Nuclear Instruments and Methods in Physics Research B xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Defect creation via dissociative recombination of ionic centers in solid Ne matrices

E.V. Savchenko [a,*], I.V. Khyzhniy [a], S.A. Uyutnov [a], M.A. Bludov [a], G.B. Gumenchuk [b], V.E. Bondybey [b]

[a] Institute for Low Temperature Physics and Engineering NASU, 61103 Kharkov, Ukraine
[b] Lehrstuhl für Physikalische Chemie II TUM, 85747 Garching, Germany

ARTICLE INFO

Article history:
Received 8 May 2015
Received in revised form 5 August 2015
Accepted 20 August 2015
Available online xxxx

Keywords:
Dissociative recombination
Defect formation
Activation spectroscopy
Rare Gas Solids

ABSTRACT

Recombination of the intrinsic ionic centers Ne_2^+ (self-trapped holes) with the detrapped electrons in solid Ne matrices and relaxation channels have been studied. The experiments were performed employing combination of the cathodoluminescence (CL) with current and optical activation spectroscopy techniques. CL spectra were recorded simultaneously in the VUV and visible range. Yields of spectrally resolved thermally and photon-stimulated luminescence (TSL, PSL) and thermally and photon-stimulated exoelectron emission (TSEE, PSEE) were measured in the time-correlated manner. It was found that the recombination reaction proceeds with irreversible dissociation of the transient Ne_2^{**} centers and the dissociative recombination (DR) products exit the matrix cage. Products of the DR reaction are found to be in 3s and 3p states. The detection of "defect" components in the TSL and PSL points to the defect formation via DR in Ne matrices. The temperature range of the electron traps stability is elucidated. A long-lasting "afteremission" of electrons and afterglow of VUV photons observed on switching off the irradiation suggest the accumulation of the uncompensated negative charge.

1. Introduction

An important role of the electronic excitations in radiation damage of non-metallic materials continues to attract much attention [1,2]. Particular attention has been given to the study of defect creation mechanisms. This topic was comprehensively studied in model insulators – Rare Gas Solids (RGS) with an emphasis on the role of exciton self-trapping ([3–6] and refs. therein). In solid Xe, Kr and Ar excitons are self-trapped into the two-center or molecular self-trapped excitons M-STE. In solid Ne the main channel of the exciton self-trapping is the self-trapping into the one-center atomic-type states, so-called A-STE states [1]. The state-selective study performed with the synchrotron radiation in the range of the exciton $n = 2\Gamma(3/2)$ absorption (20.2 eV) gave a direct evidence of the formation and accumulation of point lattice defects via the excitonic mechanism [7]. Another process stimulated via an electronic subsystem is a particle desorption. First report on observation of excited Ne atoms (in the $^3P_1$ and $^1P_1$ states) desorption under selective excitation in the excitonic range was presented in ref. [8]. Authors of ref. [9] succeeded in measurements of absolute yields of metastable Ne atoms in the $^3P_0$ and $^3P_2$ states stimulated by excitons. Desorption of the excited atoms was interpreted in a frame of the "cavity ejection" mechanism due to the repulsive interaction between the excited atom and surrounding with a negative electron affinity [1]. Desorption of Ne_2^* ($^3\Sigma_u$) excimers under excitation in the range of valence excitons (corresponding a hole production in a 2p shell) was detected by analysis of a plume of desorbing particles emitted from the Ne film surface [10].

Upon excitation with ionizing radiation another mechanism can take place, i.e. the dissociative recombination (DR) of self-trapped holes (STH), rare-gas dimer ions Rg_2^+, with electrons, which contributes to the desorption and, as one could expect, to defect formation. The DR mechanism as a source of desorption was suggested in ref. [11] to explain the desorption of excited atoms and molecules from solid Ar. Strong enhancement of the excimer emission of Ar_2^* by electron-hole recombination observed in ref. [12] corroborates with this assumption. Contribution of the DR mechanism in excimers Ne_2^* desorption was also assumed in ref. [13]. The question on the role of charged centers and DR in defect formation remains to be still open. It is worth noting that the interest to a research of ionizing radiation effects in RGS is associated with their applications as scintillators [14], moderators [15], and as solid matrices in radiation cryochemistry [16].

Solid Ne is characterized by slow energy relaxation processes [1]. "Hot" (unrelaxed) emissions are observed for both type centers, molecular centers and atomic ones. So, Ne_2^* excimers emit

* Corresponding author.

http://dx.doi.org/10.1016/j.nimb.2015.08.042
0168-583X/

predominantly vibrationally hot luminescence both in the bulk and upon the desorption as it was found in ref. [17]. Hot electronic transitions of atomic type are observed in the VUV range, transitions from $^3P_1$ and $^1P_1$ to the ground state $^1S_0$ [17,18], as well as in the visible range, $3p_i \rightarrow 3s_k$ transitions [19–21]. Emissions from highly excited states bear fingerprints of relaxation processes from primary charge states. Since activation spectroscopy is a powerful tool to probe charged species, relaxation processes and defect levels, there is a clear need to apply activation spectroscopy methods to get relevant information concerning these points. First measurements of thermally stimulated luminescence (TSL) and thermally stimulated exoelectron emission (TSEE) from pre-irradiated by an electron beam solid Ne were reported in refs. [22,23]. However, in these works only the total yield of the TSL was measured. In order to reconstruct a mechanism and the final product states of relaxation as well as to elucidate the contribution of charged states, a spectrally resolved study of TSL (including the TSL from the highly excited $3p_i$ states) complemented by TSEE study is needed.

In the present paper, the results of new experiments performed employing combination of the cathodoluminescence (CL) method with current and optical activation spectroscopy techniques are presented. Low-energy electrons were used for excitation in view of their high ionization cross-section [24]. CL spectra were measured simultaneously in the VUV and visible range. Because of the high sensitivity of TSL and TSEE to a sample structure and impurity concentration the yields of TSEE and spectrally resolved TSL were monitored simultaneously on the same sample in a manner similar to that suggested in ref. [25]. The study was complemented by the measurements of photon-stimulated emission of electrons (PSEE) and spectrally resolved photon-stimulated luminescence (PSL).

2. Experimental

Experiments were carried out in a special multifunctional chamber described in Section 7 of ref. [26]. Films of solid Ne were grown by deposition of Ne gas with a purity of 99.998% onto a cold metal substrate mounted in the high-vacuum chamber with a base pressure of 10^{-8} mbar. An open surface allowed studying the luminescence in a wide spectral range – from visible to vacuum ultraviolet (VUV). The substrate was cooled by a liquid He cryostat and during deposition was kept typically at 4.5 K. Optically transparent films of 100 μm thicknesses were used. The sample thickness and the deposition rate were determined by measuring the pressure decrease in a known volume of the Ne reservoir in the gas-handling system. After preparation the films were irradiated with an electron beam. To simulate the effect of secondary electrons generated by energetic particles, the low-energy (500 eV) electrons were used. The beam was focused in such a way to provide irradiation of the sample area of 1 cm^2. A current density of about 100 μA cm^{-2} was kept. The sample heating during irradiation did not exceed 0.4 K. In some experiments samples were grown under irradiation with a 150 eV electron beam to generate charged species throughout the entire thickness of the samples. The luminescence spectra were recorded simultaneously in VUV and visible range using two ports of the experimental chamber. The spectra ensured also control over the presence of impurities in the films. Traces of nitrogen and oxygen were detected.

Simultaneous measurements of post-irradiation relaxation emissions of photons and electrons were performed immediately on switching off the electron beam. Decay curves of the "afterglow" at chosen wavelengths and "afteremission" current (delayed emissions of photons and electrons observed) were recorded first at the irradiation temperature (4.8 K). When the "afterglow" and "afteremission" current had decayed to essentially zero, the thermally stimulated relaxation emissions of photons (TSL) and electrons (TSEE) were measured upon heating. TSEE current was detected with an electrode kept at a small positive potential +9 V and connected to a current amplifier. The substrate was kept at ground electric potential. TSL yields were measured simultaneously in visible and VUV ranges by the same registration system as used in the measurements of cathodoluminescence. The substrate temperature measured by a Si diode and heating mode can be set as needed by means of the program specially designed for this purpose. In the current experiments a linear heating at a constant rate of 3.2 K min^{-1} was used.

For measurements of PSEE and spectrally resolved PSL yields, we used an OSRAM green laser operating at the wavelength 520 nm. While Ne samples are transparent in visible and infrared range, their heating under laser beam can be caused only by heat transfer from the substrate. The sample heating monitored during experiments did not exceed 0.5 K.

3. Results and discussion

In solid Ne, which has extremely wide band gap (21.58 eV), free holes generated by ionizing radiation interact with a deformable lattice, forming the STHs, the intrinsic positively charged centers of dimer configuration Ne_2^+, which can be considered as molecular ionic centers in solid Ne matrix similar to V_k centers (self-trapped holes) in alkali halides. Electrons exhibit the free-like behavior as it has been clearly indicated in the experiments performed by muon spin rotation/relaxation (μ^+SR) technique [27] and supported by the observation of TSEE [22,23]. The important point is a large mean free path of electrons in the conduction band of all high structural quality RGS [28] that allows to use the TSEE method to get information on both the surface and bulk traps (the radiation-induced traps/defects among them). A combined study of processes, observed after completing the irradiation – TSL and TSEE, offers the way of monitoring the behavior of charged centers of both signs via concurrent measurements of TSEE current and recombination luminescence of STHs.

Fig. 1 shows the CL spectrum of solid Ne in the VUV range probed then with the TSL measurements. The most intense components b are related to the $^3P_1 \rightarrow {}^1S_0$ transition. The narrow "0" peak coinciding in energy with the $^3P_1 \rightarrow {}^1S_0$ transition in the gas phase was identified as an emission from the desorbing atoms in the excited state [17]. The components labeled by "1" and "2" stem

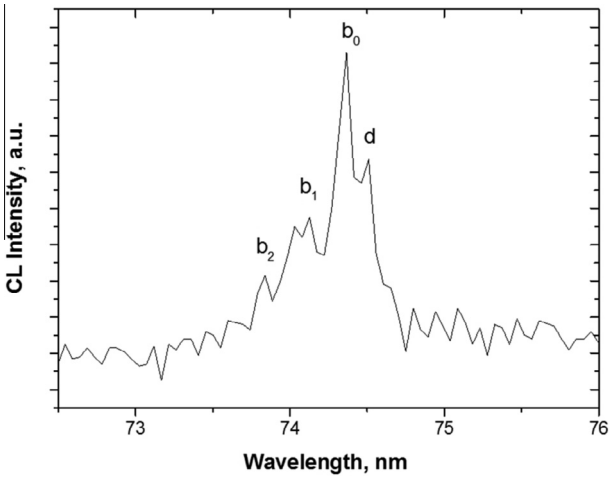

Fig. 1. Spectrum of the VUV CL taken from Ne sample excited with a 500 eV electron beam.

Please cite this article in press as: E.V. Savchenko et al., Defect creation via dissociative recombination of ionic centers in solid Ne matrices, Nucl. Instr. Meth. B (2015), http://dx.doi.org/10.1016/j.nimb.2015.08.042