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Radiation resistance diagnostics of wide-gap optical materials

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ABSTRACT

Novel approach in the detection of radiation damage created by ion beams in optical materials was demonstrated. Protons of the energy of 100 keV and fluence of 10^{17} cm^{-2} create sufficient amount of crystal lattice defects in the thin surface layer for testing of optical materials needed for future fusion reactors. These structural defects can be detected and analysed using the spectra of cathodoluminescence excited in the irradiated layer by an electron beam with adjustable energy. The method was verified by the enhanced intensity of F-type luminescence that reflects the creation of radiation-induced oxygen vacancies in MgO and Al_2O_3 crystals. Low radiation resistance of nominally pure $(Lu_{1-x}Gd_x)_2SiO_5$ crystals was demonstrated by almost total suppression of intrinsic luminescence after the same irradiation.

1. Introduction

Optical materials and insulators will play a substantial role in diagnostic systems of future deuterium–tritium fusion reactors, which have to withstand 14-MeV neutron irradiation of unprecedented intensity. The development of extremely neutron-resistant optical materials is an important task of the EUROfusion consortium research programme started in 2014 [1]. Neutron radiation induces numerous defects of different type in the materials. Radiation induced optical absorption and undesired light emission (luminescence) are the main problems/limitations for optical components (windows, lenses, fibers). The investigation of these optical phenomena under the operating conditions of future fusion reactors still lies ahead. According to rough estimations, optical elements in future fusion reactors should endure the irradiation with the damage level from 0.1 to 1 displacements per atom (dpa) [2]. However, at the moment there are no sources of 14 MeV neutrons with sufficient flux prohibiting experimental investigations. Fortunately, optical parameters can be determined in a very thin layer of tiny samples that enables to use ion beams for this task. The usage of protons or molecular hydrogen ion beams is most easy and convenient way to test some selected optical materials by the suggested diagnostic procedure. The level of proton energies used in standard implanters (hundreds of keV) differs considerably from 14 MeV, but enables to concentrate all the induced damage in a thin near-surface layer and, therefore, the needed fluence can be achieved within reasonable irradiation time using a standard high current ion implanter.

To detect elementary structural defects (vacancies and interstitials) within the proton-irradiated layer, a highly sensitive luminescence method can be used. A selected luminescence (impurity/defect related or intrinsic one) should be dependent, directly or in an indirect way, on the radiation creation of structural defects. For example, luminescence bands of F^+ and F centres (one or two electrons in the field of an oxygen vacancy, respectively) are well-known in most optical materials. It is important to excite the luminescence within the same near-surface layer that was previously irradiated by protons, and the most convenient excitation source for this task is an electron beam with adjustable energy, in other words, the cathodoluminescence (CL) technique.

2. Experimental

In the present study, the 200 keV hydrogen molecular beam (corresponding to protons of 100 keV) was applied using KIIA 500 kV ion implanter of Ion Beam Laboratory at the University of Helsinki. Molecular beam allows to get higher beam flux and, accordingly, to shorten the irradiation time needed for a prescribed fluence. The Coulomb explosion of the H_2^+ molecule in the target material causes some depth profile spread for protons, but this circumstance is not substantial for the goals of our experiment [3]. The SRIM (www.srim.org) calculations for MgO target enable to estimate the irradiated thickness (400–600 nm) and the needed fluence (10^{17} protons/cm^2) to get the damage level of ~0.5 dpa at the maximum of damage distribution (see Fig. 1). Using molecular

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beam current of ~0.25 μA/cm^2, irradiation time of 8–9 h provides the fluence of 10^{17} protons/cm^2.

Nominally pure single crystals of MgO and α-Al_2O_3, well-known compounds of high radiation resistance as well as one representative of scintillator materials – single crystals of $(Lu_{1-x}Gd_x)_2SiO_5$, were used as test samples. Electron beam of 10 keV energy and 0.5 μA current was the luminescence excitation source, which, according to the CASINO simulation [4], overlaps well with the penetration depth of protons into above mentioned compounds (an example for MgO is shown in Fig. 1, together with the penetration depth distribution for 7 and 10 keV electrons, for comparison). As one can see, the 10 keV electrons cover the whole spatial depth of ion irradiation enabling maximum luminescence intensity. CL setup at the Institute of Physics in Tartu is equipped with a vacuum cryostat (5–400 K) and two monochromators covering spectral range from NIR (~1700 nm) to VUV (~110 nm) - ARC SpectraPro 2300i monochromator with various gratings and detectors or a self-made vacuum double monochromator with a Hamamatsu photomultiplier R6836. Electron gun (Kimball Physics EGG-3101) can be used both in steady and pulse (10 ns, 5 kHz) mode. The Becker&Hickl MSA-300 multiscaler allows to detect luminescence kinetics (decay curves). To avoid surface charging under electron beam excitation, the 3-nm Pt films were deposited on all samples. It was also possible to observe by the naked eye a visible luminescence through windows of the sample chamber of the implanter during proton irradiation (see text below and Fig. 3).

3. Results and discussion

It is generally accepted that several radiation-induced absorption bands in wide gap metal oxides manifest the creation of oxygen vacancies that capture one or two electrons each and are known as F^+ and F centres, respectively. The photoexcitation in the region of these absorption bands leads to the appearance of so-called F^+- and F-emission. The optical characteristics of F^+ and F centres were thoroughly studied in MgO and Al_2O_3 single crystals, thermochemically coloured or irradiated with fast neutrons and swift heavy ions (see, e.g. [5–11], and references therein).

Thermally coloured MgO crystals contain high concentration of F centres (absorption peak at 5.03 eV, emission - 2.4 eV), fast neutrons mainly create F^+ centres (absorption peak at 4.95 eV, emission band at 3.15 eV), while oxygen vacancies (V_O) dominate in ~GeV-ion-irradiated samples. It is worth noting that the detected F- or F^+-emissions in the CL spectrum definitely confirm the presence of V_O, although an additional analysis is needed to estimate a selective contribution of F, F^+ and V_O. An electron beam forms numerous electron-hole pairs and these carriers interact with the existing F-type defects. As a result, for example, the F-emission arises at the recombination of conduction electrons with F^+ centres, while the F^+-emission dominates in the CL spectrum of a neutron-irradiated sample with a large amount of V_O serving as efficient radiative traps of electrons [9,10].

Fig. 2 presents the CL spectra measured for virgin and proton-irradiated MgO and Al_2O_3 single crystals at 78 K. Because of a highly sensitive luminescence method, as-grown F-type defects are detected in the CL spectrum of a nominally pure MgO crystal in the form of F- and F^+-emissions. The intensity of CL related to F-type defects at 2.3–3.9 eV significantly increases in a proton-irradiated sample. Similar to the case of heavy-ion irradiation, the enhanced F^+-emission confirms the radiation-induced creation of V_O. In addition to the F- and F^+-emissions, CL of the irradiated MgO sample also contains a component (decomposition gives the additional maximum at ~2.9 eV) tentatively ascribed to the crystal lattice stress (presence of bivacancies) [12,13]. A similar increase of F-type centres intensity in CL has been detected in an irradiated α-Al_2O_3 crystal (Fig. 2b), where the absorption bands of F and F^+ centres are peaked at 6.1 eV (F-emission at 3 eV) and 4.8 eV (F^+-emission at 3.75 eV), respectively [6,7,10,11].

In addition to the detection of a typical emission of F-type centres, the radiation damage of wide gap metal oxides can be estimated via comparison of the intrinsic emission intensity in a virgin and an irradiated sample. It is well established that excitons are very sensitive to structural defects of solids (see, e.g. [14]). Two types of excitons were revealed in solids long ago. Besides free excitons (FEs) that manifest themselves at the long-wavelength edge of fundamental absorption as narrow emission lines and are thoroughly studied in semiconductors, in wide-gap crystals there can exist self-trapped excitons (STEs) with typical broadband emission arising after interaction of FEs with the field of acoustic

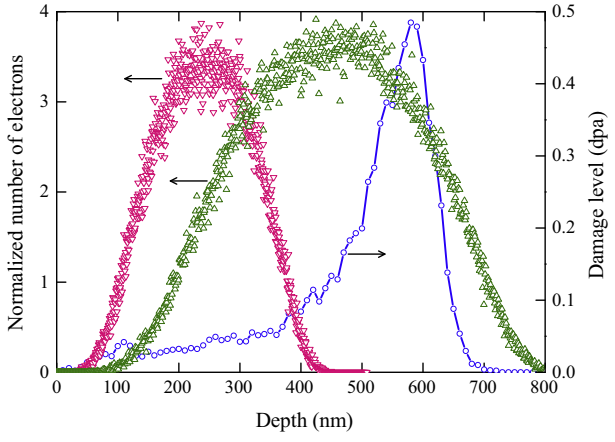

Fig. 1. Displacements per atom (dpa) caused by 100 keV protons (○○○) and penetration depth distributions for electrons (7 keV – ▽▽▽, 10 keV – △△△) in a MgO crystal, calculated using SRIM code and CASINO software, respectively.

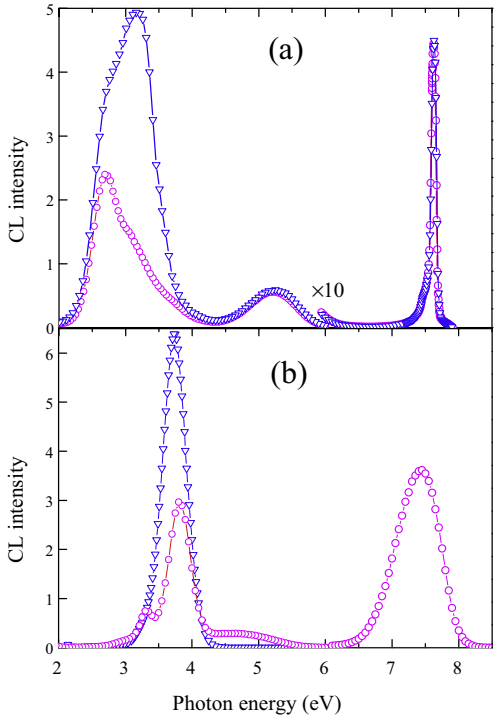

Fig. 2. Cathodoluminescence spectra measured for MgO (a) and Al_2O_3 (b) single crystals at 78 K before (circles) and after (triangles) irradiation by 100 keV protons (10^{17} cm^{-2}) at room temperature. CL was excited by an electron beam of 10 keV and 0.5 μA.