Analytical theory of electron-beam-induced damage in organic materials

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We calculate analytically the damage produced in a slab of organic material irradiated by an electron beam as a function of electron energy. The treatment is based on a Boltzmann-type transport equation. We assume that the damage is directly related to the number of carbon K-shell ionizations produced by the electron bombardment. An acceptable agreement between our calculations and experimental data is found.

I. INTRODUCTION

When energetic electrons impinge upon materials many interactions take place which are related to the energy-loss process of the incident electrons in the medium. One of the effects derived from this electron-material interaction is the electron-beam-induced damage, which becomes especially important in organic specimens and polymers[1,2] analyzed by electron microscopy. This damage may produce a serious degradation of the sample, in terms of a loss of mass, a loss of its structural order (if any), mechanical instability, and molecular alterations.[3] In fact, for many nonmetallic samples there can be more potentially damaging events than potentially information-producing events. Obviously, if the mechanism of radiation damage is known and understood quantitatively, and not only qualitatively, more effective remedial techniques may be applied to prevent some undesirable effects.[1–4]

Several mechanisms responsible for the electron-beam-induced damage of organic materials have been suggested,[1,2,5–7] usually without quantitative evaluation. Recent experiments by Howie *et al.*[8] find that for certain hydrocarbon materials the damage correlates with the process of K-shell ionizations of the carbon atoms. The existence of a sharp threshold in the electron-beam energy dependence of the measured data[8] excludes outer-shell excitation as the primary damaging process in certain materials. The relation between the K-shell ionization process and the resulting damage is thought to be via Coulomb repulsion and chemical bond breakage of the multiply ionized atoms that result when an inner-shell vacancy is filled by an Auger process.

For a quantitative understanding of the experimental results, an analytical model is proposed in Ref. 8, valid for an infinite irradiated target, which predicts a continuously increasing damage production rate for increasing beam energies above a certain threshold. The experiments, however, were performed[8] with various slab thicknesses, and result in a peak in the damage production rate for a given beam energy. This shortcoming of the theoretical description will be remedied here. The analysis is based on a Boltzmann-type transport equation for the path-length distribution of K-shell events. The analytical method is presented in Sec. II and in Sec. III we discuss some results.

II. ANALYTICAL TREATMENT

In order to simplify the model of energy loss we assume, as in Ref. 9, that the electrons of the medium contribute to the energy loss of the beam in two groups: valence electrons (of the carbon plus the hydrogen) and carbon K-shell electrons. The validity of this separation of interactions between outer and inner electrons is reasonable because the most internal electrons contribute relatively little to the total stopping power ($\lesssim 10\%$–15% of the total stopping power[10] for electrons of energies $\lesssim 10$ keV incident on organic solids).

A complete description of energetic electron beams slowing down in a medium, and the generation of inner-shell ionizations, follows from the distribution function of the (primary and generated) electrons in spatial, angular, and energy variables. We undertake a more modest approach, which allows, however, a quantitative comparison with experimental results.

The description is based on the path length distribution of inner-shell ionizations, defined as follows. $G(E,r)dr$ is the average number of carbon K-shell ionizations produced by an incident electron of energy E in the path length interval $(r,r+dr)$ slowing down in an infinite medium. To set up an equation for this distribution consider an electron starting at $r=0$ with energy $E+dE$ and allow it to move a small path length dR. The balance equation

$$G(E+dE,r)dr = dR\, n_C \int_{E_K}^{E} d\sigma_K(E,T)\,[\delta(r-dR)dr + G(E-T,r-dR)dr + G(T-E_K,r-dR)dr] + \left(1 - dR\, n_C \int_{E_K}^{E} d\sigma_K(E,T)\right) G(E,r-dR)dr, \quad (1)$$

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contains, in the rhs, three contributions. The first two terms inside the integral give the probability that a carbon K-shell ionization occurs both in the interval dR, and in the path-length interval $(r, r+dr)$ due to the incident electron of energy E-T, where T is the energy transferred to a carbon K-shell electron. The third term inside the integral takes into account the fact that an electron which loses an energy T in producing a K-shell ionization, generates a secondary electron with an energy $(T\text{-}E_K)$ which is potentially capable of producing additional K-shell ionizations. E_K is the K-shell ionization threshold energy. The fourth term gives the probability that in traveling dR the incident electron is slowed down by the valence electrons in the medium but no K-shell ionizations take place. In this latter case $dR = dE/S_V(E)$, where $S_V(E)$ is the valence electron contribution to the stopping power. $d\sigma_K(E,T)$ is the differential cross section for a K-shell ionization by an electron of energy E with an energy loss T. The carbon density of the target is n_C. The straggling in the energy loss to valence-band electrons will be neglected. Retaining only up to first-order terms in dE and dR, we obtain the following integro-differential equation:

$$-\frac{\partial G(E,r)}{\partial r} = n_C \int_{E_K}^{E} d\sigma_K(E,T)\,[G(E,r) - G(E-T,r) - G(T-E_K,r) - \delta(r)] + S_V(E)\frac{\partial G(E,r)}{\partial E}. \quad (2)$$

The average number of K-shell ionizations produced by an electron starting with energy E in a finite medium of thickness t, $G(E)$, is obtained via integration of the path-length distribution, $G(E,r)$, along the electron path inside the target

$$G(E) = \oint dr\, G(E,r). \quad (3)$$

Note that the point where the electron starts its motion is embedded in an infinite medium, and a correction for multiple crossing of this surface should be made.

With the simplifying assumption

$$d\sigma_K(E,T) = \sigma_K(E)\delta(T-\bar{E}_K)dT,$$

where $\bar{E}_K$ is a mean energy transferred to the carbon K-shell electron, and assuming that the secondary electrons do not contribute to further K-shell ionizations, integration of Eq. (2) for all values of r yields the differential equation derived in Ref. 8:

$$S_V(E)\frac{dG_\infty(E)}{dE} = n_C\sigma_K(E) \times [1 + G_\infty(E-\bar{E}_K) - G_\infty(E)], \quad (4)$$

for $G_\infty(E)$, the average number of K-shell ionizations produced by an electron slowing down from an initial energy E in an infinite medium. The function $G_\infty(E)$ increases with E without limit.

III. RESULTS AND DISCUSSION

Solution to the integro-differential Eq. (2) has been obtained by using the method of spatial moments.[11] The stopping power $S_V(E)$ due to valence electrons is taken from Ref. 12. The electron gas density is obtained by considering four electrons per carbon atom plus one electron per hydrogen, with a carbon density $n_C = 0.0586$ Å^{-3} for p-terphenyl.[8] This gives a one-electron radius $r_s = 1.79\ a_0$ (where a_0 is the Bohr radius). We have used for E_K the atomic carbon K-shell binding energy, 282 eV (Ref. 10), although the average energy transferred in each ionization may be greater.

Values of the K-shell ionization cross section, $\sigma_K(E)$, by electron impact, for different elements, are given experimentally, semiempirically, and theoretically by many authors.[10,13,14] The differential ionization cross section is taken from Ref. 12.

To obtain the total number of K-shell ionizations, $G(E)$, the integration in Eq. (3) must be carried over the "effective thickness" of the slab for each energy, $t_{\text{eff}}(E)$, which is larger than the film thickness t due to scattering of the incident electron, and has been estimated following Al-Ahmad and Watt.[15] The effective film thickness is comparable to the film thickness t for the low-energy electrons, and the ratio $(t_{\text{eff}} - t)/t$ decreases rapidly with increasing E, becoming less than a few percent for $E > 5$ keV. Figure 1 shows the calculated values of $G(E)$ for p-terphenyl, $C_6H_4\ (C_6H_5)_2$. Experimental values[8] of the electron-beam-induced damage in p-terphenyl slabs ($120\ \text{nm} \leqslant t \leqslant 200\ \text{nm}$) as a function of the beam energy are also presented in this figure. Contrary to previous claims,[13] neither the experimental damage points nor the predicted damage curve are proportional to the carbon K-shell ionization cross section. The process of target preparation, measurement, and the relation between the measured quantities and the associated damage magnitudes is discussed in Ref. 8. As we can observe in Fig. 1, the agreement between experimental and theoretical values is good in the energy region we have studied, better in the shape of the

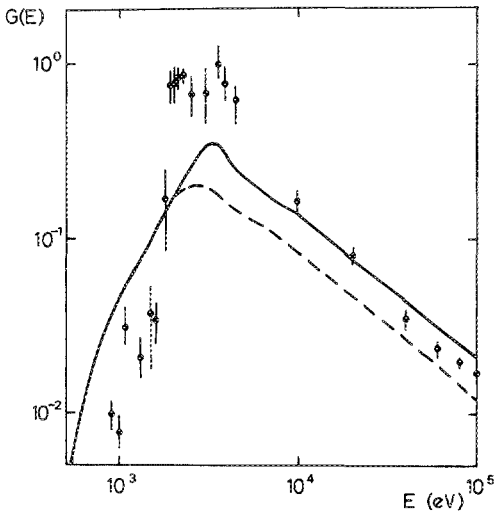

FIG. 1. Average number of carbon K-shell ionizations as a function of the incident electron energy for a finite slab of p-terphenyl. Closed circles: experimental data from F. J. Rocca (Ph.D. thesis, University of Cambridge, UK, 1985). Full line: this work ($t = 200$ nm), and dashed line: this work ($t = 120$ nm). In both cases we have corrected the target thickness, t, for electron scattering.

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damage curve than in its intensity.

At this point we consider the relation between the K-shell ionization process and the damage mechanism. When a K-shell electron is ejected, the vacancy it leaves is filled within 10^{-17}–10^{-12} s by a less tightly bound electron. This is followed by the emission of an Auger electron, after which the atom remains positively doubly charged; if the concentration of doubly ionized atoms is large and their life time is sufficient, the coulombic repulsion may be strong enough to produce chemical bond breakage and, consequently, to alter the structure of the specimen in a similar manner to the Auger-initiated desorption of ions from surfaces[16,17] or to the formation of charged-particle induced tracks in solids.[18]

IV. CONCLUSIONS

We have proposed a transport equation to describe the damage, in a slab of organic material bombarded by an electron beam, as due to carbon K-shell ionizations originated by the incident electrons plus the generated secondary electrons. An acceptable agreement is found between the experimental damage data[8] and the calculated number of K-shell ionizations in the carbon atoms of p-terphenyl. The agreement is better in the location of the maximum of the damage function than in its intensity. The disagreement at low energies (i.e., experimental data below the predicted values) may be due to a concentration of the damage near the surface.[19]

Some improvements of the model may be obtained if we incorporate the effects of electron backscattering and a more realistic description of the stopping power through the dielectric function of the medium. The ideas and procedure developed in this work may be applied to other materials to predict the production of damage as a function of beam energy.

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$$\Delta t = \frac{\pi N_A \rho Z(Z+1)e^4}{A m_0^2 v^4}(1-\beta^2)t^2\left\{\ln\left[\frac{4\pi Z^{4/3}\rho N_A}{A}\left(\frac{\hbar}{m_0 v}\right)^2 t\right] - \frac{1}{2}\right\}.$$

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