by laser light (2.76 eV).

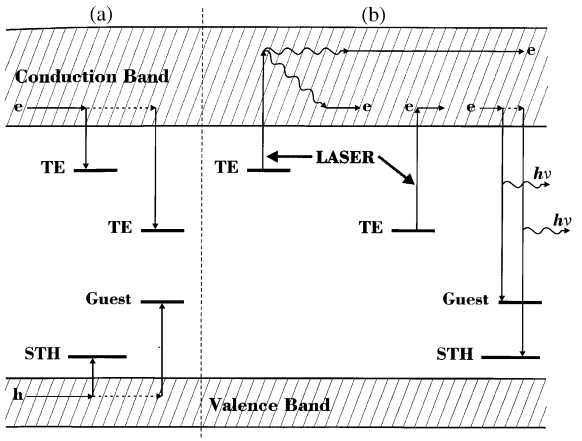

Fig. 4. Schematic illustration of photon-stimulated relaxation processes (b), the trapping of charge carriers is shown in (a).

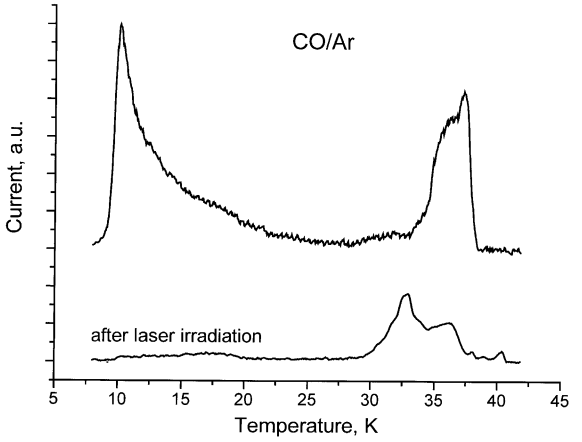

Fig. 5. Thermally stimulated current from CO doped solid Ar after irradiation by laser beam (low curve), upper curve—the TSEE yield from the identical sample non-exposed to laser light.

the electrons from the shallow traps by laser light was checked combining TSEE and PSEE measurements. The TSEE yield from CO doped solid Ar after the laser irradiation is shown in Fig. 5 (low curve) in comparison with the TSEE yield of the sample, which was grown at the same conditions but was not irradiated by laser. A photobleaching of the low-temperature peaks is clearly seen. The results obtained support the suggested mechanism of energy conversion and relaxation in solid Ar containing charge carriers and reactive neutral species.

4. Summary

Using activation spectroscopy methods—TSEE, TSL and PSEE we investigated electronic and atomic processes of relaxation in metastable solid Ar doped with O_2, N_2 and CO. Comparison of the thermally stimulated yields of electrons and photons over the wide spectral range and analysis of photon-stimulated exoelectron emission made it possible for the first time to discriminate between reactions of neutral species and charge carriers, elucidate their interconnection and suggest the mechanism of energy transfer from neutral reactive intermediates to the charge carriers.

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