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Electron traps in solid Xe

Ivan V. Khyzhniy, Sergey A. Uyutnov, Elena V. Savchenko

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine
47 Lenin Ave., Kharkov 61103, Ukraine
E-mail: khyzhniy@gmail.com

Galina B. Gumenchuk, Alexey N. Ponomaryov, and Vladimir E. Bondybey

Lehrstuhl for Physicalische Chemie II TUM, 85747 Garching, Germany

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Correlated real-time measurements of thermally stimulated luminescence and exoelectron emission from solid Xe pre-irradiated with an electron beam were performed. The study enabled us to distinguish between surface and bulk traps in solid Xe and to identify a peak related to electronically induced defects. The activation energy corresponding to annihilation of these defects was estimated by the following methods: the method of different heating rates, the initial-rise method, and the curve cleaning technique with fitting of the thermally stimulated luminescence glow curve.

PACS: 78.60.Kn Thermoluminescence;
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Introduction

Processes related to energy and structural relaxation in cryogenic solids are of considerable interest for fundamental condensed-matter physics and related fields such as solid-state chemical reactions, cryochemistry, and dosimetry. Activation spectroscopy methods are powerful tools for the study of relaxation processes as well as for trap-level analysis. The method of thermally stimulated luminescence (TSL) based on measurements of total and spectrally-resolved yields is used most commonly. However, this method has its limits in solids containing neutral and charged reactive species because both species can recombine and emit light. Therefore the most effective approach to the investigation of relaxation processes is a combination of TSL and current spectroscopy methods, such as thermally stimulated exoelectron emission (TSEE).

The widest band gap insulators — rare gas solids (RGS) — are excellent model objects for studying the processes of energy and charge transfer in solids irradiated by ionizing radiation. Exposure of RGS to ionizing radiation results in the generation of electron–hole pairs (fragments of molecules, radicals in case of doped RGS) followed by a sequence of relaxation processes involving a variety of radiation induced defects – structural defects, self-trapped/trapped holes, electrons trapped at lattice imperfections or by impurities with a positive electron affinity. Those centers are capable to store a part of the energy absorbed during excitation for quite a long time at low temperatures.

To the best of our knowledge there was only one prior investigation of TSL from nominally pure solid Xe pre-irradiated by x-rays [1]. However, the origin of electron traps still remained unclear. Here we present recent results on thermally activated processes in solid Xe, pre-irradiated by a low energy electron beam studied by optical and current activation spectroscopy methods. Some preliminary results were obtained in [2,3].

Experiment

Taking into account the strong sensitivity of TSL and TSEE methods to the sample prehistory our group has developed an experimental setup for simultaneous monitoring of several relaxation channels in pre-irradiated cryogenic solids: concurrent measuring of TSL yield, TSEE yield, and the yield of sputtered atoms. This set of methods combined with luminescence analysis was applied for the first time to study the intrinsic recombination of

charged particles in pre-irradiated solid Xe. The energy transfer processes and defect energy levels were probed by TSEE and TSL measurements.

For the preparation of Xe cryocrystals, a high purity gas (99.9996%) was used. Before the experiment the gas inlet system was pumped and degassed by heating under pumping. The samples were condensed from the gas phase under isobaric conditions ($P = 10^{-7}$ bar) on a metal substrate cooled by a closed-cycle 2-stage Leybold RGD 580 cryostat. The deposition rate was kept at about 10^{-2} μm/s. A typical sample thickness was 100 μm. The quality of the samples was controlled spectroscopically. Before the irradiation, the samples were annealed at the temperature of 58 K during 30 min. The samples were irradiated with an electron beam of variable energy (100–500 eV). These values of electron energy are not sufficient to form lattice defects in solid Xe by a knock-on mechanism. The current density was maintained at 30 $\mu A cm^{-2}$. The substrate was grounded. The dose was increased by increasing the exposure time. The irradiation and recording of cathodoluminescence spectra were performed at low temperature ($T \le 10$ K) in order to exclude the conventional thermal mechanism of defect creation and to avoid the annealing of the radiation-induced defects. On completion of the irradiation, the spectrum of the TSL and TSEE yield were recorded using different heating rates (2, 3.2 and 5 $K \cdot min^{-1}$). The total yield of TSL was measured with a PMT sensitive to VUV light. The spectra in the visible range were recorded by a multichannel Ocean Optics S2000 Spectrometer based on CCD detectors operating in the range of 170–1100 nm. This spectrometer allows monitoring the temporal evolution of the spectra in the operating range. In TSEE experiments, the emission of electrons from pre-irradiated samples was detected with an Au-coated Faraday plate kept at a small positive potential +9 V. The current from the Faraday plate was amplified by a FEMTO DLPCA 100 current amplifier. The signal was reversed in polarity by an inverter and digitized in a PC.

Results and discussion

The typical TSL and TSEE curves from nominally pure solid Xe are shown in Fig. 1. After deposition, the sample of solid Xe was annealed at T = 58 K, then re-cooled to 10 K and irradiated by an electron beam (500 eV) during 30 min. The heating rate in this case was 3.2 K/min.

We have found a correlation between TSL and TSEE peaks, which was caused by the fact that electrons released from the same kind of traps can either recombine with positively charged particles or reach the sample surface and escape from the sample to the vacuum. Similar correlation of TSL and TSEE maxima was found in solid Ne and Ar [4,5] which are characterized by a negative electron affinity ($E_a = -1.3$ eV for Ne and $E_a = -0.4$ eV for Ar) [6]. In this case, there is no barrier for electrons to escape the surface of the sample. In view of the positive electron affinity of solid Xe (0.5 eV) [6], there is an energy barrier for electrons to leave the sample. One could expect that the maxima in the TSEE curve should be shifted to the high-temperature side as compared to those in TSL. However, as seen from Fig. 1, there is no such shift. The absence of a shift between the TSL and TSEE maxima can be caused by an accumulation of negative space charge during irradiation of the samples by the electron beam. The electric field formed by this space charge is enough for free electrons to overcome the energy barrier caused by the positive electron affinity of solid Xe.

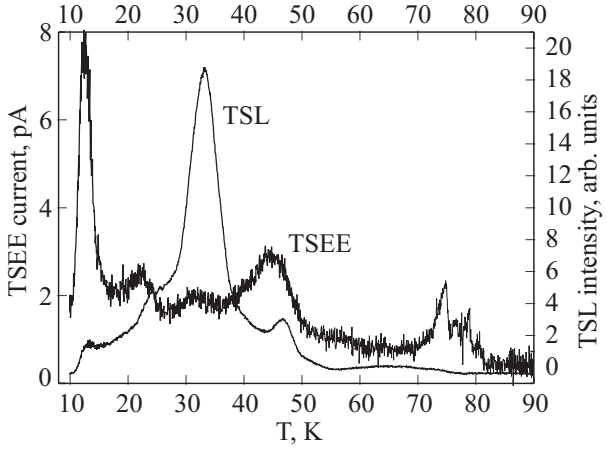

Fig. 1. Correlation of peaks in TSL and TSEE curves from solid Xe

The first low temperature peak (12 K) in both curves is caused by the release of electrons from the shallow traps in solid Xe, which are thought to be structural defects on the sample surface. This interpretation is supported by the dependence of the TSL glow curve on the energy of irradiating electrons (Fig. 2). There is no strong dependence of this peak on energy as observed for the peaks at higher temperatures. Its maximum intensity hardly increases

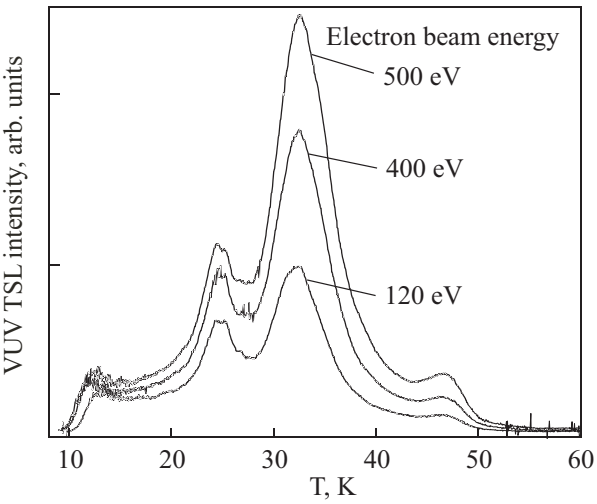

Fig. 2. Dependence of the TSL yield in the VUV range on the energy of irradiating electron beam.

with energy. The penetration depth of electrons depends on energy and bulk-related peaks should increase with increasing of electron beam energy. A small shift of the first peak in Fig. 2 to the low temperature side with increase of electron beam energy can be caused by the space charge created during irradiation. The doses of irradiation were the same for all the curves in Fig. 2, but electrons with higher energies produce more charge centers in the bulk of the sample. This leads to larger space charge. We performed also experiments on sample thickness dependence of TSL glow curve. The intensity of the first peak remained constant for several samples of different thicknesses. The higher-temperature peaks rose with increasing of sample thickness. We thus conclude that the first low-temperature peak is surface-related while the others stem from the recombination of some centers in the bulk.

In order to elucidate the nature of the peak at $T \approx 24$ K, we performed experiments with doped solid Xe. The intensity of this peak is suppressed in samples with a small amount of nitrogen (Fig. 3) while doping with oxygen resulted in an increase of its intensity. It was shown, in the case of solid Ar [7,8] that at a temperature 23 K the guest oxygen atoms (dopants or from the residual gas in the vacuum chamber) become mobile enough to move through the crystal and recombine forming the molecule O_2^* which is detected by spectroscopic means. We suppose that a similar mechanism takes place in solid Xe. Detailed investigation of relaxation channels in solid Xe doped with oxygen was reported in [9].

The peaks at 24 K and 33 K were also observed in the spectrally resolved yields of TSL from solid Xe doped with oxygen at the wavelength corresponding to the Hertzberg emission lines of the O_2^* molecule (Fig. 4). Note that the peak at $T = 33$ K is not as strongly dependent on the presence of oxygen as the peak at $T = 24$ K. This is due to de-trapping of electrons by the light emitted

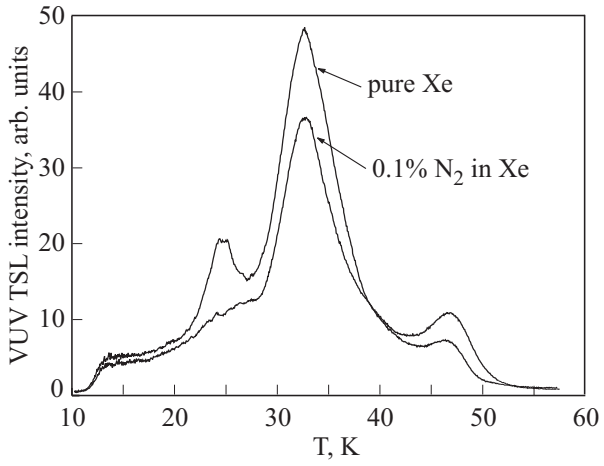

Fig. 3. Comparison of TSL yields in the VUV range from pure solid Xe and solid Xe doped with 0.1% of N_2. Samples were irradiated after annealing at $T = 58$ K.

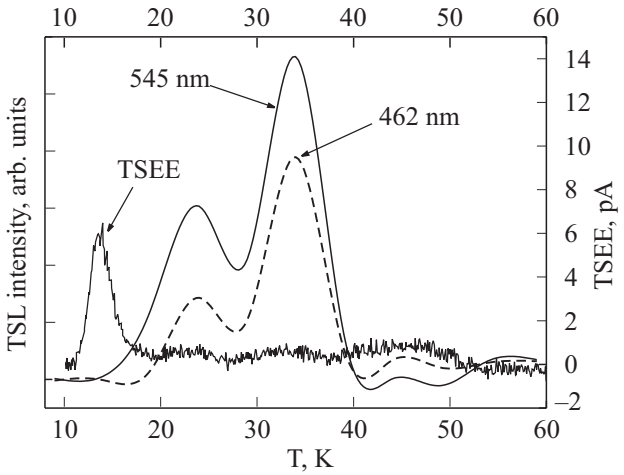

Fig. 4. Spectrally resolved TSL yield on the lines 545 and 462 nm from the region of the Herzberg progression and TSEE curve from solid Xe doped with O_2. The heating rate was 5 K/min.

at $T = 24$ K. The most of electrons are released from the corresponding traps at $T = 24$ K. The bleaching of electron traps in solid Ar by visible light was investigated in [10]. An investigation of diffusion and recombination of O atoms in a Xe matrix and identification of spectral lines was performed in [11].

Analyzing our experimental data we reached the conclusion that dopant-related relaxation processes in solid Xe can occur by the following mechanism. The O atoms in the Xe matrix start to diffuse at certain temperature through the lattice and recombine forming an excited molecule O_2^*. The visible range photons emitted during radiative transition of O_2^* to the ground state can promote electrons from deeper traps to the conduction band. Mobile electrons in the conduction band can directly leave the sample or recombine radiatively with self-trapped Xe_2^* holes yielding the VUV emission. One can consider this reaction as an «internal photon source» promoting electrons to the conduction band and affecting the relaxation paths. Note that the triggering of relaxation paths including VUV emission due to the thermally stimulated diffusion of neutral O atoms followed by molecules formation and their radiative decay leads to the conversion of photons from the visible to the VUV range. The experiments thus reveal a prominent part of dopants in relaxation processes and point to an interconnection between atomic and electronic relaxation channels.

The peak at 33 K (the most intense in TSL) obviously has a more complex origin. In our experiments the position of its maximum depended on the dose of irradiation. It points out that this peak consists of at least two components. One of them is caused by the above mentioned temperature-driven chemical reaction of oxygen atoms and the other results from annihilation of radiation-induced defects in solid Xe.

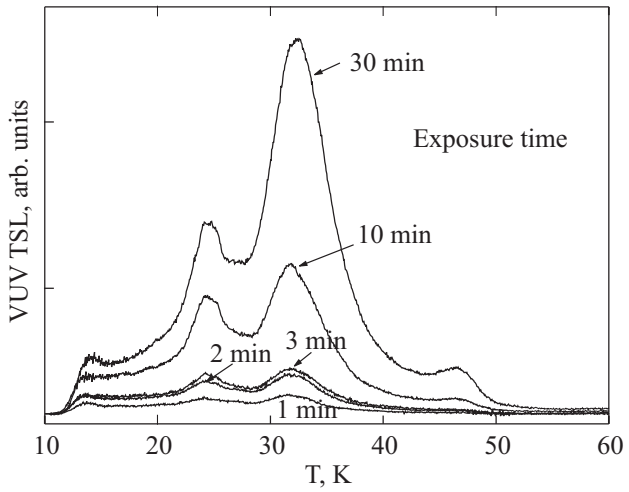

Fig. 5. Dose dependence of the TSL glow curve from solid Xe. Samples were irradiated with an electron beam after annealing at T = 58 K.

Figure 5 shows the dependence of the TSL glow curve on the dose of irradiation by an electron beam. The most pronounced dose dependence is observed for the 33 K peak. It indicates that not only lattice defects (traps for electrons) initially present in the sample are populated during irradiation but also those defects formed by the electron beam.

It is useful to compare dose dependence of the peak at T = 33 K with the dose dependence of defect-related features in the cathodoluminescence spectrum of solid Xe. The most pronounced feature in the cathodoluminscence spectra of all rare-gas solids is the well-known M-band. It consists of two components — M_1 (related to the molecular centers in the defect sites of the lattice) and M_2 (related to the molecular centers formed in the regular lattice at the exciton self-trapping) [3,12]. The shape of the M band profoundly varies with exposure time. Those changes are caused by the intensity redistribution between the two components of its internal structure — M_1 and M_2. The distinct enhancement of the «defect» sub-band M_1 upon irradiation indicates an increase in the number of defect sites, i.e. an accumulation of permanent lattice defects formed via an electronic subsystem by an excitonic mechanism [3]. Dose dependencies of the M_1 sub-band intensity in cathodoluminescence spectra and the yield of the related TSL peak (T = 33 K) in pre-irradiated solid Xe are shown in Fig. 6. Correlation between an increase of the TSL peaks and M_1 sub-bands of cathodoluminescence indicates their relation to the radiation induced defects.

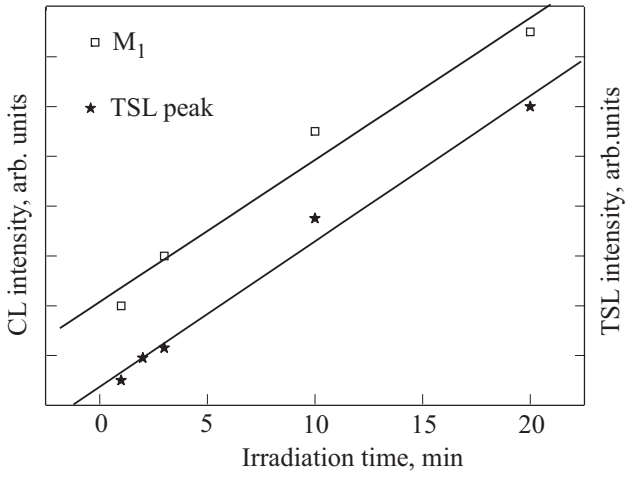

Fig. 6. Correlation between the increase with exposure time of the TSL peaks and the M_1 sub-bands in cathodoluminescence spectrum of solid Xe.

The configuration of radiation-induced defects and the scheme for the «excited state» mechanism of Frenkel-pair formation induced by exciton self-trapping into the molecular state was described in [3]. In order to estimate from the TSL glow curve an activation energy corresponding to annihilation of radiation-induced defects in solid Xe we used several experimental methods: the method of different heating rates (1.6, 3.2 and 5 K min^{-1}), the initial-rise method, and the curve cleaning technique with fitting of the TSL glow curve [13]. The activation energy corresponding to 33 K peak is found to be 42 ±5 meV. The results obtained by different experimental methods are in good agreement. The value E_a = 42 ±5 meV is a characteristic activation energy of radiation-induced defects annihilation in solid Xe.

Summary

The set of activation spectroscopy methods (TSL and TSEE) in combination with luminescence analysis was applied for the first time to study the intrinsic recombination of charge particles in solid Xe pre-irradiated by an electron beam. Surface and bulk-related peaks were identified. The dose dependence study enabled us to identify the peak as being related to the annihilation of radiation-induced defects. The corresponding activation energy was estimated.

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