

## Understanding Radiation Damage in Beam-Sensitive TEM Specimens

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Damage to materials that are particularly beam-sensitive (characteristic dose  $< 10^7$  e/nm<sup>2</sup>) arises mainly from radiolysis. Knock-on displacement occurs as well, but is negligible for organic specimens [1]. The radiolysis mechanism can be complicated but a simplified treatment, based on experimental data rather than first-principles calculation, may offer a useful guide to the principles involved.

Electron-beam radiolysis starts with inelastic scattering of a primary electron, resulting in either a single-electron excitation or a plasmon that decays rapidly (sub-fs), generating valence-electron transitions. All these transitions are rapid (fs) and atomic nuclei have inertia so according to the Franck-Condon principle, the atoms involved enter an excited final state at an elevated vibrational level, although they are expected to relax to a lower vibronic level within few ps. If the lifetime  $\tau$  of the excited state is sufficiently long, the participating atoms (vibrating at a frequency  $\nu$ ) may acquire sufficient momentum to separate, with a probability  $P$  given by:

$$P = \nu \tau \exp[-E_a/(kT_{\text{eff}})] \quad (1)$$

where  $T_{\text{eff}}$  is an effective temperature, proportional to a mean-square amplitude of nuclear vibration, and  $E_a$  is a dissociation energy; see Fig. 1a.

Fading of the diffraction patterns recorded from organic crystals suggests that  $P$  typically falls by a factor of ten as the sample temperature is reduced from 300 K to 100 K [2]. According to Eq.(1), this requires a 10% reduction in  $T_{\text{eff}}$ , similar to the decrease (between these two temperatures) in the mean-square vibration amplitude calculated for  $sp^3$ -bonded carbon [3]. Taking  $\nu \sim 4 \times 10^{13}$  Hz (C-C bond) and  $\tau \sim 10$  ns (for example) leads to the temperature dependence shown in Fig. 1b, predicting that the radiation sensitivity should fall by only a further 20% when the specimen temperature is reduced below  $T = 100$  K.

C-H bonds have a higher vibrational frequency, due to the small mass of the hydrogen atom. Hydrogen is quickly released from organic compounds and can diffuse through the specimen even at low temperatures. Replacement of hydrogen by a heavier element (mass  $M$ ) is found to reduce the radiation sensitivity, one likely cause being a reduction in the vibration frequency  $\nu$ , which is proportional to  $M^{1/2}$ . On this basis, substituting D for H in coronene would be expected to reduce the radiation sensitivity by a factor of  $2^{1/2}$ , whereas the observed value is about two [4]. Likewise, substituting Cl for H in copper phthalocyanine should result in a 4-fold reduction, compared to an observed value  $\sim 20$  [5]. The extra factor here is likely to be the cage effect [6], which can be thought of as an increase in the barrier height  $E_a$  due to the presence of larger neighbouring atoms.

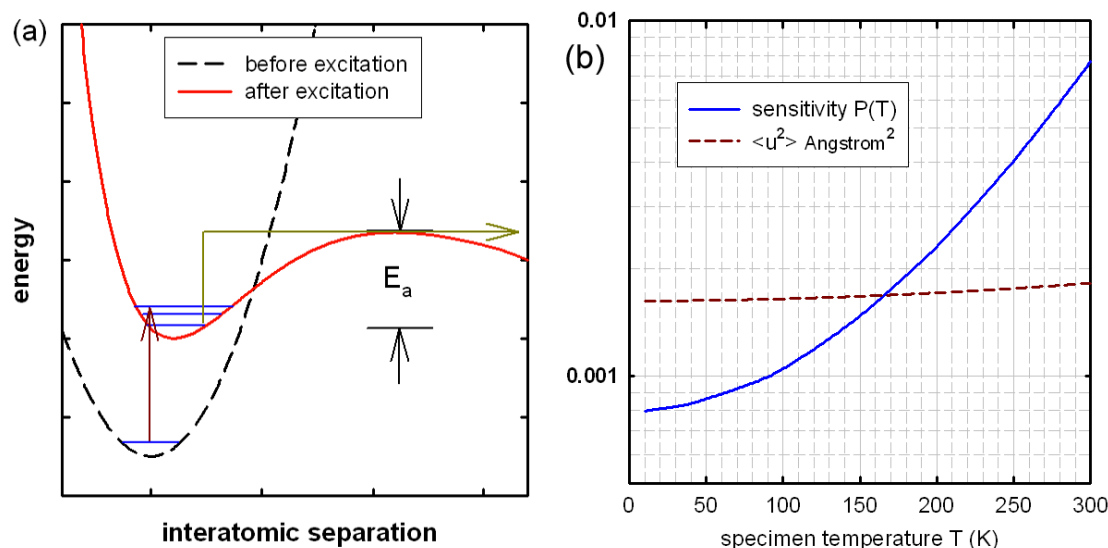
A secondary stage of radiolysis entails damage created by secondary electrons released by ionization in the primary stage. This process may account for 80% of the damage to polymers such as PMMA [7]. Radiolysis in alkali halides involves excitonic states that decay to create lattice vacancies, which at elevated temperatures aggregate to form defects that are visible in TEM images [8].

The tertiary stage of damage involves diffusive motion of the chemical species that are generated by atomic displacement, including escape from specimen surfaces (mass loss), which can be detrimental to the larger-scale structure of a specimen and to EELS or EDX elemental-analysis measurements. An equation similar to Eq.(1) appears applicable, with  $E_a$  representing an activation energy for radiation-enhanced diffusion.

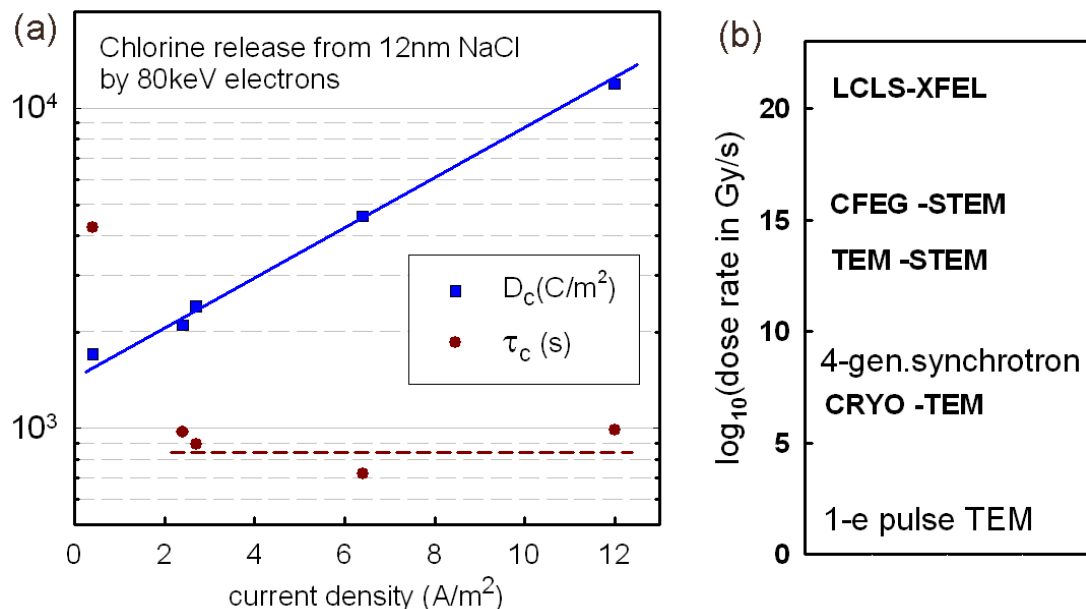
Because tertiary damage involves longer time scales, it can be partially outrun by using a high dose rate. An example is shown in Fig. 2, which shows the characteristic dose  $D_c$  for radiolytic release of chlorine from a NaCl film of thickness  $t = 12$  nm.  $D_c$  increases with current density  $J$ , indicating an inverse dose-rate effect, and the characteristic time  $\tau_c = D_c/J$  reaches a constant value (dashed line in Fig. 2), allowing an estimate of the diffusion coefficient:  $C \sim t^2/(4\tau_c) \sim 10^{-15}$  cm<sup>2</sup>/s. Extrapolating 600-1000 K measurements [9] to  $T = 300$  K gives  $C \sim 10^{-31}$  cm<sup>2</sup>/s, suggesting that the electron flux reduced  $E_a$  by about 1 eV relative to normal (thermal) diffusion.

Radiolysis by x-rays has much in common with the electron case: keV photons generate photoelectrons, which excite secondary electrons that cause nearly all of the damage. The crystals used for x-ray diffraction are often tens of hundreds of  $\mu\text{m}$  in size and diffusion of all chemical species except H is thought to be arrested by cooling the sample to 100 K.

In contrast, TEM specimens are of the order of 100 nm in thickness, making mass loss from organic samples at 100 K easily measurable. Even so, a large part of this process can be outrun by using STEM analysis or imaging, where a high current density in a small probe can be achieved without causing significant heating [10]. The dose rate is then higher than that possible with synchrotron x-rays, although less than that given by an x-ray free-electron laser (XFEL); see Fig. 2b. Because of Coulomb repulsion, the possibility of outrunning all stages of radiation damage with electrons seems remote [11].



**Figure 1.** Fig 1. (a) Primary stage of radiolysis in terms of schematic potentials and transitions of valence electrons. (b) Temperature dependence of  $P$  calculated using Eq.(1), shown in comparison with the mean-square vibration amplitude for diamond [3].



**Figure 2.** Fig 2. (a) Characteristic dose  $D_c$  and characteristic time  $\tau_c$  for removing 63% of chlorine from a 12nm film of NaCl by 80keV-electron radiolysis, as a function of current density. (b) Typical dose rates (in Gy/s = J/kg/s) for x-ray and electron-beam instruments. The value displayed for a pulsed-beam TEM (one electron/pulse) is time-averaged, assuming 0.1 ms between pulses; the rate during each 300fs pulse is similar to the cryo-TEM value.

#### References

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