ENR-MAT.01.UT 2023 Report

Investigation of defects and disorder in nonirradiated and irradiated Doped Diamond and Related Materials for fusion diagnostic applications (DDRM) – Theoretical and Experimental analysis

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Our **goal** is to combine experimental investigations of new functional materials used in diagnostics, heating and current drive applications in fusion reactors with large-scale theoretical calculations to provide an exhaustive understanding of material behaviour and predict the corresponding properties which are of high relevance for DEMO.

Combination of traditional techniques (optical absorption, IR spectroscopy, luminescence, EPR) with Raman and neutron scattering, determination of electrical/microwave properties via high frequency FABRY-PEROT-resonators and THz spectroscopy and electrical and thermal conductivity measurements in order to **monitor the development of the radiation damage** in doped diamond and related materials. Of great importance – determination of a specific role of impurities, which could improve/worsen radiation resistance.

***The main project tasks are divided between four Work Packages*:**

WP1. Advanced characterization of functional materials before and after irradiation

WP2. Investigation of electric, dielectric and mechanical properties of nonirradiated and irradiated materials

WP3. Theoretical modelling of the doping and radiation-induced effects

WP4. Material expertise for fusion applications (series of meetings)

Plans (Task specification) for 2023

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1. Literature review on radiation defect thermal annealing in selected materials ***Fully***
2. Comparative analysis of the thermal annealing of radiation damage via OA, EPR, TSL, RAMAN/IR of the selected samples irradiated at different fluences . ***Fully***
3. Computational modelling of the influence of radiation-induced disordering on the annealing kinetics of radiation defects in diamond ***Fully***
4. Detailed comparative analysis of dielectrical electrical, and EBCSD properties of selected materials irradiated with varying fluences ***Partly***
5. EBSD measurements of both diamond types and the interface passivation layers ***Fully***
6. First principles calculations of radiation defects in AlN and SiO
7. Comparative 2D mapping of the oversized irradiated samples by Raman, IR and CL ***Fully***
8. Modeling of radiation defect annealing in AlN and SiO.
9. Comparative inelastic and small angle neutron scattering of selected heavily irradiated samples at ILL ***Partly***

Tasks 2 and 7. Comparative analysis / 2D mapping … (UT, ISSP-UL)

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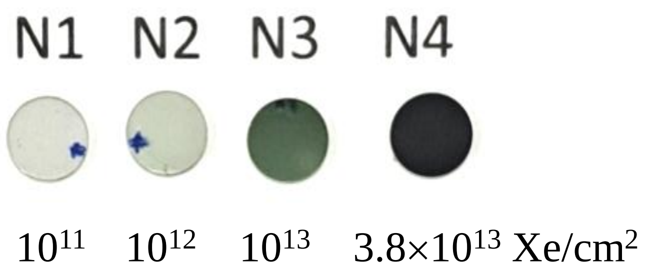
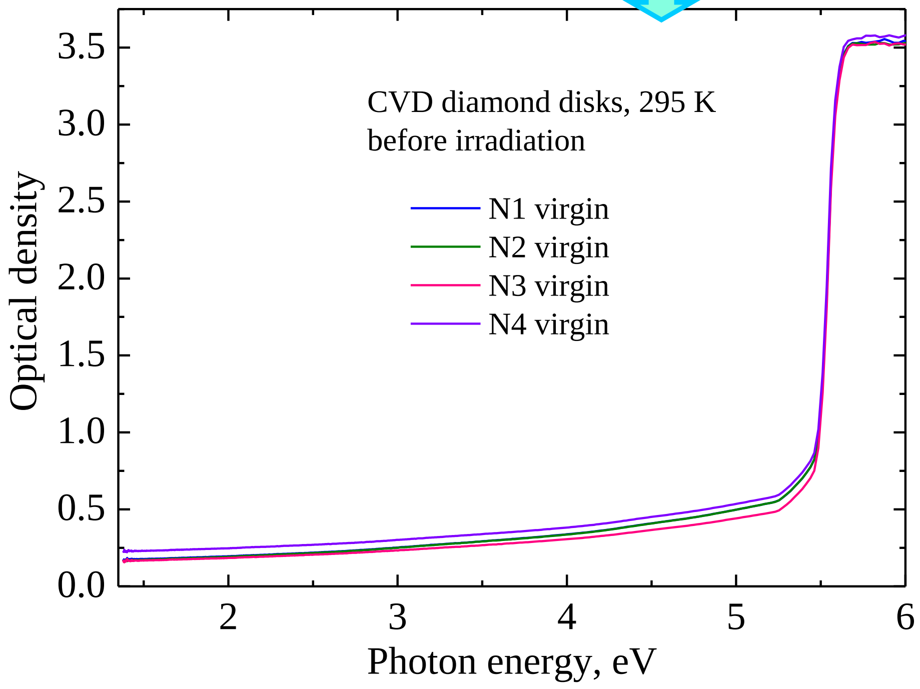
5-mm-diameter (0.4 mm thickness, *Diamond Materials, Freiburg*) novel disks of CVD diamond have been characterized via *optical absorption, CL, FTIR and Raman* methods **before and after** irradiation by 231-MeV ^{132}Xe ions at RT (Astana Kazakhstan) with 4 different fluences. According to SRIM, ion range R= 18.7 μm.



Absorption spectra for pristine and irradiated CVD diamond disks. RT, JASCO-V660 spectrophotometer.



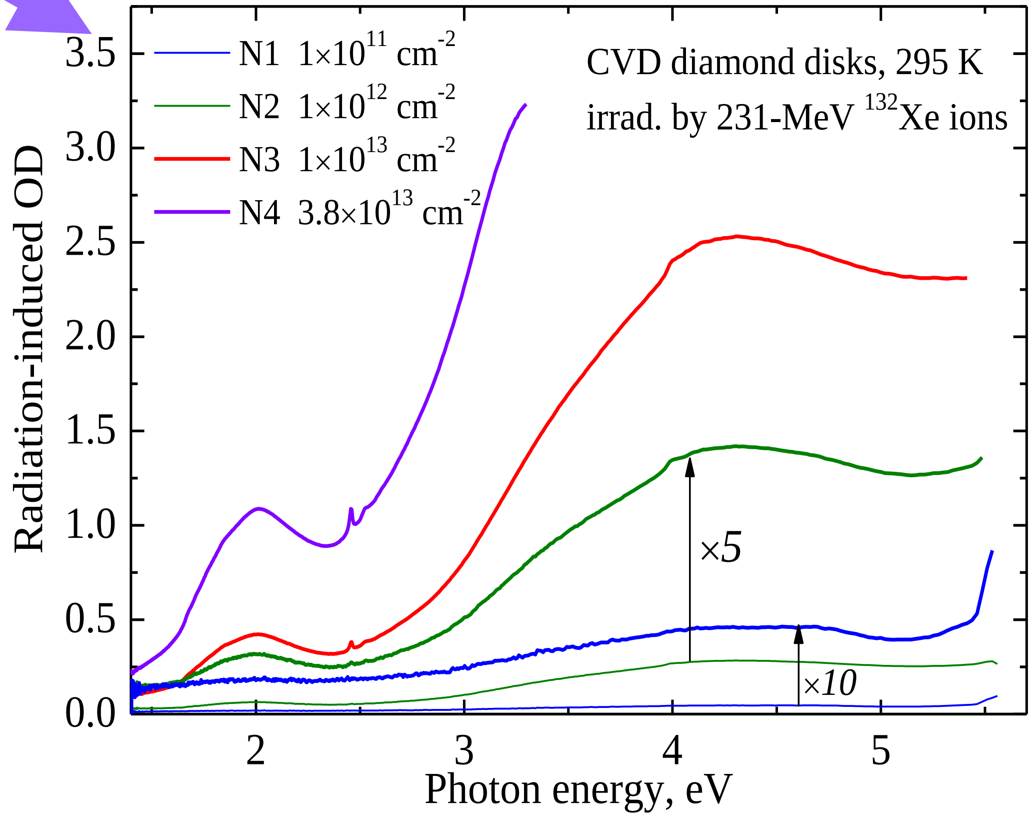


Fig. 1. RIOA spectra of CVD diamond disks (absorption of pristine sample is subtracted) exposed to 231-MeV xenon ions with different fluences. For best visualization low-fluence curves are multiplied by a certain factor.

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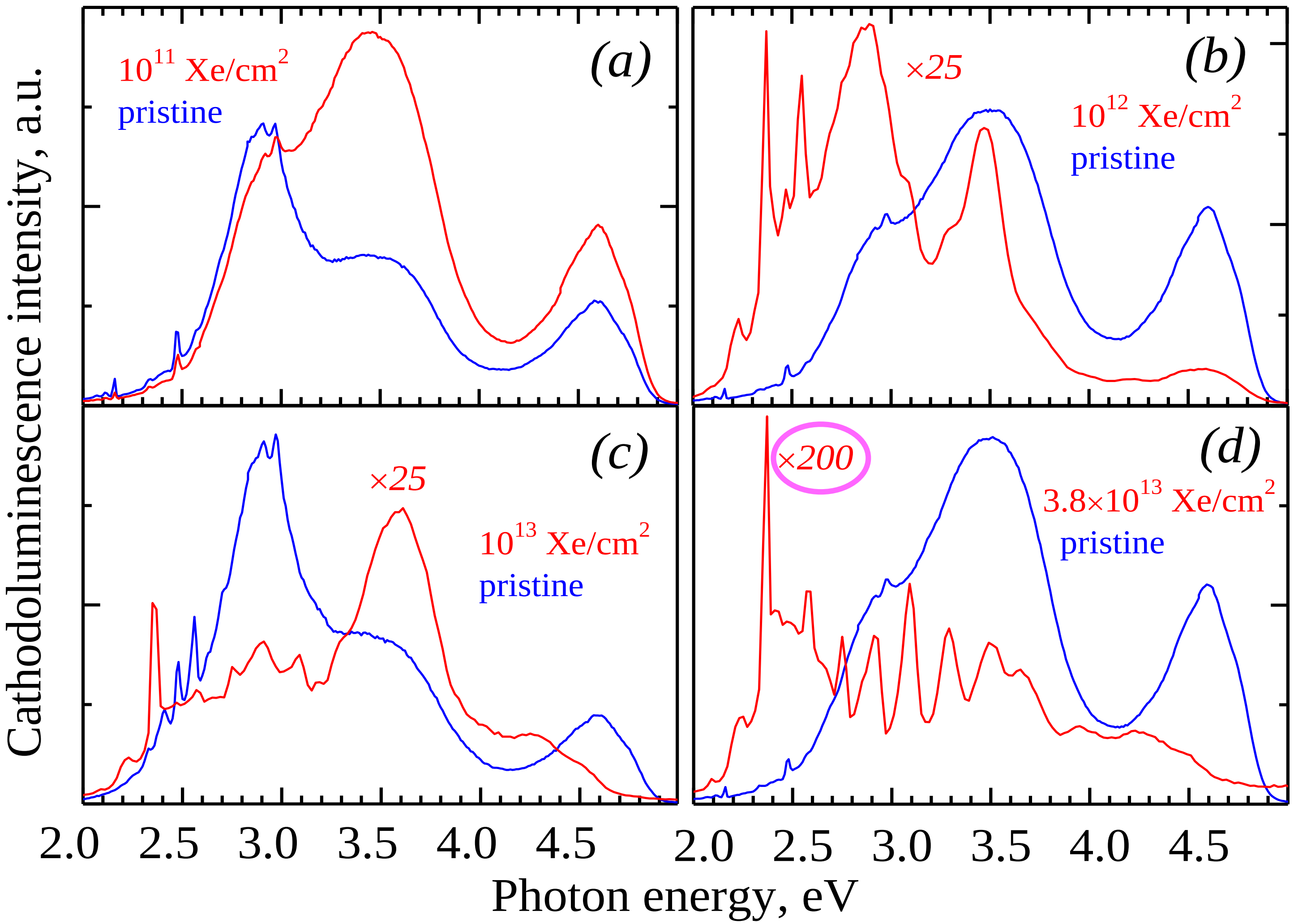
Cathodoluminescence for pristine/irradiated diamond discs.
Steady-state regime, 10-keV electron beam, 5 K



Again, new pristine samples do not demonstrated the heterogeneity estimated via CL. As a result, the analysis of CL spectra for Xe-irradiated discs did not allow to establish a clear fluence-effect relationship.

Fig. 2. Steady-state CL spectra measured at 5 K under 10-keV electron excitation of CVD diamond disks before (pristine, blue lines) and after expose to 231-MeV xenon ions with different fluences (red lines). Ordinates of some curves for irradiated samples are multiplied by a prescribed factor.

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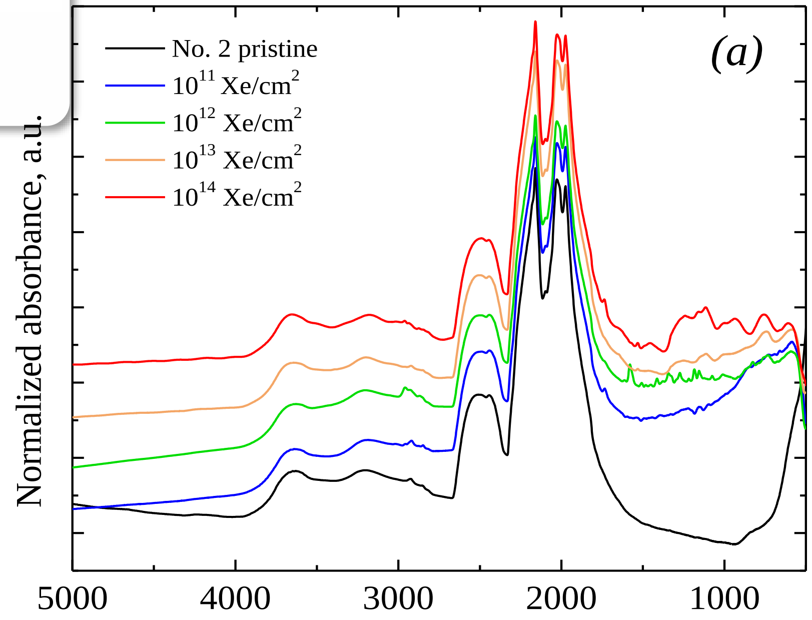
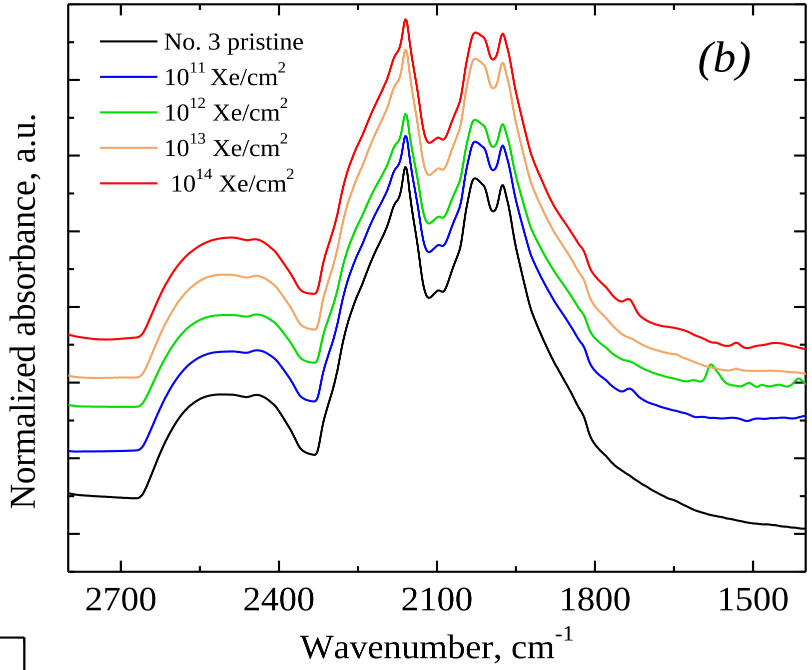
Tasks 2 and 7. Comparative analysis / 2D mapping … (UT, ISSP-UL)

… via FTIR





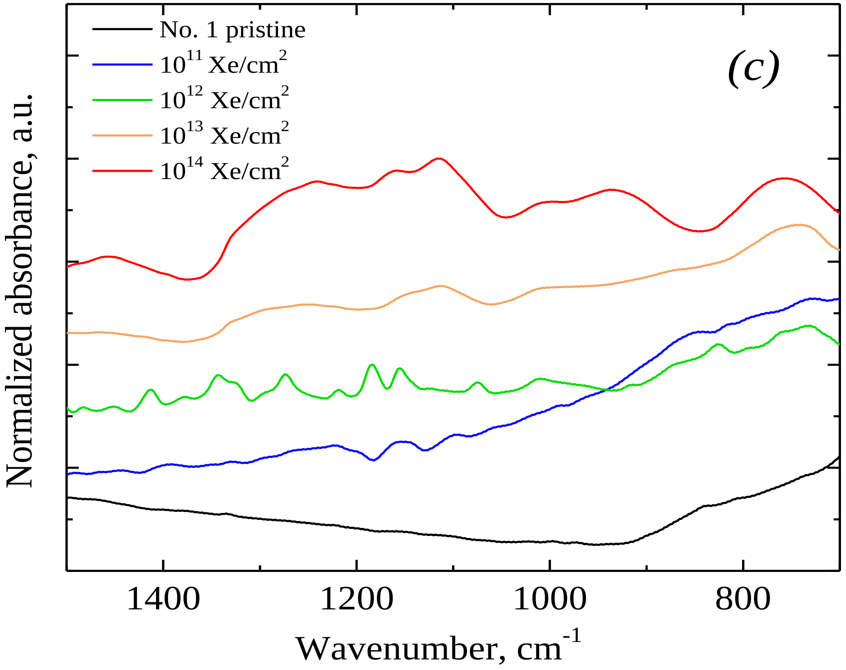
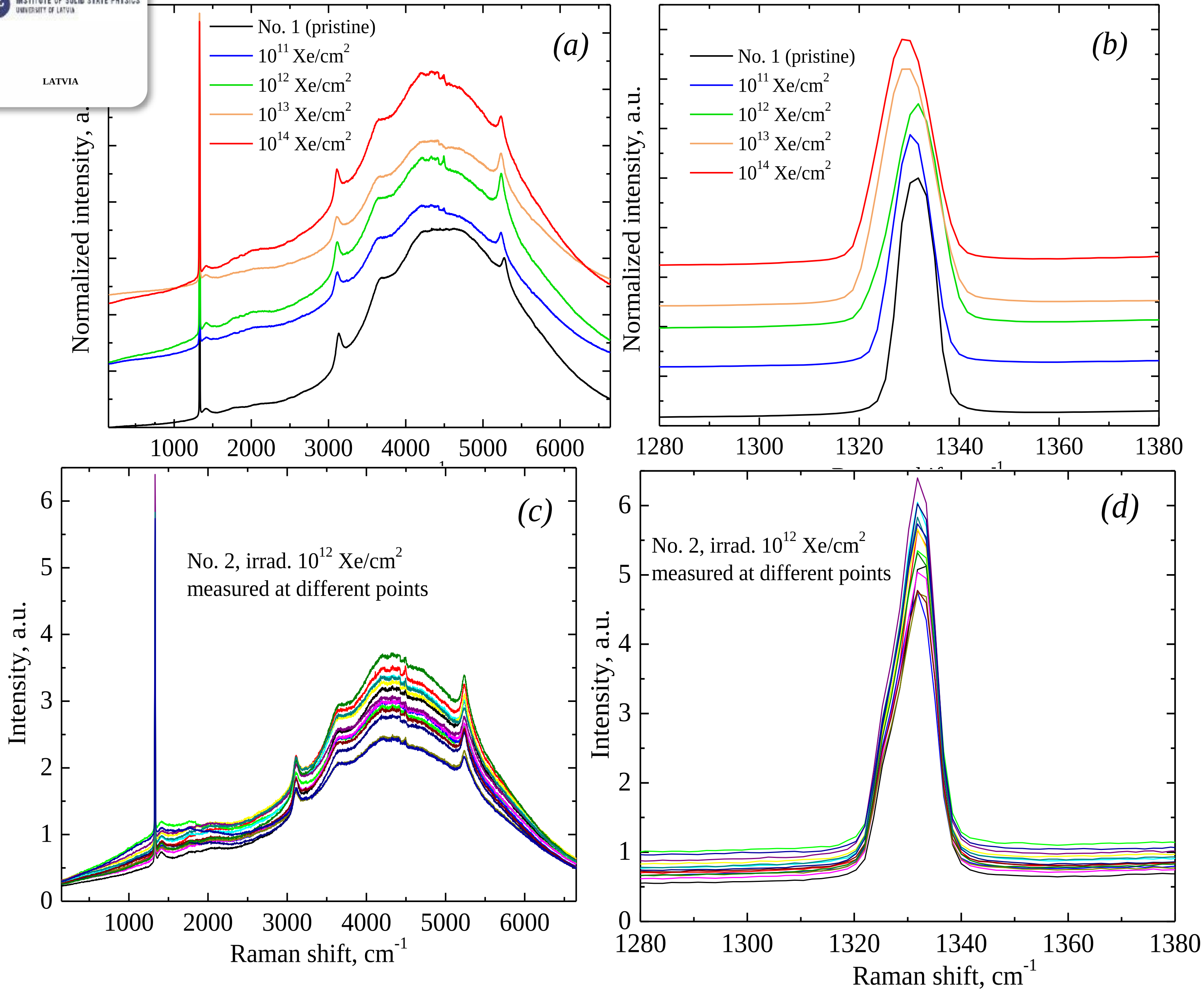


Fig. 3. FTIR absorbance spectra of CVD diamond disks before (pristine) and after expose to 231-MeV xenon ions with different fluence. The spectra are similar for all four disks under investigation (labelled by number in a relevant figure part).

3*b* - the characteristic C–C band at 2600-1600 cm^{-1} shows no significant alteration before and after Xe-irradiation of diamond.

3*c* - Irradiation → appearance of N defect bands 1700-500 cm^{-1}. This change likely relates to a modification in the state of N defects.

Tasks 2 and 7. Comparative analysis / 2D mapping … (UT, ISSP-UL)



… via Raman spectroscopy

Raman spectra contain a single mode at 1332 cm^{-1}. The bands related to nitrogen vacancies (NV^0 at 1400 and NV^- at at 3100 cm^{-1}) – no substantial changes for pristine and irradiated CVD disks.

The 1332-cm^{-1} modes (see part *b*) broadens, shifts to lower frequencies, and transforms to asymmetric with irradiation fluence – a local structural disorder induced in diamond by Xe-irradiation.

Parts *(c)* and *(d)* – 2D mapping

Fig. 4. Raman spectra of CVD diamond disks before and after expose to 231-MeV Xe ions with different fluence. The spectra are measured at 14 different spot positions of 525-nm laser excitation on disk No. 2 irradiated with 10^{12} Xe/cm^2 (*2D*-mapping – parts *(c)* and *(d)* for different spectral regions).

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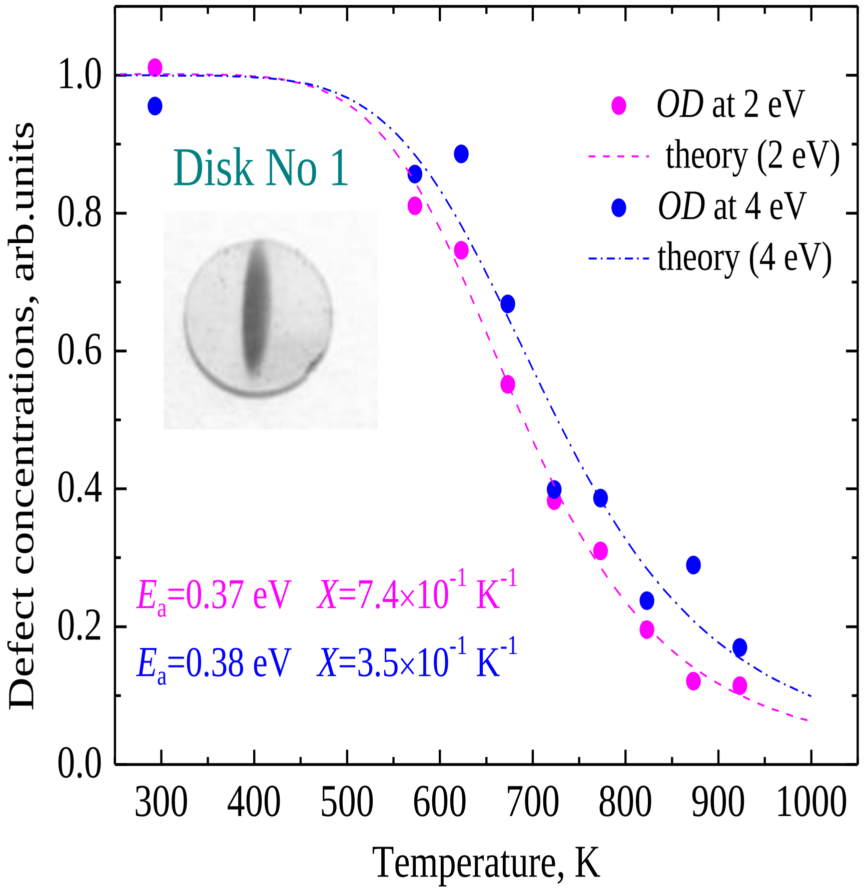
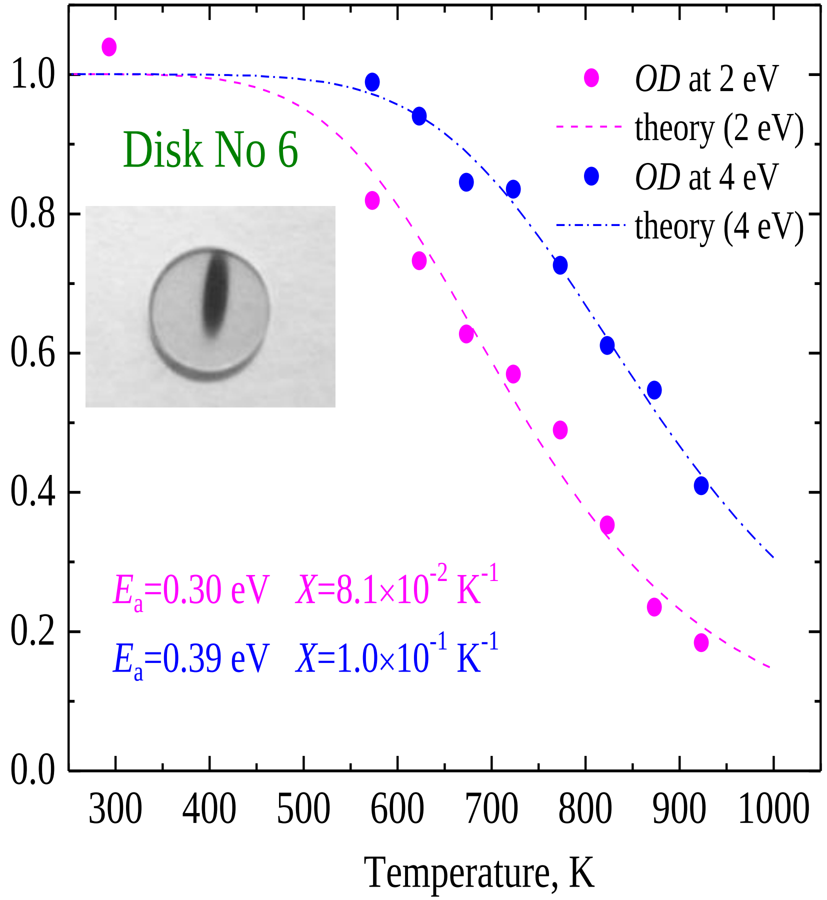
Task 3. … modelling defect annealing kinetics in diamonddefects in diamond (ISSP-UL)

Modelling of the annealing kinetics of oxygen vacancy-interstitial pairs (GR1 defect with RIOA at 2 eV and R11 at about 4 eV, respectively) in a previous set of irradiated CVD diamond (by 36-MeV ^{127}I ions within ERDA analysis).





The decay of both defects occurs with similar E_a thus confirming their complementary character. The E_a of interstitials are 0.3-0.4 eV and slightly depend on fluence.

Precise analysis of the defect annealing and possible validation of Mayer-Neldel rule for a set of Xe-ion-irradiated CVD diamonds is in progress.

Fig. 5. Defect annealing kinetics in irradiated diamonds. Symbols - experiment, dashed lines – theory.

Tasks 4. Detailed comparative analysis of … EBSD … irradiated with varying fluences (KIT)

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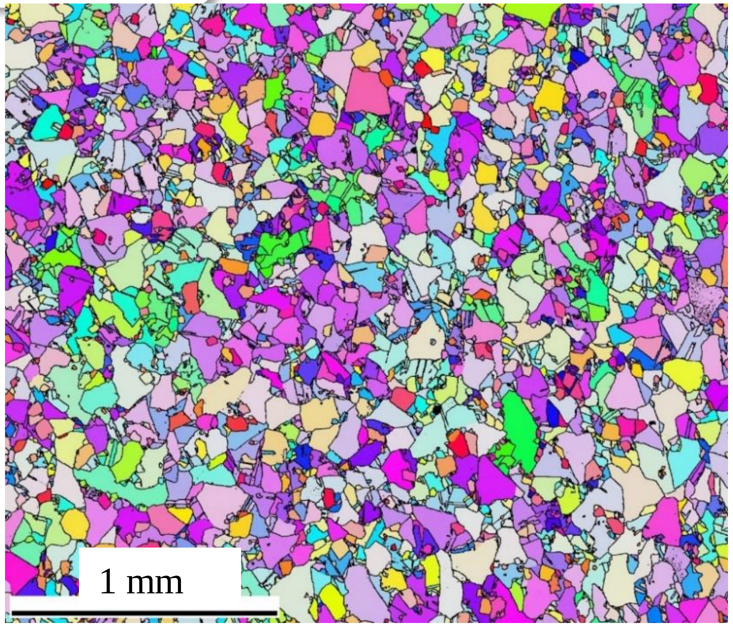
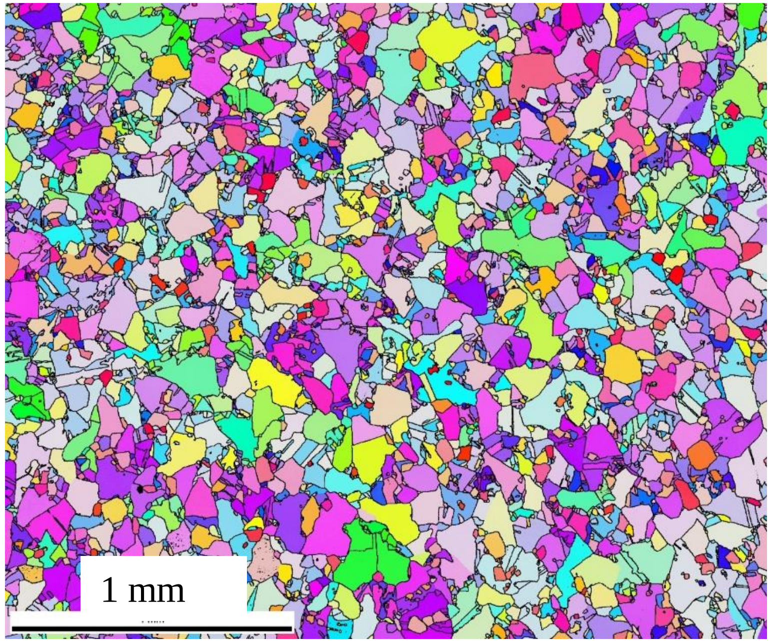
Electron backscatter diffraction (*EBSD*) – grain orientation in polycrystalline diamond

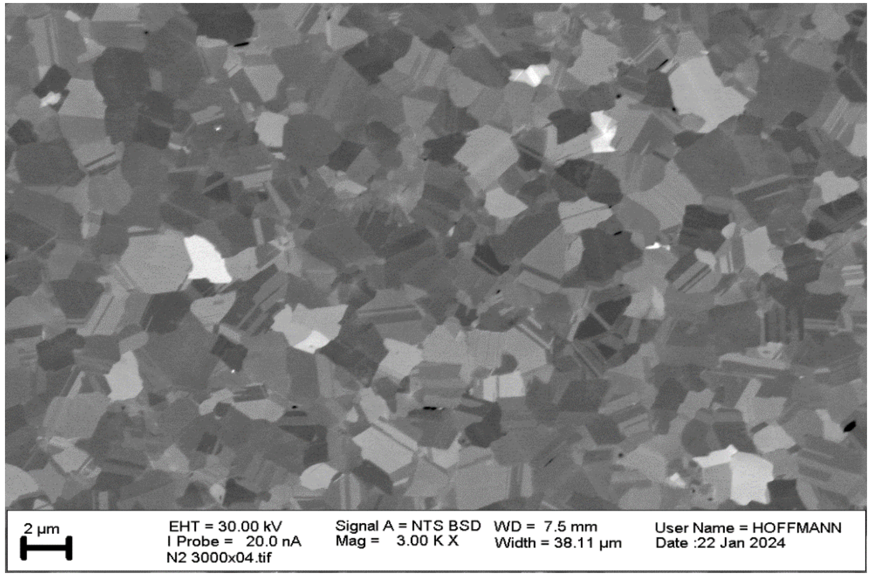


Color coded maps for Xe-irradiated CVD diamond discs (crystallographic directions parallel to the growth direction, irradiated side = growth side, black lines represent boundaries >15° misorientation).

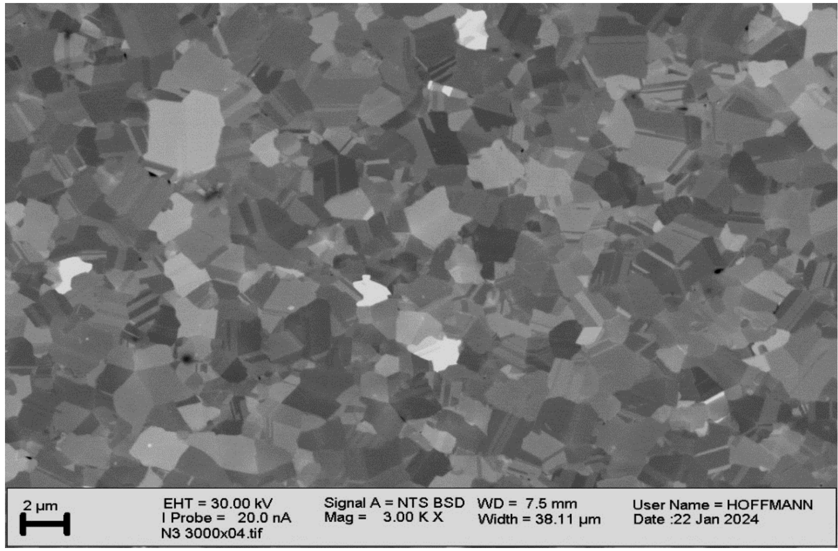
Sample N1, 10^{11} cm^{-2}, 6400 grains (center region)

Sample N4 3.8×10^{13} cm^{-2}, 5900 grains (center region)





Samples **N2** and **N3** were Xe-irradiated from nucleation site (NS), the grain size was too small to get an EBSD evaluation. Therefore, an electronic backscatter image was measured



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Tasks 4. Detailed comparative analysis of … EBSD … irradiated with varying fluences (*KIT*)

Electron backscatter diffraction (*EBSD*) – grain orientation in polycrystalline diamond

ID	irradiated side	Xe ion fluence /cm^{-2}	average grain size (>15°)by number /µm	average grain size (>15°) by area /µm	fraction all (Σ3) CSL boundary* %
N1	growth side	10E11	22.2	83.5	60 (45)
N2	nucleation side	10E12	x	x	x
N3	nucleation side	10E13	x	x	x
N4	growth side	3.8x10E13	23.7	85.2	60 (43)

Comparison of pristine/irradiated samples shows – there is no influence on the microstructure caused by irradiation with the Xe ions, independent on the ion fluence. The defects introduces by irradiation are on a much smaller scale and can not be detected with EBSD technique.

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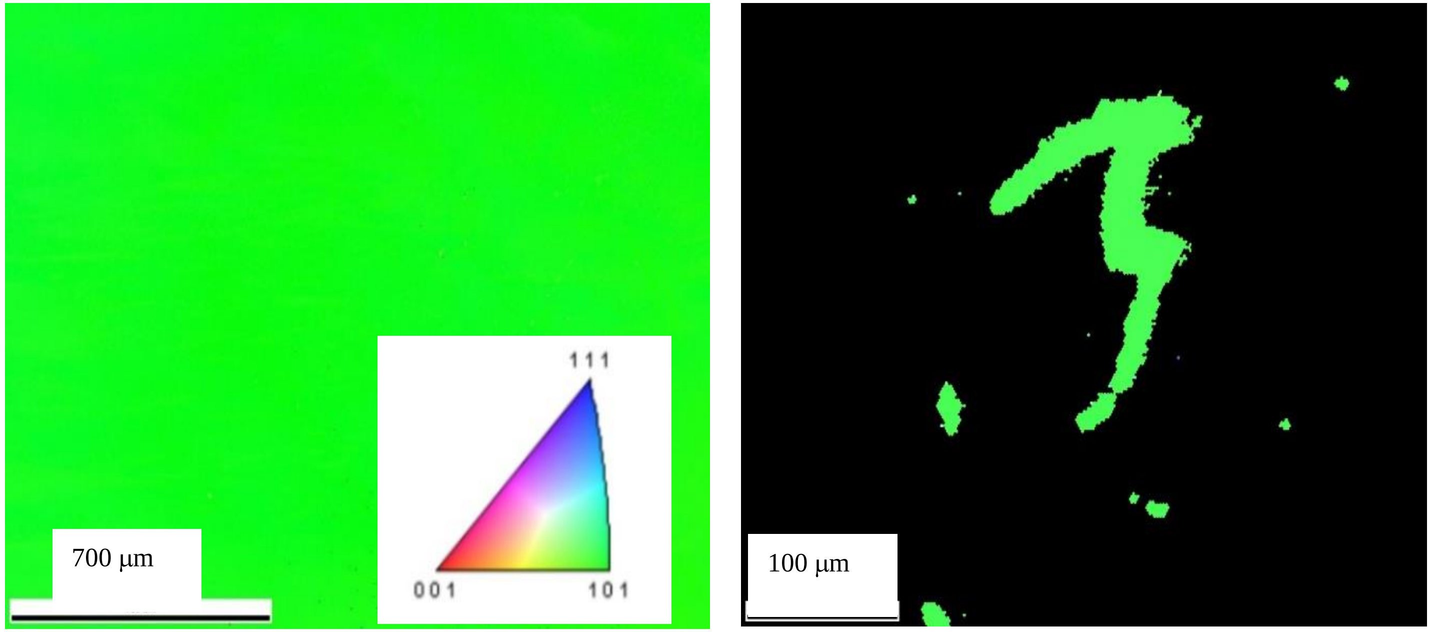
Tasks 5. EBSD measurements … of diamond and the interface passivation layers (KIT)

The crystallographic properties of a **single crystalline diamond passivated** with a layer of SiO (ca. 100 nm thick)



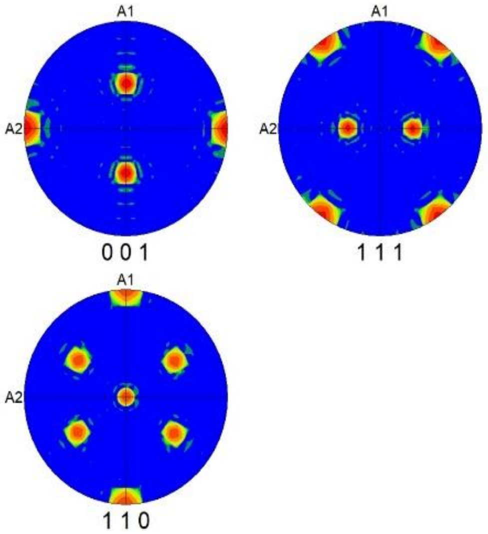


Fig. 6. EBSD charts for a single crystal diamond (left, inverse poole mapping) and SiO-coated side with a green-colored damaged regions (right). Pole figures for the basic crystallographic directions for the uncoated side.

The uncoated side is a perfect single crystal without any grain boundaries.

According to the EBSD data, the SiO-coating is presumably not crystalline (no diffraction patterns in undamaged coated areas).
Green-colored regions – a small damage of the SiO surface due to sample handling.

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Tasks 6 and 8. First principles calculations of defects … in AlN. Modeling of defect annealing … in SiO (ISSP-UL)

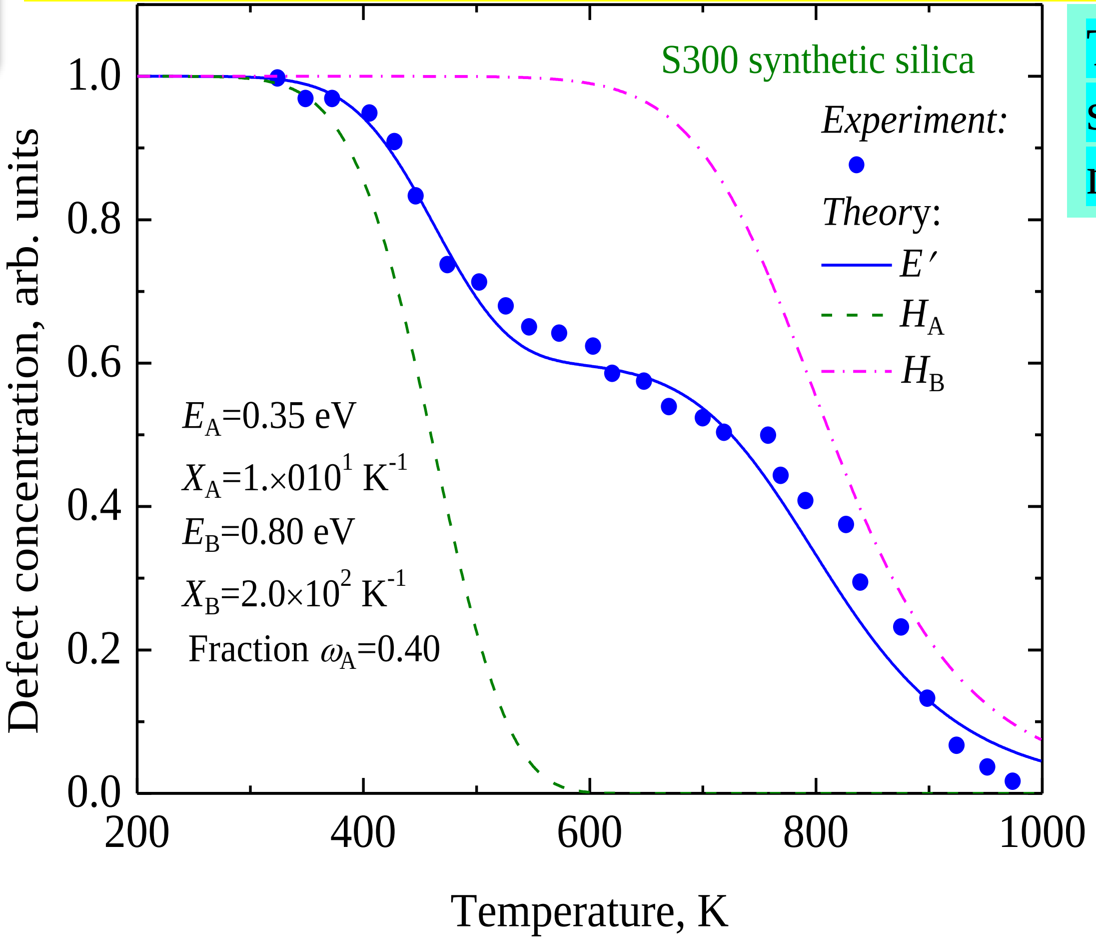

Fig. 7. The experimental annealing kinetics of the *E*' centers (symbols) in a dry synthetic S300 silica with 1 ppm of OH (from Ref. [12]). Lines – theory for the *E*' (solid) and complementary oxygen interstitials (dashed).

Theoretical analysis of the defect annealing in silica samples with different OH content irradiated by neutrons or gamma-rays (from literature data).

The kinetics is modelled assuming two types of oxygen interstitials which recombine with immobile E' centers (an oxygen vacancy), the estimated migration energies E_a of which are 0.35 and 0.80 eV, respectively (dotted lines).

Mobile interstitials (labelled as H_A and H_B) are tentatively associated with the non-bridging oxygen hole centers and the O_2^- peroxy radicals.

The main results on the first principles calculations of the atomic/electronic structure; vibrational spectra and basic radiation defects in AlN were presented in 2022. The relevant paper is now submitted to *Condens. Matter*. (*ID 36688*).

Publications related to the project

[1] L.L. Rusevich, E.A. Kotomin, A.I. Popov, G. Aiello, T.A. Scherer, A. Lushchik. The vibrational and dielectric properties of diamond with N impurities: First principles study. *Diamond Relat. Mater.* **130** (2022) 109399. doi:10.1016/j.diamond.2022.109399, *ID33490*

[2] A. Antuzevics, E. Elsts, M. Kemere, A. Lushchik, A. Moskina, T.A. Scherer, A.I. Popov, Thermal annealing of neutron irradiation generated paramagnetic defects in transparent Al_2O_3 ceramics. *Opt. Mater.* **135** (2023) 113250. doi:10.1016/j.optmat.2022.113250, *ID33491*

[3] V. Seeman, A.I. Popov, E. Shablonin, E. Vasil'chenko, A. Lushchik, EPR-active dimer centers with S = 1 in α-Al_2O_3 single crystals irradiated by fast neutrons, *J. Nucl. Mater.*, **569** (2022) 153933. doi:10.1016/j.jnucmat.2022.153933, *ID33492*

[4] N. Mironova-Ulmane, M.G. Brik, J. Grube, et al., EPR, optical and thermometric studies of Cr^{3+} ions in the α-Al_2O_3 synthetic single crystal, *Opt. Mater.* **132** (2022) 112859. doi:10.1016/j.optmat.2022.112859, *ID33493*

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[5] V. Kuzovkov, E. Kotomin, R. Vila, Theoretical analysis of thermal annealing kinetics of radiation defects in silica, *J. Nucl. Mater*. **579** (2023) 154381. doi:10.1016/j.jnucmat.2023.154381 *ID34869*

[6] A. Platonenko, W.C. Mackrodt, R. Dovesi, The Electronic structures and energies of the lowest excited states of the N_s^0, N_s^+, N_s^- and N_s-H defects in diamond, *Materials* **16** (2023) 1979. doi:10.3390/ma16051979, *ID34871*

[7] W.C. Mackrodt, A. Platonenko, F. Pascale, R. Dovesi, The energies and charge and spin distributions in the low-lying levels of singlet and triplet N_2V defects in diamond from direct variational calculations of the excited state, *J. Chem. Phys*. **160** (2024) 034705. doi:10.1063/5.0178893, *ID3668*9

[8] E. Feldbach, A. Krasnikov, A.I. Popov, V. Seeman, E. Shablonin, A. Lushchik, Cathodoluminescence as a tool for monitoring radiation damage recovery in corundum, *J. Lumin.* (2024) 120490. doi:10.1016/j.jlumin.2024.120490, *ID36711*

[9] A. Platonenko, E.A. Kotomin, A. Popov, Hybrid DFT calculations on vibrational properties of vacancy defects in hexagonal AlN crystals, *Condensed Matter (MDPI)*, submitted. *ID36688*

[10] A. Antuzevics, A.I. Popov, T.A. Scherer, V.N. Kuzovkov, E.A. Kotomin, A. Lushchik, Thermal annealing of radiation defects in neutron irradiated silica, *Opt. Mater.*, submitted *ID36710*

[11] L.L. Rusevich, A. Lushchik, T.A. Scherer, G. Aiello, A.I. Popov, E.A. Kotomin, The electronic, vibrational and dielectric properties of diamond crystals with neutral vacancies: First principles study. *Opt. Mater.*, submitted, *ID35232*

Aleksandrs Platoņenko, First principles modelling and characterization of radiation point defects in α-Al_2O_3 and $MgAl_2O_4$ crystals, ***PhD (in Physics)*** *Thesis*, Supv. Deniss Grjaznovs, University of Latvia (2023). https://dspace.lu.lv/dspace/handle/7/63041

Alise Podelinska, Vibrational spectroscopy of radiation resistive ceramics for fusion applications, ***Master Thesis***, Supv. Anatolijs Popovs, University of Latvia (June 2023). https://dspace.lu.lv/dspace/handle/7/64355

Plans for 2024

- Thermal annealing of radiation defects in CVD diamond disks irradiated by 231-MeV Xe ions with 4 different fluences (*already in progress*).
- Modelling of defect annealing in the samples irradiated with different fluences.
- Task 9. Comparative inelastic and small angle neutron scattering of selected heavily irradiated samples at ILL, ***Partly achieved*** – *still waiting for the results from Grenoble*

TASK SPECIFICATION for 2024

1. Analysis of general picture about OA, PL, RAMAN, EPR properties of three indicated heavily irradiated materials.
2. Conclusive analysis on radiation tolerance of doped diamond/sapphire and perspectives for fusion applications