

Radiation-induced defects, energy storage and release in nitrogen solids

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Abstract. New trends in the study of radiation effects in nitrogen solids with a focus on the defect-induced processes are presented. An electron beam of subthreshold energy was used to generate radiation defects via electronic subsystem. Experimental techniques developed enabled us to detect neutral and charged defects of both signs. Defect production and desorption were monitored using optical and current emission spectroscopy: cathodoluminescence CL, thermally stimulated luminescence TSL and exoelectron emission TSEE along with the detection of postdesorption. Our results show stabilization and accumulation of radiation defects – ionic centres of both signs (N_4^+ , N_3^+ , N_3^-), trapped electrons and radicals (N , N_3). The neutralization reactions: $N_4^+ + e^- \rightarrow N_4^* \rightarrow N_2^*(a'^1\Sigma_u^-) + N_2^*(a'^1\Sigma_u^-) + \Delta E_1 \rightarrow N_2 + N_2 + 2h\nu + \Delta E_2$ and $N_3^+ + e^- \rightarrow N^*(^2D) + N_2(^1\Sigma_g^+) + \Delta E_3 \rightarrow N(^4S) + N_2(^1\Sigma_g^+) + h\nu + \Delta E_3$ are shown to be the basis of defect production and anomalous low-temperature post-desorption ALTPD. The part played by pre-existing and radiation-induced defects in energy storage is discussed.

1. Introduction

Nitrogen solids represent model molecular insulating materials with a wide energy gap (15.6 eV). The intense current interest to nitrogen solids is connected with the potential use of polynitrogen compounds as environment-friendly high energy density materials HEDM [1-6]. In ref. [7] it was suggested to synthesize cluster N_4 via excited states of nitrogen. Second important aspect of interest is related to astrophysical research because nitrogen is one of the most abundant elements in the Universe [8]. Solid N_2 is used as moderators [9], source for nitrogen plasma [10] and matrix in radiation chemistry [11]. All these fields of science and applications require an understanding of radiation-induced processes. Despite a long history of solid N_2 spectroscopy such problems as defect production and defect-induced processes in nitrogen solids remained almost unexplored until recently with the exception of N radical formation.

Interaction of ionizing radiation with nitrogen solids results in generation of electron-hole pairs. Electrons are highly mobile in the low-temperature α -phase [12] and their trapping by defect sites or species with positive electron affinity produces negatively charged centers. First observation of trapped electrons in solid nitrogen was reported in [13]. Recently N_3^- centers were detected in solid nitrogen using photon-stimulated exoelectron emission PSEE [14]. Holes in solid N_2 in contrast to electrons have low mobility and can be self-trapped with tetranitrogen cation N_4^+ formation as shown



in [15] or trapped on some impurity centers. Creation of ionic species N_3^+ in electron-bombarded nitrogen films was observed by IR and UV absorption [16]. Furthermore besides of N radicals another neutral center – the azid radical N_3 , was registered in solid nitrogen pre-irradiated by electrons [17], protons [18] and synchrotron radiation [19]. Indication of a number of radiation-induced defect centers poses the question on their stability, dynamics and relaxation processes accompanied by energy transfer and conversion.

In view of such a diversity of the centers, which can be generated by irradiation, we applied a complex of complementary techniques to be able to explore the entire set of defects, their relaxation and related reactions with a focus on particles ejection from pre-irradiated solid N_2 . Cathodoluminescence CL spectroscopy as well as optical and current activation spectroscopy methods: thermally stimulated luminescence TSL and exoelectron emission TSEE along with the detection of the total yield of post-desorption, which occurs upon heating, have been applied. This enabled us to get information on radiation-induced defects and elucidate their role in defect-induced processes taking place in an electron-bombarded solid N_2 .

2. Experimental technique

We have created a comprehensive technique that enabled us to detect both neutral and charged defects of both signs. The developed experimental technique has previously been described [20, 21] therefore only important details related to the present study are given below.

2.1. Sample preparation and generation of defects

The nitrogen solids were grown by deposition of high purity (99.995%) N_2 gas onto a cooled Cu substrate mounted in a high-vacuum chamber with a base pressure of 10^{-8} mbar. A convenience of the sample preparation from the gas phase is the ability to obtain samples of the required thickness with an open surface. Such an open surface makes it possible to monitor particles desorption and defect production with luminescence techniques in a wide range of wavelength from infrared IR to vacuum ultraviolet VUV and apply current activation techniques based on exoelectron emission – TSEE and PSEE.

To irradiate the samples we used a low-energy electron beam to ensure the generation of defects through electronic subsystem, so-called sub-threshold mode. Taking into account that the threshold electron beam energy E_{thr} for production of defects in solid N_2 via the knock-on mechanism is about 1.5 keV we used beams with energies in the range 300-1500 eV. The irradiation was performed in dc regime. The current density was 3 mAcm⁻². The sample temperature was controlled with a Si sensor. The sample heating under electron beam did not exceed 0.5 K. The CL spectra were detected concurrently in the visible range and in VUV with two spectrometers. To measure the dose dependence of excited species production the CL spectra were recorded repeatedly on an exposure time or the CL intensity was recorded at the selected wavelength as a function of exposure time. Note that luminescence techniques provide access to forbidden electronic states which are difficult to populate using conventional absorption spectroscopy.

2.2 Measurement of relaxation emissions: photons, electrons and particles

Specific feature of nitrogen solids is the existence of a very long-lived metastable state of the nitrogen atoms, which appear under irradiation, resulting in long afterglow which was observed on completion of the irradiation at the wavelength of the forbidden atomic transition $^2D \rightarrow ^4S$ [22]. Simultaneously with the afterglow we observed an “afteremission” of electrons with similar characteristic decay times.

When the afterglow and “afteremission” current had decayed to essentially zero, three relaxation emissions were measured in a correlated fashion – emission of photons, electrons and particles. Relaxation processes were studied at stimulation by heating. In these experiments we used heating with a constant rate, for the most part 5 Kmin⁻¹. Partial yields of TSL were measured in the visible and VUV ranges. The measurements of thermally stimulated relaxation emissions were performed in the temperature region 5–30 K. Being promoted to the conduction band by heating detrapped electrons

either neutralize positively charged centers yielding TSL or escape from the sample yielding TSEE. Stimulated currents were detected with an electrode kept at a small positive potential $V_F = +9$ V and connected to the current amplifier. Coincidentally with TSEE and TSL detection the particles ejection (post-desorption) was recorded by pressure P monitoring. The entire control of the experiment was made with the help of a computer program developed specifically for these studies.

3. Results and discussion

Luminescence spectra in conjunction with activation spectroscopy provide extensive information on radiation-induced transformation of solids under ionizing radiation: molecule fragmentation or association, accumulation of radiation-induced species, modification of structure, desorption of excited particles, radiation-induced chemical reactions and cascades of relaxation processes involving both electronic and atomic processes. Figure 1 demonstrates the CL spectrum of solid N_2 measured in the VUV range. It consists of two forbidden molecular progressions the $a^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ and $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$.

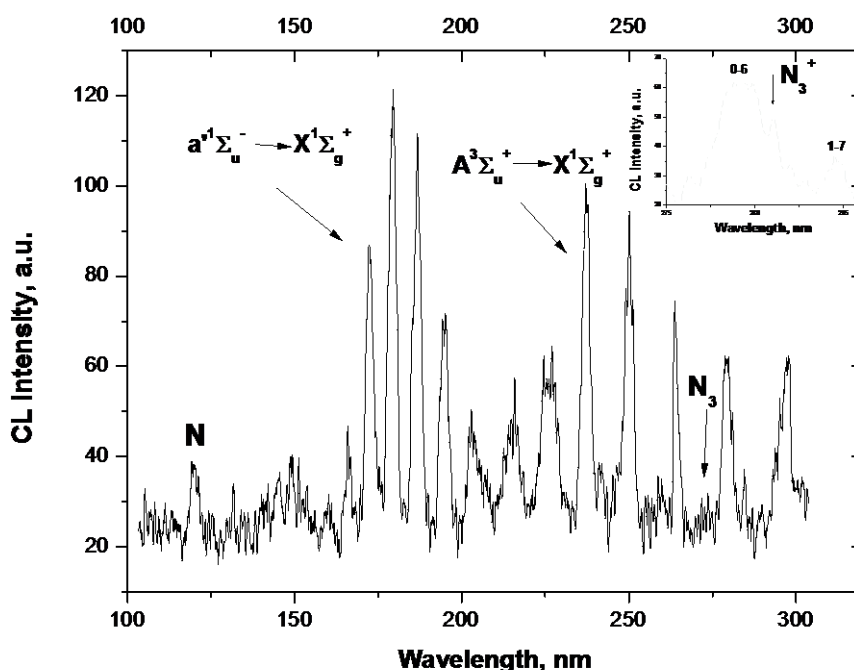
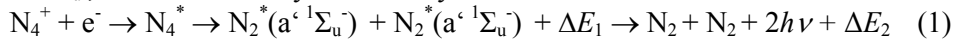


Figure 1. CL spectra of solid N_2 recorded at 5 K. Inset shows a part of spectrum recorded with higher resolution. Features related to N_3 and N_3^+ species are marked by arrows.

The vibrational bands positions of both progressions, are shifted toward longer wavelength with respect to the gas phase spectra, and are in good agreement with those observed in the early studies of VUV luminescence of solid N_2 [23, 24]. As it was found in [15] both progressions show dose dependence on an exposure time indicating accumulation of radiation-induced defects responsible for the emissions observed, which are thought to be of ionic nature. Another indication of the ionic nature of primary “reagent” in the neutralization reaction with electron was the observation TSL, nonstationary luminescence NsL and photon/stimulated luminescence PSL on vibronic bands of the singlet transition $a^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$, the yields of which correlated with exoelectron current emissions TSEE and PSEE [14, 15]. Behaviour of the relaxation emissions together with analysis of the energy diagram and potential curves of N_4 available [1, 7] resulted in the conclusion that the neutralization of tetranitrogen cation N_4^+ , in other words self-trapped hole, causes its dissociation followed by the exit

(from the parent “cage” where the neutralization has occurred) of molecules in the lowest excited singlet state $a^1\Sigma_u^-$, which then decays radiatively:



The VUV CL spectrum has several features first detected by the CL technique. This is a weak band at 273 nm assigned to the $A^2\Sigma_u^+(000) \rightarrow X^2\Pi_g(000)$ transition of N_3 radical in accordance with [16] where this transition was observed in VUV absorption spectrum of solid N_2 exposed to energetic electrons. Very low intensity of this band in our experiments is likely due to efficient formation of N_3^- centers detected with PSEE technique in our recent experiments [14]. A high value of N_3 electron affinity E_e (2.76 eV) promotes the electron attachment reaction. More intense feature which was observed in the VUV CL spectrum of higher resolution (shown in the inset in Figure 1) is the band at 281 nm. This band belongs to the transition $A^3\Pi_u(000) \rightarrow X^3\Sigma_g^-(000)$ of N_3^+ cation and coincides with the band detected in the VUV absorption of electron bombarded N_2 [16]. We detected also the atomic line N in the VUV CL spectrum which was identified as $3s\ ^4P \rightarrow 2p\ ^3S$ transition emitted by desorbing N atoms (this issue will be addressed in a subsequent publication).

Detection of the total yield of particles from pre-irradiated solid N_2 (first observed in [25]) clearly

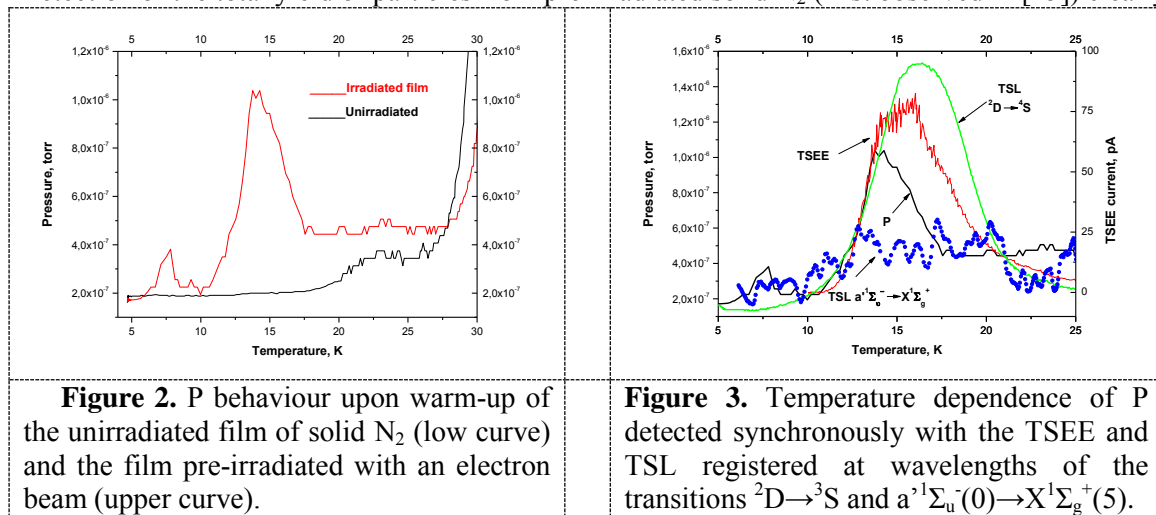
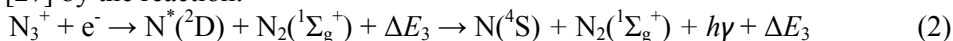


Figure 2. P behaviour upon warm-up of the unirradiated film of solid N_2 (low curve) and the film pre-irradiated with an electron beam (upper curve).

Figure 3. Temperature dependence of P detected synchronously with the TSEE and TSL registered at wavelengths of the transitions $^2D \rightarrow ^3S$ and $a^1\Sigma_u^-(0) \rightarrow X^1\Sigma_g^+(5)$.

demonstrates the radiation nature of this phenomenon. Comparison of the particle yields by P measurements from unirradiated and pre-irradiated solid N_2 films of 100 μm thick is shown in Figure 2. Note that both samples were not annealed before the experiment. For the unirradiated sample there is nearly no change in pressure up to 20 K and the sample starts to sublime at about 28 K. A sharp rise in pressure followed its decrease upon warm-up of the pre-irradiated sample was observed in the region of temperatures much lower than the characteristic sublimation temperature of solid N_2 . The most likely source of energy needed for post-desorption may be neutralization of positively charged centers survived after completion of irradiation, which are N_4^+ and N_3^+ centers. The relaxation channel described by the reaction (1) is followed by an energy release, at the stage after neutralization as well as after the radiative transition $a^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$. Note that the transition to the ground state (shown in Figure 1) terminates in vibrationally excited levels with a maximum of vibrationally excited molecules distribution at 5th level, that corresponds to about 1.45 eV. Neutralization of N_3^+ center registered in the CL spectrum also proceeds with a considerable energy release. As it was found in [26] the most probable channel of the N_3^+ dissociative recombination is the two-body channel. If both products are in the ground state the energy release in this reaction exceeds 10 eV [26], which creates preconditions for dissociation with the creation of $N(^2D)$ center. We observed accumulation of these centers upon irradiation [27] by the reaction:



In order to validate the suggestion on connection of ALTPD with neutralization reactions we measured simultaneously P, TSEE and TSL on the wavelengths of the transitions connected with

reactions (1) and (2) with the result shown in Figure 3. Detection of the TSEE yield indicates electron detrapping. Then recombination of electrons with positively charged nitrogen centers occurs followed by an energy release. The same threshold for ALTpD yield (P) and yields of TSEE and TSL, detected on the wavelengths of the transitions involved in the reaction (1) and (2) indicates that ALTpD is caused by the neutralization reactions.

To determine which traps are sources of electrons to recombine with N_4^+ and N_3^+ centers we carried out an experiment with irradiation cycles. Annealed film of solid N_2 10 μm thick was subjected to the cycles: (i) irradiation by 1.4 keV electrons, then (ii) warm-up to 25 K (while monitoring the pressure) and re-cooling to 5 K. In each subsequent cycle the sample was irradiated for a longer time and curves taken after different irradiation times are shown in Figure 4. At low irradiation time pre-existing traps (growth defects) are filled and two peaks at about 16 and 11 K are detected.

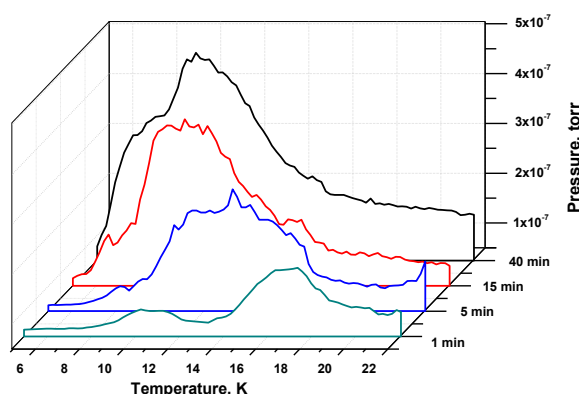


Figure 4. ALTpD yields (P) measured after irradiation during different times.

With increasing irradiation time other traps associated with radiation-induced defect centers are populated. Nonelementary curve of pressure indicates a set of defects involved. Taking into account that in a subthreshold regime defects can be formed only via electronic subsystem these radiation induced defects are most likely related to the lattice distortion at formation of atomic centers N_1 and centers, containing more than two N atoms. The radiation-induced traps appeared to be more shallow than that associated with pre-existing defects. At present it is difficult to identify separate peaks in the curves taken at irradiation times longer than 1 min (Figure 4), the trap levels distribution looks a nearly continuous. N_3^- centers representing deep traps do not contribute to ALTpD. The information obtained is of importance for different cryogenic systems in radiation environment, e.g. for astrophysical objects, moderators and for operation conditions of big particle accelerators like Large Hadron Collider at CERN where cryogenic surfaces are subjected to intense ionizing radiation.

4. Summary

The set of radiation-induced defects in N_2 solids pre-irradiated with an electron beam was detected and studied with the focus on the role of charge centers in the radiation-induced processes. The CL detection and correlated in real time measurements of spectrally resolved thermally stimulated luminescence TSL and exoelectron emission TSEE as well as detection of thermally stimulated particle ejection from pre-irradiated N_2 films were performed. This enabled us to identify N_4^+ , N_3^+ , N_3^- , N_2 and N radiation-induced defect centers in nitrogen solids exposed to an electron beam. Connection of strong anomalous low-temperature post-desorption ALTpD from pre-irradiated solid N_2 with radiation-induced defects was proved and underlying this phenomenon mechanism – the dissociative recombination of charged centers N_4^+ and N_3^+ with detrapped electrons, was elucidated.

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