Energy transfer between electrons and photoresist: Its relation to resolution

Geng Han and Franco Cerrina

Electrical and Computer Engineering and Center for NanoTechnology, University of Wisconsin, Madison, Wisconsin 53706

(Received 14 June 2000; accepted 20 July 2000)

In the study of high-energy photon and electron lithography the photoresist has been treated as a uniform and isotropic medium. As dimensions become smaller and exposure fluctuation more noticeable, we cannot ignore the processes that happen at the molecular scale. Hence, it becomes important to understand how the energy is coupled from an exciting radiation to the various molecular components of a photoresist material. In this article, we present the first step in the development of such a model. We base the analysis on the method of virtual quanta for the incoming electron, and use the dielectric function response theory to describe the medium. The results correctly describe the decreasing strength of the interaction on the electron energy, and yield an estimate of ≈2–3 nm for an average interaction distance. A simple Monte Carlo simulation is implemented to verify the effect of the fluctuations due to the virtual quanta on a line edge. © 2000 American Vacuum Society. [S0734-211X(00)03706-9]

I. INTRODUCTION

In high-energy photon and electron lithography the energy is coupled from the original radiation beam to the material along paths that are not completely understood. In x-ray and extreme ultraviolet (EUV) lithographies the excitation of core electrons creates fast photoelectrons that lose energy by scattering processes, similar to the case of electron-beam lithography. Thus we can say that the energy deposition in the exposure process is dominated by electron interactions. In high-energy lithography the photoresist is assumed to be described by a dissolution rate function that depends only on the local absorbed dose. Hence, the resist has been treated as a uniform and isotropic medium, and no study of the possible decay paths of the excitation energy exist because they are not important in this model. As dimensions become smaller and exposure fluctuation more noticeable, we cannot ignore the processes that happen at the molecular scale and it becomes important to understand how the energy is coupled from an exciting radiation to the various chemical components of a photoresist material, in particular the photoacid generator (PAG). Not only the average dose deposited but also the location of the interaction events become important in a molecular model. The detailed interaction of an electron with the resist matrix is complicated by the many molecular species (PAG, resist polymer, plasticizers, remaining solvent, etc.). As a start, we consider the case of PMMA, a relatively simple polymeric resist system.

To model the location of events, the key question to answer is how the energy is transferred from electrons to photoresist, and leads to the bond-breaking transitions. Consider a beam of 1 keV electrons passing through a PMMA box. The location of the atoms (and relative bonds) in PMMA molecules is obtained by molecular models.1 In order to put things into perspective, we have summarized the main aspects of the exposure process in Table I. From this we seek to determine a more detailed description of the interaction between electrons and PMMA. The traditional approach to the exposure process yields only expected (average) values2–4 for the energy lost by the electron. Previous work has been done to analyze the electron–photoresist interaction,5 but with incomplete results. For the reasons explained above, there is a vast amount of literature and experimental results on the interaction beam material from the beam point of view, i.e., one describing in detail the energy loss process and the energy deposited in the material, but very little information exists on the effect of the interaction on the material. The classic model by Greeneich yields an average value for the number of scissions created by the energy deposited in the material.6 A model that describes the energy transfer is complicated by the many possible paths that the transfer may take. One can define a quantum yield for the reaction of interest, i.e., the dissociation of the PAG or the scission of bonds. There are two steps that need to be explained: first, the creation of an excited state in the molecules of the resist; second, the decay of this excited state and, in particular, the fraction of energy that ends up in the PAG activation. In the case of PMMA, where there is no PAG, the process is simpler.

We seek to develop a model that eventually can be applied to predict on a molecular and bond scale the distribution and location of the interaction between electrons and materials. Since the physics of the interaction is quite complex, we first review the underlying processes in a simple model system and then apply the concepts in the development of a simplified stochastic model of PMMA-like exposure. We note that, since the following discussion involves the optical properties of the resist material, as a first step we are explicitly limiting ourselves to model systems that are not necessarily accurate representations of the full interaction between a resist and a beam of electrons. However, the basic

---

1Electronic mail: cerrina@nanotech.wisc.edu

2000 American Vacuum Society

---

I. INTRODUCTION

In high-energy photon and electron lithography the energy is coupled from the original radiation beam to the material along paths that are not completely understood. In x-ray and extreme ultraviolet (EUV) lithographies the excitation of core electrons creates fast photoelectrons that lose energy by scattering processes, similar to the case of electron-beam lithography. Thus we can say that the energy deposition in the exposure process is dominated by electron interactions. In high-energy lithography the photoresist is assumed to be described by a dissolution rate function that depends only on the local absorbed dose. Hence, the resist has been treated as a uniform and isotropic medium, and no study of the possible decay paths of the excitation energy exist because they are not important in this model. As dimensions become smaller and exposure fluctuation more noticeable, we cannot ignore the processes that happen at the molecular scale and it becomes important to understand how the energy is coupled from an exciting radiation to the various molecular components of a photoresist material. In this article, we present the first step in the development of such a model. We base the analysis on the method of virtual quanta for the incoming electron, and use the dielectric function response theory to describe the medium. The results correctly describe the decreasing strength of the interaction on the electron energy, and yield an estimate of ≈2–3 nm for an average interaction distance. A simple Monte Carlo simulation is implemented to verify the effect of the fluctuations due to the virtual quanta on a line edge. © 2000 American Vacuum Society. [S0734-211X(00)03706-9]

I. INTRODUCTION

In high-energy photon and electron lithography the energy is coupled from the original radiation beam to the material along paths that are not completely understood. In x-ray and extreme ultraviolet (EUV) lithographies the excitation of core electrons creates fast photoelectrons that lose energy by scattering processes, similar to the case of electron-beam lithography. Thus we can say that the energy deposition in the exposure process is dominated by electron interactions. In high-energy lithography the photoresist is assumed to be described by a dissolution rate function that depends only on the local absorbed dose. Hence, the resist has been treated as a uniform and isotropic medium, and no study of the possible decay paths of the excitation energy exist because they are not important in this model. As dimensions become smaller and exposure fluctuation more noticeable, we cannot ignore the processes that happen at the molecular scale and it becomes important to understand how the energy is coupled from an exciting radiation to the various molecular components of a photoresist material. In this article, we present the first step in the development of such a model. We base the analysis on the method of virtual quanta for the incoming electron, and use the dielectric function response theory to describe the medium. The results correctly describe the decreasing strength of the interaction on the electron energy, and yield an estimate of ≈2–3 nm for an average interaction distance. A simple Monte Carlo simulation is implemented to verify the effect of the fluctuations due to the virtual quanta on a line edge. © 2000 American Vacuum Society. [S0734-211X(00)03706-9]
ideas underlying the model are realistic and transferable: the inclusion of realistic parameters will be necessary to yield accurate models.

II. MODEL DESCRIPTION

How does an electron lose energy when passing through a medium? Following standard treatments, we separate the large angle elastic scattering from the energy loss process, assumed to be uniform along the electron path. When a beam of electrons is passing through a medium, the energy loss comes, of course, from the electron kinetic energy 

$$T' = T - \hbar \omega_0.$$ 

Thus, we have a new tool for computing the influence of a pulsed force on a bound oscillator.

In order to describe the interaction we need to determine the number of transitions per cubic centimeter created by the electrons that may lead to chain scissions and their spatial distribution relative to its path. We simplify the analysis by considering only the virtual photons, ignoring the other scattering processes. In the theory of optical processes, the number of transitions $W(\omega)$ per unit time per unit volume induced by a photon field in a medium of dielectric constant $\varepsilon = \varepsilon_1 + i \varepsilon_2$ by a field of strength $E(\omega)$ is

$$W(\omega) = \frac{\varepsilon_0 \omega}{2 \pi \hbar} \varepsilon_2 E^2(\omega) = \frac{\varepsilon_2}{E(\omega)} \text{material} + \frac{\varepsilon_2}{E(\omega)} \text{external field}. \quad (2)$$

The key parameters are the imaginary part of the dielectric function, which represents the material, and the external electric field, which is caused by the passing electrons. We will turn now to a discussion of these two terms.

III. ELECTRODYNAMIC INTERACTION: VIRTUAL QUANTA

Let us begin with the electric field; the discussion will be abbreviated, and follows closely the work of Jackson. We can easily compute both components of the electric field as seen by an oscillator when a electron passes by using classical expressions for the $E(b,t)$ field.

In Fig. 2 we plot the two fields, $E_b$ and $E_{\perp}$. As we can see from the curves, if the distance from the electron to the field point $b$ is fixed, both components of the $E$ field become narrower when the electron kinetic energy increases, while the height remains the same for constant $b$. Therefore, the total area under the two pulses decreases as the electron energy increases. On the other hand, both components of $E$ field become larger at smaller $b$’s.

Since both of the $E$ field components are time varying, the time dependent signal can be analyzed in the frequency domain. Figure 3 shows the Fourier transform of the two $E$ field components at fixed distance $b$. As can be seen, the bandwidth of both components becomes wider as the elec-
tron energy increases, but the strength of $E(\omega)$ becomes smaller. This is a direct result of Parseval’s theorem, that states the area under the curve is conserved under the Fourier transform. Through Planck’s equation, the frequency spectrum leads to the concept of virtual photons. In Fig. 4 we show the energy spectrum of both $E$ field components at fixed distance $b$. We note that for a given frequency, the number of virtual photon decreases as the electron kinetic energy increases. Hence, a fast electron appears to be a localized line source of white radiation, extending from the infrared to a few hundred electron volts. An increase in electron energy will make this source “bluer” but also “dimmer.” This explains satisfactorily why the interaction between electrons and matters decreases as the electron kinetic energy increases.

The total energy of the virtual photon field can be calculated by integrating over all the possible $b$’s and all the frequencies. This leads to some complex mathematics, omitted here. We note that since the calculations are based on the Coulomb potential, the formulas involved in the treatment tend to diverge for $b \rightarrow 0$. While these divergences can be removed using screening, here we keep the simpler formulation of limiting the interaction to a minimum distance $b_{\text{min}}$ (see the later discussion of this point). The reason for this is that the Coulomb potential yields an infinite frequency spectrum as $b \rightarrow 0$. However, very small values of $b$ are unphysical, because of the following:

(1) The bound valence electrons that interact with the passing charge are delocalized in chemical bonds, as shown in Table II.

(2) Because of the smallness of atomic bonds, a molecule is essentially empty space, and thus it is unlikely that the passing electron will be very close to any atom or bond (see below).

(3) Electrons have a finite spread in energy and momentum. At 1 keV,

$$b_{\text{min}} = \frac{\hbar}{mv} \approx 0.38 \text{ Å}.$$ 

The largest of the parameters will dominate the interaction and limit the value of $b$. For now we stop with the remark that, in general, $b \approx 0$ events are unlikely. The effect of screening will be the topic of a subsequent paper.

IV. MEDIUM RESPONSE

After solving for the field, let us turn to the problem of the specific location of energy deposition. It is well known that photon–matter interaction can be modeled very accurately

<table>
<thead>
<tr>
<th>Bond type</th>
<th>C–C</th>
<th>C–H</th>
<th>C–O</th>
<th>C–N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond length (Å)</td>
<td>1.5</td>
<td>1.1</td>
<td>1.43</td>
<td>1.48</td>
</tr>
</tbody>
</table>
with a distribution of Lorentz oscillators, with each oscillator describing a particular bound electron resonating at a frequency \( \hbar \omega_0 \) with damping \( \Gamma \). These oscillators are the semi-classical description of the optical absorption spectrum of the medium. It is clear that in our case we will consider the oscillator to couple to the virtual photon field; as described before, the spectrum is a function of both electron energy and distance. In our problem, the key point is that ‘‘oscillators’’ located at different distances from the electron will see both different spectra and different field strength.

To start, let us consider a single oscillator located at a distance \( b \) from the electron. To put things in perspective, we can look at the oscillator corresponding to the bond-breaking transition in PMMA as a guide in determining the resonant energy \( \hbar \omega_0 \) to use. Interestingly, the low-energy energy loss spectrum of electrons in PMMA films was measured a long time ago.\(^9\) For the sake of discussion, let us assume that the bond breaking is at 5.5 eV (217 nm), one of the transitions quoted in Ref. 9. We note that, as expected, the experimental energy loss spectrum of a fast electron is fully consistent with the dielectric function formulation of Eq. (1).

In general, we can write that the absorbed energy \( S \) for \( j \)th oscillator from an electron passing at \( b_j \) is\(^7\)

\[
d^2S(b_j, \omega) = \omega \varepsilon_2(\omega)|E(b_j, \omega)|^2(J/m^3 Hz).
\]  

(3)

Substituting the equation for \( \varepsilon_2 \) for \( N \) uniform and identical oscillators per unit volume we obtain the classical formulation

\[
d^2S(b_j, \omega) = \frac{e^2N}{m} \left( \frac{2\Gamma \omega^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2 \omega^2} \right) |E(b_j, \omega)|^2(J/m^3 Hz),
\]

(4)

where \( \Gamma = f_\omega \Gamma' \), and \( f_\omega \) is the quantum mechanical ‘‘oscillator strength.’’ The number of transitions per unit volume and frequency for \( N \) oscillators per unit volume is given by the ratio between absorbed energy and photon energy,\(^7\) and thus contains the area of the product of the Lorentzian function with the field strength \( E(\omega) \) as shown in Fig. 4. The dotted line is the imaginary part of the dielectric function that represents absorption from the material,\(^10\) and remains unchanged as the incident electron increases while the virtual photon spectrum decreases. The product of the two curves gives us the spectrum of the absorbed energy density, and the total area under the curves gives us the amount of total energy transferred. Since \( \varepsilon_2 \) is a very narrow function, the energy is coupled around the frequency \( \omega_0 \). In summary, since the energy spectrum decreases and the absorption stays constant, the number of transitions will decrease as the electron energy increases. Of course, this choice of Lorentzian function is purely for the sake of explanation and not necessarily related to a real transition.

The total number of transitions per unit volume per electron is obtained by integrating over the spectrum \((N=1)\). Considering the fact that the imaginary part of dielectric function is very narrow and centered at \( \omega_0 \), the total number of transitions is independent of \( \Gamma \) and proportional to the value of \( |E(\omega_0, b_j)|^2 \). By making the calculations more explicit we obtain

\[
\frac{dN(b_j)}{dV} = \int_0^{\infty} \frac{d^2S(\omega,b_j)}{dVd\omega} d\omega = \frac{1}{\hbar \omega_0} \frac{\pi e^2}{m} |E(\omega_0, b_j)|^2(1/m^3),
\]

(5)
a result containing modified Bessel functions, and the other symbols have standard meaning.

Let us now consider a specific volume of material, say, in the form of a box of PMMA. When the electron passes through this box, it will see a distribution of oscillators at various minimum approach distance \( b_j \), with a distribution \( D(b_j) \). If we use the number of transitions per unit volume per electron weighted by the distribution of the distance \( D(b_j) \), we can obtain the expected number of transitions per unit volume per electron to be

\[
\left\langle \frac{dN}{dV} \right\rangle = \frac{\sum_{j=1}^{n} D(b_j) dN(b_j)/dV}{\sum_{j=1}^{n} D(b_j)}.
\]

(6)

Figure 5 shows the expected number of transitions per electron per unit volume versus the electron kinetic energy. This tells us that, as the electron energy increases, the expected number of transition decreases.

Let us now look at the spatial distribution of the transitions from the electron path. Here it becomes important to have an estimate of the lower bound on \( b_{\text{min}} \). As a test, we generated a distribution of distance \( b_j \) by shooting 2400 electrons randomly into the left half side of a 40 x 40 x 40 nm\(^3\) PMMA box. If we coupled this distribution with the distribution of the number of transitions per electron versus distance, we obtain the distribution of the number of transitions versus the impact parameter \( b \), as shown in Fig. 6. This important results shows directly the expected distribution of scission events around the electron trajectory. We notice the average is 2.0 nm. In another words, if there is a 1 keV electron passing through a PMMA box, the range of the in-
teraction between that electron and the PMMA molecules is of the order of 2.0 nm from the electron trajectory.

Even for such a simplified model, it may be interesting to compare some predictions with the experiment. From our calculation shown in Fig. 5 at 1 keV the expected number of transitions per electron per volume is \( \eta = 5 \times 10^{-5} \) (1/m³). The energy loss \( \Delta E \) of 550 eV absorbed by the medium in the 40 nm thickness includes these transitions as well as nonoptical transitions (plasmons), i.e., an implicit efficiency factor is present in the equation. We obtain

\[
\frac{dN}{dE} = \eta \rho_{osc} \frac{\Delta V}{\Delta E} \approx 5 \times 10^{-5} \times 9.7 \times \frac{1}{550} = 0.028 \text{ (scission/eV)}.
\]

This number is close to the experiment value of 0.019 scissions/eV. The agreement may be coincidental, given the crude model; however, the final value is in a reasonable range.

V. MONTE CARLO SIMULATION

So far we have determined the external field caused by the electrons and the distribution of the interactions; our original goal was to determine the location of these events. Let us now apply these results to a Monte Carlo simulation. The main goal of this simulation is to observe the granularity of the bond breaking. We isolate the virtual quanta contribution by removing all the other scattering effects.

The PMMA molecules are described by the location of the atoms, and we consider that the electrons enter the left half of the box described above. We have used the freely jointed chain method to compute a realistic distribution of PMMA molecules. The molecular weight of the PMMA is 200 K, with a density \( \approx 1.0 \text{ g/cm}^3 \). The box is divided into 10 layers in the \( z \) direction, i.e., along the electron propaga-

\[
\text{Fig. 6. Top left: Distribution of } b \text{ for a PMMA box; lower left: transition density vs distance } b; \text{ right panel: expected transition distribution for the PMMA box.}
\]

\[
\text{Fig. 7. Histogram of the coupling events distribution (solid line) and its derivate plot (dashed line).}
\]
VI. SUMMARY AND CONCLUSIONS

We have introduced a simple model based on the use of the method of virtual quanta and of the dielectric function to account for the effects observed in lithography. To our knowledge this is the first time that the virtual quanta method has been analyzed in detail for application to lithography. This method, when applied to a fast electron and a material medium, provides a satisfactory and reasonable explanation of the physics of the interaction between electrons and photoresists. The general trend agrees with the experiments:

1. The electron energy is coupled to molecule bonds at their characteristic frequencies.
2. When the electron energy increases, this model correctly predicts that the energy transferred to the chemical bonds goes down.
3. The typical range of interaction between an electron and the medium is of the order of 2 nm for a 1 keV electron.

The model presented here is still crude and needs refinement. In particular, one must use a more complete dielectric function to describe in a more quantitative way the interactions, and this must explicitly include the higher energy transitions. Also, the inclusion of screening is necessary to remove the unsatisfactory truncation at \( b_{\text{min}} \). Future work will involve the definition of a more exhaustive dielectric function \( \epsilon \); other energy coupling mechanisms (e.g., backbone excitations to the photoacid generator) may be taken into account phenomenologically by considering suitable yield values from absorbed energy.

ACKNOWLEDGMENTS

This work was based in part by a grant from the Semiconductor Research Corporation, Grant No. 98-LP-452. The Center for NanoTechnology, University of Wisconsin–Madison, is supported in part by DARPA/ONR Grant No. N00014-97-1-0460.