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Mechanism of void growth in irradiated NaCl based on exiton-induced formation of divacancies at dislocations

V.I. Dubinko [a,*], D.I. Vainshtein [b], H.W. den Hartog [b]

[a] National Science Center, Kharkov Institute of Physics and Technology, Akademicheskaya 1, 310108 Kharkov, Ukraine
[b] Solid State Physics Laboratory, University of Groningen, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

Abstract

We propose a mechanism of void growth in di-atomic ionic crystals due to agglomeration of divacancies produced by interactions between dislocations and *excitons*. An exciton can cause movement of nearby dislocation jogs, resulting in the creation of equal numbers of anion and cation vacancies (Schottky defects). Owing to the heat generated locally during the exciton annihilation, the jog can be displaced while a divacancy arises in the lattice. Subsequent diffusion and agglomeration of divacancies can result in void formation and growth. We evaluate the void nucleation and growth rates in electron irradiated NaCl.
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Keywords: Radiation damage; Alkali halides; Excitons; Dislocations; Voids

1. Introduction

Exposure of alkali halides to ionizing radiation results in the formation of nano-sized halogen "bubbles" by agglomeration of H centers and of complementary inclusions of metallic "*colloids*" formed by agglomeration of F centers. H and F centers are the primary radiation-induced Frenkel pairs in the halide sub-lattice created in the crystal bulk due to decay of self-trapped exitons [1]. The H center is an interstitial halide ion with a trapped hole, and an F center is a vacancy in the halide sub-lattice with a trapped electron. The cation sub-lattice is not damaged during primary displacement processes. However, experimental results on heavily irradiated natural and synthetic NaCl crystals [2] give evidence for the formation of large vacancy voids (Fig. 1), which require agglomeration of vacancies in both anion and cation sub-lattices. One possible explanation for this phenomenon is based on dislocation climb involving the production of V_F centers (self-trapped hole neighboring a cation vacancy) due to interactions between dislocations and H centers [3,4]. A subsequent diffusion of V_F centers away from

* Corresponding author. Tel.: +7 0572 356620; fax: +7 0572 351738.
E-mail address: vdubinko@kipt.kharkov.ua (V.I. Dubinko).

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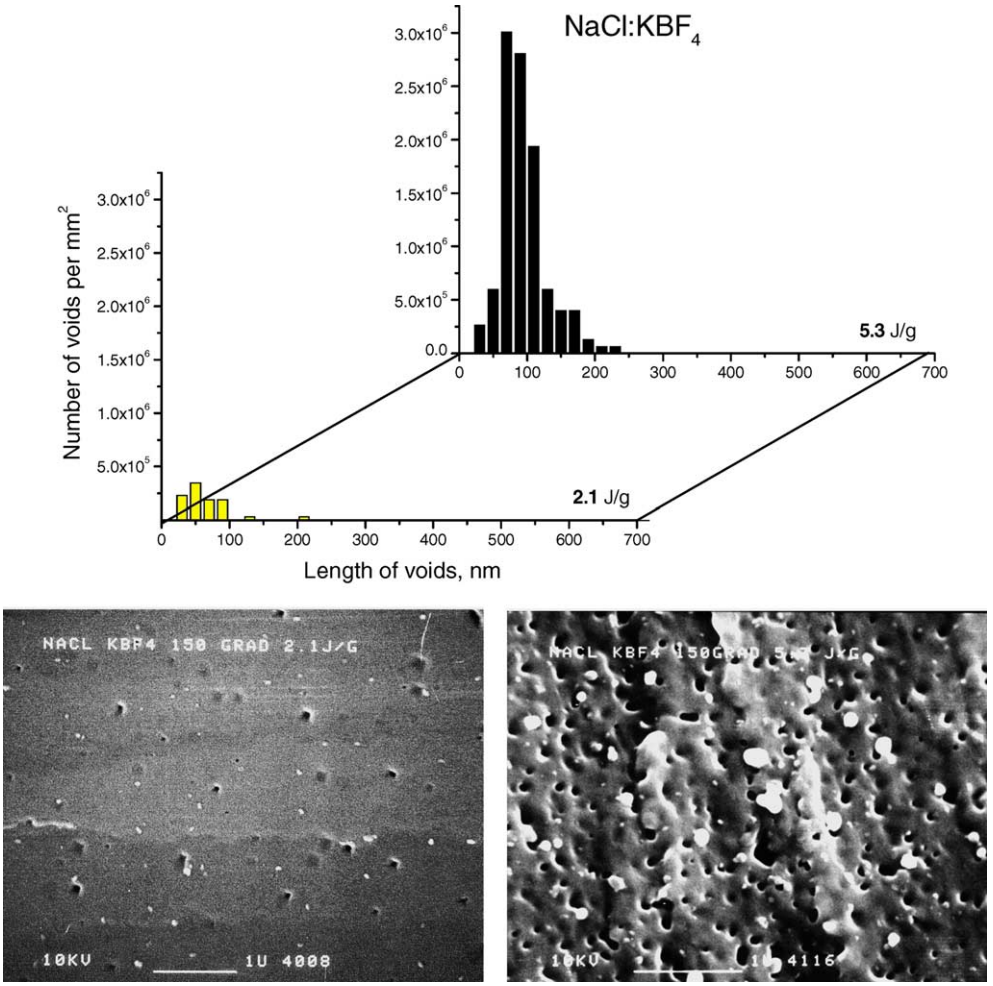

Fig. 1. SEM micrograph and the void size histogram in electron irradiated NaCl doped with 0.03% KBF_4.

dislocations and recombination with F centers would result in the formation of stoichiometric divacancies either in the bulk or at the void nuclei, formed in the colloid–bubble collisions [4], which would provide the driving force for the void growth. The collisions are mainly due to the growth of relatively large metal colloids surrounded by a high density population of halogen bubbles (Fig. 2). When the colloid surface touches an adjacent bubble, an explosive back reaction occurs, in which halogen stored in the bubble and a part of sodium in colloid recombine releasing the energy and heating the NaCl "gas" inside the cavity [5,6], which expands producing a void nucleus of the size comparable to the initial bubble size.

In this model, the void growth rate is determined by the flux of V_F centers and by the net flux of F centers (the difference between F and H center fluxes), which depends on the difference between the void bias and the mean bias of the system for the absorption of F centers. This difference is positive for void radii lager than a critical radius, R_V^{crit}, determined by the ratio of material constants related to the void and dislocation biases [3]:

$$R_V^{crit} = \frac{\alpha^{im} b}{\delta_d} \approx (1\text{–}2)b, \quad (1)$$

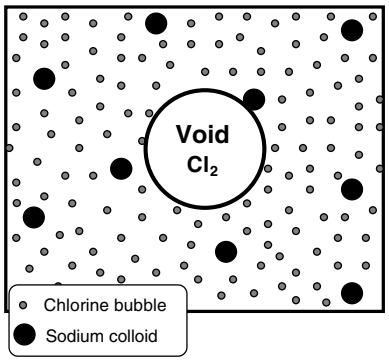

Fig. 2. Illustration of the distribution of chlorine bubbles, sodium colloids and voids in irradiated NaCl crystals [4]. The bubble size is ~1–2 nm; the colloid size ~ interbubble spacing ~5–10 nm; the void size is about intercolloid spacing ~20–30 nm, when their collisions with colloids start.

where b is the atomic spacing and α^{im} is the constant of image interaction:

$$\alpha^{\mathrm{im}} = (\alpha_{\mathrm{H}}^{\mathrm{im}} - \alpha_{\mathrm{F}}^{\mathrm{im}}), \quad \alpha_{\mathrm{n}}^{\mathrm{im}} = \left[\frac{\mu(1+\nu)^2\Omega_{\mathrm{n}}^2}{36kT(1-\nu)b^3}\right]^{1/3}. \tag{2}$$

δ_{d} is the dislocation bias for the absorption of H centers, which is determined by the ratio of relaxation volumes associated with H and F centers, $\Omega_{\mathrm{H}}/|\Omega_{\mathrm{F}}|$:

$$\delta_{\mathrm{d}} = \ln\left(\frac{\Omega_{\mathrm{H}}}{|\Omega_{\mathrm{F}}|}\right) \Big/ \ln\left(\frac{2}{L_{\mathrm{H}}k_{\mathrm{H}}}\right), \; L_{\mathrm{H}} = \frac{\mu b(1+\nu)}{3\pi kT(1-\nu)}\Omega_{\mathrm{H}}, \tag{3}$$

where ν is the Poisson ratio, μ is the shear modulus of the host matrix, k_{H} is the square root of the total sink strength for H centers, kT has its usual meaning.

Since $R_{\mathrm{V}}^{\mathrm{crit}}$ given by Eq. (1) is smaller than radius of void nuclei produced in bubble-colloid collisions, one would expect all void nuclei to grow to visible sizes. The number density of the void nuclei, N_{V}^0, can be estimated as the product of the bubble number density, $N_{\mathrm{B}} \approx 10^{18}$–$10^{19}\,\mathrm{cm}^{-3}$ and the colloid volume fraction, $V_{\mathrm{C}} \approx 10^{-2}$–$10^{-1}$: $N_{\mathrm{V}}^0 \approx N_{\mathrm{B}} \times V_{\mathrm{C}} \approx 10^{16}$–$10^{17}\,\mathrm{cm}^{-3}$. However, the observed void number densities are about 10^{13}–$10^{14}\,\mathrm{cm}^{-3}$, which means that only a very small part of void nuclei survive and grow to visible sizes. The physical reason for this low "survival" rate remained unclear in the previous model.

In the present paper, an alternative mechanism of void growth in alkali halides is considered, which is based on agglomeration of divacancies produced by interactions between dislocations and *excitons*, as was first suggested by Seitz in 1954 [7]. Voids can also emit divacancies due to the interaction with exitons, and so the balance between absorption and emission of divacancies will determine the void critical radius as well as the void nucleation and growth rates.

2. Excitonic production of Frenkel and Schottky defects

According to Seitz [7,8], an exciton can cause movement of nearby dislocation jogs, resulting in the creation of equal numbers of anion and cation vacancies – Schottky defects (SD). Owing to the heat generated locally during the exciton annihilation, the jog can be displaced while a divacancy arises in the lattice. It the previous paper [8], we have incorporated the exitonic mechanism of production of both Frenkel and Schottky defects into the rate theory and evaluated so called *local equilibrium concentrations* of SD, $c_{\mathrm{sS}}^{\mathrm{eq}}$, near spherical (colloids and voids), cylindrical (dislocations) and planar (grain boundaries) sinks, where a subscript "s" designates the type of SD (s = v for divacancies) and "S" the type of the sink (S = V for voids and S = D for dislocations).

In absence of the radiation field, one has $c_{\mathrm{sS}}^{\mathrm{eq}} = c_{\mathrm{sS}}^{\mathrm{th}}$, which can be obtained from thermodynamics. Under irradiation, $c_{\mathrm{sS}}^{\mathrm{eq}}$ is generally given by the sum of $c_{\mathrm{sS}}^{\mathrm{th}}$ and $c_{\mathrm{sS}}^{\mathrm{irr}}$, which is due to the radiation-induced emission of SD's. Here, $c_{\mathrm{sS}}^{\mathrm{irr}}$ has a purely kinetic origin and can be expressed via the *radiation-induced local emission rate* of SD, $K_{\mathrm{sS}}^{\mathrm{irr}}$ [8]:

$$K_{\mathrm{vD}}^{\mathrm{irr}} = \frac{K_{\mathrm{FP}}^0}{P_{\mathrm{FP}}}\frac{Z_{\mathrm{ex}}^{\mathrm{D}} l_{\mathrm{ex}}^2}{2\pi r_{\mathrm{D}} b}, \quad Z_{\mathrm{ex}}^{\mathrm{D}} = \frac{2\pi}{\ln(\pi/k_{\mathrm{D}}r_{\mathrm{D}})},$$
$$c_{\mathrm{vD}}^{\mathrm{irr}} = K_{\mathrm{vD}}^{\mathrm{irr}} \times \frac{b^2}{D_{\mathrm{v}}}, \tag{4}$$

$$K_{\mathrm{vV}}^{\mathrm{irr}} = \frac{K_{\mathrm{FP}}^0}{P_{\mathrm{FP}}}\frac{l_{\mathrm{ex}}^2}{bR_{\mathrm{V}}}, \quad c_{\mathrm{vV}}^{\mathrm{irr}} = K_{\mathrm{vV}}^{\mathrm{irr}} \times \frac{b^2}{D_{\mathrm{v}}}, \tag{5}$$

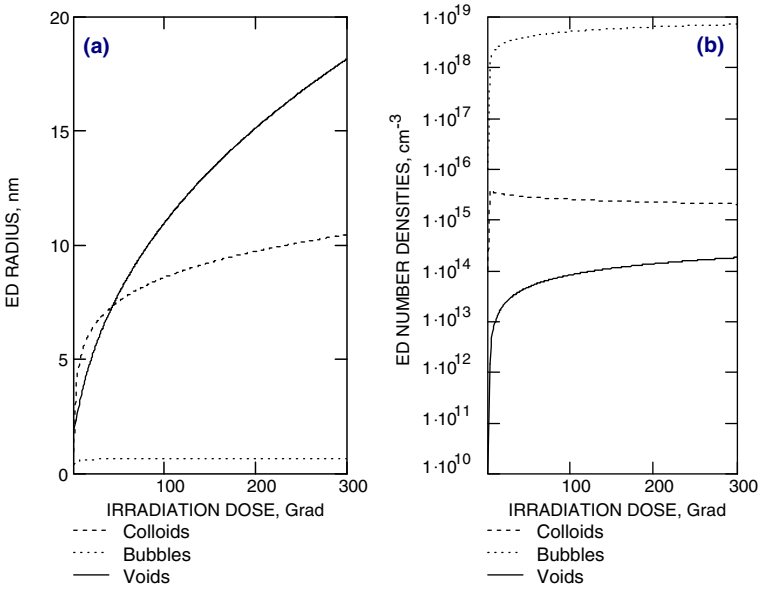

Fig. 3. Evolution of the mean size and number density of extended defects (ED) under irradiation of NaCl at 100 °C and the dose rate 1 Grad/h.

where l_{ex} is the mean free diffusion path of the exciton i.e. the average displacement of the exciton before it decays, P_{FP} is the probability of the formation of a Frenkel pair (FP) in the anion sub-lattice due to the exciton decay, K^0_{FP} is the FP production rate in the bulk crystal, Z^D_{ex} and r_D are the dislocation capture efficiency and capture radius for excitons and D_v is the divacancy diffusion coefficient.

The difference between the local equilibrium concentrations at dislocations and voids is the driving force for the void growth (or shrinkage). It can be seen that the equilibrium concentration at voids decreases with increasing void size, which determines the void critical radius as

$$R_V^{crit} = \frac{2\pi r_D}{Z^D_{ex}} \approx (3\text{–}4)b, \qquad (6)$$

implying that it is larger than the estimated radius of void nuclei produced in bubble–colloid collisions. So large voids can form only due to fluctuations in divacancy arrival and emission, which explains the low survival rate of voids. The present model provides a possibility to evaluate the nucleation and growth rate of voids as well as of colloids and bubbles in the framework of the rate theory [9]. The model results are shown in Fig. 3, from which it follows that the voids can indeed grow by the present mechanism to relatively large sizes observed experimentally.

3. Conclusion

According to the present model, chlorine bubbles are the most finely dispersed ED in the system (the inter-bubble spacing is typically about several nm) so that they start to collide with growing voids first, filling them with chlorine gas (Fig. 2). The chlorine molecules within the "bubbles" are in a solid or liquid state due to a super high pressure (in the GPa range), but after collision with a void it becomes a gas. The chlorine accumulation in voids provides a very important possibility for the explosive back reaction with metallic sodium when growing voids start hitting colloids, which can result in the void-crack transition [6] and ultimately in the explosive fracture of the material [5].

From a more general perspective, the considered above mechanism of the void formation in

alkali halides is only one manifestation of the radiation-induced emission of Schottky defects, which may be responsible for a number of various radiation effects such as the void dissolution and swelling saturation in irradiated metals [10], irradiation creep [11] and possibly the void ordering [12].

Acknowledgements

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