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Excitation-induced processes in model molecular solid – N_2

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ABSTRACT

Recent findings on electronically induced processes in N_2 molecular solids monitored by luminescence methods are presented with a focus on the electronically induced desorption. Low-energy electron beam was used for excitation to avoid the knock-on defect formation and sputtering. The samples were probed with depth by varying electron energy. VUV photon emissions from desorbing N^* atoms (the $^4P_{1/2-5/2} \rightarrow {}^4S_{3/2}$ transitions) under irradiation by electrons of subthreshold energy were observed for the first time. Their distinctive feature is a coincidence with the gas phase lines within the experimental error. New data on electronically stimulated desorption of N_2^* molecules in the electronic excited state $C^3\Pi_u$ are reported. Monitoring of nonstationary desorption NsD in combination with the detection of thermally stimulated exoelectron emission TSEE and post-desorption reveal the contribution of charge recombination reactions in the electronically induced particles ejection. Fresh approach to study of electronically induced desorption opens new type of greatly delayed desorption associated with the entry of freeing electrons in recombination process.

1. Introduction

Excited electronic states dynamics, energy storage and conversion in model molecular solid – condensed N_2, attract much attention in diverse fields of science. The keen interest to nitrogen solids is connected with the potential use of polynitrogen compounds as environment-friendly high energy density materials HEDM [1–3]. In ref. [4] it was shown that synthesis of N_4 cluster can be facilitated if implement it via excited states of nitrogen molecules. Another important aspect of interest is related to astrophysical research because nitrogen is one of the most abundant elements in the Universe [5]. Films of solid N_2 are used as moderators [6], nitrogen plasma sources, e. g. [7] and matrices in radiation chemistry [8]. Understanding of processes underlying electronically induced desorption of nitrogen is of vital importance to ensure the safe operation of high-energy particle accelerators operating at liquid helium temperature.

In all these fields of science and applications the problem of electronic excited states, their dynamics and relaxation is crucial. Electronic excitation induced by photons or electron beams can efficiently modify the properties of materials [9–11]. For molecular solids there can be a large variety of processes, e.g. molecule fragmentation, change of structure in the bulk, surface modification, charge trapping, enhanced diffusion, solid-state reactions, ejection of atoms and/or molecules, so-called desorption. Desorption of N_2 was studied under excitation with different kind of ionizing radiation, in particular, by electrons [12–16] and photons [17–19]. The most part of studies was performed using mass-spectroscopy methods which provide the information on masses of desorbing particles and their kinetic energies but no information on an electronic state of the desorbing particles. For understanding the underlying mechanisms luminescence studies are mandatory. First luminescence study of electronically induced desorption from solid nitrogen discovered the excited N_2^* ($C^3\Pi_u$) molecule desorption [20]. However the possibility of excited atom desorption remained unexplored.

In the present work, we applied luminescence spectroscopy methods in order to get information on excitation-induced processes occurring in films of solid N_2 with a focus on the electronically induced desorption. Low-energy electron beam was used for excitation to avoid the knock-on defect formation and sputtering. The measurements of cathodoluminescence CL were performed in the visible and vacuum ultraviolet VUV spectral ranges in correlated manner to monitor the radiation-induced centers production, fragmentation of molecules and excited particle ejection. Surface- and bulk-related centers were discriminated by varying the electron penetration depth and film thickness. New

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approach to the desorption study is proposed – monitoring of nonstationary desorption NsD by gradual heating the film under the beam. NsD in combination with the detection of thermally stimulated exoelectron emission TSEE and post-desorption enable us to elucidate the role of charge carriers dynamics in electronically stimulated desorption.

2. Experimental

The experimental setup and methods have been described in [21] (Sec.7). So, only related essential details are mentioned here. High-purity N_2 (99.995%) was used to grow films of different thicknesses (from 30 nm to 300 μm) by deposition from the gas phase on a Cu substrate mounted in a high-vacuum chamber. The film thicknesses were determined by measuring the pressure decrease in a known volume of the N_2 reservoir in the gas-handling system. An open sample surface allowed to record the luminescence in a wide spectral range – from visible to VUV and monitor desorption spectroscopically as well as by pressure measurements.

To irradiate the samples we used a low-energy electron beam to avoid knock-on collisions and ensure stimulation of all processes via electronic subsystem. 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 500–1500 eV. The irradiation was performed in dc regime with current density of 2 mA cm^{-2} in most cases.

The N_2 solid films temperature was controlled with a Si sensor. Samples were grown and irradiated at 5 K. The sample heating under electron beam did not exceed 0.7 K. The CL spectra were detected concurrently in the visible range and in VUV with two spectrometers. Desorption of excited particles was monitored spectroscopically. The total desorption yield was detected by pressure measuring above the sample. Special experiments were performed implementing a method similar to the previously proposed method of nonstationary luminescence NsL [22]. At the first stage the film of solid N_2 was irradiated with an intense electron beam to generate a sufficient number of charge carriers – electron-hole pairs. Electrons exhibiting very high mobility [23] are localized at defects of structure or impurities with positive electron affinity. Holes are self-trapped forming N_4^+ centers [24]. Then the pressure, characterizing desorption yield, was measured by gradual heating the film under the beam. At such a performance of the experiment detrapped electrons recombine with localized positively charged centers with an energy release. This desorption, observed under the effect of two factors – electronic excitation and heating, we call nonstationary desorption NsD. For the comparison purpose the yields of thermally stimulated exoelectron emission TSEE and post-desorption were measured. Post-desorption from preliminary irradiated solid N_2 was first detected in [25]. Its characteristic feature is strong peak of particles ejection at temperatures much lower than the characteristic sublimation temperature. For this phenomenon the abbreviation was introduced ALTpD (anomalous low temperature post-desorption).

3. Results and discussion

In the VUV and near UV ranges luminescence spectrum of solid nitrogen consists of two molecular progressions: the $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ (system of Ogawa-Tanaka-Wilkinson-Mulliken) and the Vegard-Kaplan bands $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ shown in Fig. 1. Positions of the vibrational bands of both progressions are in good agreement with those observed in the early studies of VUV luminescence of solid N_2 [26,27]. Both progressions stem from electronic

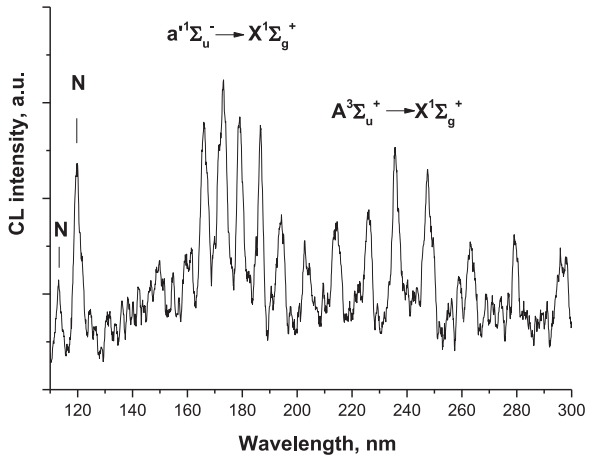

Fig. 1. CL spectrum of nitrogen film (500 nm thickness) recorded at 5 K during excitation by 0.5 keV electron beam.

excited states formed in the bulk as evident from their enhancement with increasing electron beam energy. Molecular series are red-shifted relative to the gas phase spectra. The matrix shift $\Delta = \gamma_{solid} - \gamma_{gas}$ (which is due to the interaction of the N_2^* with the surroundings) is $\Delta = -450\ cm^{-1}$ and $\Delta = -330\ cm^{-1}$ for the progressions $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ and $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$, accordingly.

In addition to the molecular bands we found atomic lines at 120 and 113.4 nm. The distinctive feature of these lines is the coincidence with the gas phase spectrum within the accuracy of our measurements. Spectral line at 120 nm belongs to the 3 s $^4P_{5/2\text{-}1/2} \rightarrow 2p^3\ ^4S_{3/2}$ transitions. Oscillator strengths for these transitions are 0.13, 0.09 and $4.4*10^{-2}$ for the component 5/2, 3/2 and 1/2 [28]. Weaker line at 113.4 nm stems from the transitions $2p^4\ ^4P_{1/2\text{–}5/2} \rightarrow 2p^3\ ^4S_{3/2}$ transitions. The width of lines in the CL spectrum is determined by the spectrometer resolution which does not allow to resolve the fine structure of these lines. The absence of matrix shift gives reason to believe that we observe the emission of N^* atoms which have left the sample surface. Note that these lines detected in Ne matrix doped with N_2 showed blue shift $\Delta_1 = 340\ cm^{-1}$ and $\Delta_2 = 700\ cm^{-1}$ (for the lines 120 nm and 113.4 nm accordingly) with respect to their positions in the gas phase [24].

Further proof of the assumption that the observed line belongs to the excited N^* atoms desorbing from the sample surface comes from probing the films with depth varying the electron beam energy. As an example, CL spectra taken during irradiation of nitrogen films with 0.5 keV and 1.5 keV electrons are shown in Fig. 2.

It is obvious from these spectra that the intensity of atomic

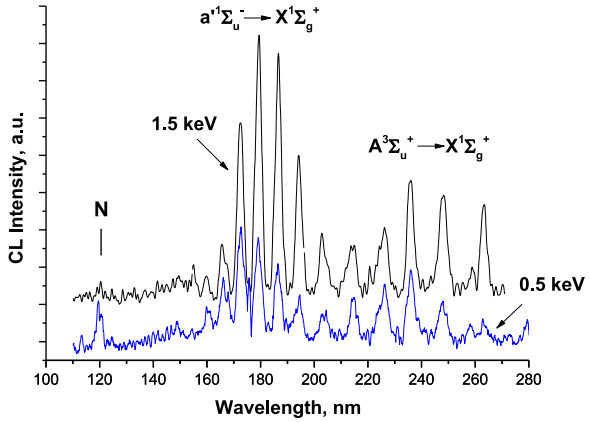

Fig. 2. CL spectra of N_2 films recorded during excitation by electrons of 0.5 keV and 1.5 keV energy. Films of 50 μm thickness were grown and irradiated at 5 K.