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A Monte Carlo study of the extent of proximity effects in e-beam and p-beam writing of PMMA

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Abstract

The generation of secondary electrons (or δ-rays) represent a significant mode of energy loss and energy delocalisation in the penetration of a charged particle into matter. Owing to the large mass disparity between electrons and protons, (1) the trajectories of penetrating protons are essentially straight while those of electrons are tortuous and (2) the fractional energy transferred to secondary electrons by protons are much less than with electrons. Although, these suggest that protons are fundamentally capable of exhibiting superior proximity effects over electrons when used in lithography, no supporting evidence has yet been presented. In the present study we utilise the Hansen–Kocbach–Stolterfoht model for proton induced secondary electron emission to develop a Monte Carlo model capable of recreating the energy deposition profiles resulting from the creation and propagation of δ-rays produced by the passage of MeV protons in PMMA. We show that protons possess more confined energy deposition profiles than electrons.

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Keywords: δ-rays; e-Beam writing; p-Beam writing; Monte Carlo; Energy deposition

1. Introduction

In electron and proton (e and p)-beam writing a resist is selectively modified by the deposition of energy to impart a latent image of the desired structure which may be brought forth by subsequent chemical etching. At present, e-beam writing can produce structures with sub-10 nm feature sizes [1] whereas p-beam writing has achieved feature sizes of the order of 20 nm [2]. The slightly reduced performance of p-beam writing is mainly due to the increased technical difficulties in focusing MeV protons to small spot sizes, coupled with the lack of development of a high brightness proton ion source. These technical problems are now being addressed. However, if the proximity effects (PE) prevalent in the two techniques are considered, p-beam writing emerges superior for producing deeper structures with high aspect ratios, while still retaining spatial resolution, as will be shown in this work.

Proximity effects, in relation to e- and p-beam writing, may be defined as the undesirable, unintended deposition of energy in those regions of the resist unaddressed by the primary beam. What PE there are in MeV protons are due predominantly to the generation of secondary electrons or δ-rays. With electrons however, the significant scattering of the primary particles themselves contribute to the PE, in addition to the δ-rays. Further, this scattering occurs at relatively shallow depths into the resist. Much effort has been expended towards studying and correcting for these electron PE [3–5]. An approximate explanation for this greater PE of electrons can be presented using the first Born approximation although higher order approximations are necessary at low electron energies where there is strong electron–electron coupling. The rate of energy loss of a fast charged particle impinging into a material, be it an electron or proton, depends not on its' energy but its' velocity ($\frac{dE}{dS} \propto \frac{z^2}{v^2}$ [6,7]). A proton and an

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electron with a similar velocity, will suffer a similar rate of energy loss. Owing to the minuteness of the electron's mass its total kinetic energy is depleted more quickly than the protons'. Since, the elastic scattering cross-sections (e.g. Rutherford), tend to be larger at lower energies, the electrons then tend to participate in more scattering.

With the intention of furthering our understanding of the extent of the influence of PE on e- and p-beam writing we have undertaken a preliminary computational study with the positive resist, PMMA (polymethylmethacrylate) as the target material. The goal of the study is to extract the 3D energy deposition profiles which can then be correlated to the bond scissioning and consequent reduction in molecular weight incurred by the passage of the particles [4]. This variation in the molecular weight manifests itself in the chemical development step by creating differential etch rates. Our study is bifurcated into (1) a Monte Carlo (MC) determination of the 3D energy deposition profiles and (2) a time evolution simulation of the chemical development. Details and results of the former, henceforth referred to as δ-*Simulator*, will be the presented in this article while the latter, referred to as δ-*Etcher*, will be presented in a subsequent publication.

Other simulations constructed for the understanding of the energy deposition profiles do exist. The MC proton propagation in water has been studied in [8–12] and has a biological bias. An analytical formalism has been adopted in [9,13–15] again to address biologically relevant material. A few MC simulations for electron bombardment are [16–18].

2. Simulating energy deposition: δ-*Simulator*

δ-*Simulator* aims at extracting the 3D energy deposition profiles resulting from the passage of a charged particle (electron or proton). To this end, we not only need to incorporate the primary particle's energy loss due to δ-ray generation but also the secondary electron generation due to the δ-rays themselves so as to better reproduce the energy spread [16–18]. This requires the adoption of an Event-by-Event or Direct MC formalism which is more complicated but more suitable than the *Continuous Slowing Down Approximation* (CSDA) MC method where the energy loss between two elastic scattering events is approximated by averaging the energy loss (e.g. using the Bethe formula). The Direct MC formalism attempts to rectify the shortcomings inherent in the CSDA approach by simulating all significant inelastic scattering events participated by a particle, in addition to the elastic ones. A Direct MC approach is more demanding with respect to the scattering cross-sectional information necessary. More details of the Direct MC approach may be found in [8,10–12,16–26]. Details of CSDA MC may be found in [27–30].

The basic components that constitute δ-*Simulator* may be listed as: simulation of (1) proton propagation, (2) proton energy loss and δ-ray generation, (3) electron propagation and (4) electron energy loss and δ-ray generation. Ideally, one may extract from these components the energy deposited in the resist by recording the details (i.e. $x, y, z, \Delta(energy)$) of the inelastic events (ionisation, excitation, plasmon generation, etc.) suffered by the propagating charged particles.

δ-*Simulator*'s adopts the Shimizu and Everhart approach for electron propagation, energy loss and δ-ray generation [19,20,25] that utilises Gryziński's expressions for L-shell cross-sections [31–33] and along with a modified Rutherford's cross-section. The formalism adopted for simulating proton propagation was that of TRIM/SRIM [34,35]. However since TRIM/SRIM is strictly a CSDA MC programme (unable to offer details of each energy loss event), its' energy loss routine was replaced with a *stochastic energy loss function (SELF)*.

2.1. Stochastic energy loss function (SELF)

The *SELF* attempts to recreate the individual, stochastic, inelastic energy loss events suffered by a proton; the sum of which is the electronic stopping. The original TRIM/SRIM code which calculates this energy loss using experimental data [35], provides only an average over a given pathlength but no information on the individual inelastic scattering events. However, this information is necessary for the implementation of δ-*Simulator*. Fig. 1, gives the distribution of this *SELF* for 2 MeV protons impinging into 0.5 μm thick PMMA. Although any given energy loss calculation for the thickness may vary stochastically, the average of a statistical ensemble is the same as that predicted by the experimental energy loss data for protons.

δ-*Simulator*'s current implementation of the *SELF* is based on the assumption that *the electronic energy loss is solely due to the generation of* δ-*rays*. The explicit modelling of the atomic excitations and the generation of volume plasmons have not been included in this preliminary work. (The energy delocalisation due to plasmons makes no contribution to the chain scissioning process [16].) However, in order to maintain agreement between the predictions of the *SELF* and the experimentally acquired energy loss data, appropriate adjustments were made to the total δ-ray generation cross-sections (Section 2.2). This adjustment entails in simply reducing the total cross-sections to approximately 97.9 % of their original values. This number, obtained by optimisation, matches the energy loss predicted by Ziegler's [35] fit of experimental data to the predictions of the *SELF*. This approach proves successful only to a penetration depth of approximately 30 μm in PMMA for 2 MeV protons. δ-*Simulator* is thus limited in validity to energies greater than approximately 1.4 MeV or depths in PMMA of less than approximately 30 μm for 2 MeV protons. This can be seen in Fig. 2.

2.2. Hansen–Kocbach–Stolterfoht (HKS) model for δ-rays

The incorporation of the stochastic generation of δ-rays within a MC formalism requires the knowledge the rele-

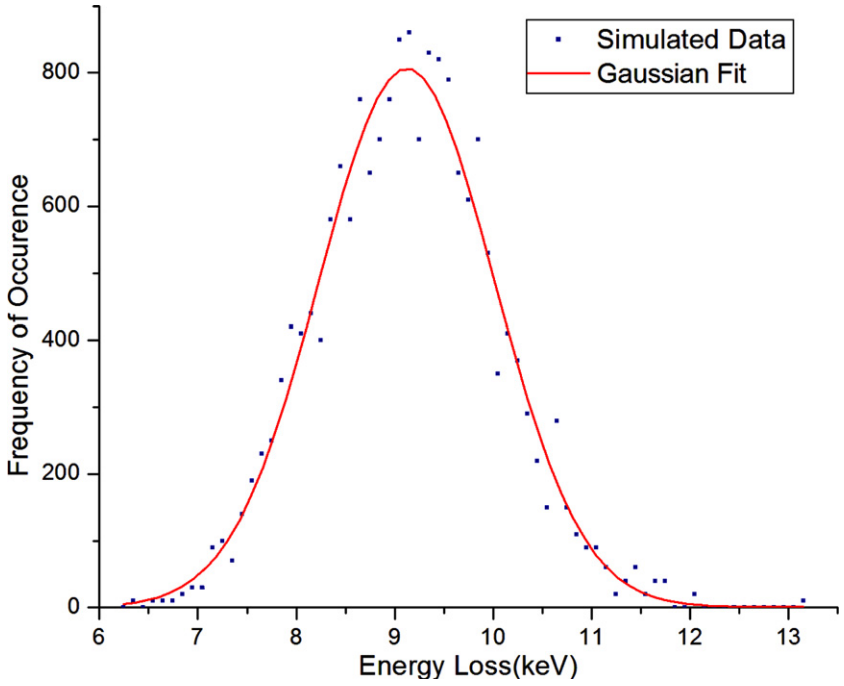

Fig. 1. The distribution of 1800 energy loss values for 2 MeV protons calculated for 0.5 μm thick PMMA using the *SELF*. The average energy loss value predicted by experimental data is 9.0 keV while *SELF* yields 9.1 keV. The FWHM predicted using the Bohr value for energy straggling [55] is 5.4 keV. The Gaussian fit to the data is asymmetrical towards the higher end as there are more ways of losing more energy. The distribution of the number of δ-rays that leads to this energy loss follows the HKS model and is given in [49].

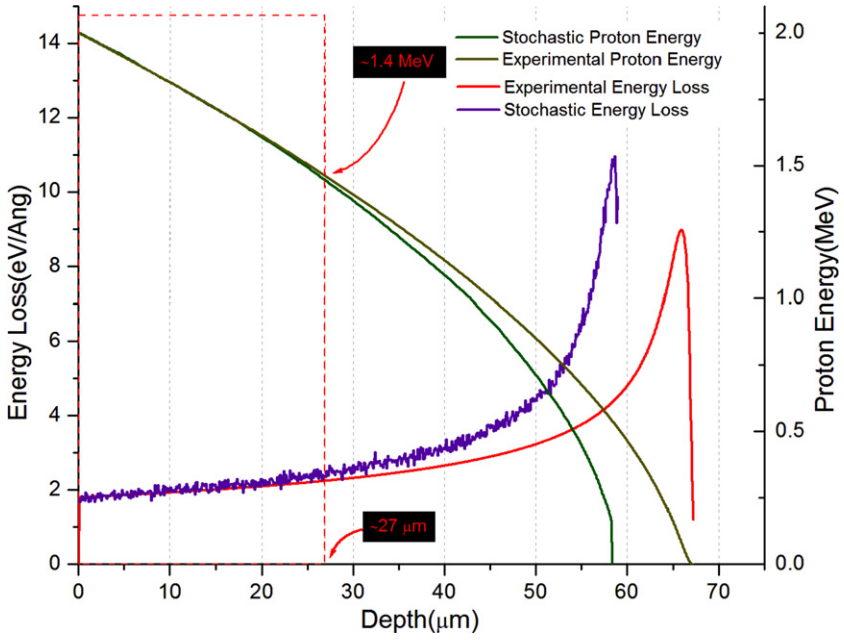

Fig. 2. Comparing the energy loss using the *SELF* with Ziegler's [35] fit of experimental data for 2 MeV protons impinging into PMMA. There is a discrepancy between the two beyond a depth of approximately 30 μm.

vant singly differential and doubly differential inelastic scattering cross-sections (SDCS and DDCS). Ionisation by the ejection of δ-rays tends to be the most probable form of reaction of an atom to a fast impinging ion [6]. There have been many attempts at modelling the δ-ray generation mechanisms ranging from purely classical formalisms through hybrid models to purely quantum mechanical ones. More detail may be found at [6,7,31–33,36–42,42–49].

The Hansen–Kocbach–Stolterfoht (HKS) [42,50] cross-sections are used in δ-*Simulator* for the generation of δ-rays. The only fitting parameters required by this model

is the binding energy, in contrast to some other models that require many parameters whose values are sometimes unavailable. Further, this model has also been successfully used elsewhere [8,51–53]. The detailed formulae for the doubly differential cross-sections (DDCS) and singly differential cross-sections (SDCS) of the *HKS* model may be obtained from [42,49].

3. Results: the extent of proximity effects

3.0.1. Positional distribution of particles

Fig. 3 shows the positional information of the simulation results for 20 keV electrons impinging into 10 μm thick PMMA. The topmost image is from the CSDA based MC programme CASINO [28–30]. The middle and bottom images show results from δ-*Simulator*. The Direct MC results have electrons that propagate further than those in the CSDA, CASINO. This is not unexpected as the Direct MC formalism can allow particles to propagate without significant energy loss. Further, the inclusion of the secondaries results in there being a greater spreading of the deposited energy.

Fig. 4 shows the results for the propagation of 2 MeV protons into 10 μm PMMA, which includes the positional information for the primary protons, their δ-rays and also the secondaries produced by these δ-rays. The spatial (and therefore the energy) spread involved in proton impacts is less prominent than for electrons.

3.1. Proximity effects for two parallel beams

Fig. 5 shows an attempt at comparing the proximity effects of electrons and protons. Here two point beams are simulated penetrating into 10 μm PMMA. Then the separation of the two beams are varied and the percentage energy that is deposited in a 2 nm region midway between the two beams is observed. The highly confined nature of the energy deposition profile due to protons is apparent. The proximity effects of the protons are superior to those of electrons for all separations. Much of the energy contained in the electron beams is delocalised so much so that only about 2% remains in the 2 nm region when the two point beams are coincident. In contrast the proton beams have as much as 91% of energy in this region when made coincident.

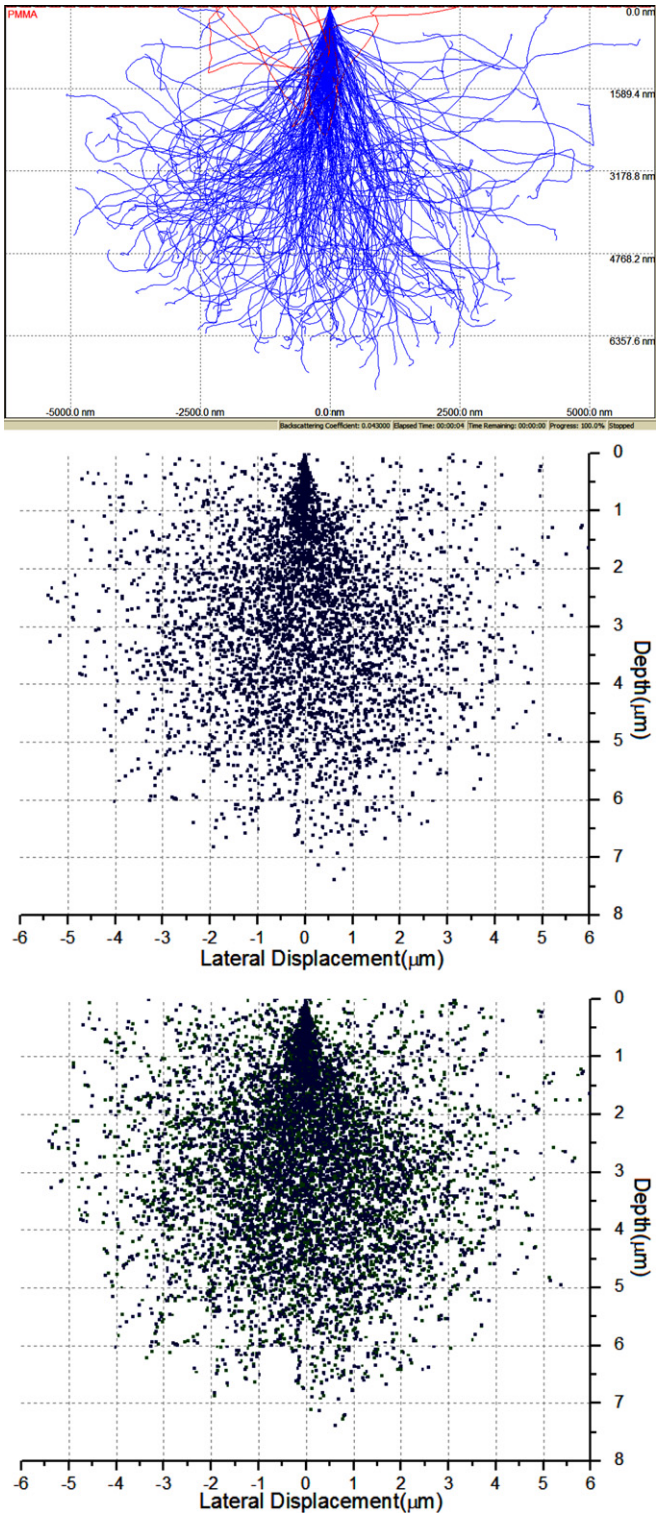

Fig. 3. Simulation of a 1000 20 keV electrons impinging into 10 μm thick PMMA. Top: Simulated using the CASINO [28–30]. Middle: Primary electrons simulated using δ-*Simulator*. Bottom: Primary + secondary electrons simulated using δ-*Simulator* (Primaries – blue, secondaries – green). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion and future work

δ-*Simulator* is unique in that it allows an almost 'event by event' approach to the simulation of the energy loss of protons in PMMA. It is not a complete 'event by event' simulation due to the TRIM component that needs to be replaced by a more appropriate Direct MC simulation for the propagation of protons, which will be more accurate for thin samples. Further, the *SELF* used in δ-*Simulator* does not explicitly incorporate other important energy loss phenomena such as plasmon generation and atomic excitations, which will make it more accurate. One of the

immediate and obvious improvements that can be administered will be the incorporation of these phenomena. For plasmons this should be possible by adopting the dielectric response approach of [16]. The incorporation of atomic excitations may have to follow the work of [21]. Another, improvement is the incorporation of actual experimental

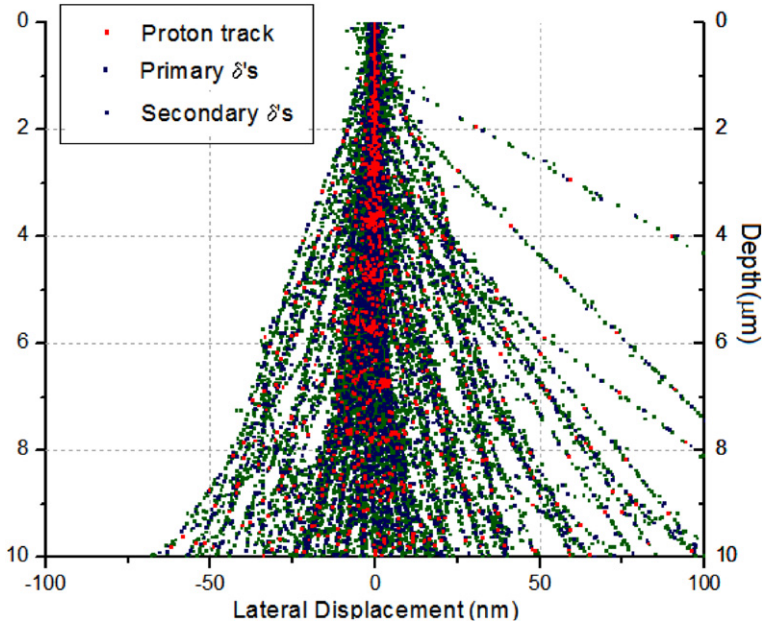

Fig. 4. Simulation of the δ-rays generated when 1000, 2 MeV protons impinge on 10 μm thick PMMA. Compare with Fig. 3. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

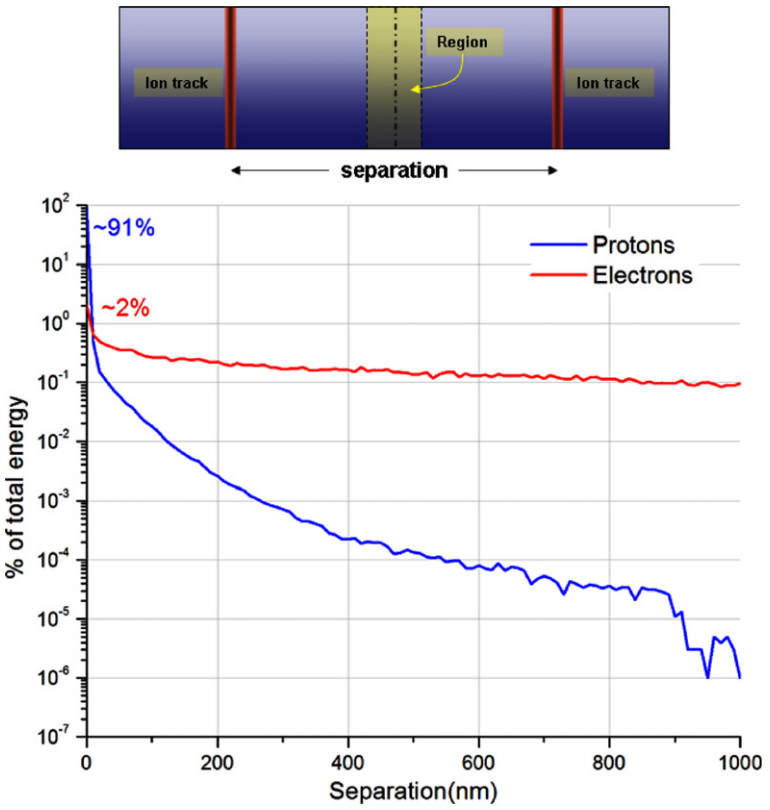

Fig. 5. Comparison of the proximity effects of 2 MeV protons and 20 keV electrons in 10 μm thick PMMA. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

cross-sectional data bases, in place of the analytic formulae. Such a database for electrons is the Lawrence Livermore National Laboratory [54] EEDL libraries. Another important detail to be worked out is the comparison of the predictions of δ-*Simulator* with experiments. For this it will be necessary to improve δ-*Etcher* which is still in its preliminary stages.

The simulation results presented so far are indicative of the superior nature of p-beam writing over e-beam writing with respect to the extent of PE. The use of protons for lithography can result in more confined energy profiles while also permitting structures of high aspect ratios.

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