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Emission spectroscopy of solid nitrogen

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HIGHLIGHTS

- Radiation effects in solid N_2 were studied by optical and current emission spectroscopy.
- Cathodoluminescence and yields of TSL, NsL, PSL, TSEE, PSEE were measured.
- Analysis of products of the electron-ion recombination reactions was performed.
- New evidences of hole self-trapping with the cation N_4^+ formation were obtained.
- "Fingerprints" of N_3^- species were detected by the PSEE.

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ABSTRACT

Monitoring of the cathodoluminescence spectra temporal evolution and concurrent measurements of optical and current relaxation emissions revealed stabilization and accumulation of the radiation-induced charged species. New results in favor of hole self-trapping with the tetranitrogen cation N_4^+ formation are presented. "Fingerprints" of N_3^- species are detected by the photon-stimulated exoelectron emission.

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1. Introduction

Nitrogen solids known for their bright luminescence gained general recognition as model molecular crystals. Interest in the research of these solids is associated with the prospect of their application as high energy-density materials (Nguyen, 2003; Zarko, 2010), their use as moderators (Ghandi and Miyake, 2011) and as matrices in radiation chemistry (Grigoriev and Trakhtenberg, 1996). Investigations of nitrogen emission spectra were undertaken to ascertain the polar light nature (Kragh, 2010). These solids also attract much attention in astrophysical research because solid nitrogen and nitrogen-containing "ices" are present in cosmic space (Clark et al., 2012). In all these fields of science radiation effects, energy storage, transformation and its release are the focus of studies. Until ricently radiation effects in solid N_2 were studied and discussed mostly in terms of neutral electronic excitations. The formation of N radicals in solid nitrogen grown from discharge or irradiated with an electron beam was detected in the first studies related to clearing up elements involved in polar light (Vegard, 1924; McLennan and Shrum, 1924). Later studies, e.g. (Bass and Broida, 1956; Oehler et al., 1977) revealed an interaction of N radicals with the surroundings. The laboratory studies of asrophysical "ices" detected the azid radical N_3 in solid nitrogen pre-irradiated by protons (Hudson and Moore, 2002), electrons (Jamieson and Kaiser, 2007) and synchrotron radiation (Wu et al., 2012).

Despite a long history of solid N_2 spectroscopy the problem of charged (ionic) species generation, stability and their reactions is only beginning to be studied. The method of activation

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spectroscopy – thermally stimulated luminescence TSL was applied to solid nitrogen by Brocklehurst and Pimentel (1962). The total yield of TSL from solid nitrogen subjected to electron beam was interpreted as a recombination of neutral N atoms, in other words, as chemiluminescence. TSL spectra in the range of atomic transition $^2D \rightarrow {}^4S$ were registered by Faure et al. (1979). However, production of TSL via charge recombination reactions was not considered. It is worth noting that numerous studies (e.g. Bernard et al., 2004; Boltnev et al., 2005, 2015) of nitrogen enriched impurity-helium condensates (IHCs) grown by injection of a helium gas jet containing admixtures into superfluid helium – the technique first developed by Gordon et al. (1974) – were focused on N radicals. However, more recent studies of TSL from IHCs with nitrogen impurity revealed accumulation of charged species (Boltnev et al., 2013; Krushinskaya et al., 2015; Pelmenev et al., 2015). The formation of $^{14}N_4^+$ and $^{15}N_4^+$ cations in Ne matrices grown from discharge was registered in IR absorption by Thompson and Jacox (1990). The cation radicals $^{14}N_4^+$ and $^{15}N_4^+$ were generated in Ne matrices under photoionization conditions and detected by ESR technique by Knight et al. (1987).

The first indication of charged centers stability in pre-irradiated solid N_2 was the detection of strong thermally stimulated exoelectron emission (TSEE) (Khyzhniy et al., 2010). Further studies of infrared and ultraviolet absorption spectra of electron-bombarded solid nitrogen disclosed the formation of ionic centers N_3^+ (Wu et al., 2013). The transformation of a set of ionic centers when going from matrix-isolated N_2 to the crystal was studied in (Savchenko et al., 2015a). "Fingerprints" of N_4^+ centers, in other words self-trapped holes, were found by analyzing the spectrally resolved TSL, nonstationary luminescence (NsL) and TSEE from solid nitrogen exposed to an electron beam. Note, that the self-trapping effects in organic molecular crystals were discussed by Song and Williams (1996). However, in such simple molecular crystals as nitrogen, to our best knowledge, these effects have remained insufficiently explored.

Here we report an extension of study of ionic centers formation in solid nitrogen. In order to generate charged species, low-energy electrons were used because of their high ionization cross-section (Elango, 1991). In view of the need to combine optical and current methods of activation spectroscopy to bring out the part of the charge centers (Savchenko and Bondybey, 2005), measurements of thermally and photon-stimulated emissions of photons and electrons from pre-irradiated samples were performed. Because of the high sensitivity of these emissions to a sample structure and to impurity concentration, the yields of electron emissions and spectrally resolved photon emissions were monitored simultaneously on the same sample in a manner similar to that suggested first in (Ponomaryov et al., 2007).

2. Experiment

The experimental technique has previously been described in more detail (Savchenko and Dmitriev, 2010, Sec.7 by Savchenko in Allodi et al., 2013), so only essential points are mentioned here. High-purity N_2 (99.995%) was used to grow films of uniform thickness (~100 μm) by deposition from the gas phase on a metal substrate mounted in a high-vacuum chamber with a base pressure of 10^{-8} mbar. An open sample 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 was kept typically at 5 K during sample deposition. The film thicknesses and the deposition rates were determined by measuring the pressure decrease in a known volume of the N_2 reservoir in the gas-handling system. After their preparation the films were irradiated with an electron beam of subthreshold energy ($E_e < E_{thr} = 1$ keV). The current density could be adjusted between 30 μAcm^{-2} and 7 mAcm^{-2}. The sample heating under beam did not exceed 0.7 K.

The luminescence spectra were recorded repeatedly on an exposure time to monitor the dose dependence of excited species formation and accumulation. Upon completion of the irradiation, the N_2 films exhibited the well-known long afterglow at the wavelength of the forbidden atomic transition $^2D \rightarrow {}^4S$ (Lofthus and Krupenie, 1977). Coincidentally 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, the thermally stimulated relaxation emissions of photons (TSL) and electrons (TSEE) were measured upon heating. Besides the total yield, spectrally resolved TSL and photon-stimulated luminescence (PSL) yields were measured. TSEE and photon-stimulated exoelectron emission (PSEE) currents were detected with an electrode kept at a positive potential +9 V and connected to a current amplifier. The substrate was kept at ground electric potential. The substrate temperature measured by a Si diode and heating mode can be set as needed by means of a program specifically designed for this purpose. In the present experiments a linear heating at a constant rate of 3.2 Kmin^{-1} was used. In order to reveal more clearly TSL band at higher temperatures, the "cleaning curve" technique was applied – irradiation at 22 K. The measurements of thermally stimulated relaxation emissions were carried out in the temperature range 4.5–40 K. PSL and PSEE yields were detected at 5 K.

In addition we used the approach, developed by our group, to probe charged centers – non-stationary luminescence (NsL). This two-stage technique is to some extent a combination of cathodoluminescence (CL) and of spectrally resolved TSL. The charged centers are first generated by an intense electron beam. The ionic species produced are then probed by the NsL which is induced by a low-density electron beam under gradual heating. As this takes place electrons released from the increasingly deeper traps recombine with positively charged species contributing to the NsL spectra. This contribution to the NsL spectrum results in non-monotonic temperature dependence of the spectrum intensity, which is defined by the trap levels structure.

For measurements of spectrally resolved PSL yield, we used the LED which emitted photons of 2.76 eV. While N_2 samples are transparent in visible and infrared range, their heating under a photon beam can only be caused by heat transfer from the substrate. The sample heating monitored during registration of photon-stimulated emissions did not exceed 0.4 K.

3. Results and discussion

In solid nitrogen, which has a wide band gap (15.6 eV), electrons are highly mobile in the range of α-phase existence, as was demonstrated by (V.G. Storchak et al., 2001), and their trapping by defect sites or species with positive electron affinity produces negatively charged centers. Fig. 1 shows thermally stimulated yields of electrons from an unannealed nitrogen film and from the film annealed at 30 K.

In the low-temperature range wide a multipeak band of TSEE was observed for the unannealed sample. The strong difference of the low-temperature band intensity for annealed and unannealed samples indicates that the band belongs to defects of growth. However their detailed identification requires further studies. At higher temperatures we observed a strong peak of nonelementary structure in the range of α-β phase transition at 35.6 K discussed by (Khyzhniy et al., 2010). After the phase transition the yield of TSEE decreases because of electron scattering in orientationally disordered β-N_2.

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