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Relaxation processes in solid methane pre-irradiated with an electron beam

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ABSTRACT

The relaxation processes in CH_4 solids irradiated by an electron beam were studied with a focus on post-irradiation phenomena. Because of absence of thermally stimulated luminescence (TSL) from pure solid methane we applied current activation spectroscopy method – thermally stimulated exoelectron emission (TSEE). Two broad features were detected near 18 and 43 K. Their relative intensity appeared to depend on irradiation time. The experiments performed with a variable voltage applied to an electrode for current detection first revealed significant accumulation of uncompensated negative charge in pre-irradiated methane films. The TSEE current was detected at negative voltages up to −35 V. Concurrently with thermally stimulated yield of electrons the total yield of thermally stimulated post-desorption (TSpD) from pre-irradiated solid methane film was detected. Correlation of TSEE and TSpD yields is discussed and compared with the temperature behavior of solid methane subjected to a neutron flux.

1. Introduction

Solid methane is one of the best cold moderators with approximately 3.5 times the efficiency of the commonly used liquid hydrogen based moderator [1]. In view of this solid CH_4 is widely used material for moderating hot neutrons to cold and ultra-cold ones. Solid methane moderators are in operation at the Argonne National Laboratory (IPNS-facility) [1,2], at the Rutherford Appleton Laboratory (ISIS-facility) [3,4], at the Indiana University (LENS-facility) [5], at the pulsed reactor IBR-2 (Joint Institute for Nuclear Research) [6], at the Tsinghua University (CPHS-facility) [7] and other neutron centers operating with cold neutron sources (e.g. [8]). Despite the attractive neutronic properties of solid methane its using in cryogenic moderators faces a problem caused by large spontaneous releases of energy. The moderator material stores a part of energy absorbed from radiation in view of frozen-in products of radiolysis. At high density of reactive species their recombination and the expansion of hydrogen, which builds up in the solid methane during irradiation by neutrons [2] result in fast energy release which destroys a moderator container. This phenomenon known as "burp" effect significantly constrains the current use of solid CH_4 moderators. In view of pressing character of this problem solid methane exposed to neutron radiation was thoroughly studied (e.g. see [1,2,6] and references therein). A review of the main characteristics of cold neutron moderator, including solid methane, was presented in [9]. The results of these explorations have confirmed the relevance of Carpenter's model, however experiments demonstrated that this phenomenon is still understood incompletely. So, according the model prediction all recombination processes should be completed at temperatures below 40 K [1,2,6]. The very first test of the solid CH_4 moderator at the Target Station 2 (TS2 at ISIS), operated at 38 K, ended because of a burp-like effect which damaged the moderator [10].

Another aspect of the keen interest to radiation effects in solid methane is caused by presence of methane and methane-containing "ices" in cosmic space [11–15]. Comets spend a considerable amount of time in the low temperature environment of the Kuiper Belt and the Oort-Opik cloud, being subjected to the continuous radiation of outer space. In these conditions solid methane might accumulate a substantial number of radiation defects, which in turn could lead to spontaneous self-accelerated heating triggering the eruption of a cryo-volcano [3]. Relationship of methane studies to prebiotic chemistry was discussed in [16].

All these fields of science and applications require an understanding of radiation effects and radiation-induced processes. Radiation-induced chemical modification of solid CH_4 has been studied extensively especially dissociation mediated chemistry [1,2,6,17–24]. Note that the role of charge states in the relaxation processes in solid CH_4 remained poorly studied in contrast to the gas phase study ([25,26] and references therein). Different channels of ionization and dissociation at electron degradation in CH_4 gas were modelled by the Monte Carlo simulations [25] and the cross section data were compiled from the

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literature for electron collisions with CH_4 molecules [26]. As it was pointed out in [27] above about 50 eV production of ionic fragments is also possible with appearance of CH_4^+, CH_3^+, CH_2^+. Neutralization of CH_4^+ results in the emergence of CH_4^* which will dissociate through the shown below main channels [26]:

$CH_4 \rightarrow CH_3 + H$

$CH_4 \rightarrow CH_2 + H_2$

$CH_4 \rightarrow CH_2 + 2H$

$CH_4 \rightarrow CH + H + H_2$

The experiments performed at the heavy ion storage ring CRYRING with gaseous methane provided information on branching ratios for the reaction products [28] and yet it should be taken into account that branching ratios for solid CH_4 radiolysis products differ from those in the gas phase [29]. Effects of energetic electrons on low-temperature phase II of pure methane ices were studied at 10 K using FTIR and mass-spectroscopy techniques [30]. The study revealed CH_x (x = 1–4) and C_2H_x (x = 2–6) species with main contribution from a methyl radical CH_3 and a hydrogen atom H. It should be particularly emphasized that activation spectroscopy techniques useful for the investigation of radiation damage were almost not used to study radiation effects in solid methane. To our best knowledge only thermally stimulated luminescence (TSL) from solid methane doped with benzene and toluene pre-irradiated with UV light was studied [31]. Considering the absence of TSL from pure solid methane and being motivated to clear up the role of charged species in relaxation of irradiated CH_4 films we applied current activation spectroscopy method – thermally stimulated exoelectron emission.

The work presents our first results on thermally stimulated relaxation processes in an electron bombarded solid methane. Choice of electrons for excitation is dictated by the fact that they are common secondary particles at any kind of ionizing radiation. Taking into account an interest to the "burp" phenomenon with fast temperature excursions of solid methane subjected to a neutron flux we focused on study of thermally stimulated relaxation emissions of neutral particles and electrons from pre-irradiated at low temperature (5 K) methane films. Combination of current spectroscopy method TSEE with correlated in real time detection of the total yield of TSpD was used. Two features were observed in TSEE and TSpD yields indicating two stages of recombination process similar to the situation in cold methane moderators subjected to a neutron flux. The accumulation of significant uncompensated negative charge in pre-irradiated with an electron beam methane films was first detected.

2. Experimental

2.1. Sample preparation and treatment with an electron beam

The developed experimental technique for a study of radiation effects in cryogenic ices has previously been described in and Section 7 of [32] therefore only essential details related to the present study are given here. Films of methane ices were grown by deposition of a certain amount of gas onto a cooled Cu substrate at 5 K mounted in a high-vacuum chamber with a base pressure of 10^{-8} mbar. We used CH_4 gas (99.97%) without further purification. The gas-handling system and vacuum chamber were degassed before each experiment. The samples of 25 and 100 µm thicknesses were grown. Temperature was monitored with a Si sensor during entire experiment. The irradiation was performed in dc regime at 5 K. The electron beam energy E_e was set to 1 keV with the current density of 1 mAcm^{-2}. The beam covered an icy sample with an area of 1 cm^2. The sample heating under electron beam did not exceed 0.5 K. The radiation dose was varied by an exposure time. An open surface of films allows the use of current activation technique, based on exoelectron emission – TSEE, and monitoring the desorption total yield by pressure P measurement both during irradiation and during subsequent heating.

2.2. Detection of relaxation emissions of electrons and particles

Because of high mobility of electrons in solid methane [33] monitoring of the TSEE provides the information on relaxation processes not only near the surface, but also in the bulk of the sample. Measurements of stimulated relaxation emissions of electrons (TSEE) and particles (TSpD) from solid CH_4 were started when the "afteremission" current had decayed to essentially zero. Special program enables us to perform measurements of TSEE and TSpD in a correlated manner. Relaxation processes were stimulated by heating with a constant rate of 5 Kmin^{-1}. Measurements were performed in the temperature range of solid methane existing (5–90 K). Being promoted to the conduction band by heating detrapped electrons either neutralize positively charged species 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. A special series of experiments was performed at a variable voltage (from +9 V up to −35 V) applied to the detecting electrode to probe a space charge accumulation in solid CH_4 films under the electron beam. Pressure gauge mounted in the sample chamber was used to monitor the total yield of desorbing particles (TSpD). For the comparison purpose the total yield of particles from unirradiated sample during its heating, so-called temperature programmed desorption (TPD), also was detected. The entire control of the experiment and the simultaneous acquisition of the TSEE yield, of the vacuum chamber pressure, as well as temperature control and recording were accomplished with the help of a computer program written for these experiments.

3. Results and discussion

After irradiation we observed decaying exponentially afteremission of electrons which is the first indication of methane films electrostatic charging. Note that excess electrons mobility in solid methane is comparable with that of electrons in solid Ar [33] what makes current methods beneficial for radiation effects study. When the afteremission current decayed to essentially zero, the sample heating was switched on. First of all we tested the effect of exposure duration on the TSEE yield.

Fig. 1 shows the TSEE yield from pre-irradiated solid CH_4 films at short exposure (10 min) and long exposure (30 min). For clarity first maxima of the TSEE yield are adjusted in intensity. The first peak is observed at about 18 K. In fact the first TSEE peak with FWHM of about

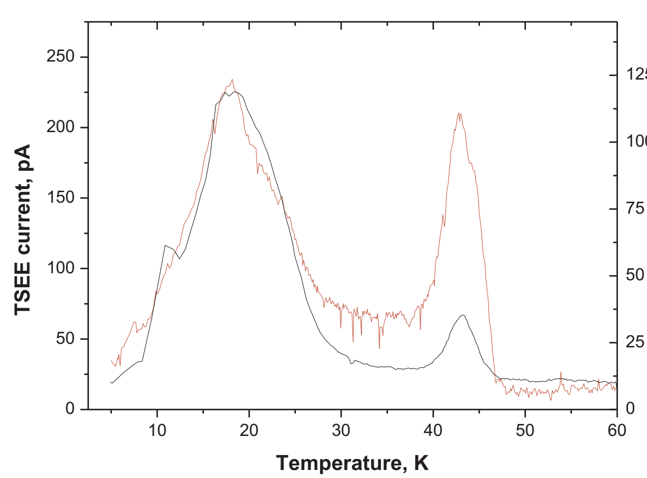

Fig. 1. Yields of TSEE current at 10 min exposure (black, right scale) and 30 min exposure (red, left scale). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)