

Photo- and Thermally Stimulated Relaxation Processes in Pre-irradiated Atomic Solids

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Abstract

Atomic and electronic relaxation processes in pre-irradiated atomic solids are considered using as an example solid Ar preliminary irradiated by an electron beam. The results of real time-correlated study are presented for the first time with an accent on found recently anomalous low temperature sputtering of Ar atoms from the surface. The experiments were performed using a set of activation spectroscopy methods – thermally stimulated exoelectron emission (TSEE,) thermally stimulated luminescence (TSL) in combination with measurements of the sputtering yield. Solid evidence of thermally induced charge recombination mechanism is obtained. Mechanism of energy transfer based on the crowdion model is discussed. Photo-stimulated sputtering from pre-irradiated Rare Gas Solids (RGS) is predicted.

Key words: atomic solids, relaxation processes, sputtering, activation spectroscopy.

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1. Introduction

Radiation effects in solids have been the object of much concentrated attention in current research spread over a variety of materials. A change of their physical and chemical properties induced by ionizing radiation attracts particular interest in view of its fundamental and technological importance. The electronic excitations in irradiated insulators initiate a sequence of elementary relaxation processes involving both atomic and electronic subsystems. The knowledge of the relaxation channels and paths in preirradiated solids is a basic issue for understanding of radiation effects, dynamics of carriers and is of high interest in surface science. Despite the extensive study of relaxation processes in different classes of materials (Elango, 1991; Song and Williams, 1996; Itoh and Stoneham, 2001; Luschik and Luschik, 1989) a considerable gap still exists in understanding of elementary steps, pathways and cross connection of these processes.

Rare gas (Rg) atoms at low temperatures form the simplest weakly bound atomic solids, which are easily modeled theoretically and this makes them especially well suited for investigation of a variety of processes common to condensed media in general. The problem of interest is the topical problem of cross connection between atomic and electronic processes. Due to combination of weak van der Waals interatomic forces with a strong electron-lattice interaction Rare-gas solids (RGS) offer the best opportunity to get new insight into the problem. Such phenomena as electronically induced lattice defect formation (Song and Williams, 1996; Savchenko et al, 1994, 1998, 2005a; Fu and Song, 1997) and related surface phenomenon – electronically induced sputtering of the lattice atoms (Song and Williams, 1996; Johnson and Schou, 1993; Zimmerer, 1994, 1998; Hudel et al., 1991; Belov et al., 2000; Bass et al., 1999; Grigorashchenko et al., 1997; Dujardin et al., 1998; Savchenko et al., 1997; Arakawa et al. 2003 and References

therein), so-called desorption induced by electronic transitions (DIET), were found in RGS. Several mechanisms were suggested to explain the DIET from these atomic solids. The main mechanisms are as follows: (i) a “cavity ejection” mechanism and (ii) an “excimer dissociation” mechanism. The “cavity ejection” mechanism (Zimmerer, 1994) was found in RGS with negative electron affinity E_a – in solid Ne and Ar (Song and Williams, 1996), where repulsive forces between electron cloud of excited atom or molecule (self-trapped excitons) and ground state neighboring atoms prevail. The “excimer dissociation” mechanism (Johnson and Schou, 1993; Zimmerer, 1994) involves the radiative electronic transition of excited molecular dimer Rg_2^* to a repulsive part of the ground state potential curve that results in appearance of “hot” atoms. If the events occur near the surface one can expect the sputtering. This phenomenon was observed under irradiation by slow and fast electrons, ions as well as vacuum ultraviolet (VUV) radiation.

In our experiments on radiation effects in RGS (Savchenko et al., 2002, 2003) we revealed anomalous enhanced sputtering of own atoms from the surface of Ar pre-irradiated by an electron beam. The sputtering characterized by nonmonotonous behavior was detected at temperatures much lower than the sublimation temperature T_{sb} . A comparison with the sputtering from nonirradiated sample clearly demonstrated that the phenomenon is related to radiation effect. It was suggested that the basic process responsible for the found enhanced sputtering is charge recombination reaction followed by Rg excimer formation accompanied by its radiative decay. This paper reports the results of experiments on sputtering of Ar atoms from the surface of preliminary irradiated by an electron beam solid Ar. Activation spectroscopy methods – thermally stimulated exoelectron emission (TSEE) and thermally stimulated luminescence (TSL) were used in combination with measurements of the sputtering yield. Because both TSL and TSEE are

quite sensitive to the sample structure and concentration of guest centers there is clear need to make synchronous measurements of TSL, TSEE and sputtering yield at the same sample. We present for the first time the results of real time correlation study of atomic and electronic relaxation processes with an accent on the found recently (Savchenko et al., 2002, 2003) new relaxation channel – low-temperature sputtering from pre-irradiated atomic solids.

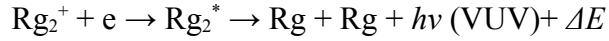
2. Experimental section

We developed a new low-temperature modification of activation spectroscopy technique – **real time-correlated study** of relaxation processes in cryogenic solids with simultaneous measurements of the TSEE, spectrally resolved TSL and the detection of total sputtering yield. The samples were grown from the gas phase by deposition on a coated with a thin layer of MgF₂ metal substrate cooled by a closed-cycle 2-stage Leybold RGD 580 cryostat. High-purity (99.999%) Ar gas was used. A base pressure in the vacuum chamber was 10⁻⁸ mbar. The samples were doped with small quantities of N₂ and O₂ (10⁻⁴). The deposition was performed with a concurrent irradiation by 120 eV electrons to generate charge centers throughout the layer. The current density was kept at 30 μAcm⁻². A typical deposition rate was 10⁻¹ μms⁻¹. We deposited Ar films of 50 – 100 μm thickness. The sample thickness and the deposition rate were determined by measuring the pressure decrease in a known volume in the gas-handling system. After sample preparation substrate was turned to the position for measurements. We measured yields of the thermally stimulated exoelectron emission (TSEE) from the samples, thermally stimulated luminescence (TSL) and total sputtering yield. The exoelectron yield was measured with an Au-coated Faraday plate kept at a small positive potential +9 V and connected to the current amplifier FEMTO DLPCA 100. A centrally located

hole in the Faraday plate permitted to detect spectra from the sample through an optical window. Spectra were recorded by a spectrometer (Multichannel S2000 Spectrometer Ocean Optics based on CCD detectors) operating in the range 170 – 1100 nm with the resolution not worse than 1.3 nm in ms time window. This spectrometer allows monitoring the temporal evolution of the spectra in the operating range. The sputtering yield was detected by measuring the pressure change in the chamber using Compac Full Range BA Pressure Gauge PBR 260. The temperature was measured with a calibrated silicon diode sensor, mounted at the substrate. The relaxation processes in Ar samples were studied in the temperature range from 7 to 42 K. The programmable temperature controller LTC 60 allowed us to maintain the desired temperature of deposition, irradiation and heating regimes. In the study presented we used step-wise heating of the samples with a step of 2 K and an interval between successive steps of 10 min. The program developed permitted to detect synchronously spectra over entire operating range, TSEE current, temperature and pressure in the chamber.

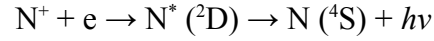
3. Results and discussion

Study of atomic and electronic relaxation processes in pre-irradiated solids offers some advantages over the study under irradiation. First of all a number of relaxation channels becomes considerably less than those during an exposure time. Primary states of relaxation cascades represent localized in the lattice metastable centers storing a part of the excitation energy. For pre-irradiated RGS they are self-trapped holes (STH) –dimer ionic centers, and electrons trapped at the lattice defects or “electron scavengers”, as well as metastable levels of guests and products of radiation-induced reactions. We suggested (Savchenko et al., 2002, 2003) that the thermally released and mobilized electrons recombine with the STH by the reaction



In the case under consideration energy stored by the charge carriers is released via radiative electronic transition of the recombination reaction product – e.g. “excimer” Ar_2^* – to the repulsive part of the ground state. The energy is released in the form of photon emission (the well-known M band 9.7 eV related to the $^1,3 \Sigma_u^+ \rightarrow ^1 \Sigma_g^+$ transition). The excess energy about 1 eV is distributed between the two Ar atoms producing “hot” ground state atoms in the lattice. Note, that this reaction was considered as a source of energy needed for the sputtering of atoms from the surface under irradiation already in earlier studies (Johnson and Schou, 1993). Thus one could expect to observe recombination-induced sputtering from pre-irradiated RGS.

Because the proposed scenario is based on a release of electrons from their traps the most straightforward way to test its validity is to perform measurements of the sputtering yield and relaxation processes induced by release of electrons e.g. – thermally stimulated current (TSC), or exoelectron emission (TSEE) and TSL from recombination reactions. We chose TSEE registered in solid Ar (Savchenko et al., 2001) and TSL. In our first observation the measurements were made by points and with the samples grown at similar conditions (Savchenko et al., 2002, 2003, 2005b). In order to make well-defined proof of the model the measurements should be made synchronously at the same sample as it was underlined. The results of correlated in real time measurements are presented below. The relevant set of curves is shown in Fig.1a. The upper curve represents pressure behaviour during the step-wise heating, the middle curve describes TSEE current and lower trace is a fingerprint of recombination luminescence. Here we present as an example TSL plotted at the wavelength of a guest N^* atom emission stemmed from the reaction:



Temperature as a function of time is depicted in part b of Fig.1. As it is seen each temperature step is followed by a sharp increase in the pressure, exoelectron current and TSL of N^* metastable atoms followed by an exponential decrease of TSEE and TSL curves down to the noise level before the next temperature step. The curves in temperature range between 20 and 30 K are shown in Fig.1c on an enlarged scale. The behaviour of this sort is characteristic for TSL measured by Isothermal-Decay method (Vij, 1998) at step-wise heating of irradiated solids and was observed in the experiments on radiation effects in solid Ne (Frankowski et al., 2004). The fact that the sputtering yield shows the same behaviour demonstrates the common intrinsic origin of these relaxation processes. All of them are initiated by the release of electrons from their traps to the conduction band followed by charge transport by highly mobile electrons to positively charged centers in the bulk and near the surface. Slightly different distribution of the intensities of the peaks by temperature can be explained if take into account that the recombination luminescence and exoelectron emission despite the common origin are competitive processes and the yield of the recombination induced sputtering depends on interplay between these relaxation paths.

The base line for pressure shows a tendency to increase in the range of temperatures close to T_{sb} . Following decrease of the base line is caused by evaporation of the sample. Additional feature observed as a shoulder in the temperature range 23-40 K is thought to be due to slow diffusion controlled processes in the lattice. Note, that at these temperatures guest atoms as N start to diffuse and form molecules by the neutral atom recombination. This reaction is followed by the emission of visible light called by chemiluminescence. This process was considered to be a source of the energy needed for

electron detrapping (Savchenko and Bondybey, 2005). So one can expect the sputtering from pre-irradiated RGS induced by photons. Decrease of N^* emission in parallel with an increase of N_2^* emission at these temperatures seems to support this assumption. But for the certain conclusion more detailed experiments with different dopants are required.

A question is raised as to mechanism of energy transfer to the surface. It was found in a molecular dynamics study of energy transfer in solid Ar (Cenian and Habriel, 2001) that the energy can be transferred over large distances about 10^2 lattice constants. After thermally induced recombination of the self-trapped holes followed by the radiative decay of the Ar_2^* the excess energy is transferred to the lattice atoms in the collision cascade. The kinetic energy is transmitted preferentially along the close-packed [110] direction. This process can be described in a crowdion model. It was found in (Natsik et al., 2001) that crowdions – nonlinear solitary waves of displacements arising in close-packed atomic rows – exist in atomic Ar cryocrystals with a FCC lattice. One can see from the analysis of crowdion parameters: the crowdion width $\lambda/b=2.76$ (b is the interatomic distance) and the crowdion effective mass $m=0.3$ (in units of the atomic mass) that the interaction of the distinguished atomic row with the matrix surrounding is relatively weak. The crowdion energy E_s is found to be quite large $E_s=0.3$ eV, however E_s is less than the energy ($E=0.5$ eV) transferred to the ground state Ar atoms at the radiative electronic transition of Ar_2^* to the ground state. An existence of crowdions explains how the recombination events occurring in the bulk can contribute to the sputtering of atoms from the surface.

4. Summary

We present for the first time the results of real time-correlated study of electronic and atomic relaxation in atomic solids with an accent on the found recently new relaxation channel in pre-irradiated solid Ar. Experiments were performed using a set of activation spectroscopy methods – thermally stimulated exoelectron emission (TSEE), thermally stimulated luminescence (TSL) in combination with measurements of the sputtering yields. Strong proof of the recombination mechanism of the anomalous sputtering is presented. It is shown that the stimulating factor for the low temperature sputtering from pre-irradiated solid Ar is thermally induced electron detrapping followed by the hole-electron recombination reaction. Possible models of the anomalous sputtering are discussed and the crowdion mechanism of the atom ejection from the surface is proposed. Photo-stimulated sputtering from pre-irradiated RGS is predicted.

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Figure captions:

Fig.1 (a) Measured simultaneously sputtering yield (pressure in the chamber) – curve 1, thermally stimulated exoelectron emission (curve 2) and TSL on the wavelength of ${}^2D \rightarrow {}^4S$ transition of N atom; (b) Temperature as a function of time; (c) some part of plot (a) presented on an enlarged scale.

Figures:

Fig. 1(a)

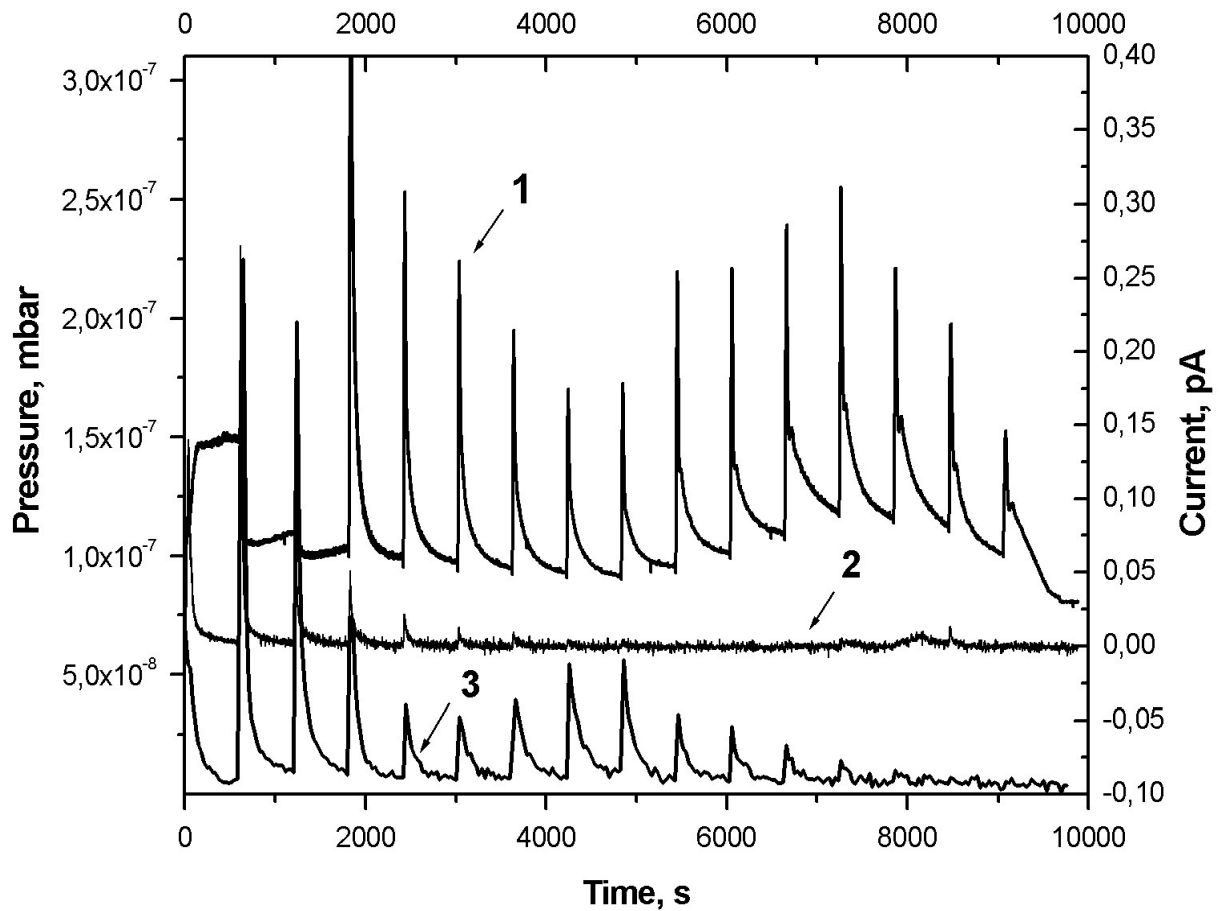


Fig. 1(b)

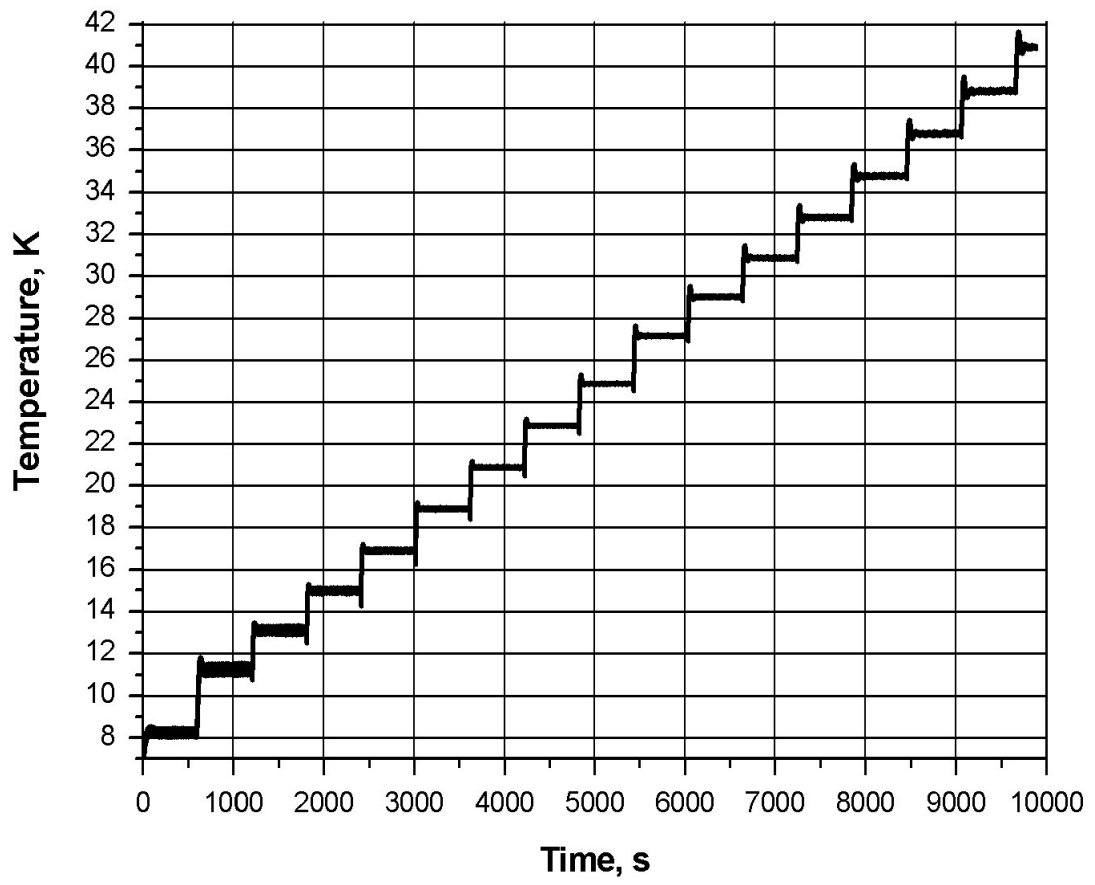


Fig. 1(c)

