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Stability of Charge Centers in Solid Ar

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The technique of thermally stimulated exoelectron emission (TSEE) was used for the first time for a study of thermal stability of charged centers in solid Ar. The data obtained demonstrate the efficiency of combining the TSEE study with thermally stimulated luminescence (TSL) for trap-level analysis. High thermal stability of charge centers at low temperatures was found.

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1. INTRODUCTION

The field of ionic states spectroscopy has lately developed into a very active topic of the study of cryogenic solids. Interest in the problem is stimulated both by current fundamental and applied research. The specific properties of these solids (small binding energy, simple electronic and crystal structure) offer the best opportunity to get an insight into different phenomena in solids at a molecular level of understanding and to develop promising technical applications in solid-state photochemistry, laser techniques, radiation physics, material science and methods for the detection of nuclear radiation.

The question of the stability of charge centers attracts particular attention because of their prominent role in different electronically induced phenomena like desorption of atoms and molecules from the surface of cry-

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ocrystals, defect formation, diffusion. Ionic centers can be used as a medium for solid state VUV, near UV and IR lasers, and their usage for energy storage was also considered. There are, however, still significant gaps in our knowledge on the stability of charged centers in cryogenic solids.

Stability of charged centers generated in an overall neutral matrix suggests a presence of spatially separated and immobile centers of opposite signs. Holes are self-trapped in the lattice of all atomic cryocrystals due to strong interaction with acoustic phonons and can be considered as intrinsic ionic centers in the matrix. It was found that the intrinsic ionic centers in atomic cryocrystals have a configuration of molecular ionic dimers Rg_2^+[1–3]. Electrons can be self-trapped in a "bubble" structure in solid He and Ne[4]. While in these solids electrons appear to be dressed by strong lattice interactions, in solid Ar, Kr and Xe free electron states are more stable and electrons can be trapped only at local energy levels within the forbidden band.

Thermally stimulated luminescence - TSL from preirradiated solids is a very valuable tool for an investigation of trapping levels in solids[5], and several studies of TSL from nominally pure atomic cryocrystals[6–8] and from doped ones[9–13] were reported. However, in cryocrystals exposed to ionizing radiation or grown from discharge, one can observe upon heating an emission of light due to the diffusion of reactive neutral species followed by their recombination, and the discrimination of these processes often appears to be a nontrivial task. Indeed, a combination of the TSL measurements and the thermally stimulated conductivity (TSC) seems to be an effective way and results were obtained for doped Ar solids[11].

In this paper we present a new approach to study of the thermal stability of charged centers in cryocrystals — thermally stimulated exoelectron emission (TSEE). The mechanism underlying TSEE is in fact the same as for TSL. Positively charged centers and electrons are created in insulating materials exposed to ionizing radiation. Thermally released electrons get raised to the conduction band. If they reach enough energy to overcome the potential barrier at the surface and the attraction of the image charge on the surface, they can leave the solid and can be detected with an electrode of positive potential fixed near the sample. Specific feature of cryogenic solids is relatively high mobility of dopant atoms at low temperatures[13]. Thermally stimulated reactions of neutral species can also result in light emission. To discriminate the contributions from charge recombination and chemical reactions of neutral species, we combined the TSL and TSEE methods. Here we report the first results on TSEE and TSL correlation studies in solid Ar preirradiated by an electron beam.

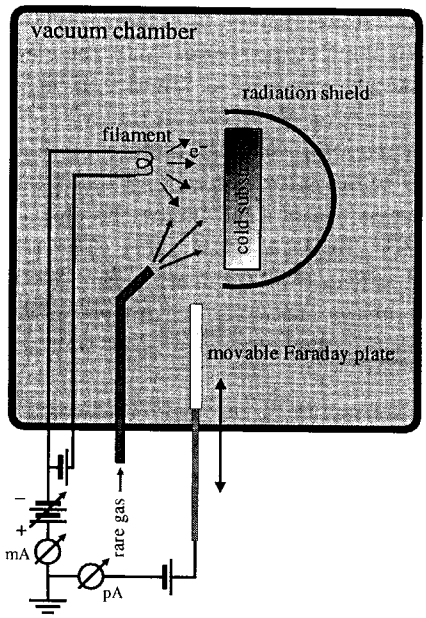

Fig. 1. Schematic drawing of the experimental chamber.

2. EXPERIMENT

Ionic centers were generated in solid Ar *in situ* in two ways: (1) by deposition of rare gases under an electron beam and (2) by electron beam irradiation of neutral solids. High-purity (99.9990%) Ar gas was deposited on an Ag-coated copper substrate, cooled by a Leybold RGD 580 closed-cycle cryostsat. A typical deposition rate was kept at about 10^{-2} μm/s. Before the experiment, the gas inlet system was pumped by turbomolecular pumps and degassed by heating under pumping. The pressure in the deposition chamber was 10^{-7} mbar. The presence of impurities was monitored by the recording mass spectrum and by the measurement of infrared absorption spectrum. The mass spectrum of the residual gases contained N_2, O_2, H_2O, CO_2. The contamination was smaller than 10^{-4}. The sample thickness was determined by measuring the pressure decrease in a known volume and observing the fringes of the spectrum. A typical sample thickness was 100 μm. In both cases we used an electron beam of low energy: 200 eV in case (1) and up

to 500 eV in case (2). A hot tungsten filament served as a source of the electron beam (Fig. 1). The current density of the electrom beam during 1 hour deposition in case (1) was kept at about 0.03 $mAcm^{-2}$ and during 0.5 hour irradiation in case (2) at about 0.1 $mAcm^{-2}$.

To minimize the recombination of ionic centers with electrons in the solids, the deposition temperature in case (1) and temperature during irradiation in case (2) were maintained below the characteristic temperature of the first peak of TSL in Ar at T = 12 K. The temperature was measured with 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 control the heating rate.

In the TSEE experiments, a movable gold-coated Faraday plate was used. It was located in front of the sample at a distance of 5 mm for the current mesuremnts. The substrate was kept at the ground potential and a small positive potential (9 V) was applied to the plate. The current from the Farday plate was amplified by a FEMTO DLPCA 100 current amplifier, 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 total yield of TSL was detected with a PMT. To extend the wavelength range available we introduced into the cryostat chamber a convertor of vacuum ultraviolet radiation into visible light. In doing so, we were able to detect luminescence in the range from 800 nm up to 10 nm. The measurements were carried out in the temperature range of 8–50 K.

3. RESULTS AND DISCUSSION

The TSEE from solid Ar preirradiated by an electron beam was studied for the first time. The reasons for this choice were as follows: (i) Ar has a negative electron affinity of -0.3 eV[14]. This means that an electron in a conduction band will experience an increase of kinetic energy when it exits from the sample surface. (ii) It was found[15] that the electron yield produced by MeV H^+ ions is extremely large — several orders of magnitude larger than that observed from metals and larger than that from other insulators. Moreover it appears to be strongly affected by a weak external electric field. (iii) Because a large electron escape depth of about 500 nm was found[16] one can expect to get information about both kinds of shallow electron traps — traps in the bulk and surface traps.

The dependence of the yield of the electron emission measured as a function of the temperature of a preirradiated sample (also called a glow

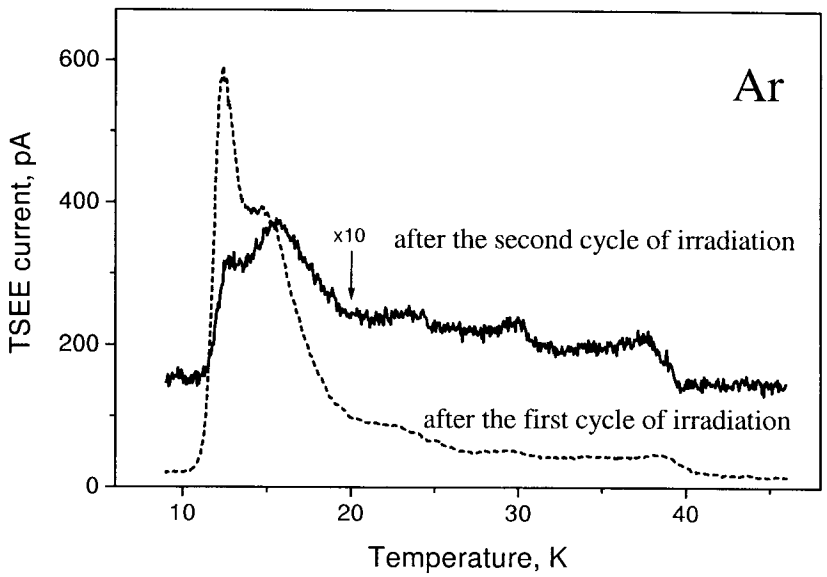

Fig. 2. TSEE current curves of solid Ar.

curve) is shown in Fig. 2. It was measured at a linear heating rate of 3 K/min. The currents detected were on the scale of 0.6–0.03 nA. Charge centers were generated with method (2). The sample was grown at T=20 K and then irradiated at T=9 K during 1 hour. The glow curve recorded after the first cycle of irradiation (dashed line) shows peaks at 12, 15, 22, 29 and 38 K. Heating up to 46 K during the TSEE measurment resulted in a more pronounced glow curve structure and intensity redistribution between peaks. Low-temperature peaks appeared to be suppressed in comparison with peaks at higher temperatures as one can expect under thermocycling. The overall decrease in the thermally stimulated current is thought to be due to partial evaporation of the sample. The highest temperature point under heating was well above the sublimation temperature T=30 K. In addition to this, the irradiation itself, even by low-energy electrons, results in an electronically induced sputtering of solid Ar[17]. Changing the Faraday plate polarity (+9 V $\rightarrow$ -9V) resulted in a suppression of the TSEE signal, which was however still detectable. This means that the surface of the Ar sample has a negative potential with respect to the Faraday plate, i.e. negative charges are accumulated during irradiation by an electron beam. No signatures from positively charged species were observed. The TSEE glow curves give direct evidence of the appearence of mobile negatively charged

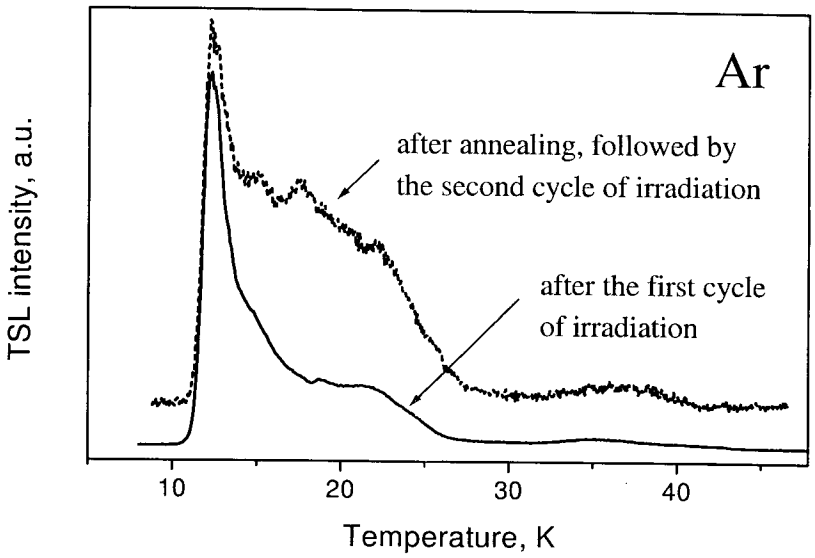

Fig. 3. Glow curves of TSL from solid Ar.

carriers (more likely electrons) upon heating of the preirradiated samples.

Note that a transient current of negatively charged species was observed in the experiment with mass-selected ions in an Ar matrix[18]after irradiation by an electron beam. The relevant trace from Ref. 18 shows a narrow peak at about 12 K and wide one with features at about 21 and 27 K. The origin of this thermally stimultated current was not discussed in Ref. 18. Taking into account the results of our measurements of TSEE one can suggest that this transient current arises due to the release of electrons from shallow traps in the Ar matrix.

TSL-glow curves of solid Ar irradiated by an electron beam after deposition with method (2) are presented in Fig. 3. They were measured at the same linear heating rate. The TSL yield from an unannealed sample of solid Ar deposited and then irradiated at T=9 K is shown in the lower trace of Fig. 3. The curve in the upper trace was taken from the same sample after the first cycle of annealing up to 55 K, which occurred during the TSL recording. The intensity of TSL after annealing followed by the second cycle of irradiation decreased and a redistribution of the intensity in the glow curve was observed. To facilitate easy comparison the glow curves were normalized by the first peak height. It is clearly seen that the intensity of the low-temperature peak at 12 K decreased with respect to peaks at

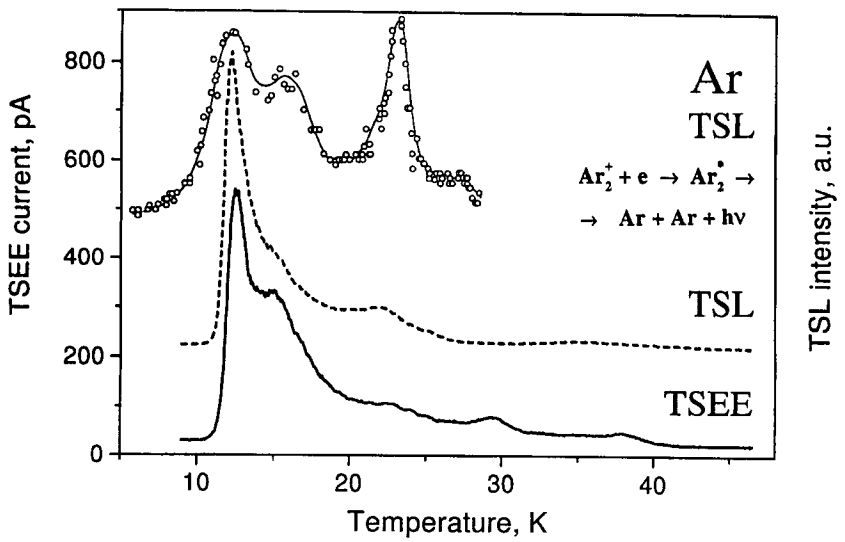

Fig. 4. Total yield of TSL and that of TSEE from solid Ar measured in this work (low curves). Upper curve - spectrally resolved TSL recorded at the photon energy E=9.7 eV [3].

higher temperatures, and the curve showed some structure at 15, 17, 22 and 37 K. Despite the fact that the glow curve taken after short-time annealing shows inhomogeneous broadening, positions of peaks in this curve coincide fairly well with those obtained for the samples of solid Ar grown in a closed cell at 60 K[8] and irradiated by a 1 keV electron beam. It was checked using irradiation at higher temperatures which resulted in the disappearence of all peaks at lower temperatures. Note that the emission of electrons and light can be detected even several hours after irradiation.

Indeed, the shape of glow curves depends on the sample structure. However, the samples grown in an identical way exhibited quite reproducible glow curves of both TSL and TSEE. Fig. 4 comparises of the total yield of TSL and that of TSEE taken after the first cycle of irradiation. A correlation between TSL peaks and TSEE peaks at 12, 15, 22 and 37 K indicates the presence of electron traps contributing to both processes — recombination of charged particales and electron emission from the solid. Note that all peaks at 12, 15, 22 K were observed also in a spectrally resolved glow curve (upper curve in Fig. 4) resulting from the recombination of self-trapped holes with electrons[3]. This demonstrates that these peaks in TSEE and integrated

TSL are characteristic of the electron trap-levels in solid Ar. Analysis of glow curves changes under annealing suggests that the low-temperature peak at 12 K is related to surface traps and traps at inner interfaces in the sample. The peak at 15 K exhibiting pronounced dose dependence should be assigned to radiation-induced defects. It was shown[3] that excitation of solid Ar by low-energy electrons results in a formation of Frenkel pairs — vacancies and interstitials of the "dumb-bell" configuration <100>. The broad peak at about 16 K was observed also in the thermally stimulated conductivity (TSC) yield from Ar doped with different dopants - Ag and Au [11]. The peak around 22 K detected in TSEE, in the total yield of TSL and in the course of recombination of self-trapped holes with electrons was observed also in glow curve taken from solid Ar [7] irradiated by X-rays at 15 K.

It is interesting that the peak at 23 K was recorded also both in thermally stimulated bulk conductivity and by monitoring emission from matrix-isolated O_2 molecules (the Herzberg progression) [11]. It was suggested there that this peak in TSL is caused by chemiluminescence due to the recombination of O^- ions with neutral O atoms. In our experiments the abundance of oxygen impurities is quite low, and the probability of the 23 k peak being due to O^- diffusion is small. It appears more likely that at least in our study it is due to activation of trapped electrons. An origin of the peak at 29 K is not clear. It was observed only in TSEE glow curves taken from different samples and it was not found in TSL. This may be caused by the difference in contributions of the surface and bulk traps in the emission of light and electrons. However, this peak was recorded in the TSL of Ar cryocrystals irradiated by X-rays[7].

4. CONCLUSION

The TSEE from solid Ar preirradiated by an electron beam was detected for the first time. A correlation between the TSEE peaks and TSL ones was found pointing to common mechanism underlying both TSEE and TSL — recombination of charge centers due to a high mobility of released electrons. An analysis of glow curves will be presented in another publication. Our studies indicated a high thermal stability of charge centers in solid Ar at low temperatures.

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