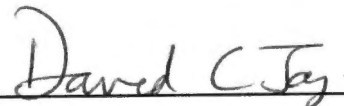


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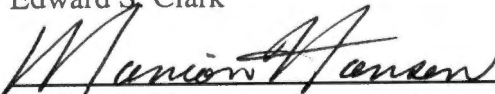


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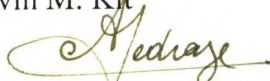
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**Electron Beam Induced Conductivity Effect of Polymer Resists and
Charging Induced Electron Beam Deflection Simulation in Electron
Beam Lithography.**

A Dissertation Presented for the Doctor of Philosophy Degree

The University of Tennessee, Knoxville

Justin Jia-Jen Hwu

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ABSTRACT

The electron beam induced conductivity (EBIC) effect of polymer materials was investigated and three electron beam resists, PBS, EBR900, and ZEP7000, were used as target materials in this research. An external bias method was applied for the direct measurements of EBIC current and the EBIC conductivity was then derived. The change of carrier drift velocity and the carrier concentration under field is believed to be the reason for the conductivity increase and the approach of the asymptotic values in the initial state EBIC characteristics. The temperature effect on EBIC was illustrated by EBR900 and a simple single trap level analysis gave good agreement in explanation of initial state conductivity dependence on temperature change. The dependence of initial state EBIC values on dose rates and bias was also determined and an empirical form of EBIC-bias relationship was established for the electron beam deflection modeling.

The long term EBIC characteristics of resists were investigated under different dose rates. The variation of EBIC versus time was explained by a transient theory that considers rates of carrier generation, carrier trapping, carrier detrapping, and carrier recombination contribution. The trapping model analysis on steady state EBIC results revealed that PBS has a uniform distribution of traps, while EBR900 and ZEP7000 fall in the same category that has exponential distribution of traps. The steady state EBIC gain was also determined for the three resists and the onset of the plasma region was observed for EBR900 and ZEP7000.

Monte Carlo simulation on electron beam range advised that only the positive charging layer needed to be considered for charging simulation and the image method was applied for the construction of the surface potential calculation.

A simulation model for the calculation of electron beam deflection owing to resist charging was developed in the second part of this research. Charging patterns of circles and squares of different dimensions were considered. Both SIMION and MATHEMATICA were used as simulation tools and the limitation of SIMION was illustrated and discussed. The model programmed in MATHEMATICA simulated electron beam deflection during e-beam writing. With the combination of the empirical EBIC–bias relationship of EBR900, the model simulated surface potential decay after irradiation and the results showed good agreement with literature values. The extent of deflection per surface potential was shown to increase with pattern dimension size under the same secondary electron emission yield, while the maximum deflection per surface potential per unit area decreased as the pattern dimension decreased.

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LIST OF SYMBOLS

A	Irradiation area
A_d	Beam diameter
A	Atomic weight
D	Dielectric constant
$\dot{D}$	Dose rate
$\dot{D}_0$	Reference dose rate at 1 rad/s
d	Depth or electron landing position from a charging pattern edge
d_s	Escape depth of secondary electron
d_p	Electron penetration depth in solid
d	Mass density
E	Electric field or electron energy
E_b	Beam energy
E_x	Electric field in x direction
E_z	Electric field in z direction
E_r	Electric field in r direction
e	Electron charge unit
G	EBIC gain
g	Conductivity
g_d	Delayed EBIC conductivity
g_{DARK}	Dark conductivity
I	Current
I_b	Incident beam current
I_{EBIC}	EBIC current
J	Mean ionization potential
J_b	Primary beam current density
K	Preexponent constant of Fowler's power law
K'	Constant for delayed EBIC equation
k	Boltzmann constant
L	Sample thickness
m	Electron mass
N	Total concentration of immobile carriers
N_c	Degeneracy of the extended band
N_d	Concentration of deep-trapped carriers
N_p	Number of electron-hole pairs generated per incident electron
N_t	Density of the trapping level
N_0	Avogadro's number
n_c	Free carrier concentration in extended band
n_s	Concentration of shallow-trapped carriers
n_t	Trapped carrier concentration
P	Electric power consumption
p	Probability

p	Carrier generation rate
Q	Total charge
q_i	Individual charge packet
R	Ratio of n_c to N , or resistance
R	Electron beam range
S	Mass distance unit; the product of d and s
S_x	Electron trajectory in x direction
s	Travel path in Monte Carlo simulation
s_b	Schubweg or mean free path of carrier
T	Absolute temperature
t	Time
U	Activation energy
V	Bias or surface potential
Z	Atomic number
α	Recombination rate coefficient
α_s	Screening factor for Rutherford elastic cross section
α_1	Trapping rate coefficient
α_2	Detrapping rate coefficient
α_3	Recombination rate coefficient
δ	Secondary electron emission coefficient
ϵ	Relative permittivity
ϵ_0	Permittivity in vacuum
η	Backscattered electron emission coefficient
λ	Electron mean free path
μ	Trap-modulated mobility
μ_+	Mobility of positive carrier
μ_-	Mobility of negative carrier
μ_0	Free mobility of carrier
ρ	Charge density
ρ_+	Density of positive charge
ρ_-	Density of negative charge
σ_E	Screened Rutherford elastic cross section
τ	Lifetime of carrier
τ_+	Lifetime of positive carrier
τ_-	Lifetime of negative carrier
v	Drift velocity of carrier
ϕ	Scattering angle
ψ	Azimuthal angle
Ψ	Work function
φ	Electrical potential
Φ	Solid angle

CHAPTER 1

INTRODUCTION

The advent of integrated circuit (IC) microdevices started the era of modern microelectronics and initiated ways of new electronics applications that were not possible or practical with discrete devices before. The miniaturization and simultaneous fabrication of transistors, resistors, capacitors, and interconnects on a silicon wafer makes possible today's advanced computational and communication technologies; and this is solely made available with modern lithographic procedures that rely essentially on polymer-based photoresists.

From the Moore's law prediction the devices on a chip will double in roughly every year, which means in approximately every 18 months the linear minimum feature size will shrink by half[1]. The current semiconductor fabrication technology in 1999 for 256 MB dynamic random access memory (DRAM) has reached 0.18 micrometer for half-pitch dense line spacing; the next generation of 0.15 micrometer technology is under its final pre-application evaluation and will be available next year. It is expected that by 2006 the fabrication technology will reach 0.1 micrometer (100 nanometer) milestone for 4 GB DRAM memory fabrication[2]. According to the statistics the semiconductor industry in the United States has enjoyed a constant growth at an average rate of approximately 15% annually over the past three and half decades. It is evident to say the semiconductor industry is currently one of the most vital and fast developing cutting-edge industries in this country, as well as a major power engine that drives US economy.

As the size of devices continues to shrink in semiconductor manufacturing, new problems related with the material characteristics and challenges from the developments of needed new process techniques are emerging. For example, one of the most significant current problems is the charging of photo and electron beam resists during electron beam tool applications. Charging degrades electron microscope imaging, produces systematic errors in critical dimension (CD) measurements, and results in fatal distortions of the patterns during the electron beam writing of photomasks. My research, therefore, concentrates on the charging behavior of polymer resist materials due to electron beam irradiation and the charging effect in electron beam tools applications because photoresist process is the key step in lithography. Since thirty-five percent of chip manufacturing cost today is associated with lithography, the economic importance of this study is very substantial.

The function of photoresist is to transfer a pattern to a material. This is done by using a combination of photoresists and photomasks. (During the first step in lithography, the patterns are transferred from a photomask into a photoresist layer spin coated onto a substrate. After exposure, patterns are formed in the resist layer by a development process, which will then be ²transferred onto the substrate by subsequent etching, metal deposition, ion implantation, etc. to fabricate transistors, interconnections, and other features simultaneously.)

A key technique in high performance lithography is the production of the photomask that defines the optical or x-ray illumination. This task is performed by electron beam lithography that is the direct electron beam pattern writing on electron

beam resists. The masks used in contemporary IC fabrication are mainly made by electron beam lithography owing to the readily accessibility of sophisticated computer controlled electron beam writing systems and their capability of offering focused electron beam source with spot size down to 2 to 10 nanometer diameter range for local precise pattern formation[3-5]. The commonly used photomasks today are the chromium coated glass plates. The blank masks are firstly spin coated with electron beam resists, this is then followed by the electron beam pattern writing and development of the resist layer and removal of the exposed chromium. In the finishing step the resist layer is stripped to form the final patterned masks. Charging during the first electron beam writing stage interferes with the position of the writing beam, degrades and distorts the precision of the patterns or can result in an unacceptable mask pattern. Since a typical mask is worth about \$50,000, this is a serious and expensive problem.

As discussed later, charging is the result of two distinct processes, a static effect which depends on the net inflow or emission of charged particles, and a dynamic effect resulting from the generation and subsequent trapping of electrons and holes as a result of electron beam irradiation. An important aspect of dynamic charging, so called because it varies with such parameters as beam current and beam dose rate, is the phenomenon of electron beam induced conductivity (EBIC). This effect, discovered three decades ago by photoconductivity studies, is well known to occur in most of semiconductor and some inorganic materials. However, its role on polymers, particular on resist materials is still not fully investigated today. I shall start our theoretical approach by using the established band gap model from conventional solid state physics to explain certain characteristic

electrical behaviors in photoresists, and an experimental method for measuring the dynamic properties of the EBIC effect will be performed. A charging model incorporating both static and dynamic charging with our experimental EBIC data will be proposed, and from this the spatial electric field and potential distributions in and above the resist will be derived and their contribution to the electron beam flight deflection will also be evaluated and compared with current available literature results. In the end we hope to combine our experimental data and computer simulation to establish a photoresist charging model that is capable of performing feedforward electron beam deflection compensation for electron beam tools, such as in SEM imaging, inspection, CD measurement and e-beam lithography applications.

CHAPTER 2

LITERATURE REVIEW

2.1. Historical Background of Electronic Beam Induced Conductivity (EBIC)

Research

It is well known that the electrical conductivity of insulators and semiconductors can be increased by exposing the substance to light (the effect, often called β -conductivity, also known as photoconductivity) or irradiation like x-ray, gamma irradiation, or electron beam. Among different types of irradiation, the effect caused by light was first discovered about 120 years ago and it was thought to be a specific material property of a few substances for years before the corresponding theory was constructed. This same theory is still used today as a backbone for the explanation of radiation-induced conductivity for most insulators with reasonable agreement. However, modifications are developed to better suit materials of different categories.

The effect of photoconductivity was first found on selenium[6] but it did not receive much attention till the discovery of cuprous oxide (Cu_2O) in 1916. Since then systematic research showed that other materials, particular sulphides and alkali halides, were found to display the same effect although to different extents.

The first observation on the conductivity increase due to electron bombardment was done on paraffin film by Becker[7]. Later in 1948[8, 9] the electron beam induced conductivity (EBIC) effect in diamond crystals was reported. Early research on electron beam induced conductivity was done mainly on inorganic materials, such as silica[10],

arsenic sulphide[11], antimony sulphide[11], alumina[12], mica[13, 14], zinc sulphide[15], etc.

Starting in the 1950's, the increasing use of polymer materials in electrical insulation applications, particularly in environments involving ionizing radiations, posed the need to understand the charge transport properties of polymers, therefore the interest on polymer-substance radiation-induced conductivity studies were initiated. X-ray, electron beam, β , and γ -rays were used as irradiation sources; in the early years, polyethylene[16-19], polyethyleneterephthalate[14, 20, 21], polytetrafluoroethylene[17, 18, 20], and polystyrene[22, 23] were among the materials studied most; the following research also led to the discovery that carriers of different polarity dominate charge transport processes in different polymer materials[24-26].

2.2 Threshold Effect and Gain

Both pulse and continuous electron beam irradiations are used in EBIC studies. For pulse irradiation, a quantity called the EBIC gain is defined as the ratio of the charge generated inside the film to the pulse charge injected; the EBIC gain for continuous irradiation is then defined as the ratio of the induced EBIC current to the incoming beam current. Early EBIC studies report low gains in the range of 10^{-4} to 10^{-5} or even lower[7, 27-31]. This is because both high energy electron beams and sophisticated techniques of thin film preparation were not available at that time. A common conclusion reached by the early researchers was the transmission of carriers and the resultant increase of gain

were observed only when the energy of the electrons appreciably exceeded a certain value, known as the "threshold effect".

The threshold effect was reported to happen at the beam energy that made the electrons penetrate half thickness of the film [11, 12]. Bowlit and Ehrenberg[32] determined the relationship between space charge and the threshold effect; in their research a two-beam bombardment was performed; the build-up of space charge after the first irradiation was then released by the second bombardment irradiating from the back side of the film. The extent of space charge in films in which the incoming beam energy was below the threshold energy was determined as well. (From their research it was confirmed that threshold effect starts to emerge at which the beam penetration depth reaches half of the sample thickness.)

The studies on light and x-ray induced conductivity resulted in the advent of a theoretical framework that accounts for charge carrier generation and transport in crystals and semiconductors during irradiation[33-36]. The research on photoconductivity illustrated that it is the generation of electron-hole pairs during irradiation that contributes to the conductivity change. This theory was expanded to explain the similar effects observed from insulators. (Since the band theory cannot fully explain the conductivity behavior in amorphous insulators, the idea of space-charge-limited current transport was proposed.) Mott and Gurney[37] first proposed the mechanism of space-charge-limited currents in solids; they simplified the analysis of space-charge injection by assuming the substance is an ideal insulator in absence of traps.

2.3 Concept of Irradiated and Non-Irradiated Regions

The existence of a threshold effect implies that a substance forms two distinct regions during electron beam irradiation; the sample depth within the range of beam comprises the irradiated layer, while a non-irradiated layer is formed from beyond the end of range to the rear sample surface. During electron beam irradiation, the charge carriers generated inside the irradiation region are driven out to the non-irradiated region by a field if an external bias is applied across the sample thickness; the field can still be present even if the external bias is absent, since the escape of secondary electrons near the front surface and the final trapping of incoming electrons close to the end of electron range creates layers of opposite polarity. The carriers from the irradiated region are trapped in the non-irradiated region; the process continues until the charge trapped in the non-irradiation region creates a potential that is high enough to take up the whole potential drop across the thickness, assuming the field in the sample does not reach the dielectric breakdown level during the process. The schematic representation of the electric field in a dielectric bombarded by electrons is illustrated in Figure 2.1. The early threshold study indicated that there should be regions of different carrier transport properties to account for the field buildup and resultant EBIC effect during and after irradiation. This idea was first explained in terms of internal space charge by Spear[11] and revealed by other researchers [12, 15, 32, 38, 39]; the analytical model considering a dielectric as a series of two regions under bombardment was proposed by Nunes de Oliveira and Gross later[40] and other groups[41, 42]; it will be reviewed concisely in the following section.

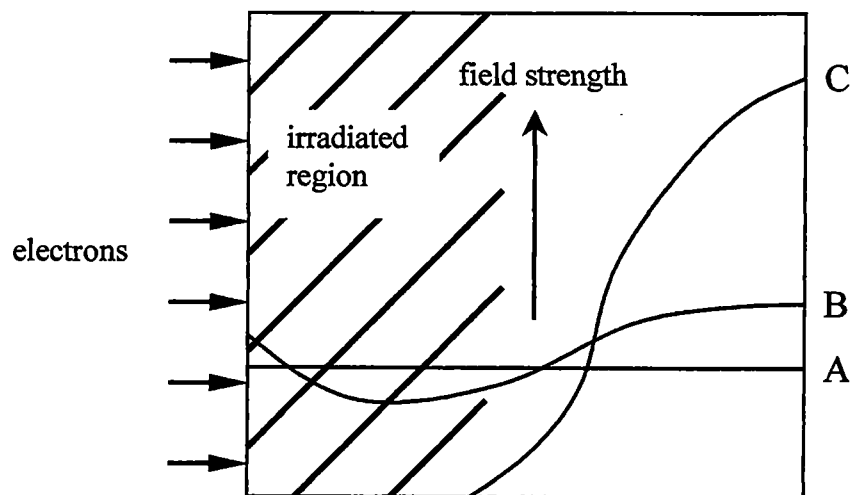


Figure 2.1. Schematic representation of the electric field in a dielectric bombarded by non-penetrating electrons; the left electrode is positive. A, before irradiation; B, after a brief pulse of irradiation; C, equilibrium under steady state irradiation. The dash line refers to the condition that the mobility of negative carrier is much higher than that of the positive carriers.[15]

2.3.1 Analytical Model of Irradiated and Non-Irradiated Regions

The analytical model proposes the zones of irradiated and non-irradiated regions coexisting during and after bombardment; the former is governed by the enhanced conductivity since the primary beam generates electron-hole pairs in the region while the space-charge limited current flow dominates the carrier transport in the latter zone (Figure 2.2).

The incident electrons penetrate through the front electrode and undergo a series of elastic and inelastic scatterings; eventually they lose all the energy and rest in the first region shown as d_1 . The electron-hole pair generated by the inelastic scattering in this region is driven by the field from both the applied bias and space charge created during irradiation. The depth d_1 may be written according to the consideration of the combined effects of elastic scattering and energy loss[43]:

$$d_1 = 0.0276 \cdot A \cdot E_b^{1.67} / Z^{0.89} \cdot d \quad (2.1)$$

where E_b is the incident beam energy, A the atomic weight, Z the atomic number, and d the density of the sample. The induced current in this region, based on the photoconductive gain equation[35], is

$$I_1 = N_p \cdot \mu \cdot \tau \cdot I_b \cdot V_1 / d_1^2 \quad (2.2)$$

where N_p is the number of carrier pairs generated by a primary electron, $\mu \cdot \tau$ is the net effect of carrier mobilities and lifetimes and $\mu \cdot \tau$ equals $\mu_+ \cdot \tau_+ + \mu_- \cdot \tau_-$ where $\mu_{\pm}$ and $\tau_{\pm}$ are the carrier mobilities and lifetimes of different polarity carriers before recombination, I_b is the primary beam current measured by electrons per second, V_1 is the potential

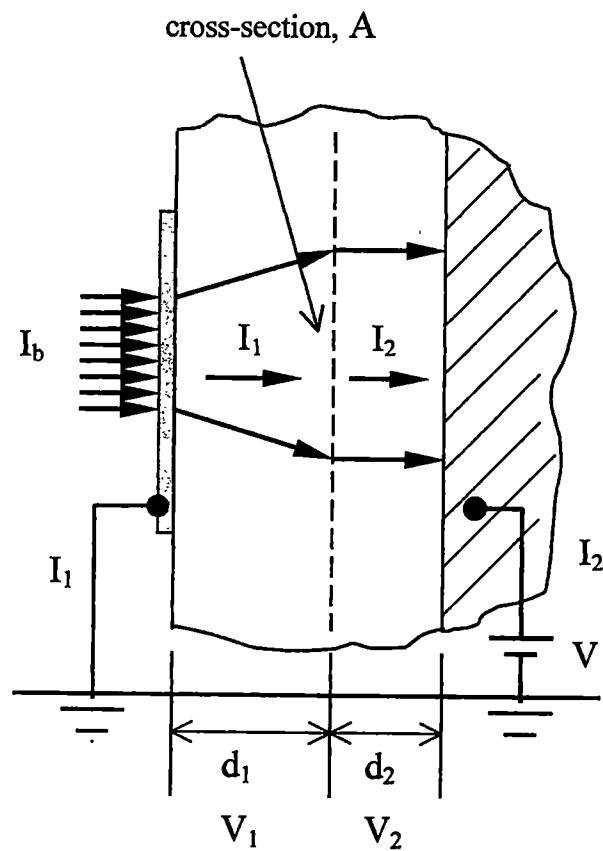


Figure 2.2. Illustration of irradiated and non-irradiated regions and their circuit arrangement. The thickness d_1 is determined by the electron range.[41]

appearing across range d_1 . V_1 can be determined by the relative resistivities in region d_1 and d_2 and the space charge might exist in the interface[41].

The region beyond the irradiation zone is likely to have higher electrical resistance than the value mentioned above. Assuming the interface and the back electrode are injecting contacts, space-charge-limited conduction may be expected to occur. For simplification in derivation, only carriers of one sign are assumed to be mobile and they are taken to drift across the path d_2 while carriers of the opposite sign are quickly trapped; the distribution of traps is assumed to be shallow and can be treated equivalently as traps in a single level. The conduction current in d_2 is thus represented as[44]

$$I_2 = \epsilon \cdot \mu \cdot A \cdot V_2^2 / (e \cdot d_2^3) \quad (2.3)$$

where ϵ the permittivity, μ the trap-modulated mobility that is different from the free mobility due to trapping of carriers (this will be discussed in Chapter 3.4), A is the cross-sectional area and is determined by the initial cross section of the beam and the subsequent scattering processes in the depth d_1 , V_2 is the potential across d_2 , e is the electronic charge. For interface of negligible thickness, the following relationship exists

$$V_1 + V_2 = V \quad (2.4)$$

and

$$d_1 + d_2 = d \quad (2.5)$$

The EBIC gain G is written as

$$G = I_2 / I_b \quad (2.6)$$

combining equation (2.2)-(2.5) the gain can also be written as

$$G = \pm \epsilon \cdot \mu \cdot A \cdot V_2^2 / (e \cdot I_b \cdot (d - d_1)^3) \quad (2.7)$$

where the positive sign is taken when V_2 is positive. One might expect to see the maximum of g when the penetrating beam condition is reached. However, this is not necessary the case since the maximum of gain is determined by the relative resistances in region d_1 and d_2 .

The predicted potential distributions across the dielectric and gain characteristics are shown in Figure 2.3.

2.4 Charging Effect in Electron Beam Irradiation

The electron beam tools of different kinds are commonly used in today's semiconductor manufacturing, such as the applications of scanning electron microscope in sample imaging, inspection, CD measurement, and direct electron beam writing during photo or x-ray masks patterning. Local charging of workpiece experienced during e-beam tool applications has become a pervasive problem and it will even be an more significant factor that influences the precision of CD measurements and electron beam lithography in the future as the device size continues to shrink. In this section we shall review the current research progress on charging effect experienced in electron beam lithography and justify our research proposal for establishing a suitable dynamic charging model.

The charging of the workpiece during e-beam direct writing has been identified as a factor that causes pattern displacement errors. The error as a result of charging is becoming more significant as the pattern dimensions continue to shrink. Various

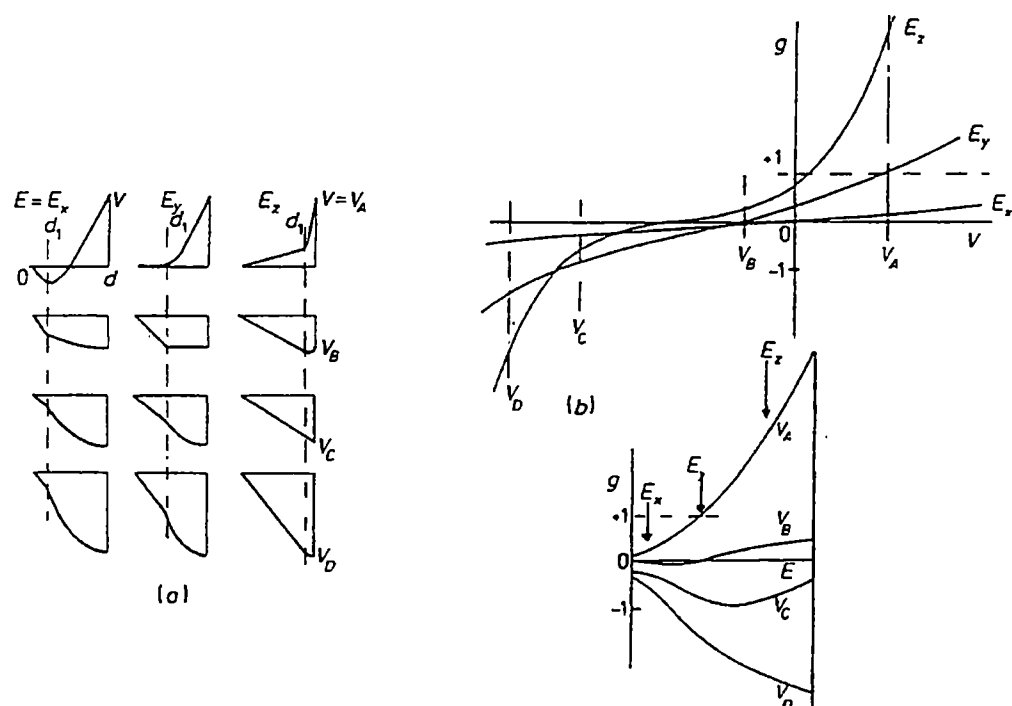


Figure 2.3. The illustration of potential and field distributions of a sample with irradiated and non-irradiated regions. (a) Sketches of potential distributions across a bias dielectric for different V and d_1 . Bias voltage is in the increasing order from V_A to V_D . (b) Gain versus V and gain versus E corresponding to 2(a).[41]

approaches toward the estimation of the deflection error due to substrate charging have been conducted, including experimental and relevant models that estimate the amount of e-beam deflection[45-54].

Angelopoulos *et al.* [49, 52] reported the pattern displacement error in the range of greater than 5 μm in their 2-step pattern writing electron beam deflection experiment. However, no deflection estimation model was proposed to correlate with their experimental observation. They noticed that their presumed charging-free reference pattern interfered with the following writing pattern and resulted in a displacement error of $\cong 0.5\mu\text{m}$ in the first step of second pattern writing for nonconducting interlayer resist samples. This error range agreed with the calculation done by a simplified model, which predicts the interaction between surface charge and electron beam is strong and long range[51, 54].

Ingino *et al.*[46] presented two models for the calculation of beam deflection in e-beam writing procedure. In their report an experimental setup for the estimation of resist surface potential was also proposed and later revised[45]. A destination error of 1 to 1.7 μm for a 10kV beam at 10mm working distance was reported from the models' calculation, and the use of a top ground plate to resemble the zero potential pole piece was suggested by the models for better space field calculation.

The patterns have been written during an e-beam process all contribute the field that interferes the area that is going to be written because of the nature of slow charge decay and the long range characteristic of electrostatics interaction. The field strength in beam deflection predictions depends on the dimension of the charged area assigned in

calculation. So far most of the models proposed deal with single areas in the millimeter size range, which might overestimate the deflection error due to size selection and underestimate the deflection at the same time for their single geometry definition. Based on the above review there is still room for better simulation in more realistic dimension, such as in micrometer dimension range.

CHAPTER 3

THEORETICAL BACKGROUND

3.1 Band Gap Model and Localized States

The band gap model, derived from band theory calculations in conventional solid-state physics, describes charge-transport processes well in ordered materials. It has also been applied to explain electronic processes in certain amorphous semiconductors and polymers as a best approximation, even though the actual band structure of amorphous materials is far too complicated to calculate. The amorphous and microcrystalline dielectrics of our concern still possess short-range order to certain extent; this allows the band gap model to be appropriately applied over a microscopic range and serves as a useful model with which a wide range of observations are explained.

The electronic processes of an ordered material can well be explained by the band theory. In a crystalline material, the interaction between an electron and the constituent atoms is periodic in three dimensions. The interaction forms different energy levels for electrons and holes as described by the Bloch solutions of the Schrödinger equation and called the band structure of the crystal. The band structure of a crystal determines the charge carrier transport processes of the crystal itself. In a crystalline semiconductor or insulator, the band structure consists of a filled valence band and an empty conduction band along with a well-defined energy gap separates them in between. Impurities and structural defects in the material form concentrations of localized energy levels in the energy gap, and these energy levels serve as traps for electrons or holes or even

recombination centers for trapped charge to recombine with carriers of opposite polarity (Figure 3.1a). The electron traps have energy states close to the bottom edge of the conduction band while the hole traps have the energy states that are just above the valence band. At a given temperature, electrons from the valence band or impurity donors can be excited to the conduction band if electrons are the dominant charge carriers. The excited electrons are either trapped in the higher energy state traps or move freely in the conduction band; the rate of excitation, recombination, trapping, and detrapping form a dynamic equilibrium and render a equilibrium conductivity at this temperature. Similarly, the impurity can accept electrons from the valence band and leave free-moving holes in the valence band if holes are the charge carriers. Again the various mechanisms mentioned above happen in a same manner and contribute a steady conductivity level by hole transport at a given temperature.

Band theory has been applied to explain the electrical conductivity of molecular crystals such as benzene, naphthalene, anthracene, tetracene, etc [55]. The crystal of these organic materials can be treated as an array of molecular molecules. Since the intermolecular interaction is generally weak and the wave functions have low couplings, the band structure calculation from the Bloch solution results in very narrow bands (Figure 3.1b). The increase of the effective mass of electrons and holes results in a slow response in an external field, therefore a low electrical conductivity is seen in these materials [56, 57].

In more highly disordered materials, such as amorphous molecular materials and polymers, a well-defined band structure may not exist. It is believed that the so called

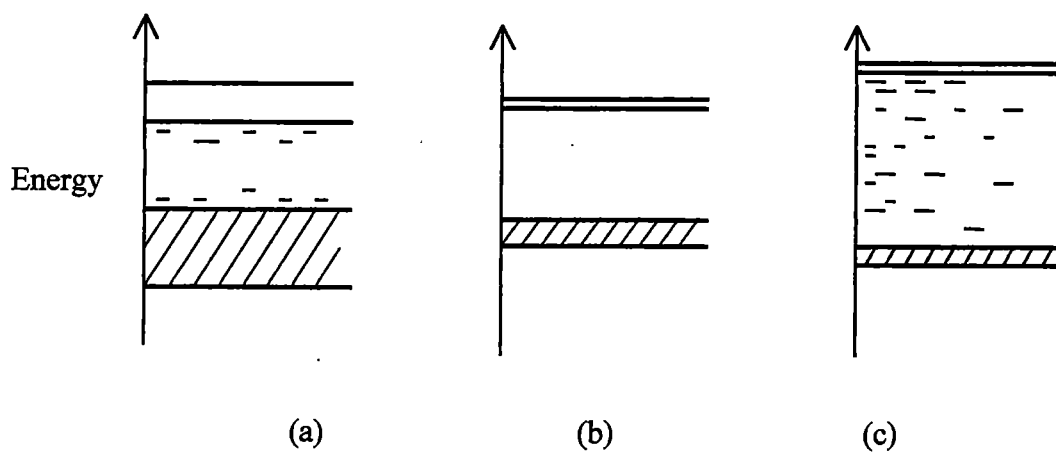


Figure 3.1. The band structures of (a) a crystal with defects, (b) molecular ordered materials, (c) an amorphous material with short-range order.

“energy band” structures are arrays of localized states with similar energies (Figure 3.1c). They can be in neutral state serving as carrier donors, acceptors, or carrier traps, as well as in ionized states after excitation and serve as filled traps or recombination sites. Since the localized states can be high in concentration and vary closely in energy, the mechanism of charge carrier transport in disordered materials is proposed as carrier jumping across the discrete states in these “band” like energy levels, a transport process that is much less efficient than that in semiconductors.

Hopping of charge carriers over the localized energy states has been proposed as the mechanism of charge transport in molecular crystals and amorphous materials under the electric field[55, 58]. Unlike the ordered materials, the excited carriers are not freely moving in the energy levels at low temperature and hopping is a temperature activated process. The hopping process can be intermolecular, or even intramolecular in polymers if available levels are present in the same molecules.

It is known that intrinsic defects, such as structural defects and impurity centers in materials, contribute trapping sites for carriers in charged electrets studies [59]. For polymers, the amorphous-crystalline interfaces, branching, chain ends and entanglements, pendant groups, etc all contribute the formation of traps. Besides, various conformation and molecular motion along a polymer chain provide even more possible localized states. The following modes of molecular motion are suggested as possible localized states and most of them can be discerned from thermally stimulated discharge (TSD) experiments of electrets; they are listed in the increasing energy order:[60]

- 1) side-chain motions

- 2) motion of two four-carbon moieties in the main chain (the Schatzki crankshaft effect)
- 3) motion of moieties containing heteroatoms in the polymer chain
- 4) motion of segments containing 50-100 backbone atoms, i.e., glass transition temperature
- 5) motion of the entire chain as a unit
- 6) crystal melting
- 7) change in crystalline structure
- 8) motion of side chains in the crystallite
- 9) crystalline-amorphous interactions including interfacial friction

Some trap energy states have been estimated. Duke and Fabish[23] argue the side groups on polymer chain can also serve as trapping states and different structure variations could result in the energy-level variation of the range of 1 eV. The existence of lower energy states does not guarantee hopping to occur, it is the activation energy of the whole process along with the ease of detrapping that determine the possibility of hopping. Hopping and space-charge-limited current flow are the mechanisms of insulator conduction. The mechanism of space-charge-limited current flow is one of the carrier transport mechanisms; it will be discussed in the Chapter 3.3 in which photoconductivity principles are generalized for EBIC theory illustration.

3.2 Trap Level Distribution and Multiple Trapping Model

The research of the distribution of traps has been an important topic since the information revealed could lead to the better understanding of material characteristics or

the processing history. Concepts and understanding of carrier generation, trapping, detrapping, and recombination stem from the early photoconductivity research study[35]. Based on x-ray induced conductivity studies, Fowler proposed a trapping model on the assumption of a continuous trap energy distribution[61]. The steady-state radiation-induced conductivity poses a power law relationship with the irradiation dose rate $\dot{D}$

$$g = K (\dot{D} / \dot{D}_0)^\Delta \quad (3.1)$$

where $\dot{D}_0$ is the reference beam dose rate taken as 1 rad/s and K the constant that contains the contribution of g at 1 rad/s. The exponent Δ is in the range of 0.5 to 1. A uniform distribution of energy trap levels renders 1 for Δ . A trap level in the gap with its distribution falls exponentially with energy level gives Δ between 0.5 and 1. The limiting case of steep exponential distribution is equivalent to all traps having a single energy level, and $\Delta = 0.5$ is predicted for this.

The decay of irradiation-induced conductivity can also be given by the form

$$g = K' \cdot g_0 \cdot (1 + t/\tau)^{-1} \quad (3.2)$$

where K' is the constant and τ the time constant of the system.

Typically, current from thermally stimulated discharge (TSD) experiments shows multiple peaks; this indicates the carriers reside in more than one energy level.

The fundamental analysis for multiple trapping was established by Scher and Montroll[62] and the continuous-time random walk (CTRW) model based on the prediction of the stochastic hopping transport was also developed by various groups[63-65]. CTRW model fails to explain the observations that the apparent activation energy

for the charge collection process depends on the fraction of charge collected; the alternate multiple-trapping model[66, 67] is then developed to fit the experimental observation on the temperature dependence of activation energy.

3.3 Photoconductivity Principles and Relevant Models

Photoconductivity is briefly introduced here since the photoconductivity and EBIC effect which will be introduced below are principally the same in terms of electron-hole pair generation. The main difference between photoexcitation and electron beam irradiation for carrier generation is the former is kept in charge neutrality, while the latter forms space charge distribution during and after electron beam irradiation.

Photoconductivity is a process in which the absorption of light by a solid results in a change of electrical conductivity and it is a quantum process. A beam of light releases energy to electrons in both localized states and in the valence band; they are excited to conduction band and equal number of holes are generated in the same time. The increase of electron and hole densities in conduction and valence bands results in the increase of conductivity.

One of the important issues in photoconductivity is the time dependence of the photocurrent and this is controlled by the characteristics of carrier recombination. The recombination process is the main cause that terminates free electrons and holes. There are two possible ways of recombining carriers: the direct recombination of free carriers of opposite polarity and the indirect recombination through the localized sites in the band gap. The former process needs to happen in the valence band, but this rarely occurs since

free carriers in the conduction band need to release their energy all in one event and go directly to their ground state; this is favored process only if a perfect crystal is assumed. The chemical impurities and physical imperfections are known to occur at the range of 10^{15} cm^{-3} or greater. This corresponds to a departure from perfection of one part in 10^8 . Besides, it is known that the response times of photoconductors can easily be influenced by defect density as low as 10^{10} cm^{-3} [35]. The localized levels introduced by impurities and imperfections in a solid make the latter process the dominant one in the real materials; it is therefore easy for electrons and holes to be trapped in shallow energy states and recombine with opposite carriers that are promoted by an energy that is small than the energy gap.

The systematic treatment for photoconductivity and related problems were summarized by Rose[33-35]. A theory evolving from photoconductivity with consideration of randomly distributed traps of discrete levels was proposed by Simmons and Taylor[68]. Treatment of photoconductivity and charge transport by random walk theory has also been developed [62, 69].

3.4 Carrier Mobilities in Polymers

The transportation of carriers inside a sample under the influence of electric field results in the current measured and the conducting characteristic of a sample. The carrier mobility μ , defined as the drift velocity of carriers per unit field strength, bears the unit of $\text{cm}^2\text{V}^{-1}\text{sec}^{-1}$. For electrons in the conduction band or holes in the valence band the drift velocity v of free carriers is defined as

$$v = \mu_0 \cdot E \quad (3.3)$$

where μ_0 is the free mobility of electron or hole and E is the field. The free mobility is a material constant; it is not a strong function of temperature and free mobilities of different insulators are reported to be in the range from 10^{-3} to $1 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$ [70].

At a temperature above absolute zero, the free carrier concentration in the conduction and valence bands, n_c , and trapped carrier concentration in different energy levels, n_t , are in a thermal equilibrium; the ratio of n_c to total immobile carrier density, i.e., $(n_c + n_t)$ is designated as R . A trap-modulated mobility is thus proposed to represent the overall effective mobility in which the equilibrium distribution of carriers is considered, it is given as

$$\mu = \mu_0 \cdot n_c / N = \mu_0 \cdot R; N = n_c + n_t \quad (3.4)$$

The trap-modulated mobility is a strong function of temperature. For a single electron trapping level at a given temperature, the trap density ratio n_c/n_t is given as [71]

$$n_c/n_t = (N_c/N_t) \cdot \exp(-U/kT) \quad (3.5)$$

where N_c is the degeneracy density of the conduction level, N_t the density of traps, U the activation energy. The trap-modulated mobility therefore, by combining equation (3.4) and (3.5), equals

$$\mu = \mu_0 / (1 + (N_t/N_c) \cdot \exp(U/kT)) \quad (3.6)$$

At high temperature μ approaches μ_0 ; for low temperature $\mu \cong \mu_0 \cdot (N_c/N_t) \cdot \exp(-U/kT)$. For typical insulators one has $N_c \cong 10^{19} \text{ cm}^{-3}$ and $N_t \cong 10^{17} \text{ cm}^{-3}$, with μ_0 in the range of $10^{-3} \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$ and 0.5 eV for U , $\mu \sim 5 \times 10^{-10} \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$, which is of the range of mobility values reported for polymers [26, 72-75].

The lower limit of free mobility can be estimated if the carrier recombination rate is known; this is the famous Langevin's relation [76-78] and it is given as

$$\alpha/\mu_0 = e/(\epsilon\epsilon_0) \quad (3.7)$$

where α is the recombination coefficient between carriers of opposite polarity in $\text{cm}^3 \text{s}^{-1}$, e is the electron charge, and ϵ and ϵ_0 are the relative permittivity of the insulator and permittivity in vacuum respectively. A trap-modulated mobility estimation can also be done by consideration of Fowler's recombination law[33, 34, 61]. The radiation-induced conductivity g can be written as

$$g = e \cdot n_c \cdot \mu_0 = e \cdot N \cdot \mu \quad (3.8)$$

and the recombination law at steady state is[61]

$$p = \alpha \cdot n_c \cdot N \quad (3.9)$$

where p is the carrier generation rate. Combining equation (3.7) to (3.9) one obtains

$$\mu = g^2/(e \cdot p \cdot \epsilon\epsilon_0) \quad (3.10)$$

The "Schubweg", or the mean free path of carrier, s_b , can be estimated if it is small compared with the sample thickness L . The movement of a carrier with a charge e over a distance s_b normal to the electrodes of a parallel plane capacitor results in an external induction charge $e \cdot s_b/L$ [79]. If the carrier generation rate is p over the sample irradiation volume $A \cdot L$, the radiation-induced current I will be given as

$$I_{\text{EBIC}} = A \cdot L \cdot e \cdot p \cdot s_b/L \quad (3.11a)$$

and

$$s_b/L = I_{\text{EBIC}}/A \cdot L \cdot e \cdot p \quad (3.11b)$$

s_b can therefore be estimated once after p is known.

3.5 Ramo's Theory

The current measured during the EBIC experiments is the contribution of the carriers moving under the field inside the specimen. A simple theorem proposed by Ramo[7, 80] illustrates how charge transport, induction current, and conductance are coupled. This theory directly relates to the carrier transport inside a dielectric and the induction EBIC current measured outside the circuit loop; it will be applied in our research calculations for carrier transport information.

Consider a charge Q placed in a parallel plate capacitor of gap L as shown in Figure 3.2. The work required in moving this charge over a distance dx along the field is $Q \cdot (V/L) \cdot dx$, which is supplied by the battery outside the capacitor. From the energy balance we know

$$Q \cdot (V/L) \cdot dx = V \cdot dq \quad (3.12)$$

where dq is the charge flows in the outside loop. The time variation of equation (3.12) thus gives the information about the drift velocity and carrier concentration of carriers in a dielectric under the influence of a electric field (V/L).

3.6 Radiation Chemistry of Photoresists

Both poly(olefin sulfone) (PBS) and poly(methyl methacrylate) derivative type (EBR900 and ZEP7000) positive electron beam photoresists are used in our research. The chemical structures will be illustrated in Chapter 4.2. In this section I shall give a brief discussion of the radiation chemistry in these photoresists.

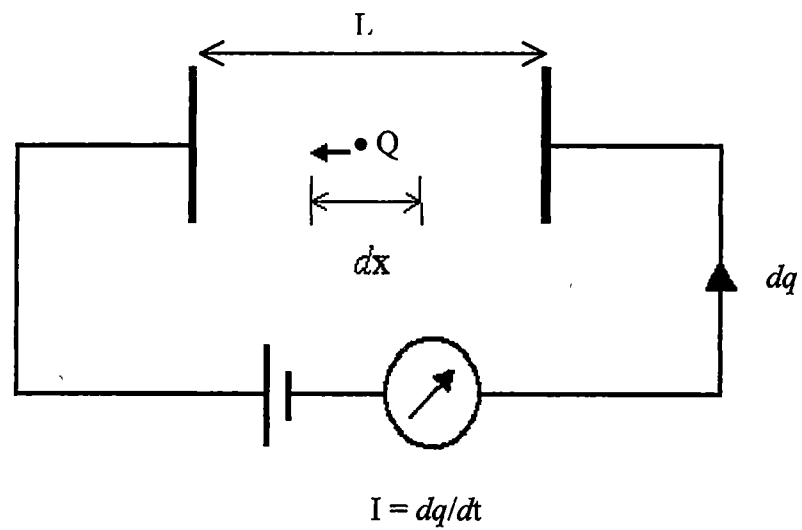
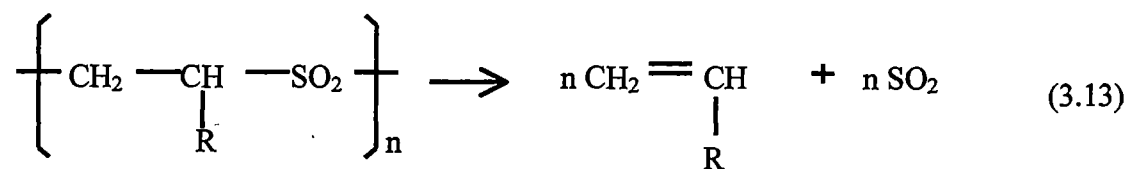


Figure 3.2. Illustration of Ramo's theorem: the movement of charge Q inside the capacitor causes an induced current dI measurable from the ammeter outside.

3.6.1. Poly(olefin sulfone) Photoresist

The high energy electron beam initiates backbone scission in all three positive resists. For poly(butene-1-sulfone), it is the relatively weak C-S bond on the chain (62 kcal/mole for C-S bond to 83kcal/mole for C-C bond) that undergoes breakage during electron beam irradiation. In the exposure it is known that the scission reaction on C-S bonds happens first, followed by the spontaneous depolymerization of the alternating chain[81, 82]



From the diaryl sulfone analogy radiation chemistry study it is proposed that the first step in the process is the loss of an electron from the molecule[83]



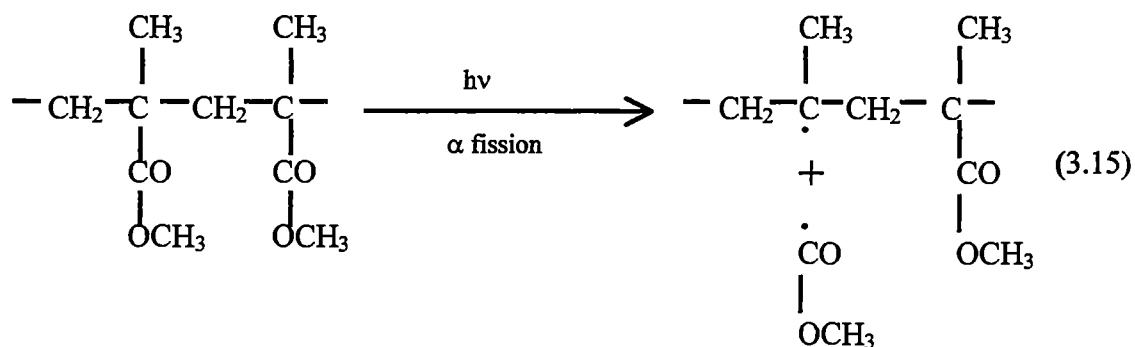
The loss of the electron results in the formation of a vacancy in the σ (S-C) bonding orbital, this weak S-C bond is thus susceptible to thermal or kinetic energy transfer by the ionization events or the energized incoming electrons. Therefore a high yield of scission is obtained. Typically, the sensitivity of commercial available PBS resists is at the range of $1\mu\text{C}/\text{cm}^2$ for 10 KeV electron beam.

PBS resist can be developed thermally or by convensional solvent method[5] after electron beam exposure. The exposed area of the resist can evaporate at elevated temperature or even during electron beam writing owing to local heat buildup[84]. This is a benefit of PBS system since the solvent development procedure can be eliminated,

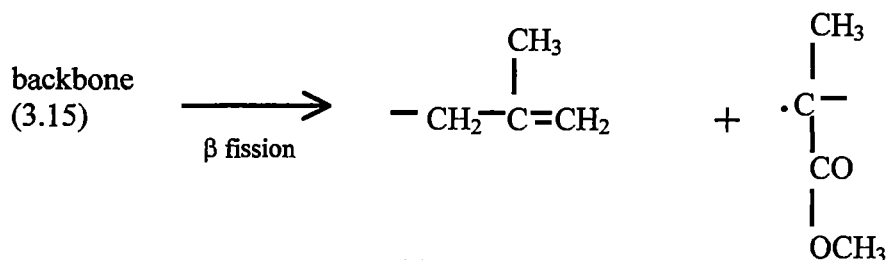
but the contamination of vacuum chamber and the resulting shortening lifetime of electron gun is the drawback.

3.6.2 Poly(methyl methacrylate) Resist and Derivatives

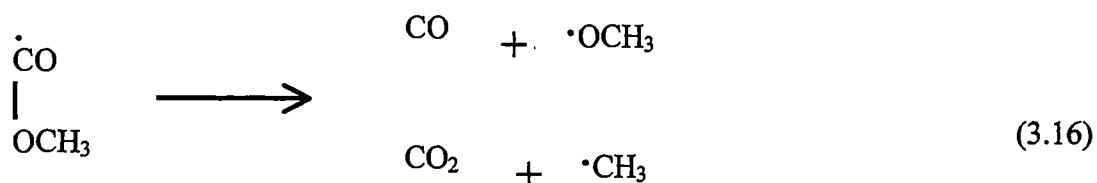
Not only serve as deep-UV photoresists, PMMA and its derivatives are also the main stream electron beam resists today. PMMA series resists are characterized by their good wetting and adhesive properties among photoresists. Backbone scission occurs on the α carbon by the carbonyl group, it is called Norrish-type I process and is shown in the following reaction scheme.



(3.15) goes through further β fission and results in backbone breakage and formation of gases



broken side group



Reaction kinetics studies[85, 86] showed that the instability of the radical formed during the α scission step hinders the whole reaction rate and thus renders low sensitivity of PMMA in electron beam resist applications. There are ways proposed to weaken the α C-C bonds, such as the introduction of electron-withdrawing halogen substituents at the α carbon on the backbone or at the ester side group (EBR900), or copolymerization with radiatively more susceptible components.(ZEP7000) These all contribute the stability of the radical formed during scission, thus the sensitivity of these PMMA derivatives are increased.

3.7 Monte Carlo Simulation

The determination of the spatial distribution of the primary electrons in a dielectric is a key step for the double layer model calculation and this step is done by Monte Carlo simulation. The principle of Monte Carlo simulation on electron trajectory in solids is to use a finite number of random sampling events to simulate a real electron-solid interaction. In the simulation, the electron mean free path and the corresponding energy loss due to elastic and inelastic scattering processes are randomly generated and incorporated as a start for a following step as an electron travels inside a solid. Every event begins with an electron of assigned energy and ends when all its kinetic energy is

released through scattering and it comes to a stop or a desired energy minimum is reached. The selection of the size of sampling base need to compromise the calculation time required from a modern PC and the justification to represent a real electron-solid interaction. Without this technique, the information of electron-solid interaction and the resultant spatial charge distribution will only be available from experiments, which is time-consuming and sometimes not feasible.

The Monte Carlo simulation evolved as a mathematical process and it has many applications in statistics and physics related area, such as radioactive decay and transmission of cosmic rays through barriers. The first Monte Carlo method applied on charged particles was reported by Hebbard and Wilson[87]; since then other works in this field had been done by different groups and consequently the framework of Monte Carlo simulation on electron-solid interaction had been established[88].

Scattering angle influence on electron path in solid contributed from elastic and inelastic scattering processes are summarized by Joy[88]. I herein discuss the single scattering model since it confines scattering angle change as results of elastic scattering event and it agrees with experiments with large sampling base. The assumptions in the single scattering model are illustrated as follows:

- 1) Only the elastic scattering events contribute the deflection of electrons while traveling in a solid. Elastic scattering is a process that an incident electron undergoes the Coulombic attraction from the positively charged nucleus of the target atom and the repulsion from the orbital electrons of the nucleus, less than 1eV of energy is transferred from the beam electron to the target atom. The elastic scattering, described by the

screened Rutherford cross section (will be discussed later), results in a scattering range from 5° to 180° [89]. The inelastic scattering process, however, introduced deflections of the order of $\Delta E/E$. For a 10keV electron which losses 15 eV during an inelastic event, the deflection resulting from this energy loss will be about $15/10,000$ radians, which is only about 0.1° change in direction of travel and therefore can be regarded as insignificant and neglected.

2) The energy loss of the incident electrons is assumed to be a continuous process along their path instead of as the result of discrete inelastic scattering events. In reality both the continuous energy loss process like Bremsstrahlung generation and the discontinuous processes like Auger electron and characteristic x-ray peak generation happen at the same time. In single scattering model the total energy loss process of an incident electron is averaged and described by the Bethe relationship which will also be discussed in the following.

The basic geometry for the simulation calculation is illustrated in Figure 3.3. Consider an electron traveling from a spatial position P_{n-1} and experiencing a scattering event at P_n with a direction change at P_n , the distance between P_{n-1} and P_n is the elastic mean free path, the directional change at P_n is described by ϕ . The electron will further travels from P_n and experiences another scattering event at P_{n+1} . The elastic mean free path is related with the screened Rutherford elastic cross section σ_E by the following relation[90]:

$$\sigma_E = 5.21 \times 10^{-21} \cdot \frac{Z^2}{E^2} \cdot \frac{4\alpha_s}{\alpha_s(1+\alpha_s)} \left(\frac{E+511}{E+1024} \right)^2 \quad (3.17)$$

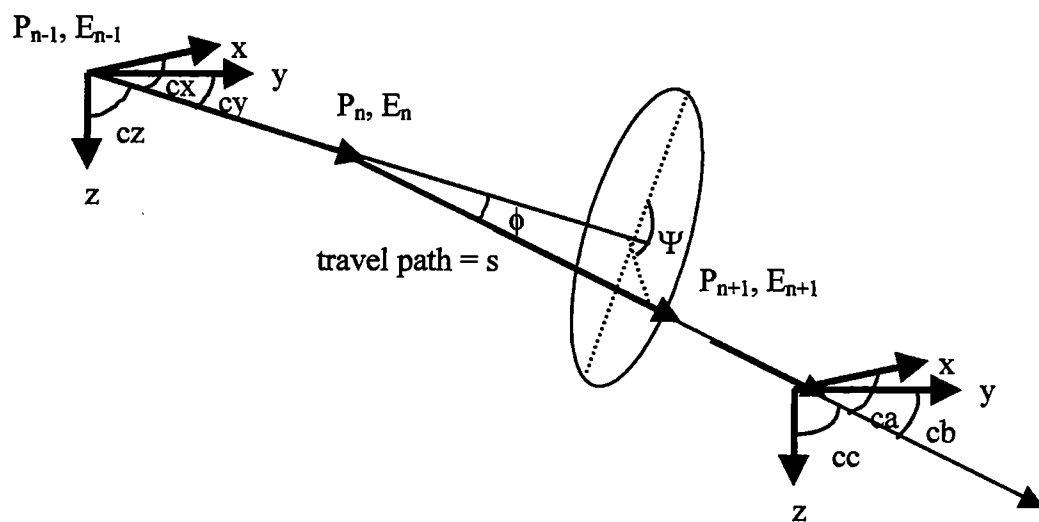


Figure 3.3. Definition of coordinate system used in the Monte Carlo simulation.

where E is the electron energy in keV, Z is the atomic number of the target, α_s is the screening factor that accounts for the fact that the incident electron does not see all the charge on the nucleus owing to the screening effect from the orbiting electrons the nucleus has. The factor α_s is evaluated using an analytical approximation[91]:

$$\alpha_s = 3.4 \times 10^{-3} \cdot (Z^{0.67}/E) \quad (3.18)$$

the mean free path λ is related with the cross section σ_E by

$$\lambda = A/(N_0 \cdot d \cdot \sigma_E) \quad (3.19)$$

where N_0 is the Avogadro's number, A the atomic weight of the target in g/mole, and d the target density in g/cm³. The λ obtained from equation (3.19) is the averaged elastic mean free path that an incident electron will travel between successive elastic scattering events. The range of λ is about 10 to hundreds angstroms for a 10keV beam, the calculated λ for selected targets are illustrated in Table 3.1.

The actual mean free path an electron travels in successive elastic scattering events is in a random manner; the probability of an electron traveling distance s with an averaged mean free path λ is given as

$$p(s) = \exp(-s/\lambda) \quad (3.20)$$

The estimation of s can be found by solving the integration

$$RND = \frac{\int_0^s \exp(-s/\lambda) ds}{\int_0^\infty \exp(-s/\lambda) ds} \quad (3.21)$$

which gives

Table 3.1. Elastic mean free path of electrons in selective materials.[88]

Element	Z	λ at 100 keV	λ at 10 keV
carbon	6	1310 Å	170 Å
silicon	14	1112 Å	127 Å
copper	29	297 Å	35 Å
gold	79	89 Å	10 Å

$$\text{RND} = 1 - \exp(-s/\lambda) \quad (3.22)$$

therefore

$$s = -\lambda \cdot \ln(1 - \text{RND}) \equiv -\lambda \cdot \ln(\text{RND}) \quad (3.23)$$

RND in equation (3.21) to (3.23) is a random number ranging from 0 to 1 and is generated by computer during simulation. In equation (3.23) $1 - \text{RND}$ is rewritten as RND since they both are randomly generated.

The scattering angle ϕ is determined from the angular dependence of screened Rutherford cross section as[92]

$$\sigma_E' = 5.21 \times 10^{-21} \cdot \frac{Z^2}{E^2} \left(\frac{E + 511}{E + 1024} \right)^2 \frac{1}{(\sin^2(\phi/2) + \alpha_s)^2} \quad (3.24)$$

and the scattering angle can be determined by the integration[90]

$$\text{RND} = \int_{\Omega} \frac{\sigma_E'(\phi)}{\sigma_E'} d\Omega \quad (3.25)$$

equation (3.25) yields the relation for the scattering angle ϕ with RND and α as

$$\cos(\phi) = 1 - 2 \cdot \alpha_s \cdot \text{RND} / (1 + \alpha_s - \text{RND}) \quad (3.26)$$

The electron scattered at P_n with angle ϕ is free to travel with an azimuthal angle ψ , again the determination of ψ is by a random number RND as

$$\psi = 2\pi \cdot \text{RND} \quad (3.27)$$

here the generation of RND is independent of the random numbers in equation (3.23) and (3.26). The relative position of P_{n+1} to P_n can be determined after the traveling path s , the scattering angle ϕ , and the azimuthal angle ψ are calculated. The coordinates x_{n+1} , y_{n+1} , z_{n+1} at P_{n+1} is related with P_n (x_n , y_n , z_n) as

$$x_{n+1} = x_n + s \cdot ca \quad (3.28a)$$

$$y_{n+1} = y_n + s \cdot cb \quad (3.28b)$$

$$z_{n+1} = z_n + s \cdot cc \quad (3.28c)$$

where ca , cb , and cc are direction cosines at P_n and they are related to the direction cosines cx , cy , cz that generated in the previous scattering. ca , cb , cc are transformed from cx , cy , cz as [88] and [93]

$$ca = (cx \cdot \cos(\phi)) + (V1 \cdot V3) + (cy \cdot V2 \cdot V4) \quad (3.29a)$$

$$cb = (cy \cdot \cos(\phi)) + (V4 \cdot (cz \cdot V1 - cx \cdot V2)) \quad (3.29b)$$

$$cc = (cz \cdot \cos(\phi)) + (V2 \cdot V3) - (cy \cdot V1 \cdot V4) \quad (3.29c)$$

where

$$V1 = AN \cdot \sin(\phi) \quad (3.30a)$$

$$V2 = AN \cdot AM \cdot \sin(\phi) \quad (3.30b)$$

$$V3 = \cos(\psi) \quad (3.30c)$$

$$V4 = \sin(\psi) \quad (3.30d)$$

and

$$AN = -(cx/cz) \quad (3.31a)$$

$$AM = \frac{1}{\sqrt{(1 + AN^2)}} \quad (3.31b)$$

Note that in our derivation the direction cosines have the following property

$$ca^2 + cb^2 + cc^2 = cx^2 + cy^2 + cz^2 = 1 \quad (3.32)$$

The energy loss of the incident electron traveling from P_n to P_{n+1} composes of different mechanisms, such as Coulombic interaction between the electron and nuclei of

target atoms and discrete inelastic scattering events. Bethe proposed an electron slowing down concept that includes all the possible energy-releasing mechanisms[94, 95]; in his argument different energy-releasing mechanisms are considered and are represented by a model which is continuous along the mean free path. This model is modified by Joy and Luo[96] for better experimental agreements in low energy region, and it is given as

$$\frac{dE}{dS} = -78,500 \cdot \frac{Z}{A \cdot E} \cdot \ln \left(\frac{1.166(E + 0.85J)}{J} \right) \quad (3.33)$$

$\frac{dE}{dS}$ is sometimes referred as the “stopping power” of the target. S , called the “mass distance unit”, is the product of sample density $d(\text{g/cm}^3)$ and path length $s(\text{cm})$ the electron travels, Z and A are the atomic number and atomic weight of the target respectively, E is the incident beam energy, and J is the mean ionization potential(keV) and is determined by experiments. Berger and Seltzer[97] proposed the following empirical J form that gives good agreements with different elements:

$$J = \left(9.76Z + \frac{58.5}{Z^{0.19}} \right) \cdot 10^{-3} \quad (3.34)$$

For compound materials, the appropriate Z for equation (3.34) is the mean atomic number derived from the stoichiometric contribution of all elements a compound has if the composition is known. For more complicated materials with uncertain compositions, J values are only available through experiments. Some literature J values of compounds are listed in Table 3.2.

Table 3.2. Measured values of mean ionization potential J.[88]

material	J (eV)	material	J (eV)	material	J (eV)
Nylon	63.9	aluminium oxide	145	Adipose tissue	63
Teflon	99.1	calcium oxide	166	bone	107
Paraffin wax	48.3	lithium fluoride	94	muscle	75
PMMA	74.0	silicon dioxide	139	skin	74
polyethylene	57.4	sodium iodine	452	air (1 atm)	86
polystyrene	68.7	Pyrex glass	134	blood	75
plastic	64.7	photographic	64.7	liquid water	75
scintillator		emulsion			

3.8 The Double Layer Model

The space charge distribution during and after electron beam irradiation is the result from combining the contributions of incoming beam scattering, secondary and back scattered electron emission, and electron-hole pair generation. Major research efforts have been focussed on estimating the space charge distribution[40-42, 98-121]and the resultant electric field and corresponding surface potential prediction [99-101, 109, 112, 113, 118, 119, 122-127].

The fundamental thought about applying two volumes of charge of different polarities in representing charge distribution caused by electron beam irradiation and the relevant electric field and potential calculation is illustrated as follows. When an insulating material is bombarded by an incident electron beam, secondary electrons are emitted from the shallow depth within about 50nm from the surface[128, 129] and so leave the volume positively charged. After a series of elastic and inelastic scattering, the incoming electrons come to rest in the insulator at some depth within the electron range. There primary electrons form a negatively charged volume inside the dielectric and the density of charge goes up along the depth direction as the depth approaches the incoming electrons' penetrating range. Assuming the escape depth of secondary electrons and the penetrating range of electrons are d_s and d_p , respectively, the two volumes of positive and negative charge distributions can be represented by cylinders of heights d_s and d_p with suitable diameters (Figure 3.4). However, owing to the fact that the electron penetrating range is far greater than the secondary escape depth, i.e. $d_p \gg d_s$, the charge density in

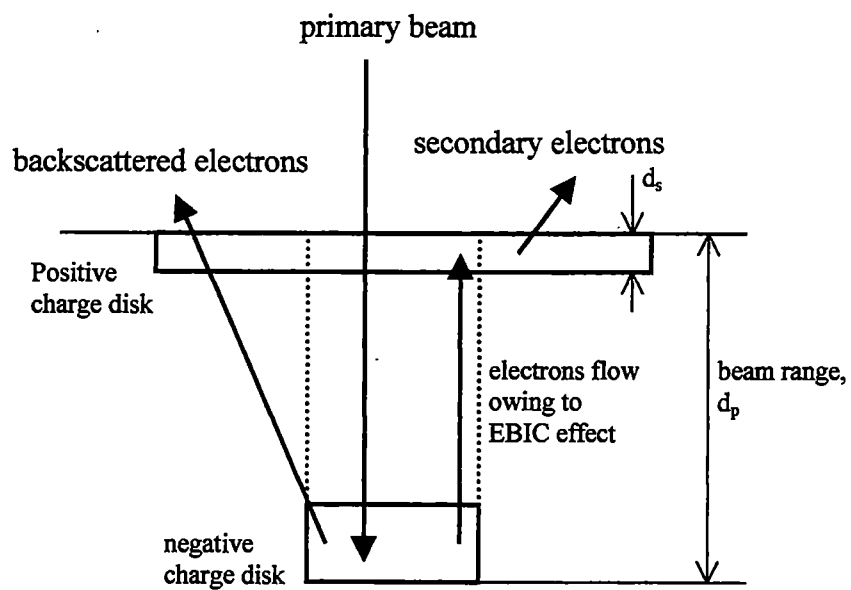


Figure 3.4. Illustration of the double layer model.

these two volumes will have order of magnitude difference regardless of the fact that the total stored charges Q_+ and Q_- inside the cylinders can have the same order of magnitude if both the secondary electron yield δ and back scattered electron yield η are taken into consideration.

The field and potential inside and above the insulator can be estimated by classical electrostatics after the diameters of the charged volumes are set; they are the results of the contributions from the positive and negative charge volumes and the image charge the volumes create. The field calculations can be done individually first, then superimposed together since electric field are summed in the vector space. The calculation work was systematically discussed by Cazaux in 1986 [113] and we herein briefly review the key derivation as follows.

Consider a charged disk of radius a and thickness dz (at position z_0 to $z_0 + dz$) shown in Figure 3.5, from classical electrostatics the two differential field components $E_r(r, z)$ and $E_z(r, z)$ at point $P(r, z)$ are [130]

$$dE_r(r, z) = (\rho \cdot dz_0 / 2\pi\epsilon\epsilon_0) \cdot (r_1/r) \cdot [(1-k^2/2) \cdot J_1(k) - J_2(k)] \quad (3.35)$$

and

$$dE_z(r, z) = (\rho \cdot dz_0 / 4\pi\epsilon\epsilon_0) \cdot d\Phi \quad (3.36)$$

where $r_1 = [4a^2 + (z - z_0)^2]^{1/2}$, $k = 2a/r$, ρ and $\epsilon\epsilon_0$ are charge density and permittivity of the dielectric, Φ is the solid angle from which the disk is seen from P , and $J_1(k)$ and $J_2(k)$ are the elliptic integrals defined as

$$J_1(k) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2 \theta}} \quad (3.37a)$$

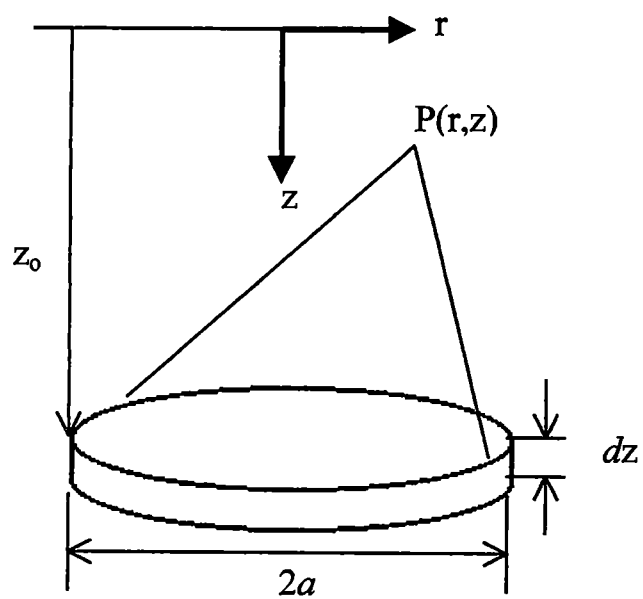


Figure 3.5. The geometry of a differential uniformly charged disk in the double layer model.

and

$$J_2(k) = \int_0^{\pi/2} \sqrt{1 - k^2 \sin^2 \theta} \cdot d\theta \quad (3.37b)$$

The field at point P(r, z) is obtained by integration of equation (3.35) and (3.36) over the cylinder height d; either a defocused ($d \ll a$) or highly focused ($a \ll d$) condition will simplify the integration process. For the defocused condition, the z field component E_z is

$$E_z(0, z) = (\rho/2\epsilon\epsilon_0) \cdot f_{z,i}(0, z) \quad \text{or} \quad (\rho/2\epsilon\epsilon_0) \cdot f_{z,o}(0, z) \quad (3.38)$$

The subscript i and o represent "inside" or "outside" the cylinder. $f_{z,i}(0, z)$ and $f_{z,o}(0, z)$ are

$$f_{z,i}(0, z) = 2z - d + [(z - d)^2 + a^2]^{1/2} - (z^2 + a^2)^{1/2} \quad (3.39)$$

and

$$f_{z,o}(0, z) = [(z - d)^2 + a^2]^{1/2} - (z^2 + a^2)^{1/2} \pm d, \quad (3.40)$$

+ for $z > d$ and - for $z < 0$.

The r field component can only be determined by numerical integration.

However, certain circumstances may make analytical approximation appropriate. Very close to the z-axis of the cylinder, the r field component can be estimated by solving Gauss's theorem from the following relationship

$$E_r(r, z) + r/2 \cdot \partial E_z(0, z) / \partial z = C \quad (3.41)$$

$C = \rho/2\epsilon\epsilon_0$ for $0 < z < d$ and $C = 0$ for $z < 0$ or $z > d$.

The potential will also be solved numerically by Poisson's equation in the dielectrics and by Laplace's equation outside the cylinder. This will be done by

commercial simulation tools like SIMION™ and METHEMATICA™ and it will be discussed in the later part of my disertation.

The field inside the dielectric will increase continuously till it reaches the breakdown strength ($\sim 10^7$ V/cm) if a perfect insulator is under electron beam bombardment, i.e., no recombination or any other effect happens to reduce the space charge formed during irradiation. This is not the case for a real situation since EBIC and recombination effects will happen in certain extent during and after irradiation. If, at the onset of the bombardment and the recombination and EBIC effects are negligibly small, the charge densities of the cylinders can be estimated as

$$\rho_+ = J_b \cdot \delta \cdot t / d_s \quad (3.42)$$

$$\rho_- = J_b \cdot (\eta - 1) \cdot t / d_p \quad (3.43)$$

for a very short period of time, where δ and η are the secondary and backscattered electron emission coefficients respectively, and J_b is the primary beam current density.

Considering the EBIC effect during irradiation, Cazaux suggested an analogy to the discharge of a capacitor through a resistor and proposed a form of changing density, for ρ_+ it is [113]

$$\rho_+ = \rho_+(\infty) \cdot (1 - \exp(-t/\tau)) \quad (3.44)$$

where $\rho_+(\infty) = (J_b \cdot \delta \cdot t / d_s) \cdot \tau$. τ is shorter than the natural recombination time constant ε/g_d when the incoming beam is off, and g_d represents the delayed EBIC conductivity.

The dynamic variation of trapped charges can now be illustrated by the following set of equations

$$dQ_+/dt = -I_b \cdot \delta + I_{EBIC} \quad (3.45)$$

$$dQ_-/dt = I_b \cdot (1-\eta) - I_{EBIC} \quad (3.46)$$

with initial conditions of $Q_+ = Q_- = 0$ at $t = 0$.

where δ and I_{EBIC} are both functions of time. The variation of δ can be derived by the concept of escape probability[131, 132]. For small variation of surface potential (~ several volts) the secondary emission coefficient δ can be regarded as a constant during calculation.

The EBIC effect is assumed to take place in between the cylinders of opposite charge during and after electron beam irradiation. The EBIC conductivity g and the delayed counter part g_d can be experimentally determined by the bias method in the experimental section. The time variation of g and g_d are fitted by suitable analytical form and the correspondent I_{EBIC} is given as

$$I_{EBIC} = g \cdot \Delta V \cdot A_d / d \quad (3.47)$$

where ΔV is the potential drop from the sample surface to the penetrating depth and it can be replaced by V_1 in equation (2.2), and A_d is the incoming beam diameter. Melchinger and Hofmann simplified their calculation with steady state g used instead and made reasonable agreements with certain experimental results in their Auger electron spectroscopy charging experiments[119]. An experimental-determined g should further improve the accuracy of our field and potential prediction.

The diameter of the positive-charged cylinder in double layer model derivation is chosen to be larger than that of the negative-charged one owing to the consideration of the mechanism of secondary electron generation. The lower mean energy and average

emergence angle of backscattered electrons contribute the fact that backscattered electrons are more efficient in exciting secondary electrons than primary electrons[132].(Figure 3.6) In a range of primary electrons with different energy that can generate secondary electrons, about 40% to 80% of the secondary electrons emitted from the sample surface are generated by backscattered electrons other than primary electrons[129]. Backscattered electrons can reach surface areas far from where the primary beam spot strikes on the specimen surface; The low average emergence angle of backscattered electrons make them more favorable for the excitation of secondary electrons; therefore, the horizontal dimension of the positive-charged volume after secondary electron emission is larger than that of the negative-charged counterpart.

The charge-induced field and potential obtained from the double layer model calculation can therefore provide one to estimate the deflection of electron beam in e-beam tool applications, particular in e-beam direct writing and SEM critical dimension (CD) measurements operations.

3.9 The Electrostatics Principles and Simulations of Electron Beam Deflection from Charging

3.9.1 The Electrostatics Principles

The electric field and potential resulting from sample charging during and after electron beam irradiation is derived from classical electrostatics[133]. For simplification of modeling we carry out our discussion and simulation in the Cartesian coordinate system and the orientation of coordinate system with respect to a photoresist mask layout

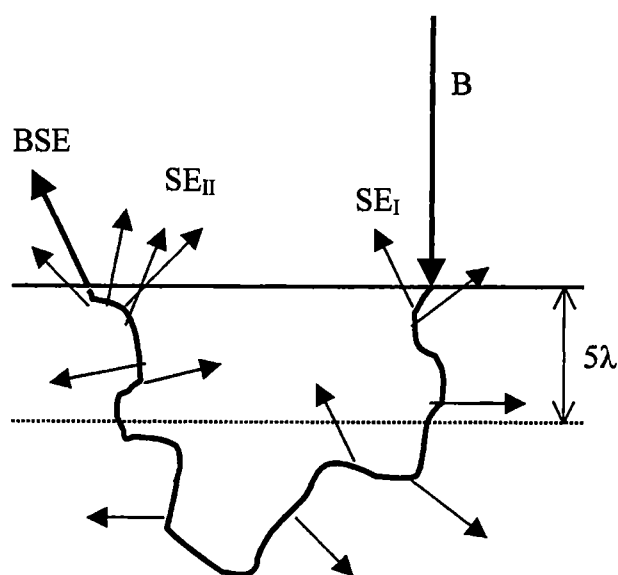


Figure 3.6. Schematic illustration of the origin of two sources of secondary electrons emit from a sample. Incident beam electrons (B) generate secondary electrons (SE_I) upon entering the sample. Backscattered electrons (BSE) generate secondary electrons (SE_{II}) while leaving the sample. λ is the average mean free path for secondary electrons.

used for the EBIC experiment is illustrated in Figure 3.7.

From Coulomb's force law the field introduced from a group of point charge is given as

$$\mathbf{E}(\mathbf{r}) = \left(\frac{1}{4\pi\epsilon\epsilon_0} \right) \sum_{i=1}^N \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|^2} \hat{\mathbf{n}}_i \quad (3.48)$$

where the electric field $\mathbf{E}(\mathbf{r})$ is determined by the space charge group q_i ; $\mathbf{r}$ and $\mathbf{r}_i$ are the position vectors for the test charge and the individual charge q_i ; ϵ is the dielectric constant of the media; ϵ_0 is the permittivity in vacuum and is given as 8.85×10^{-12} F/m. $\hat{\mathbf{n}}_i$ represents a unit vector which points from q_i to the test charge if q_i is positive. The electric potential is a scalar function; by definition it equals

$$\phi(\mathbf{r}) = \left(\frac{1}{4\pi\epsilon\epsilon_0} \right) \sum_{i=1}^N \frac{q_i}{|\mathbf{r} - \mathbf{r}_i|} \quad (3.49)$$

both the electric potential and field are related by the following relationship:

$$\mathbf{E} = -\text{grad } \phi = -\left\{ \hat{\mathbf{x}} \frac{\partial}{\partial x} + \hat{\mathbf{y}} \frac{\partial}{\partial y} + \hat{\mathbf{z}} \frac{\partial}{\partial z} \right\} \phi \quad (3.50)$$

The spatial distribution of field and potential can be calculated from the Poisson's equation; it is derived from the Gauss's equation and equation (3.50), it is given as:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \phi = - \left(\frac{1}{4\pi\epsilon\epsilon_0} \right) 4\pi\rho \quad (3.51)$$

The homogeneous form of the equation (3.51), i.e. for $\rho = 0$, is called the Laplace's equation. This is the condition for the potential distribution in vacuum and

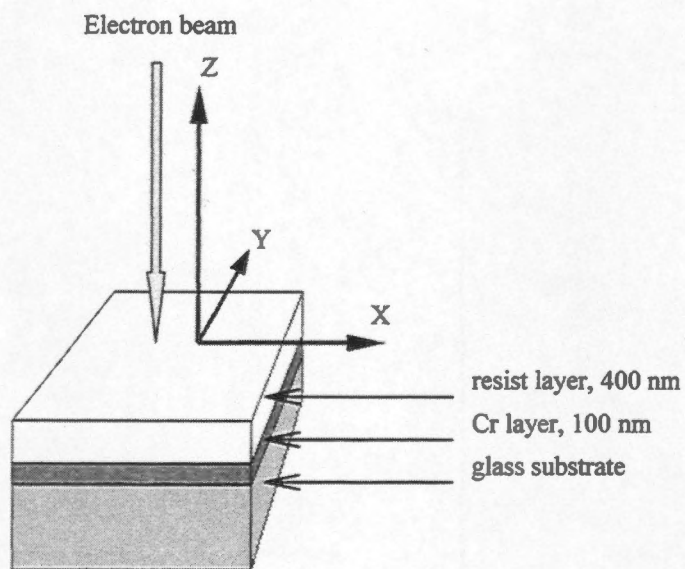


Figure 3.7. The orientation of the Cartesian coordinate system with respect to a photoresist mask layout.

above a charged surface. It is from the Laplace's equation that the potential distribution is solved by SIMION6™.

3.9.2 The Electron Beam Deflection Simulations

To simplify the scope of complication in simulation it is assumed that the electron beam irradiated area equals the area of charging, i.e., no lateral charge diffusion and no lateral EBIC effect are considered in our work. The charging areas are simulated as electrodes with assigned potential values in SIMION. Laplace's equation (equation (3.51)) is used in the SIMION spatial potential calculation and the electric field in vacuum is then determined by the spatial potential gradient illustrated from equation (3.50). By flying incident electrons of given energy close to the edge of the electrode, the beam deflection is determined by comparing the lateral coordinate differences between the actual and desired landing positions. The SIMION simulation serves to obtain the information about the range of beam deflection at an assigned electrode potential.

The geometry of circles and squares of different dimensions are considered in MATHEMATICA electron beam deflection calculation. The electron beam used in MATHEMATICA simulation has the energy of 10 keV. The charge layers and their image charge are considered for spatial electrical field calculation. The positive charge layer resulting from the secondary and backscattered electrons is assumed to reside 15 nm below the resist surface in consideration of average escape probability of secondary electrons.[132] The location and size of negative charge layer is determined by the Monte Carlo simulation of 10 keV electrons in resist layer. The charge density is

assumed uniform through out the entire charging area. The uniform charge distribution is achieved by an equal spacing "charge packet" array whose lateral dimension equals that of the electron beam irradiation and the total charge the array has equals the amount of charge generated as a result primary beam irradiation. A positive charge packet array will have the charge that equals the number of secondary electron emitted during the primary beam irradiation, while the negative charge packet array will have the amount of charge that equals the trapped incident electrons from irradiation. The charge content in an individual packet for an array is then determined by dividing the total charge to the number of total packet points the array has in the irradiated area. The packet arrays used in circle and square are illustrated in Figure 3.8. The spatial potential distribution is determined by the Coulomb potential contribution of all the charge packets and their image counterparts in the glass substrate.

The deflection of electron flight path is calculated stepwise along the trajectory by the following set of electrostatic equation of motion

$$\begin{aligned}
 S_z &= v_{i,z} t + \frac{q E_z}{2m} t^2 \\
 v_{f,z} &= v_{i,z} + \frac{q E_z}{m} t \\
 v_{f,x} &= v_{i,x} + \frac{q E_x}{m} t \\
 \Delta S_x &= v_{i,x} t + \frac{q E_x}{2m} t^2
 \end{aligned} \tag{3.52}$$

where q the charge, m the mass of an electron respectively. t is the flight time in the trajectory step S_z , $v_{i,z}$ and $v_{f,z}$ are the initial and final velocity z -components, while $v_{i,x}$

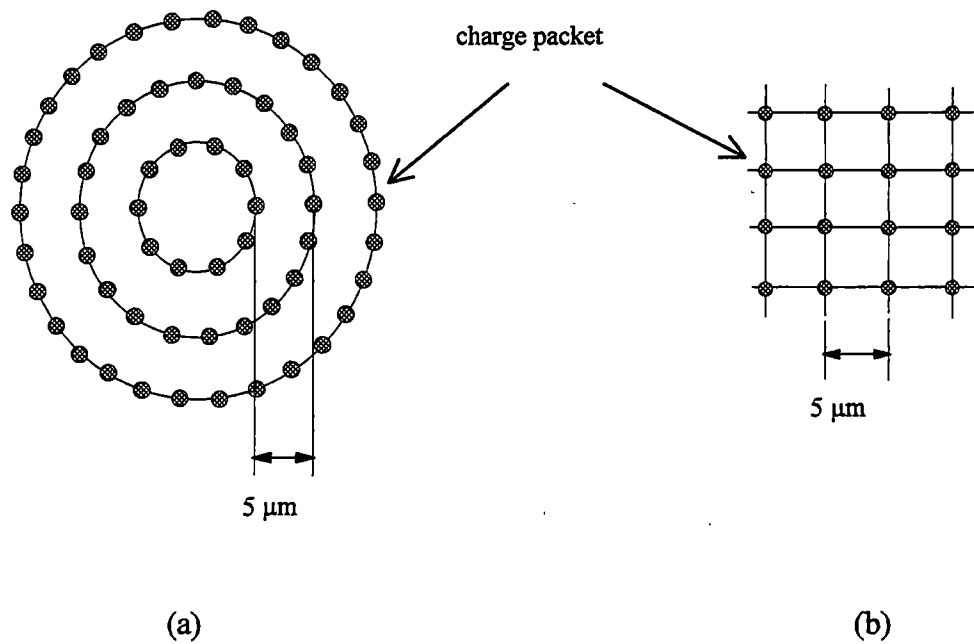


Figure 3.8. Charge packet meshes used in MATHEMATICA calculation. (a) mesh for a circle ; (b) mesh for a square.

and v_{fx} are the corresponding velocity x-components respectively. The deflection ΔS_x in each step is summed over a given length of electron flight path and reported as the total lateral deflection. It is clear that the electron beam deflection ΔS_x is defined as the distance between the actual the desired electron landing positions. In my simulation both circular and square charging patterns are considered; the definition of desired landing positions in the patterns are shown in Figure 3.9.

The size of trajectory step S_z determines the precision of calculation because the electric field components are determined each step during computation. Suitable step size S_z and total number of calculation steps are therefore critical for the precision of simulation and the efficiency in computation. In my simulation the total electron flight path will start from 1 mm and below since this meets the working distance range used in electron beam lithography; the results from different flight paths will be compared and a reasonable setup will be determined and used for all charging geometries.

The charge decay after irradiation is assumed to be dominated by the electron beam induced conductivity (EBIC) effect. The experimental relationship between EBIC conductivity g and bias potential in our experiment is used to calculate the resistance across the resist layer after irradiation. In a time increment Δt , the resistance $R(t)$ and resulting charge decay Δq are

$$R(t) = \frac{L}{g(V) \cdot A}$$

and

$$\Delta q = \frac{V \cdot g \cdot A}{L} \Delta t \quad (3.53)$$

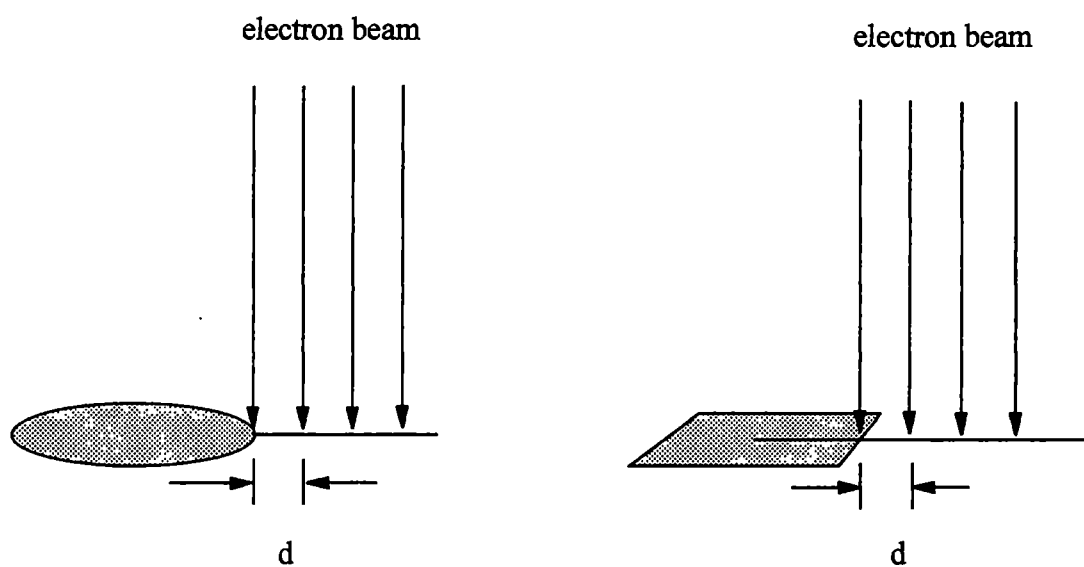


Figure 3.9. The definition of desired primary beam landing positions “d” in circular and square charging patterns. For a square pattern the primary beam is assigned to irradiate along the line extending perpendicular to the midpoint of one side.

where L and A are the resist layer thickness and irradiation area respectively, V is the surface potential. The decay of surface potential is then obtained by the loop calculation combining equation (3.53) and equation (3.49)~(3.51).

CHAPTER 4

EXPERIMENTAL

4.1 The Problem Statement

The EBIC effect of insulators has long been discovered and studied for decades. Various researches on polymer materials since 1990 have been done for areas such as carrier mobility[134-147], space charge distribution[114, 116-119, 121, 138, 148-150], field and potential created from irradiation[116, 118-120, 125, 151], and dielectric breakdown[152-155], etc. However, the majority of the research interest is done on polymers designated for electret use; the prime purpose of electron irradiation is therefore to charge the polymer materials. Besides, a suitable model to predict charging behavior of polymer under electron beam irradiation with experimental EBIC data support has yet to emerge. The EBIC effect study on photoresists is still a new frontier and this field deserves more attention since the EBIC characteristics of photoresists and the relationship between EBIC and photoresist charging during electron beam irradiation is still not clear. This research will benefit all e-beam tool applications since we concentrate on how EBIC alters surface charging behavior during and after electron beam irradiation. I also will propose a feedforward electron beam deflection correction algorithm for solving errors generated from charging problems experienced in SEM critical dimension (CD) measurements and direct e-beam writing of masks for optical and x-ray lithography.

Based on the issues mentioned, this research will focus on the following

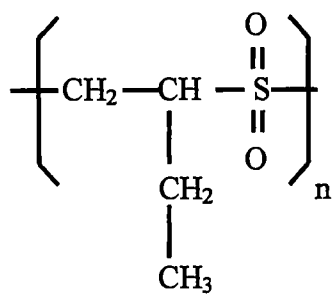
categories:

- 1) Setup a bias method experiment to measure EBIC effect.
- 2) Evaluate EBIC effect of resists during electron beam irradiation, its dependence on bias and temperature will also be investigated.
- 3) Utilize the Monte Carlo simulation to construct a double layer model that incorporates the experimental EBIC effect.
- 4) Estimate surface charging effect by SIMION and MATHEMATICA, and predict the extent of electron beam deflection due to surface charging.

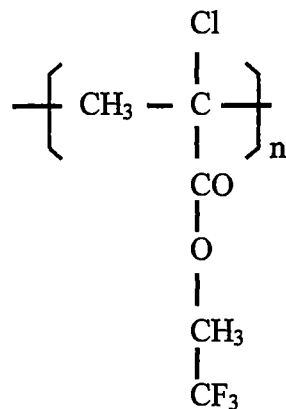
4.2 Materials

Three positive electron beam resists, poly(butene-1-sulfone), PBS, poly(2,2,2-trifluoroethyl- α -chloroacrylate), ZEP7000, and copolymer of α -chloromethacrylate and α -methylstyrene, EBR900, are used as in this research. The first is an alternating linear sulfur-containing polymer and the other two are the poly(methyl methacrylate) (PMMA) derivatives. The chemical structures of the resists are shown in Figure 4.1.

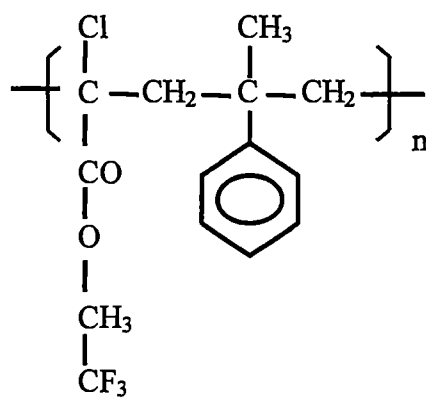
All samples comes in a standard photo mask geometry, which consists a 4000 Å resist layer spun coated on a 1000 Å chromium layer on an optical glass substrate. (Figure 4.2a) An array of 3mm diameter and 300 Å thick chromium layer “islands” were then sputter coated on the resist top surface through an aluminum mask made in our laboratory. The islands served as front electron transparent electrodes for the measurements made during beam irradiation.



PBS



EBR-900



ZEP-7000

Figure 4.1. The chemical structures of the electron beam resists.

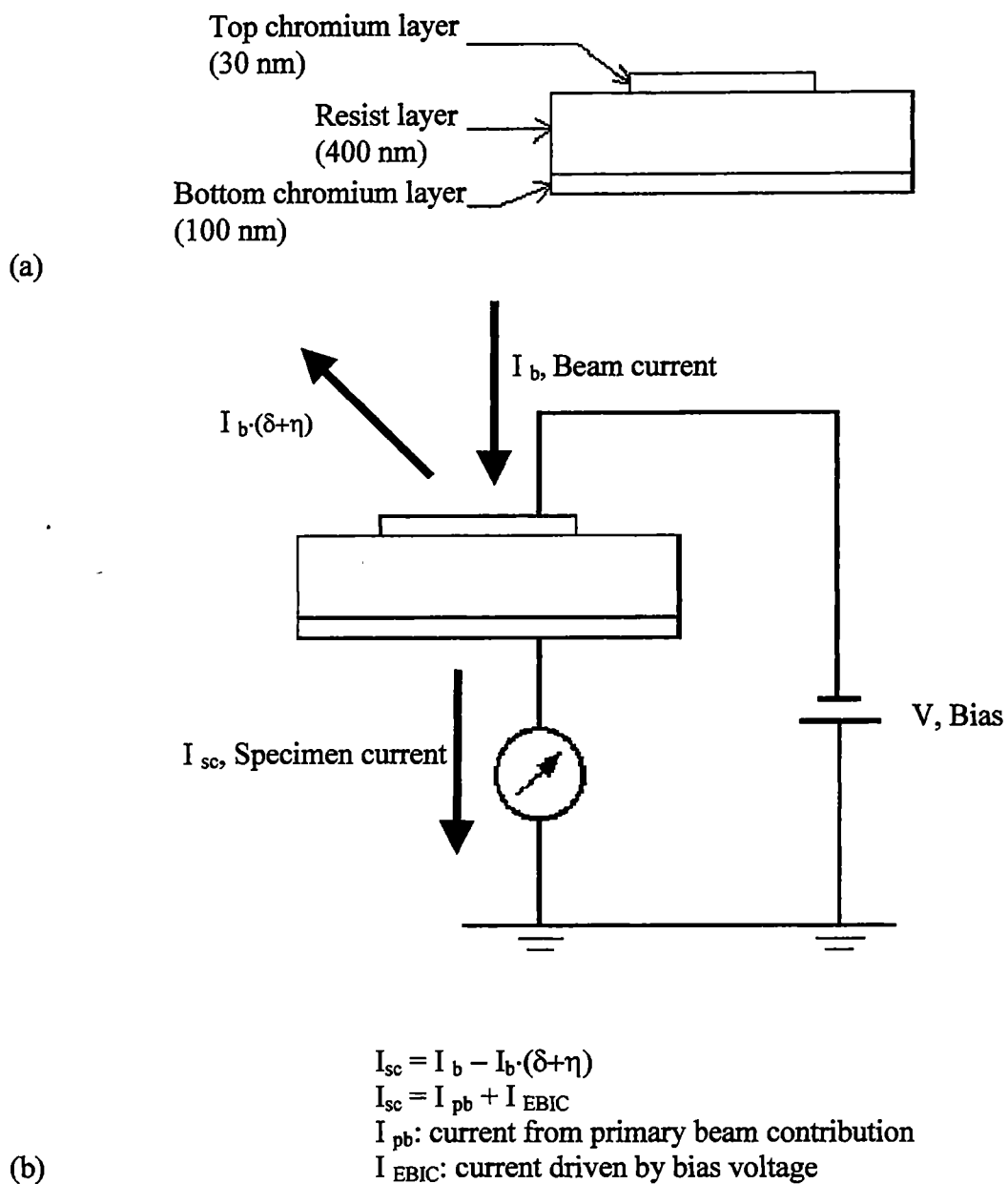


Figure 4.2. The specimen geometry and the experimental setup. (a) Specimen geometry (not to scale), (b) experimental setup.

4.3 EBIC Experiment Setup

4.3.1 Bias Method Experiments

A sample bias method [156, 157] is used in this study and a schematic illustration of the experimental setup is shown in Figure 4.2b. The specimen current I_{sc} through the sample is the contributions from both the primary electron beam and the leakage current from the bias voltage, it can be written as

$$I_{sc} = I_{pb} + I_{EBIC} \quad (4.1)$$

where I_{pb} and I_{EBIC} represent the current components driven by the primary electron beam and bias respectively. I_{sc} equals I_{pb} only when bias is zero. From Kirchhoff's law we know when a bias is applied, the bias loop satisfies

$$-I_{EBIC} \cdot R + V = 0 \quad (4.2)$$

and the resistance R of the polymer film is

$$R = L/(g \cdot A) \quad (4.3)$$

where g is the electron beam induced conductivity, L and A are the sample thickness and electron beam irradiation area respectively. Combining equation (4.2) and (4.3) one has

$$g = I_{EBIC} \cdot L / (V \cdot A) \quad (4.4)$$

In the experiment I_{EBIC} was determined after the measurements of I_{sc} and I_{pb} were done at non-zero and zero bias conditions and the electron beam induced conductivity g was then calculated from equation (4.4).

Temperature variation experiments are performed in a same experimental setup mentioned above except a water-cooled thermistor cold stage is utilized to hold

specimen at temperatures down to -30°C. The real time temperature readout is acquired by a thermocouple attached on the side of the sample to ensure an accurate temperature control throughout the experiment. The temperature variation experiment setup is illustrated with a thermistor cold stage in Figure 4.3.

4.3.2 Electron Beam Source and Data Acquisition System Design

The specimen current is measured using a Keithley™ 414A picoammeter, the output of which is connected to a PC-based data logger consisting of a 12 bit Keithley™ DAS-801 analog-to-digital card. A QUICKBASIC™ program code is used to sample the current change at 10ms intervals during the entire run and to store and present the data as a file and on screen. Bias is applied from an Hewlett Packard 712C power supply. The bias voltage is chosen in the range of 0 to 200 V as required. Electronic current limiting is employed to minimize the chance of dielectric breakdown in the resist.

A Hitachi™ S-3200N tungsten filament gun scanning electron microscope is used to provide the primary electron beam in our experiment. Acceleration energy of 10keV is used since from Monte Carlo simulation we know that the beam interaction range at this energy will extend through the thickness of resist film. This guarantees a penetrating beam condition for all the measurements. In the experiment, the beam current is converted to dose rate $\dot{D}$ by the following equation

$$\dot{D} = I_b \cdot E \cdot 10^5 / A R d \quad \text{rad} \cdot \text{s}^{-1} \quad (4.5)$$

where I_b is the primary beam current (A), E the beam accelerating voltage(V), A the scan area (cm^2), R the beam range (cm), and d the resist density (g/cm^3). 5nA and 0.5nA beam

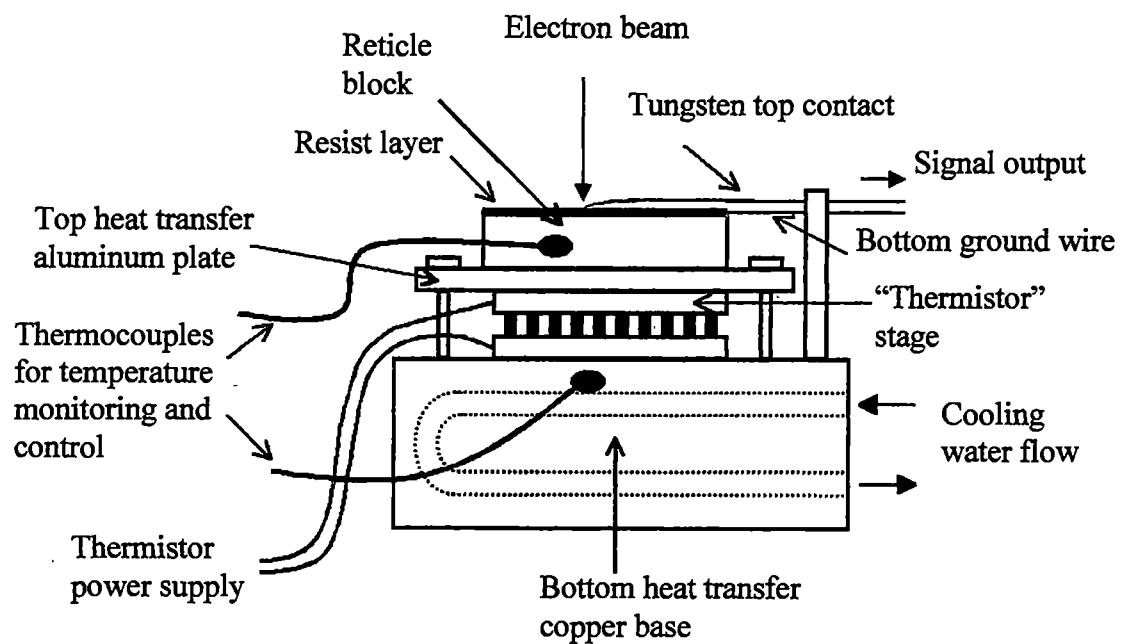


Figure 4.3. Schematic illustration of the thermistor cold stage.

currents are used and the corresponding dose rate are 3.9×10^8 (designated as high) and 3.9×10^7 (designated as low) $\text{rad} \cdot \text{s}^{-1}$ respectively under the assumption of same density value (1.2 g/cm^3) for all three resists. The electron beam is constantly irradiating the sample through the entire experiment cycle. Each experiment cycle consists of two measuring parts: a first half where a bias is connected after I_{sc} reaches a steady value, followed by the second half where the bias is then disconnected once the I_{sc} readout from the previous part reaches steady value again.

Values of the conductivity “g” are calculated from the above “bias on” and the “bias off” parts of the measurement using the raw I_{sc} data files stored on the computer. The dark conductivity g_{DARK} of the three resists are also measured under the same experimental setup except the electron beam is off. The initial state EBIC gain, defined as the ratio of I_{EBIC} to beam current I_b at end of the first bias on part, and the conductivity increase ratio, g/g_{DARK} , are both calculated for the resists.

4.4 Charging Effect Simulation and Electron Beam Deflection Calculation

The modeling of charging effect of photoresists is done with SIMION6™ and MATHEMATICA™ V.4 simulation tools from which the electron beam deflection is estimated. The SIMION is used first to obtain the information about the range of electron beam deflection at a given surface charging potential. The step-by-step simulation algorithm is carried out in MATHEMATICA and is shown as the flow chart in Figure 4.4. First, the amount of total beam dosage of $10 \mu\text{C/cm}^2$ is assigned with the choice of 0.1 to 0.2 as the secondary electron yield for the determination of total injected primary

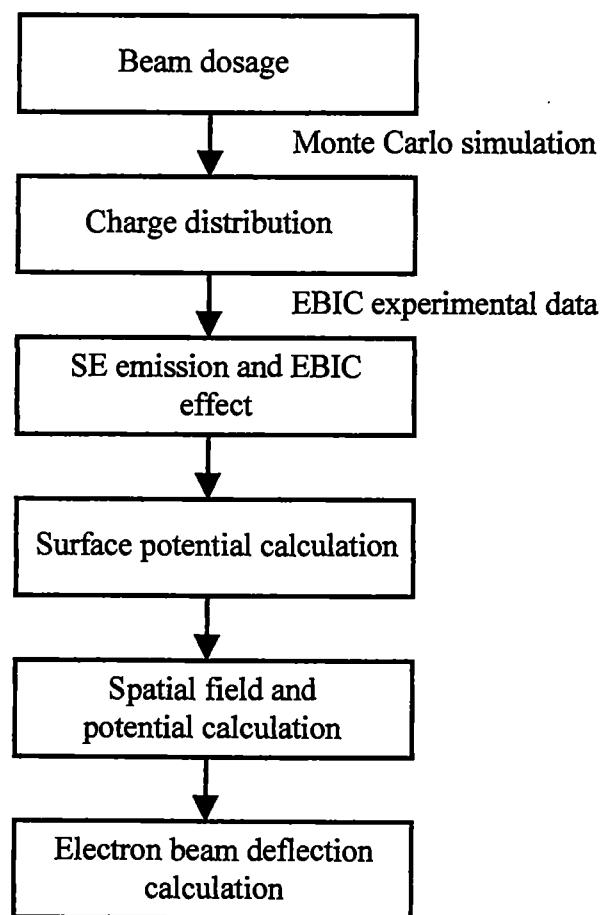


Figure 4.4. The flow chart of simulation procedure.

electrons and the generated positive charge. Second, the Monte Carlo simulation is performed, from which the profile of injected electron distribution and consequently the location of negative charge layer is determined. The EBIC effect is taken into consideration for the decay of trapped charge in the layers. Finally the spatial distribution of electric field and potential are calculated by image method with dielectric constants 3 and 6.9 for the resist and glass substrate layers using MATHEMATICA , from the spatial field information the resulting electron beam diffraction is obtained.

CHAPTER 5

RESULTS

5.1 EBIC Behavior of Photoresists

5.1.1 Initial State EBIC Characteristics

A typical raw data set for I_{sc} including both bias on and off parts is illustrated in Figure 5.1. Note that the transient current regions resulting from switching the bias voltage on and then off are in the range of seconds so that these are very long in comparison with our sampling interval (10ms) throughout the measurements. The molecular polarization frequency is in the microwave range [158], and the relaxation time of fluorinated polymers is reported to be the range of 500 μ s[141, 159]. In Figure 5.1 no current overshoot is seen at the moment of switching the bias off, therefore the polarization effect contributed by the orientation of the polar pendant groups on the polymer chain appears only in the beginning stage of the conductivity curve. The polarization effect can be neglected when the conductivity reaches the plateau region after bias is switched on, and g at this region is designated as the "initial state" conductivity.

Figure 5.2 and 5.3 show the bias-on and the subsequent bias-off experiments of the three resists at high dose rate. After bias was turned on, all the resists started with their conductivity at a maximum value, which then decayed with time to reach their initial values. From Figure 5.2 it is clear that the EBR900 resist decays much slower than

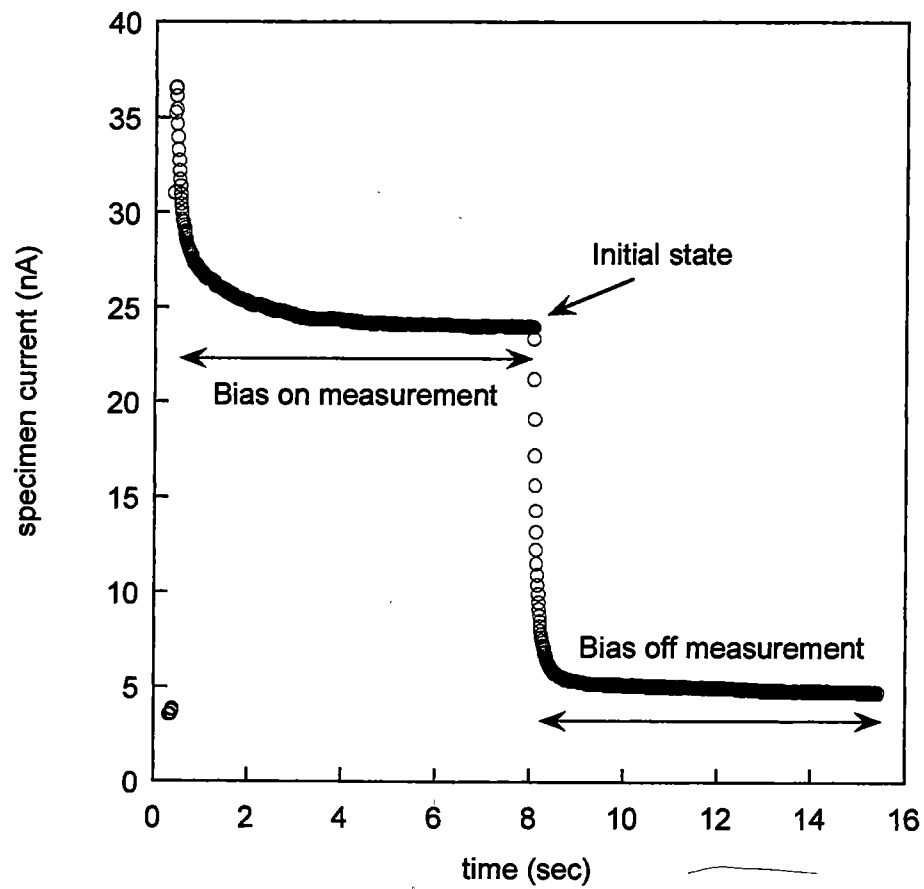


Figure 5.1. The illustration of a data set from a bias method measuring cycle.

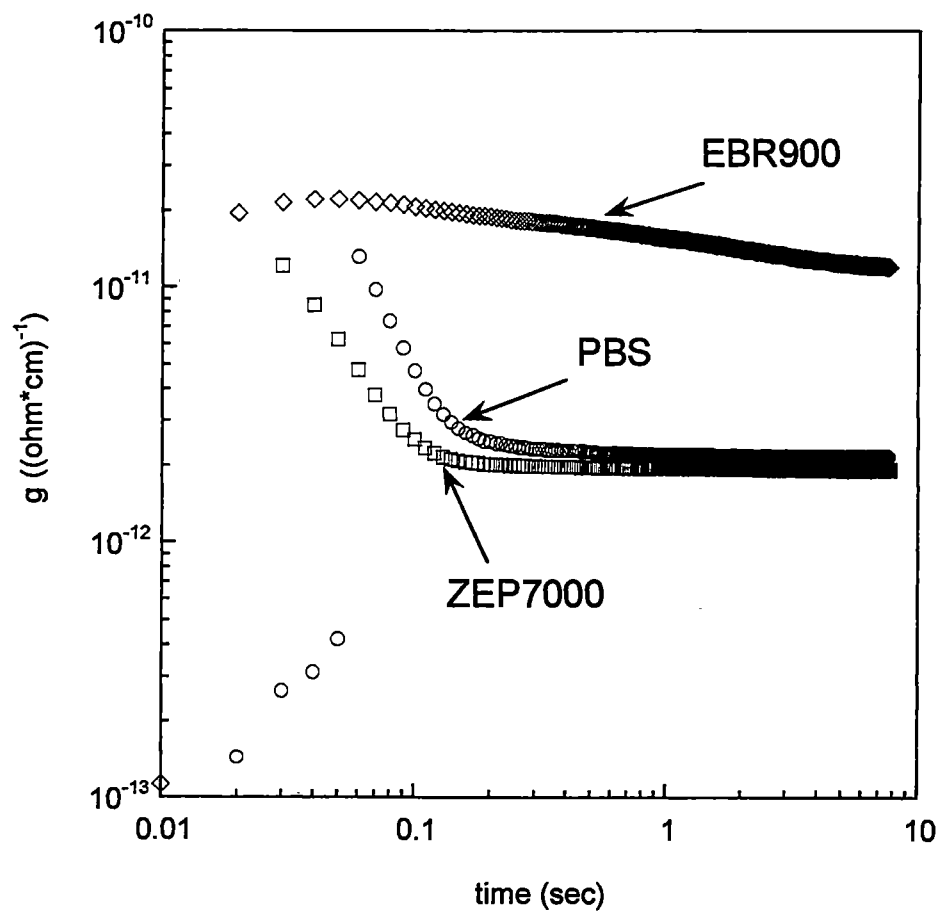


Figure 5.2. Variation of EBIC g of the three resists, bias-on experiment (high dose rate at 100 V bias).

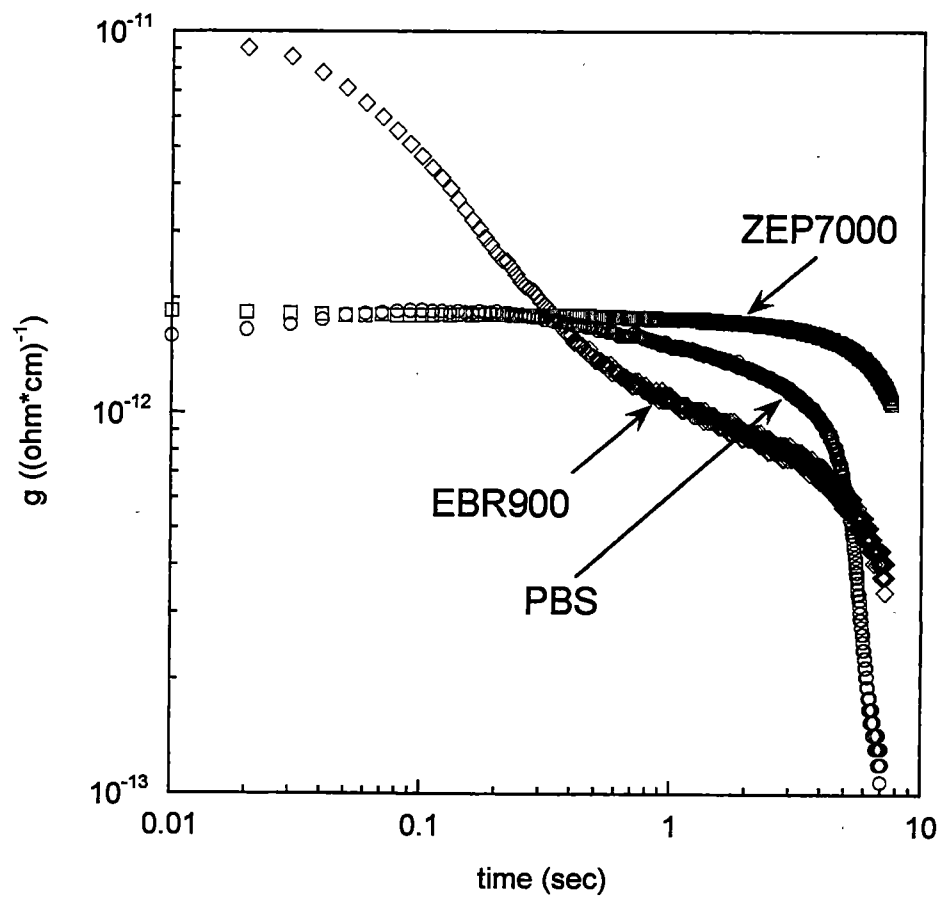


Figure 5.3. Variation of EBIC g of the three resists, bias-off experiment (high dose rate at 100 V bias).

the ZEP7000 and PBS resists because it takes a few seconds for EBR to reach the initial state, while only a fraction of a second is needed for both ZEP7000 and PBS resists. In Figure 5.3 an approximately linear decay is seen for the ZEP7000 resist; the EBR900 resist shows a steep decay region followed by a near linear decay. The PBS resist distinguishes itself from the other two resists by showing two regimes of linear decay each with a different slope.

The initial state conductivity versus bias for three different resists are shown in Figure 5.4 and 5.5 and the conductivity range of the three resists are summarized in Table 5.1. For higher dose rate experiments the g values are in the range of 1×10^{-12} to 1.6×10^{-11} (ohm-cm)⁻¹ and falling to 1×10^{-12} to 4×10^{-12} (ohm-cm)⁻¹ in the corresponding low dose rate experiments. The EBR900 sample has the highest EBIC effect among the resists. Its conductivity shows a clearly rising trend with increasing bias before it fails as a result of dielectric breakdown. The ZEP7000 resist shows the opposite trends on bias dependence in different dose rates. Its g rises as the bias increases at low dose rate experiments while g goes down as bias rises at high dose rate conditions. The PBS resist shows fluctuations in the value of g regardless of the dose variation, and no trend is discerned.

The conductivity increase ratio, defined as the ratio of the initial conductivity to the dark conductivity of the three resists, is tabulated in Table 5.2 for the three resists. The initial state EBIC gain, defined as the ratio of the EBIC current I_{EBIC} to the beam current I_b , is shown in Figure 5.6 and 5.7 for the three resists as well in both high and low dose rate experiments. The comparison of initial state EBIC gains of the three resists at a given bias is shown in Table 5.3.

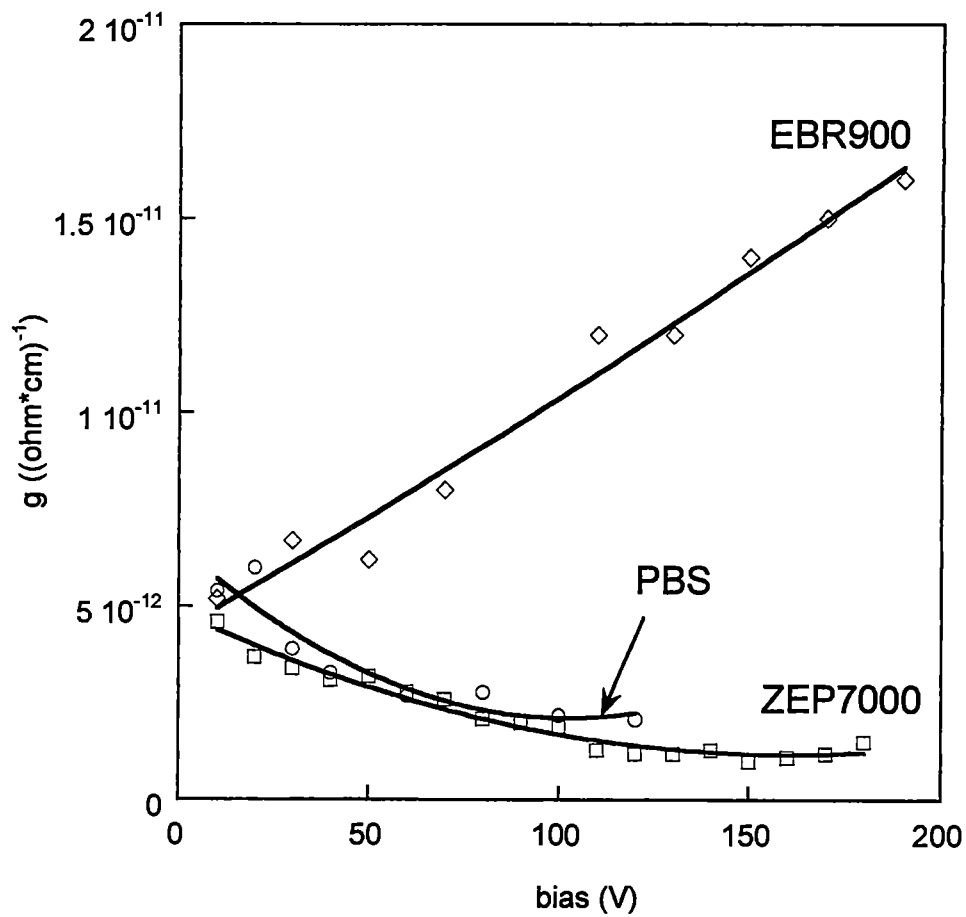


Figure 5.4. The initial state conductivity versus bias for three resists. High dose rate experiment.

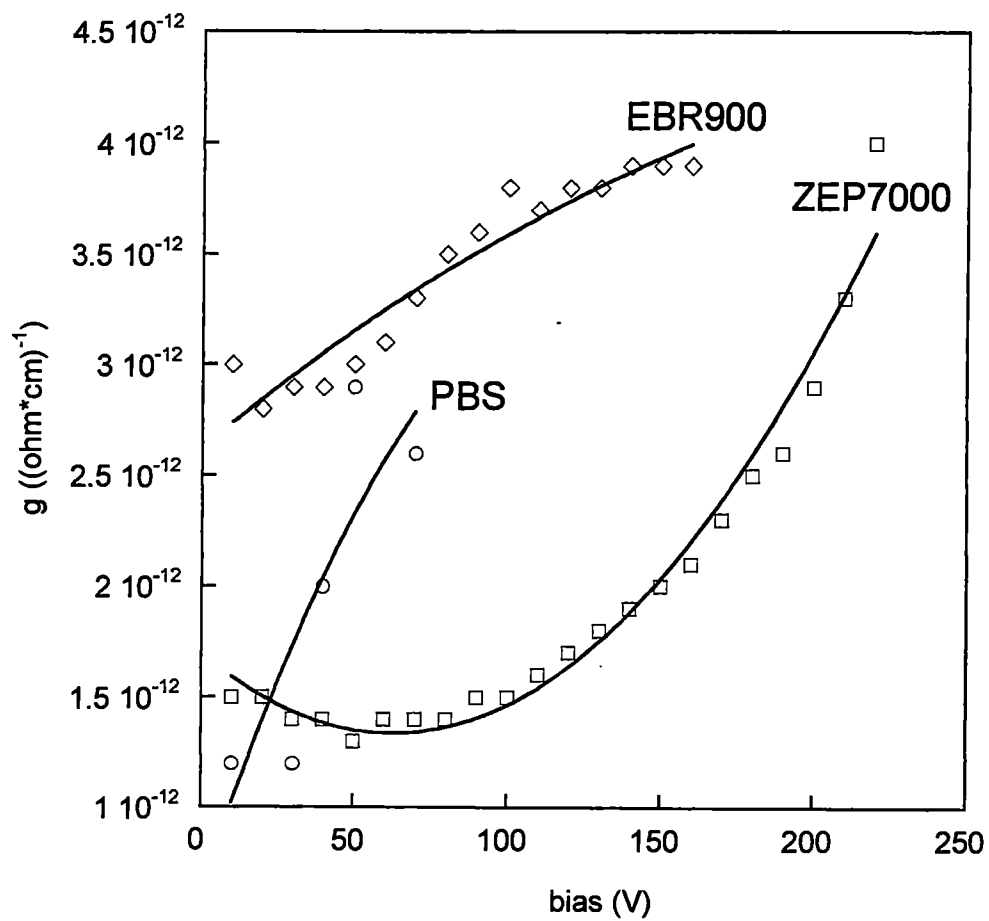


Figure 5.5. The initial state conductivity versus bias for three resists. Low dose rate experiment.

Table 5.1. Initial state conductivity g values of three resists, unit in $(\Omega\cdot\text{cm})^{-1}$.

resist	Bias range (V)	high dose rate	low dose rate
EBR900	10~190	$4.8\times 10^{-12} \sim 1.6\times 10^{-11}$	$2.8\times 10^{-12} \sim 3.9\times 10^{-12}$
ZEP7000	10~180	$1.0\times 10^{-12} \sim 4.6\times 10^{-12}$	$1.3\times 10^{-12} \sim 4.0\times 10^{-12}$
PBS	10~120	$2.1\times 10^{-12} \sim 7.6\times 10^{-12}$	$1.2\times 10^{-12} \sim 2.9\times 10^{-12}$

Table 5.2. Initial state conductivity increase ratio of three resists at 100V bias.

resist	high dose rate	low dose rate
EBR900	3.75×10^3	1.58×10^3
ZEP7000	3.7×10^2	2.92×10^2
PBS	9.56×10^2	NA

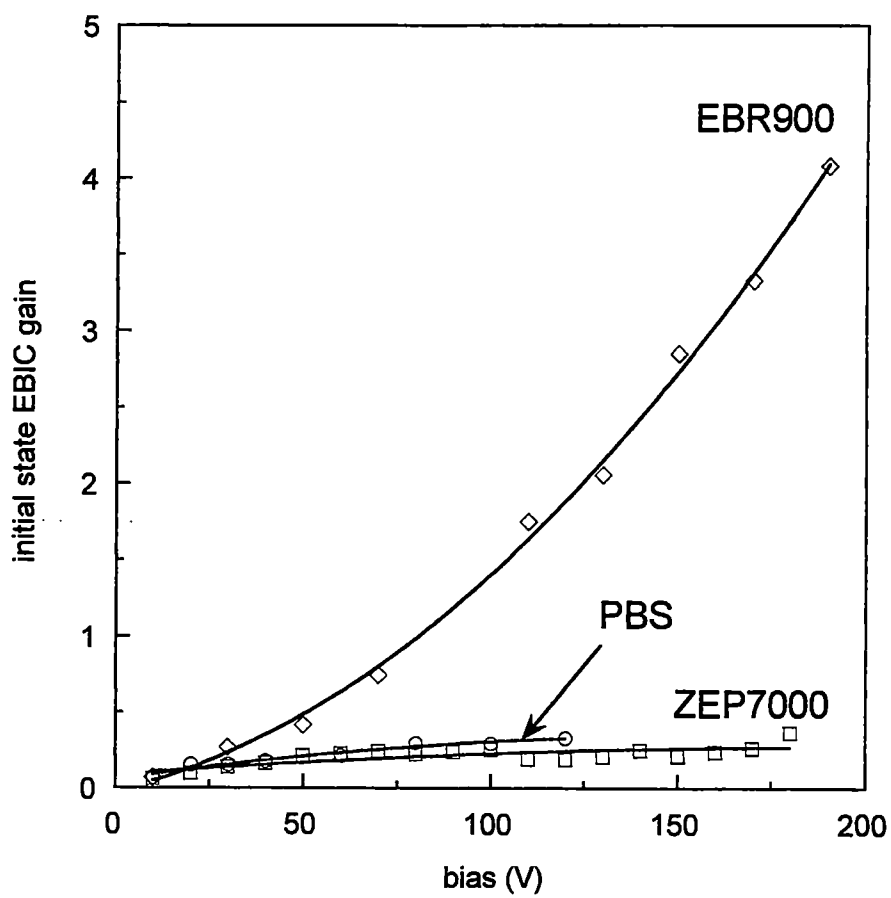


Figure 5.6. The initial state EBIC gain versus bias of the three resists. High dose rate experiment. (Beam current is 5 nA)

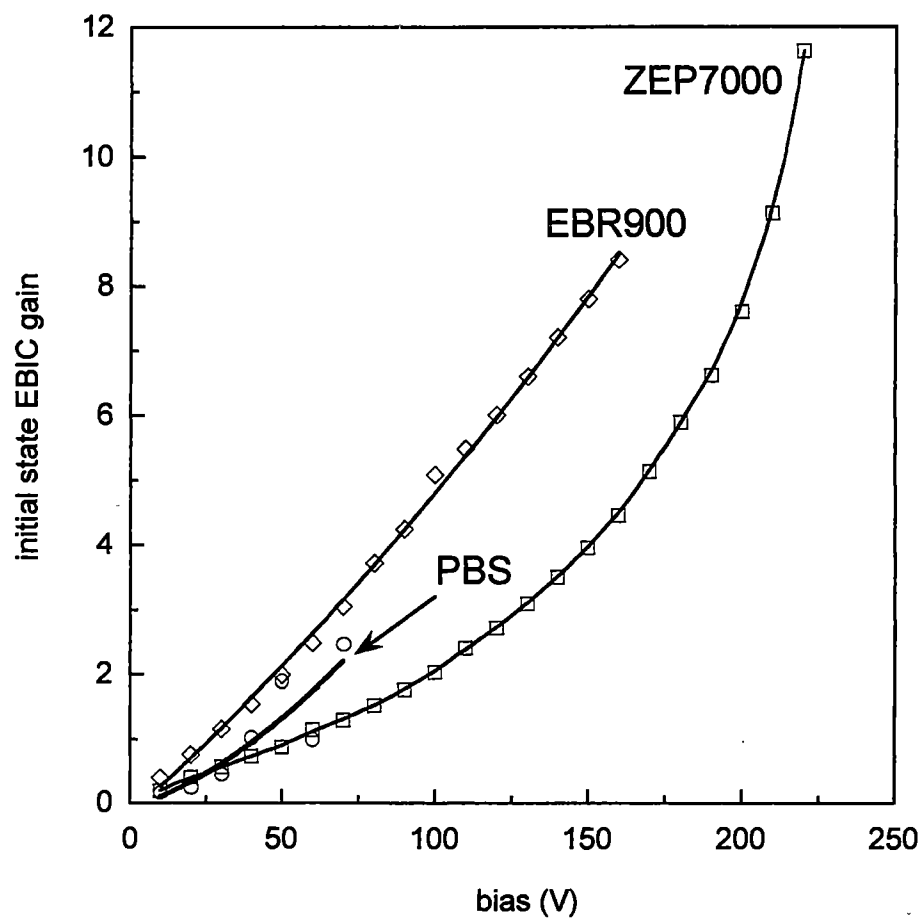


Figure 5.7. The initial state EBIC gain versus bias of the three resists. Low dose rate experiment. (Beam current is 0.5 nA)

Table 5.3. The initial state EBIC gain of the three resists. Bias voltage is 100V.

resist	high dose rate	low dose rate
EBR900	1.42	5
ZEP7000	0.30	2
PBS	0.25	NA

5.1.2 Low Temperature EBIC Characteristics

The temperature variation experiment is done with the thermistor stage at -30°C . Figure 5.8 shows the initial state conductivity of EBR900 resist vs. bias at both room temperature and -30°C .

5.1.3 Long Term and Steady State EBIC Characteristics

The long term EBIC experiments are carried out under the bias condition of 100V. Beam currents of 0.1 nA, 0.3 nA, 0.5 nA, 1 nA, and 5 nA are used for generating five different dose rates in our long term EBIC studies (Table 5.4). The conductivity g is found to vary with time and reach steady state in about two hours after recording, with the peak of g happens around 14~15 minutes after start. The conductivity g vs. time for EBR900 at different bias is shown in Figure 5.9. The steady state EBIC gain, defined as the ratio of I_{EBIC} to beam current I_b at steady state, is shown in Table 5.5 for three resists and is plotted in Figure 5.10. It is seen that the resists have higher gain at lower beam currents, which is equivalent as low dose rates.

The conductivity g versus time for different dose rates from the three resists are illustrated in Figure 5.11 ~ 5.13. It's clear that the steady state conductivity is reached near 2 hours from the start of recording; the trend of higher conductivity from higher dose rate is seen in all the resists.

The Fowler's power law (equation (3.1)) analysis is illustrated in Figure 5.14. The result shows PBS has the power law exponent of 1.02; EBR900 and ZEP7000 have the exponents of 0.7 and 0.67 respectively.

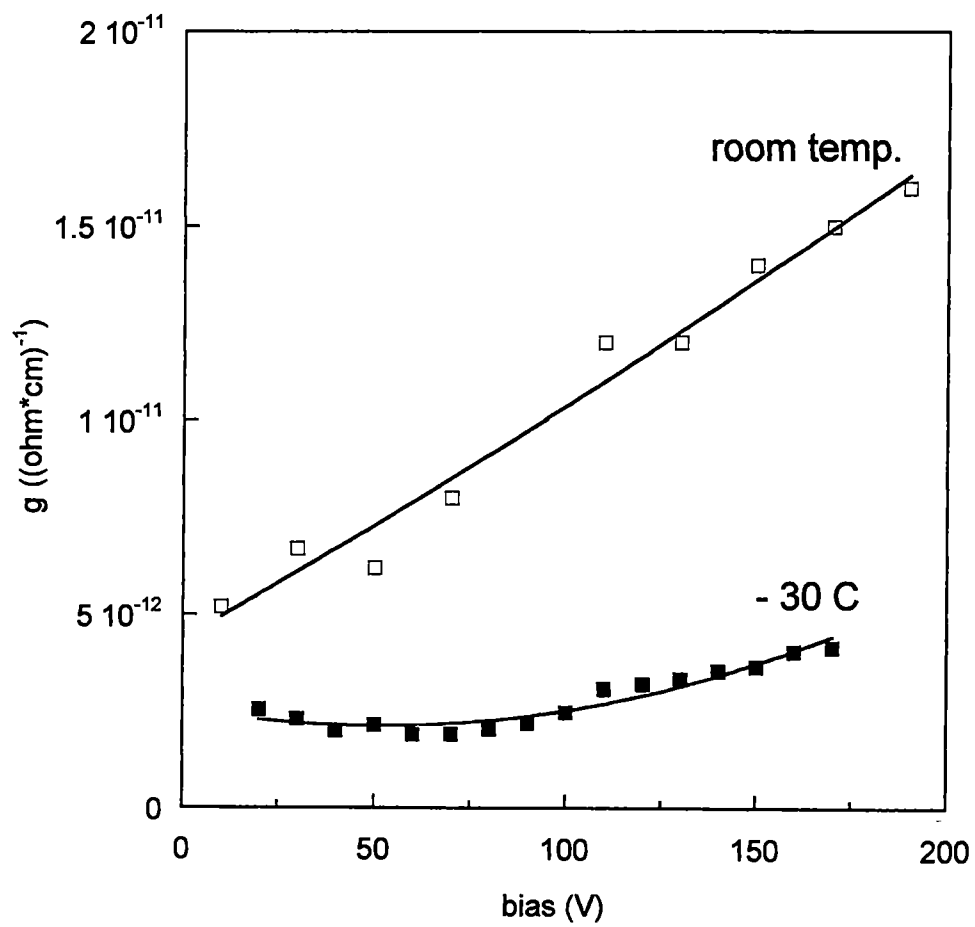


Figure 5.8. The initial state conductivity of EBR900 resist vs. bias at both room temperature and -30°C . Beam current is 5nA .

Table 5.4. The conversion table of beam currents and the corresponding dose rates. All the experiments are done in the fixed $\times 600$ magnification. The scan raster area is $2.665 \times 10^{-8} \text{ m}^2$.

beam current (nA)	0.1	0.3	0.5	1	5
dose rate (rad/s)	7.818×10^6	2.345×10^7	3.909×10^7	7.818×10^7	3.909×10^8

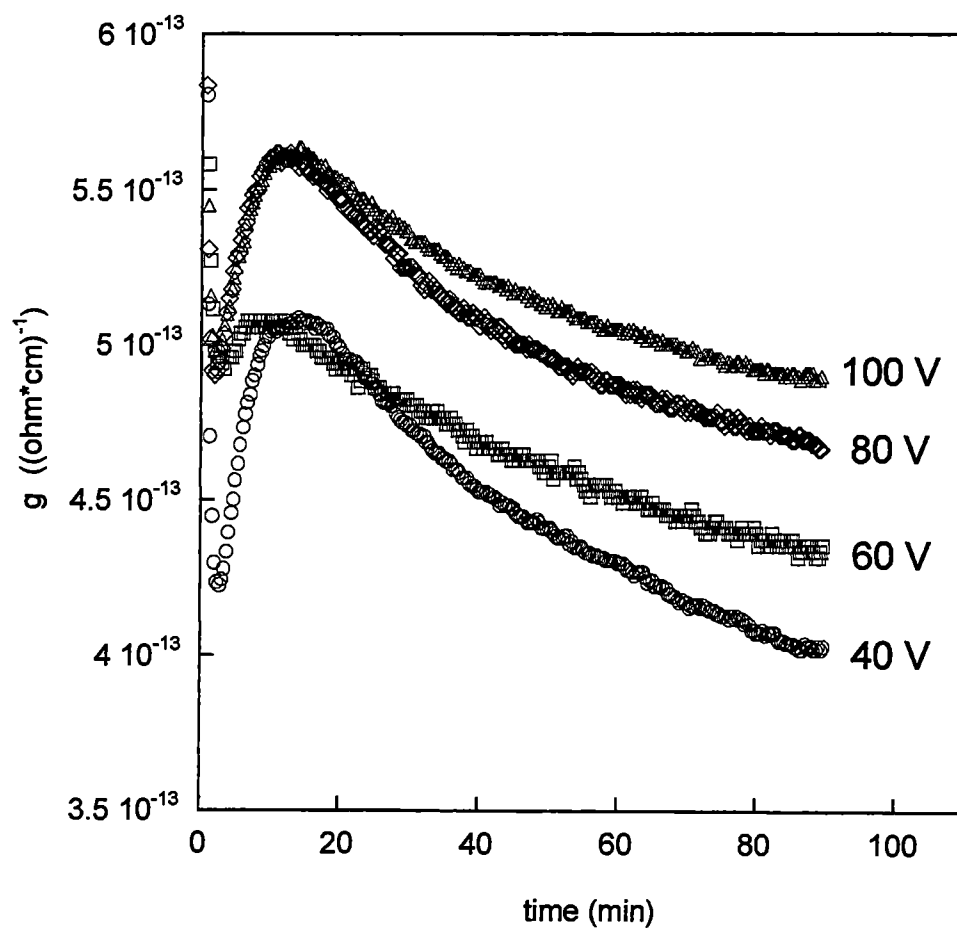


Figure 5.9. g vs. time for EBR900 resist under different bias conditions. Beam current is 0.1 nA.

Table 5.5. Steady state EBIC gain of three resists. Bias voltage is 100V.

Beam current, nA	PBS	EBR900	ZEP7000
0.1	0.15	3.26	2.65
0.3	0.11	1.2	3.98
0.5	0.16	0.3	0.64
1	0.15	0.31	0.11
5	NA	0.17	0.08

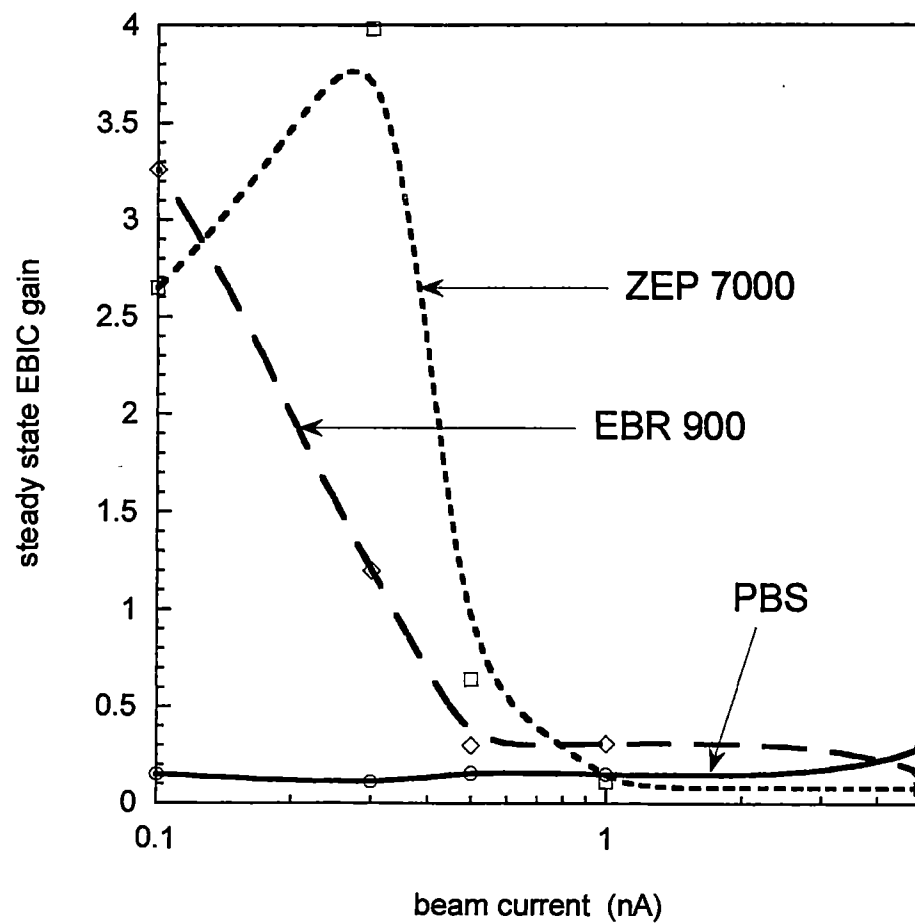


Figure 5.10. Steady state EBIC gain for three resists. The corresponding values are tabulated in Table 5.4.

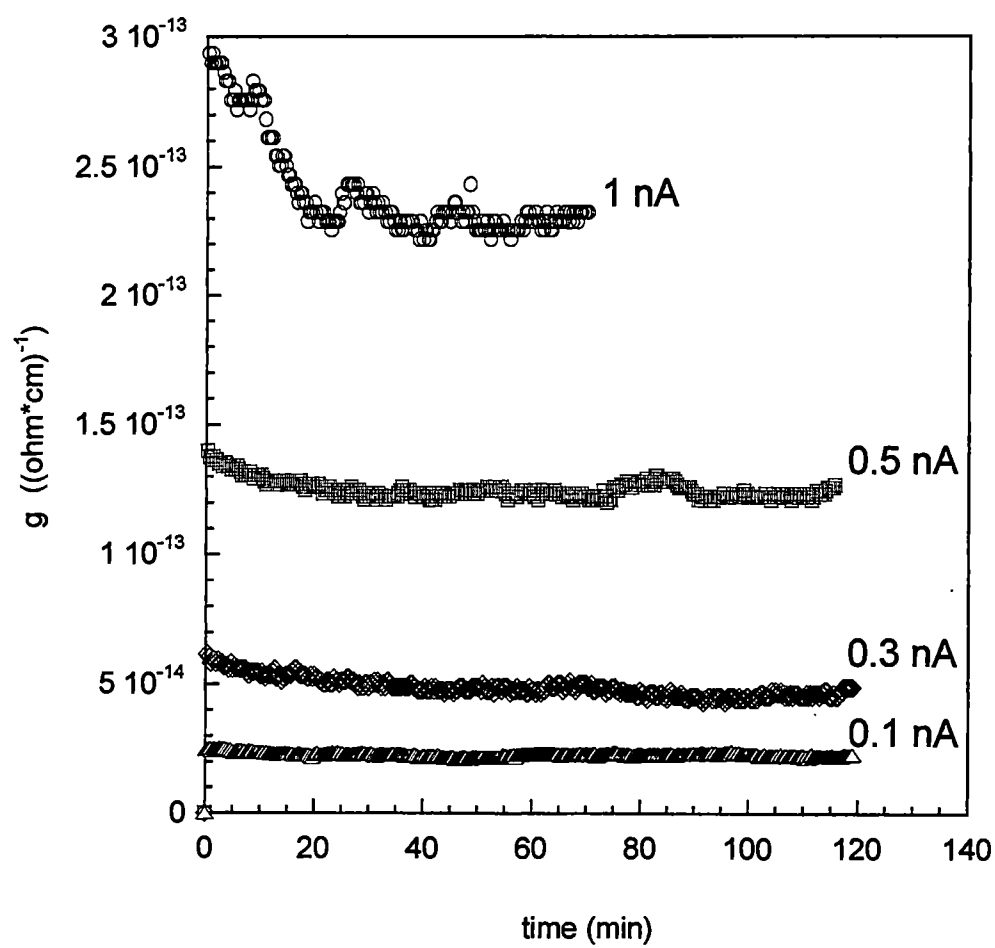


Figure 5.11. g vs. time for PBS resist under different beam current conditions. Bias voltage is 100 V.

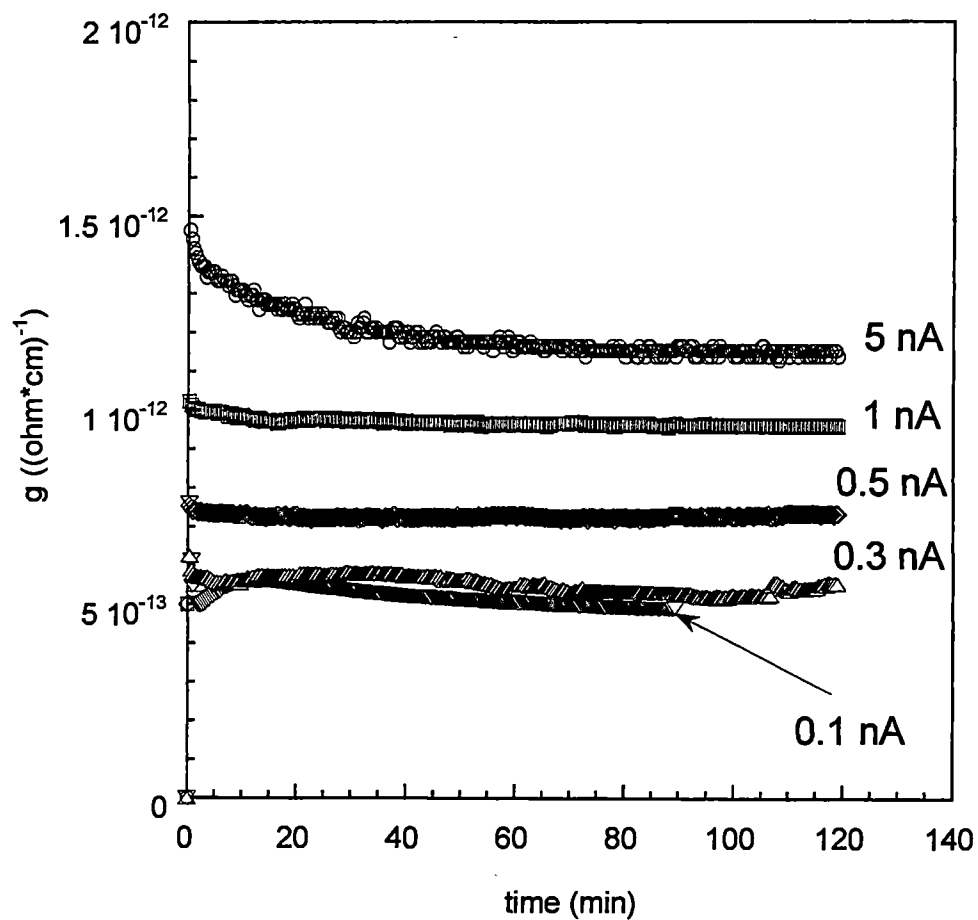


Figure 5.12. g vs. time for EBR900 resist under different beam current conditions. Bias voltage is 100 V.

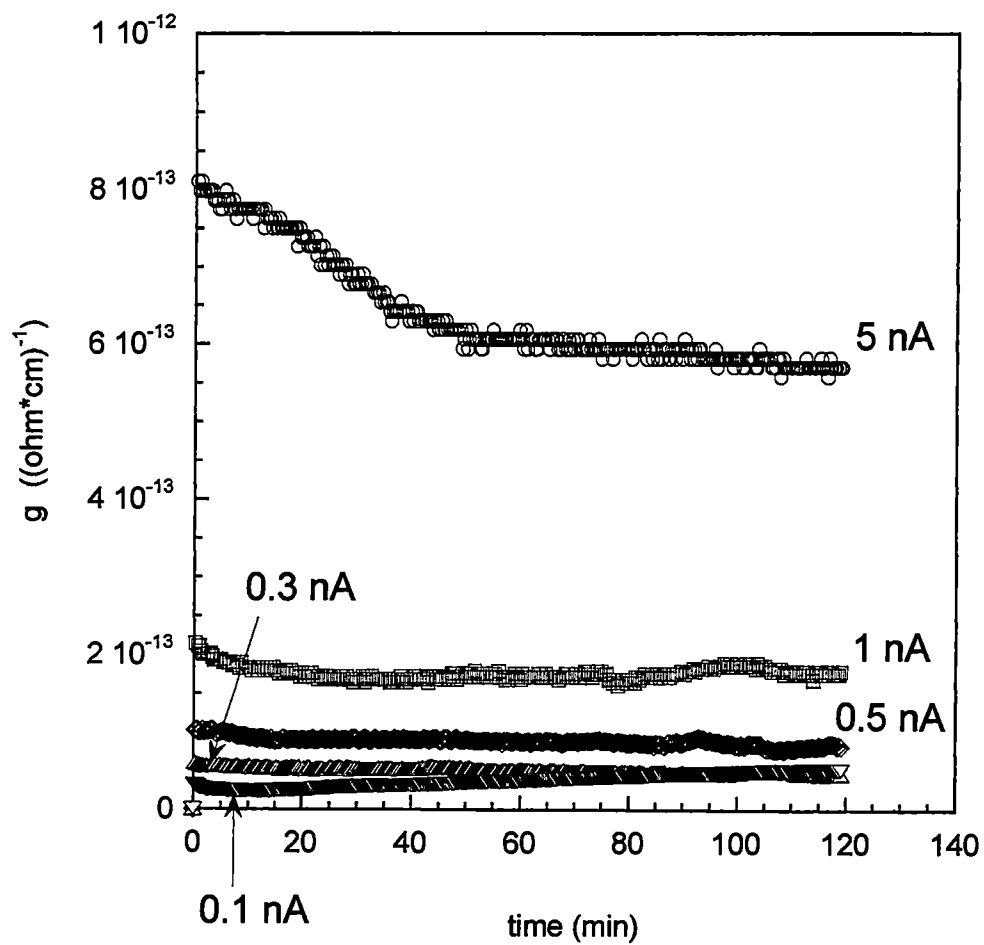


Figure 5.13. g vs. time for ZEP7000 resist under different beam current conditions. Bias voltage is 100 V.

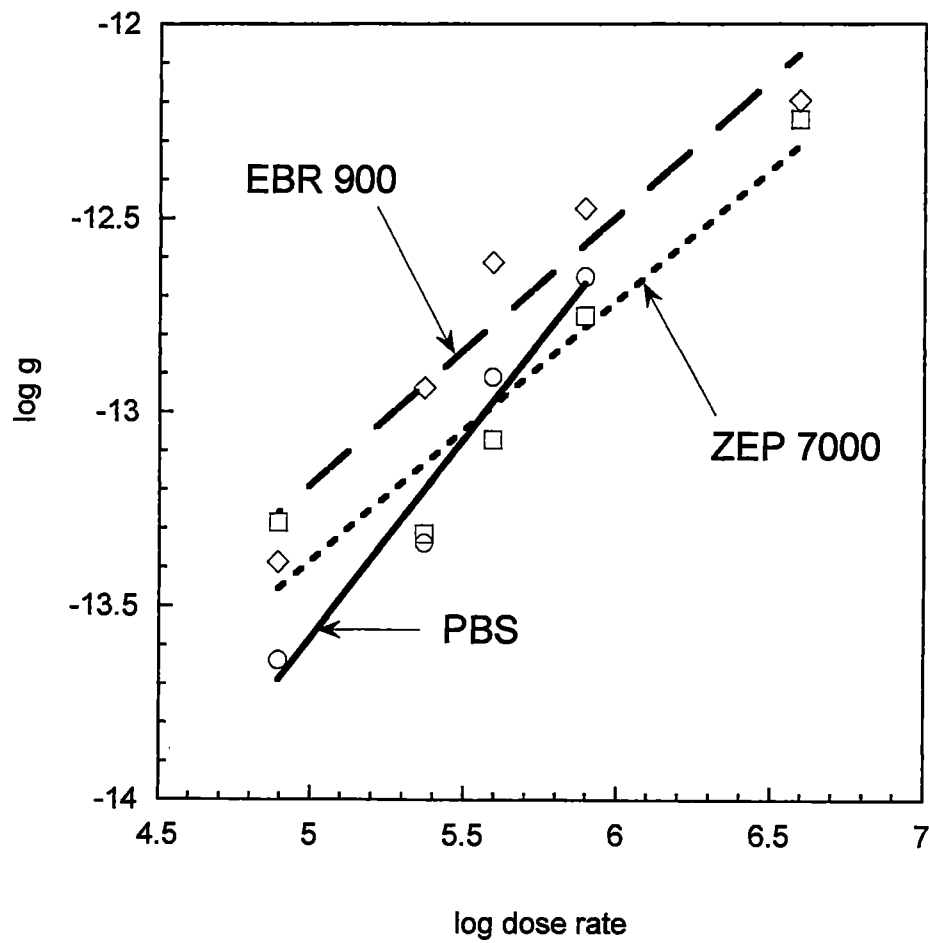


Figure 5.14. Folwer's power law for three resists. The slopes give the information about the distribution of trap level concentration.

5.2 Monte Carlo Simulations

The single scattering model was used in our Monte Carlo simulation for electron range estimation in photoresist layer and the program code written in Visual Basic in our group was used[160]. The result of a 10 keV electron beam irradiating perpendicular to the resist surface is shown in Figure 5.15. The number of electrons from 10 to 1000 were used to illustrate the trajectory in the photoresist layer. It is shown that most of the electrons penetrate the 400 nm photoresist layer. The corresponding percentage of electrons trapped within 400 nm from the resist surface and the backscattered electron yield are shown in Table 5.6.

5.3 Electron Beam Deflection Simulations

Both SIMION simulation tool and MATHEMATICA programming are applied for the electron beam deflection simulation from surface charging. Charging patterns of circles and squares of different dimensions are considered. The results of simulation are illustrated in the following sections.

5.3.1 SIMION Simulations

The first stage in electron beam deflection owing to surface charging is to estimate the range of electron beam deflection from a surface charging of known potential. Charging patterns of circles and squares of different sizes are considered and this is done by SIMION simulation tool. An electrical potential distribution illustration from a circular surface charging of 50 V is illustrated in Figure 5.16; the corresponding

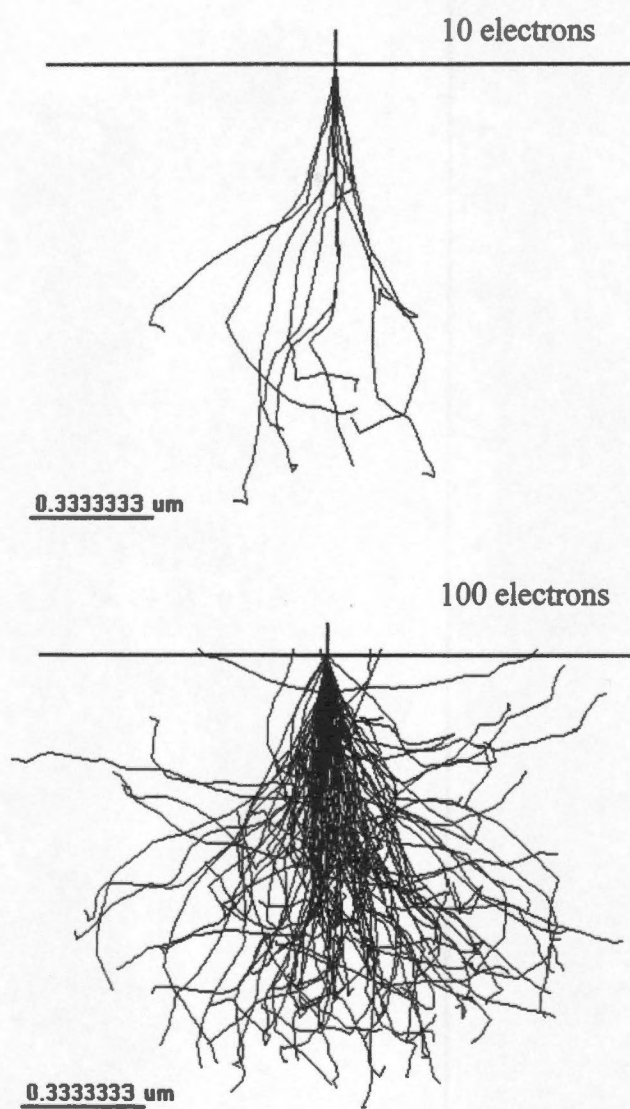


Figure 5.15. The Monte Carlo electron trajectory Simulation of photoresist material, the electron beam energy is 10 keV.

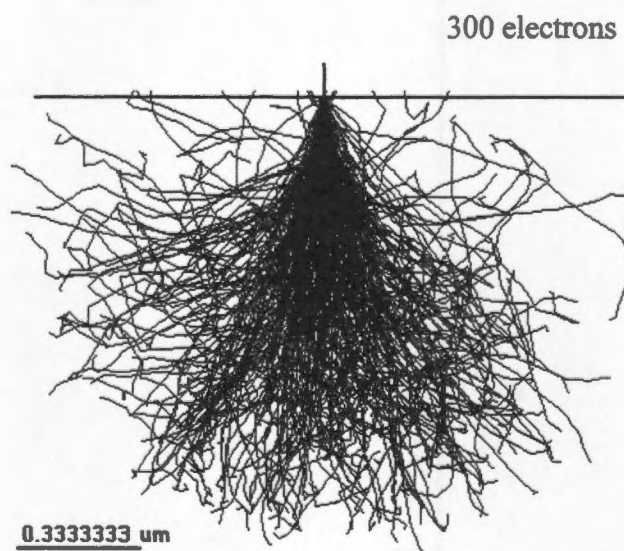
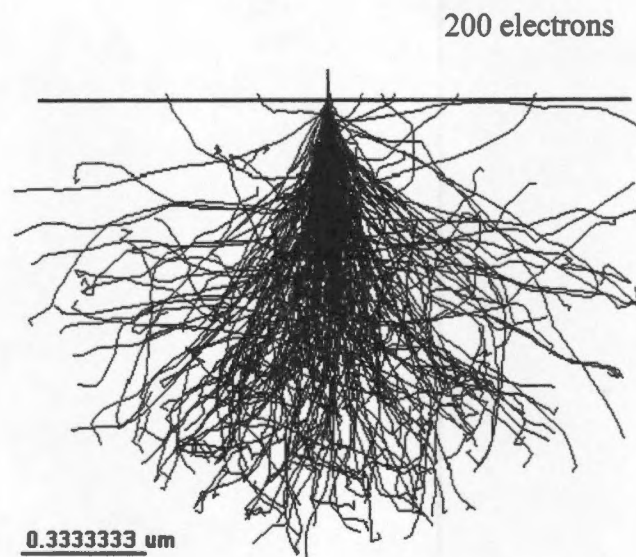


Figure 5.15. The Monte Carlo electron trajectory Simulation of photoresist material.
(continued)

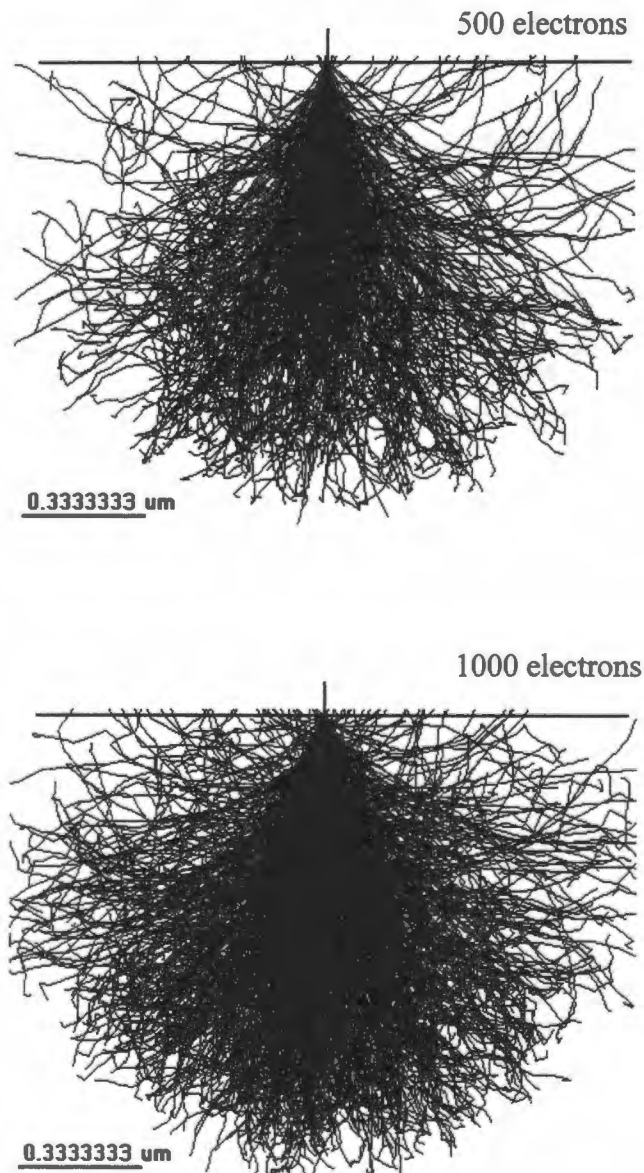


Figure 5.15. The Monte Carlo electron trajectory Simulation of photoresist material.
(continued)

Table 5.6. The backscatter electron yield from the Monte Carlo simulation. (10 simulations average)

Electron no.	10	100	200	300	500	1000
BSE η	0.07	0.05	0.055	0.064	0.054	0.053

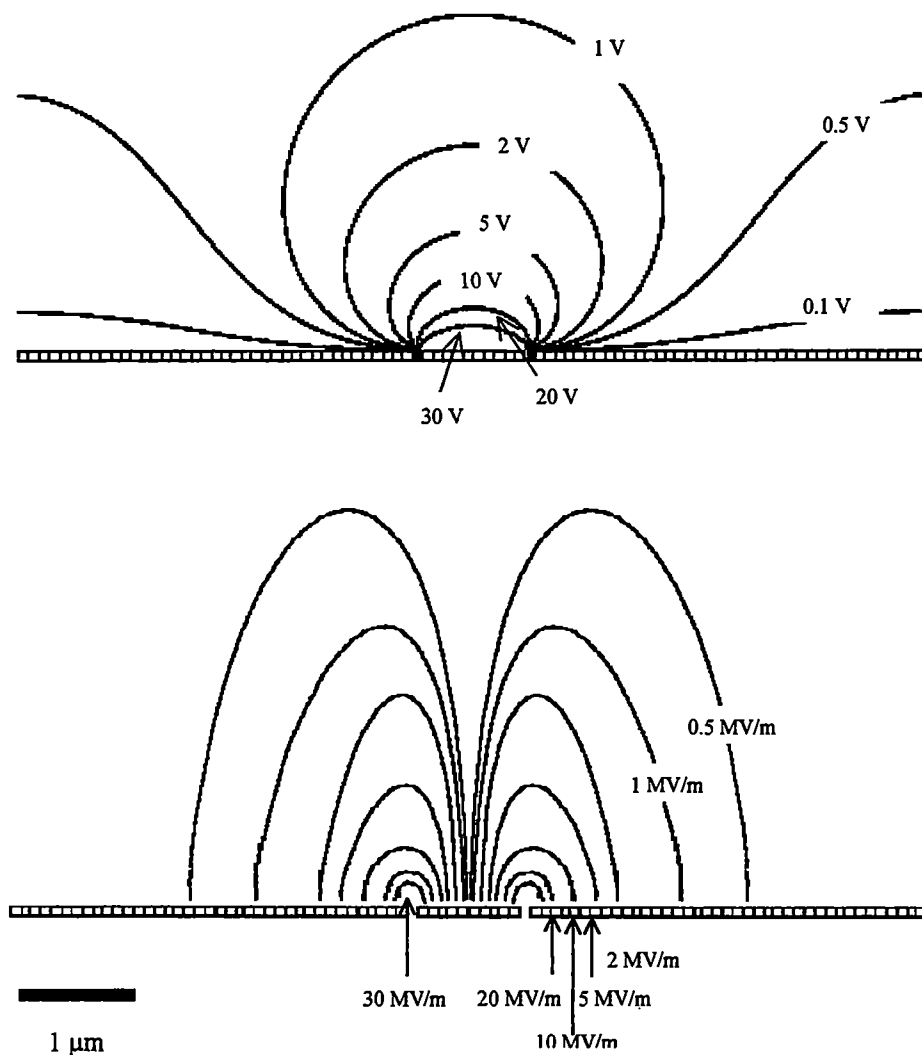


Figure 5.16. The electrical potential (top) and field distribution illustration from a circular surface charging of 50 V by SIMION simulation. The diameter of the circle is 1 μm .

landing deflection estimation from this pattern under different potential assignments is shown in Figure 5.17; the beam deflection estimation from a semi-infinite charging plane is shown in Figure 5.18.

5.3.2 MATHEMATICA Simulations

Figure 5.19 illustrates the field components in r and z directions with respect to the distance above a $1\text{ }\mu\text{m}$ diameter charging circle. The drastic lateral field decay in the first $100\text{ }\mu\text{m}$ distance away from the charging surface is observed and we consequently use the $100\text{ }\mu\text{m}$ flight path as the range for beam deflection calculation. The 2-D x - y field map that shows the relative lateral field strength in different planes above a $1\text{ }\mu\text{m}$ charging circle is illustrated in Figure 5.20. It is seen that the field maps have very similar patterns above $100\text{ }\mu\text{m}$ distance from the charging surface.

We simulate potential distribution in a 3-D manner using MATHEMATICA. The 3-D potential map is calculated in the final $5\text{ }\mu\text{m}$ distance range and shown in Figure 5.21. The results from MATHEMATICA reveal that the spatial potential has steep decay in the 5 to $10\text{ }\mu\text{m}$ range above a charging surface depending on the dimension of a charging pattern. For a $1\text{ }\mu\text{m}$ diameter charging circle the spatial potential decays from 8.899 V to 0.62 V in the $5\text{ }\mu\text{m}$ range away from the surface.

The long range nature of the electric field on electron beam deflection is estimated as well. Figure 5.22 shows the MATHEMATICA calculation for a $1\text{ }\mu\text{m}$

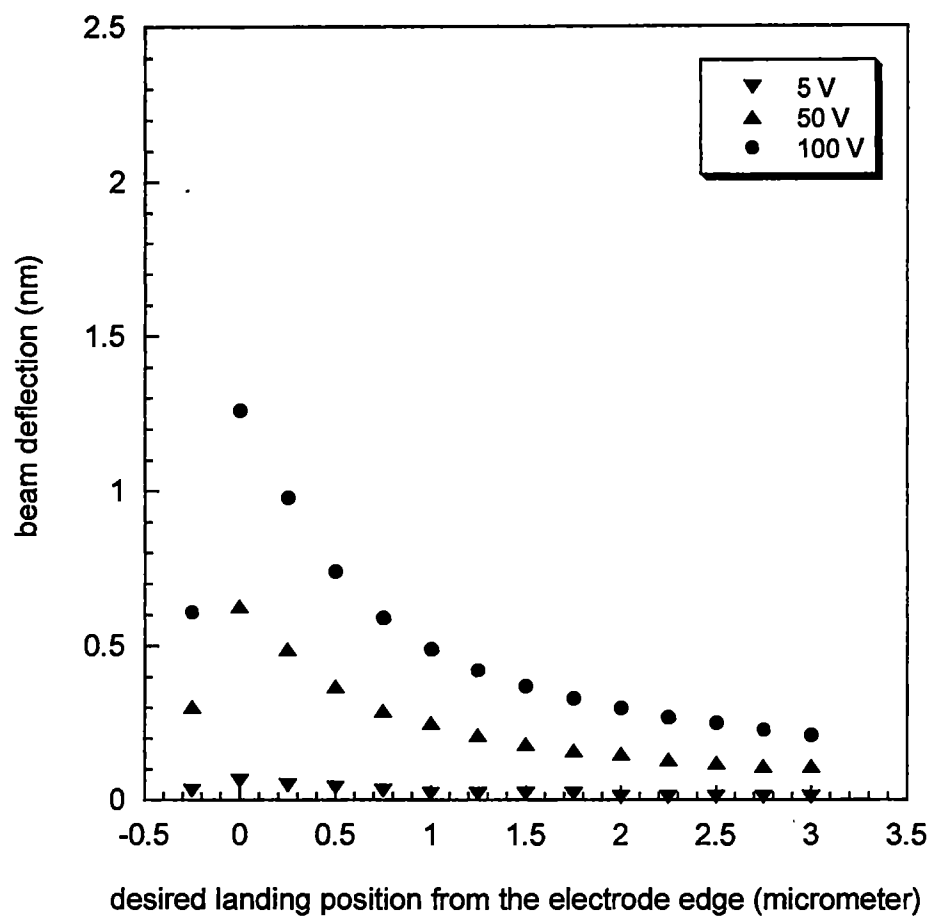


Figure 5.17. The electron beam deflection versus landing position for different surface potential settings. 1 μm charging circle from SIMION simulation.

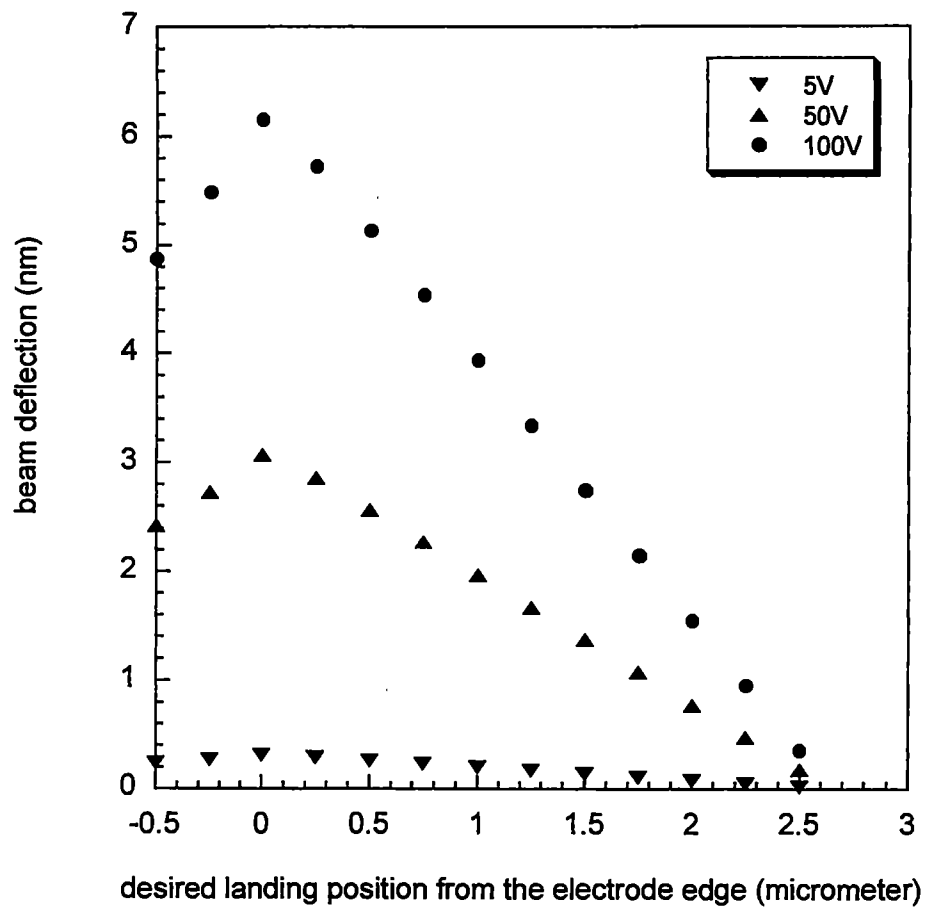


Figure 5.18. The electron beam deflection versus landing position for different surface potential settings. A semi-infinite charging plane from SIMION simulation.

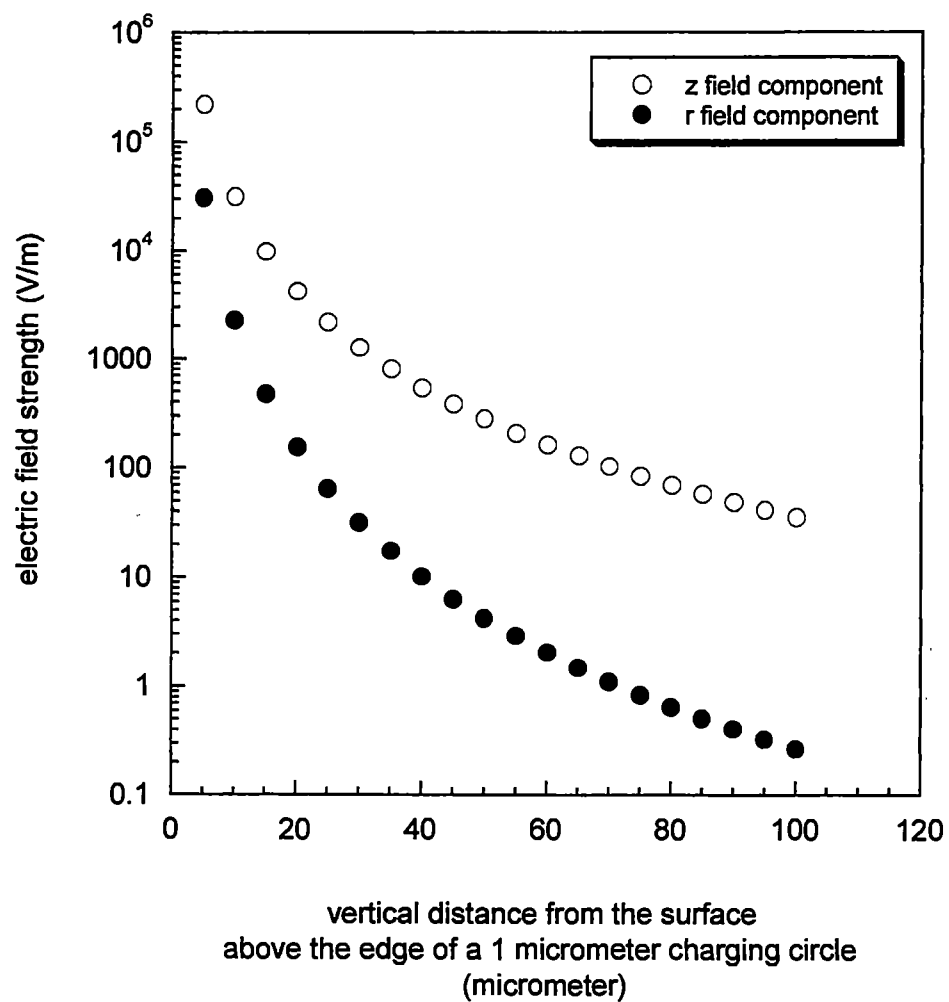


Figure 5.19. The field components result from a 1 μm diameter charging circle. MATHEMATICA simulation.

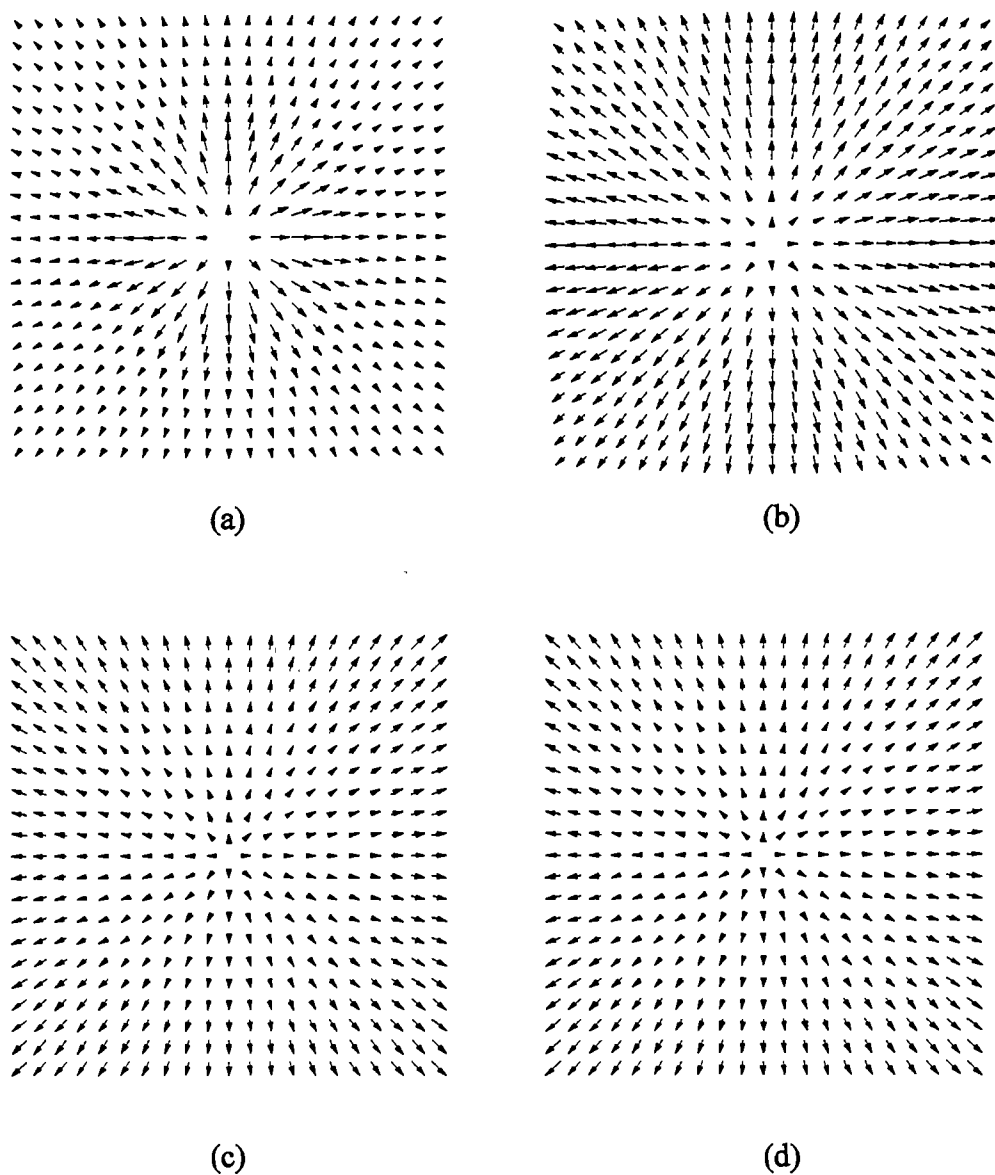


Figure 5.20. The 2-D field maps from a 1 μm diameter charging circle in different X-Y planes, every map covers a $5 \times 5 \mu\text{m}^2$ area. (a) 1 μm above charging surface; (b) 3 μm above charging surface; (c) 100 μm above charging surface; (d) 1000 μm above charging surface. MATHEMATICA simulation, SE yield = 0.1.

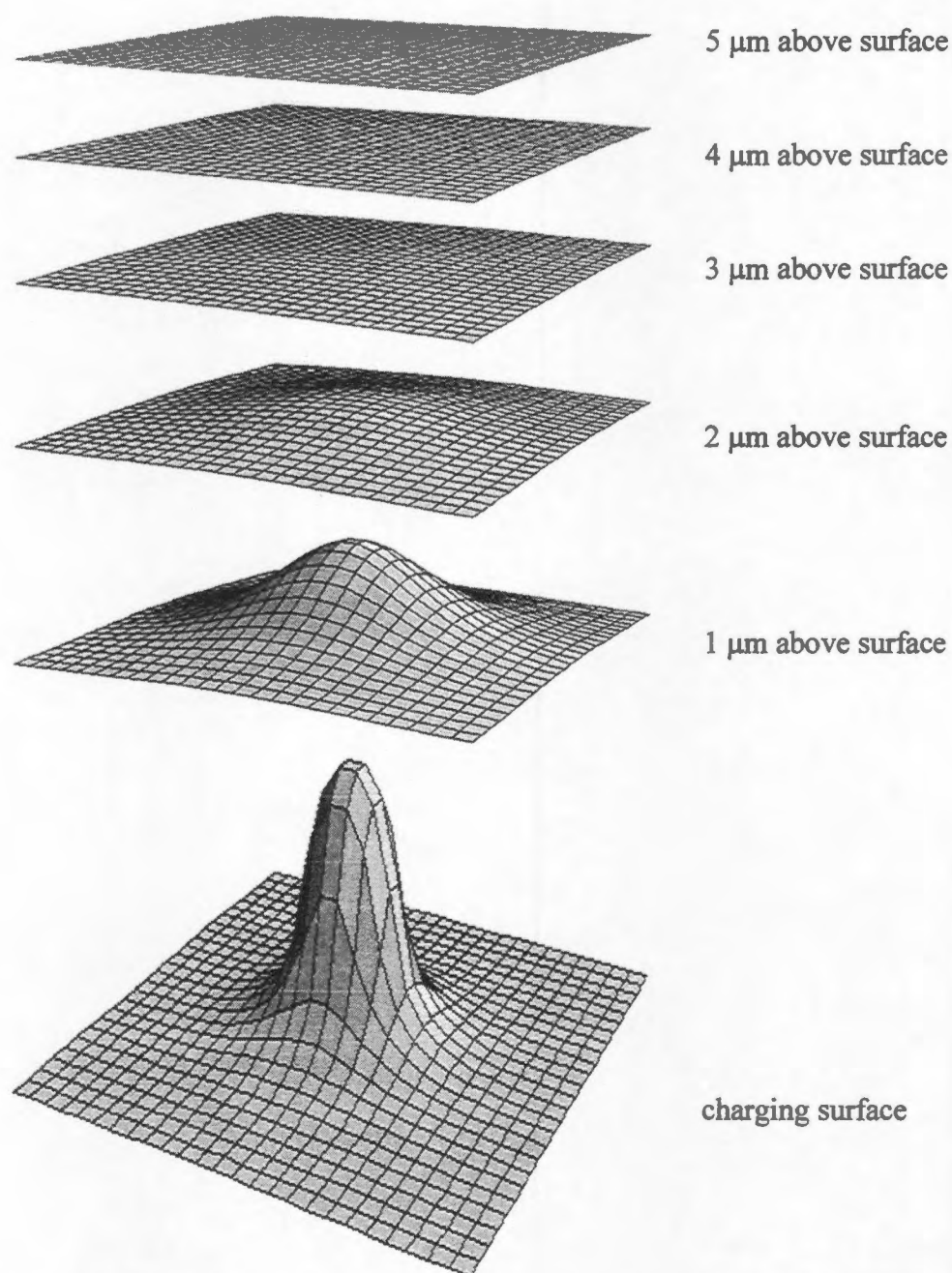


Figure 5.21. The MATHEMATICA potential map illustration above a 1 μm diameter charging circle. Every map covers the same area of $5 \times 5 \mu\text{m}^2$. The mesh size is $0.2 \times 0.2 \mu\text{m}^2$ and SE yield = 0.1. The potentials in the center (from top to bottom) are 0.620, 0.933, 1.558, 3.110, 8.899, and 57.748 Volt respectively. The vertical distances among layers are not to scale.

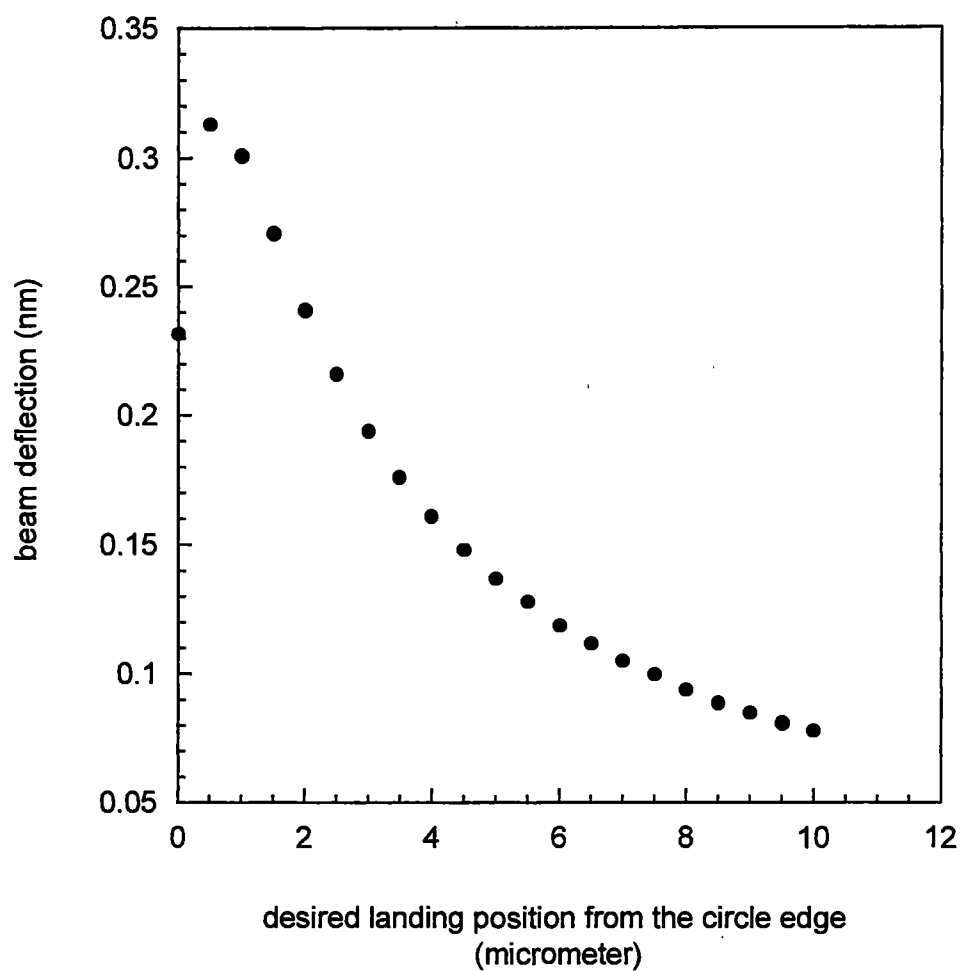


Figure 5.22. The electron beam deflection from a 1 μm diameter charging circle. MATHEMATICA simulation.

diameter charging circle. The maximum deflection is 0.314 nm at 0.6 μm outside the charging edge, the deflection falls to 0.1 nm at 7.5 μm away the charging edge.

The dimensional effect is also considered in our simulation. Figure 5.23 to 5.24 show the electron beam deflection results for 1 μm and 3 μm charging circles and Figure 5.25 to 5.27 show the electron beam deflection for squares of different size. They illustrate the electric field is more significant for a larger charging area even under a same secondary electron emission yield.

5.3.3 Surface Potential Decay Simulations

The surface potential decay after irradiation was estimated combining the experimental result in Figure 5.4 and 5.5 in Chapter 5.1.1. The correlation between g and bias for EBR900 was extracted as a representation for the decay simulation since EBR900 has a well-behaved g through out the bias range used in experiment. The fitted correlations between g and bias V are

$$g = 4.381 \times 10^{-12} + 5.6758 \times 10^{-14} \cdot V + 3.2197 \times 10^{-17} \cdot V^2 \quad (5.1)$$

for the high dose rate experiment and

$$g = 2.6238 \times 10^{-12} + 1.1522 \times 10^{-14} \cdot V - 1.8382 \times 10^{-17} \cdot V^2 \quad (5.2)$$

for the corresponding low dose rate experiment. The decay of surface potential was then calculated by equation (3.53). The results for EBR 900 resist using equation (5.2) with circular and square charging patterns of different dimensions are illustrated in Figure 5.28 and 5.29. It is clear that the surface potential drops significantly in the first second, and a

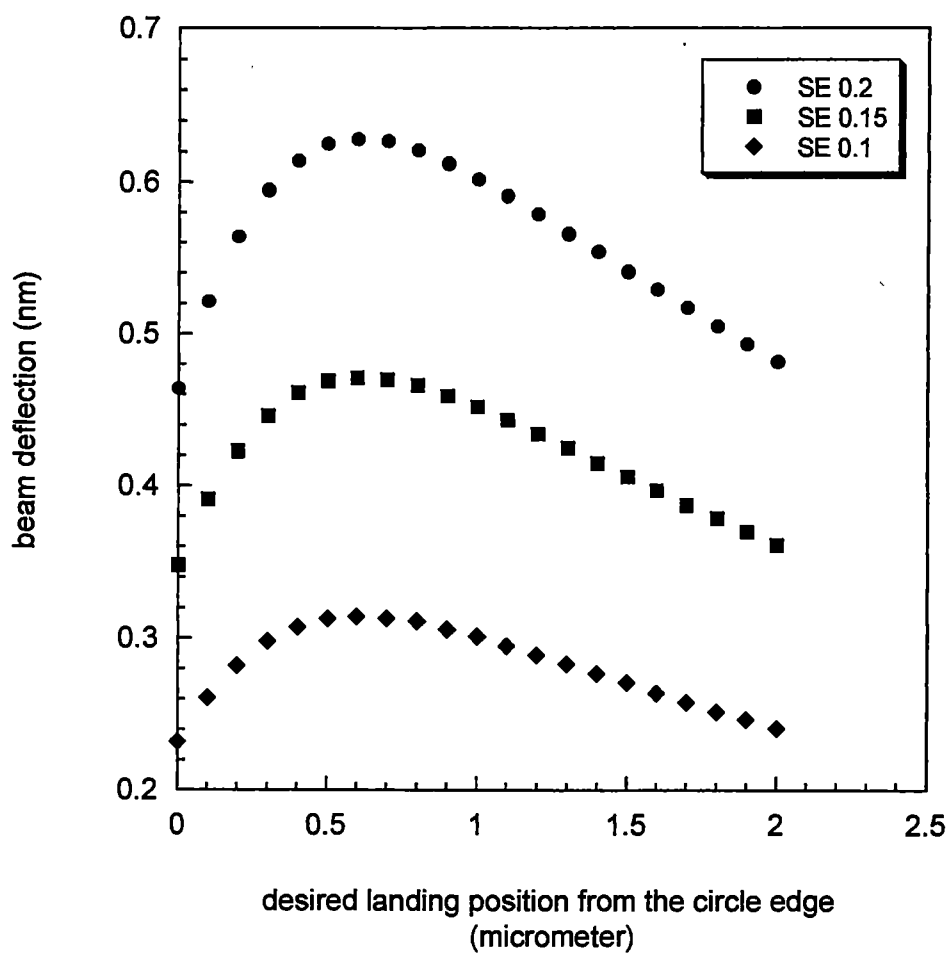


Figure 5.23. The electron beam deflection from a 1 μm diameter charging circle with different SE yield settings. MATHEMATICA simulation.

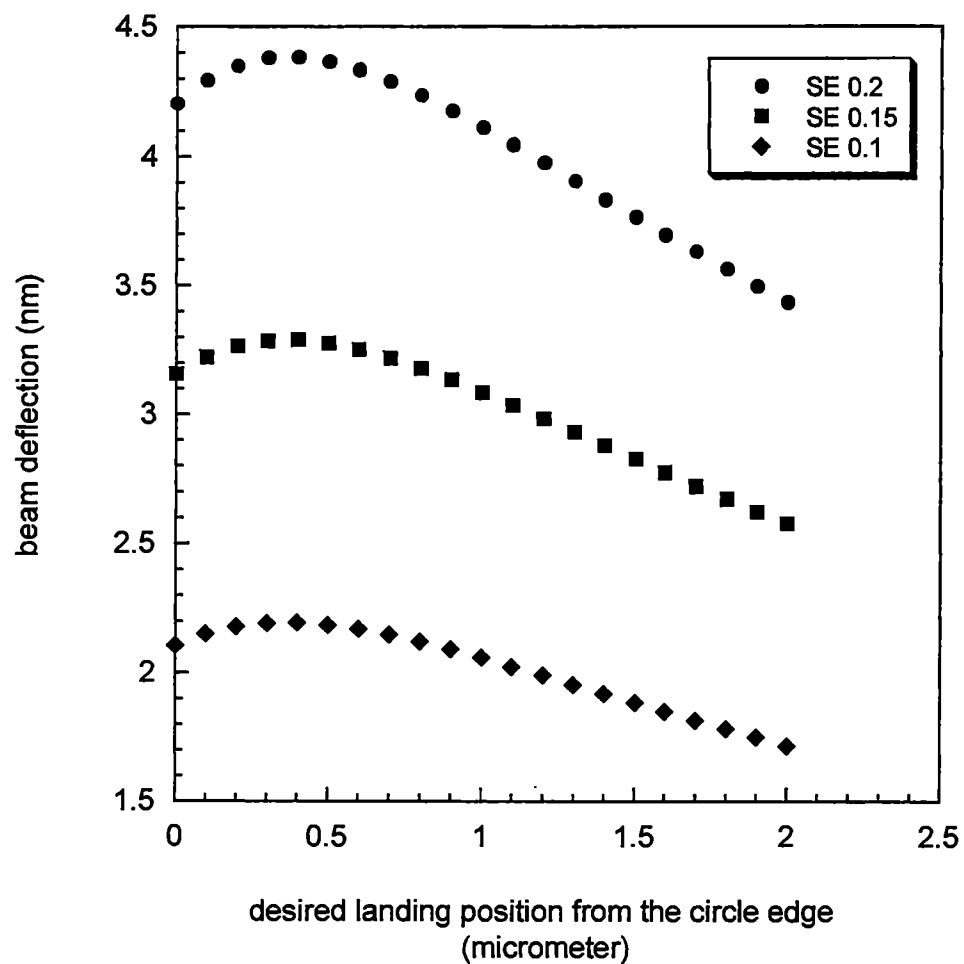


Figure 5.24. The electron beam deflection from a 3 μm diameter charging circle with different SE yield settings. MATHEMATICA simulation.

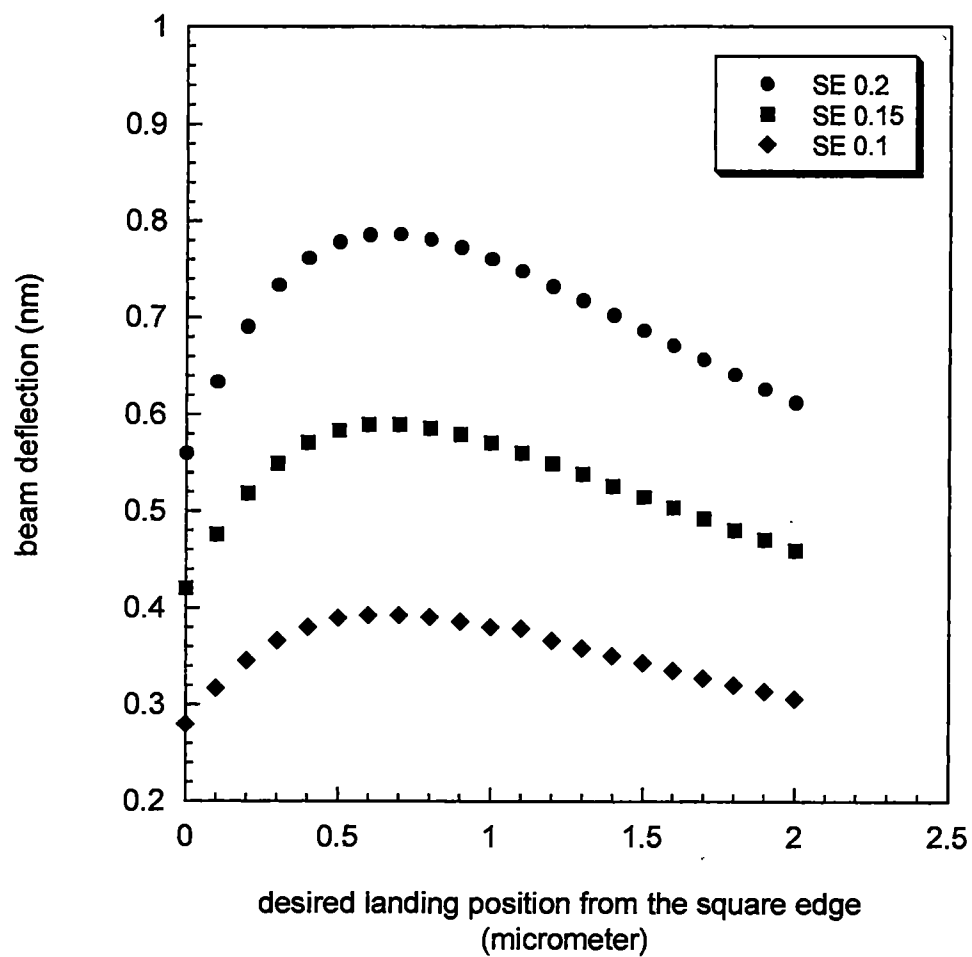


Figure 5.25. The electron beam deflection for a $1 \times 1 \mu\text{m}^2$ square with different SE yield assignments. MATHEMATICA simulation.

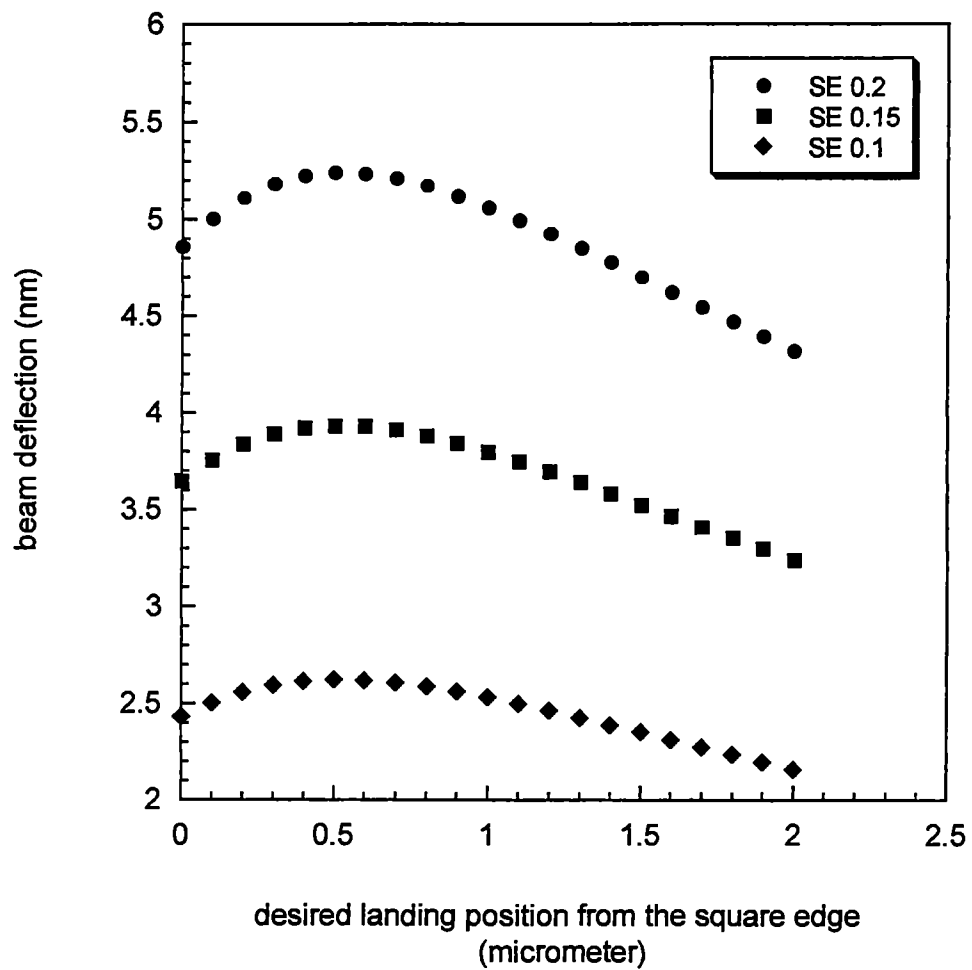


Figure 5.26. The electron beam deflection for a $3 \times 3 \mu\text{m}^2$ square with different SE yield assignments. MATHEMATICA simulation.

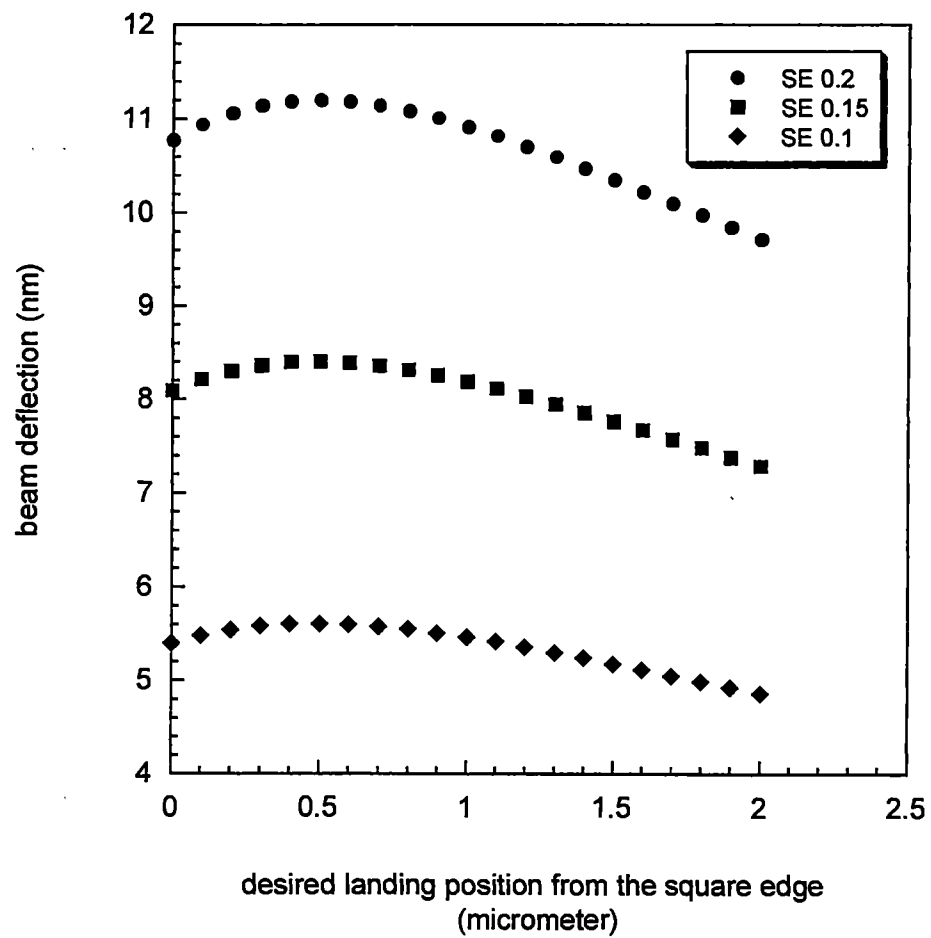


Figure 5.27. The electron beam deflection for a $5 \times 5 \mu\text{m}^2$ square with different SE yield assignments. MATHEMATICA simulation.

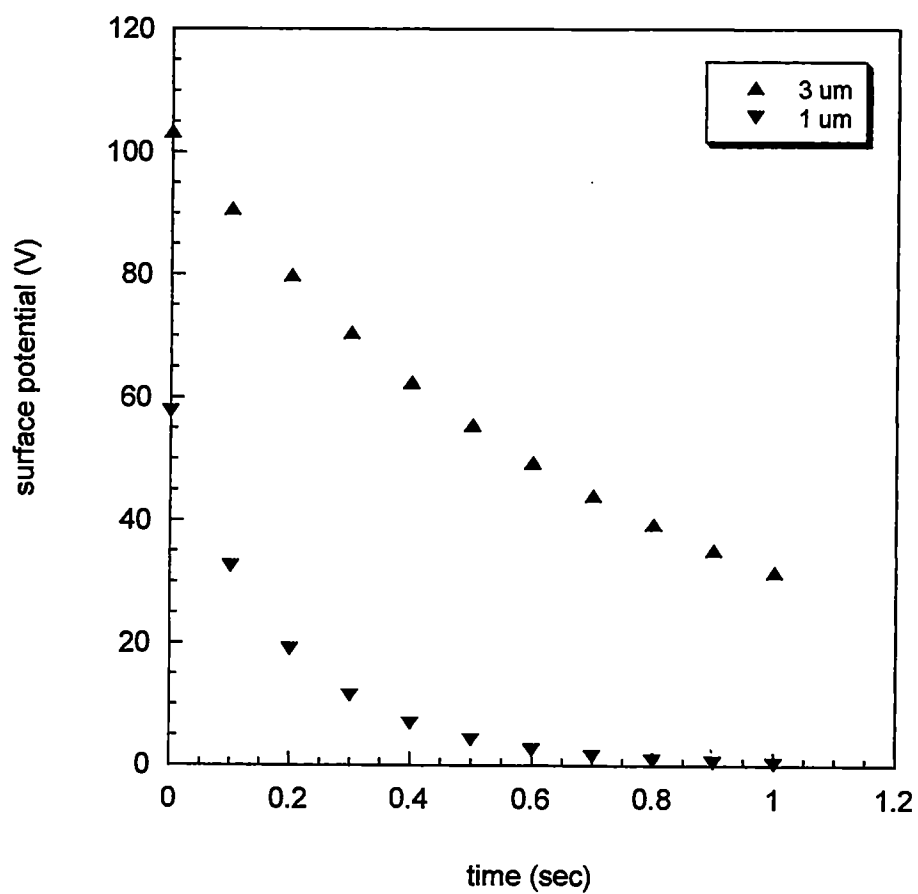


Figure 5.28. The potential decay of charging circles of different dimensions. MATHEMATICA simulation on EBR 900 resist.

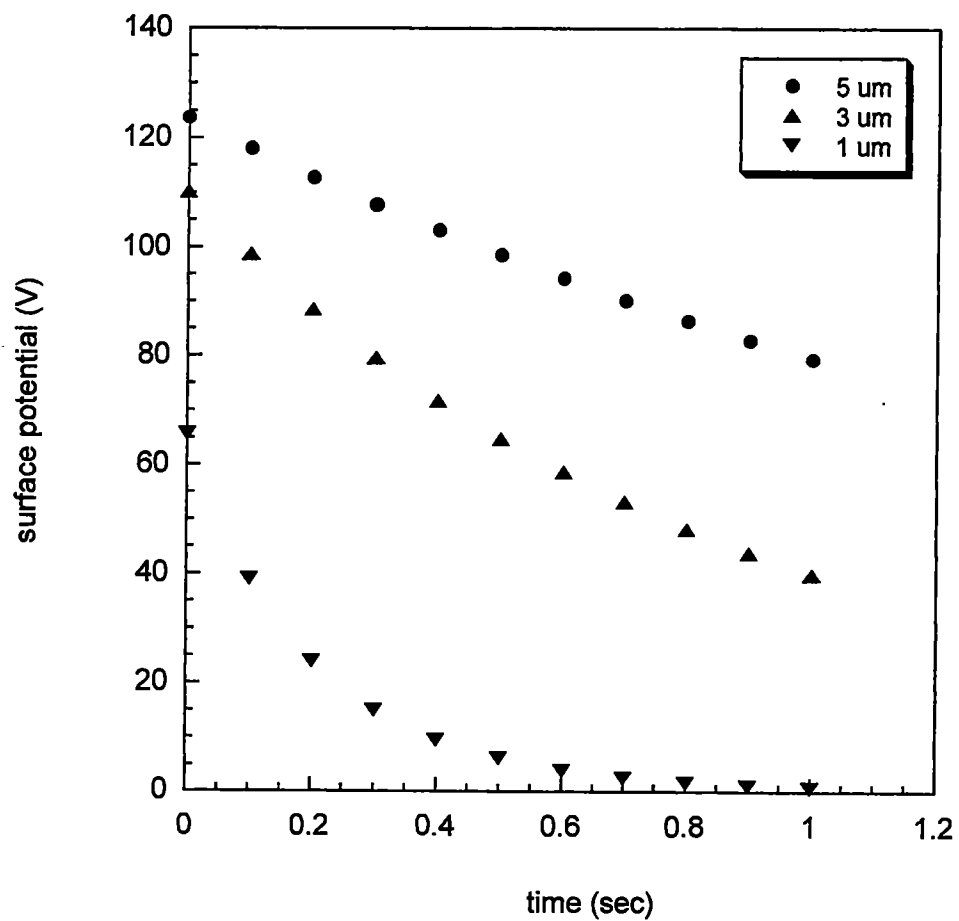


Figure 5.29. The potential decay of charging squares of different dimensions. MATHEMATICA simulation on EBR 900 resist.

pattern of smaller dimension decays faster than a larger one in both circular and square patterns.

CHAPTER 6

DISCUSSION

6.1 EBIC Characteristics of Photoresists

The initial and long term EBIC characteristics were investigated in my experiment. They will be discussed separately in the following sections.

6.1.1 Initial State EBIC Characteristics

An explanation for the observed conductivity changes during the entire experimental cycle shown in Figure 5.1 is proposed as follows. Carriers are constantly generated in the interaction volume by the primary beam during irradiation. Before a bias is applied, the rate of generation, trapping, detrapping, and that of recombination reach a dynamic equilibrium, consequently a stable specimen current is observed. When an electric field is applied, the drift velocity of carrier surges, the conductivity jumps up to a peak value then gradually drops down and reaches a new equilibrium. The polarization effect contributes the overall conductivity surge but mainly in the beginning section of the measurement after the bias is applied. I propose that the carrier concentration may go through a transient variation as a result of the drift velocity increase because the change of carrier mean free path under the field alters the carrier recombination rate. The change in the carrier mean free path promotes an increase in the carrier recombination rate and causes a decrease in the free carrier concentration; this accounts for the conductivity drop during transition. The rate of trapping can be treated

as a constant during transition since most of the traps are filled right after they are generated and before the field is applied. The rate of detrapping may undergo an increase in the same time since the applied field may trigger some shallow trapped carriers to escape (Poole-Frenkel effect[161]). The equilibrium under bias can be seen as the asymptotic tails of the conductivity levels of three resists in Figure 5.2.

After the field is turned off, the recombination rate goes through a transition again. This is shown in Figure 5.3 by three different slow conductivity decay lines for the resists. My experimental setup may account for the slow transition processes after bias is off. The penetrating beam condition generates a low field across the resist layer [103, 108]. Only the field from the positive charge layer is available to drive space charge carriers inside the irradiation volume after bias is turned off and this results in the long decay in conductivity seen in Figure 5.3.

All three resists show distinctive conductivity decay profiles as a function of time in the bias-off experiments. It seems that the behavior of the PBS resist implies two processes with different decay times; this may be related to the rate of generation for the decomposition fragments SO_2 and CH_2CHR that PBS yields during scission reaction. The difference in the PBS two decay processes is not clear but it is likely to be linked to the resist decomposition chemistry.

Figure 5.6 and 5.7 demonstrate how a simple estimation of the carrier concentration variation can be made. The EBIC current is the product of carrier electronic charge e , carrier concentration n , irradiation area A , and drift velocity v under field

$$I_{EBIC} = e \cdot n \cdot A \cdot v \quad (6.1)$$

In both cases only the beam current varies, therefore the carrier concentration will be the only variable when a resist is irradiated under different beam current with a given applied field. Since the irradiation area and beam energy are the controlled variables in our experiment, the carrier concentration ratio, by mathematical manipulation, leads to a representation by EBIC gain G ratio in the following manner

$$\begin{aligned} n_{5nA} / n_{0.5nA} &= I_{EBIC, 5nA} / I_{EBIC, 0.5nA} \\ &= (G_{5nA} / G_{0.5nA}) \cdot (5nA / 0.5nA) \\ &= (G_{5nA} / G_{0.5nA}) \cdot 10 \end{aligned} \quad (6.2)$$

Comparing the gain range in Figure 5.6 and 5.7, the EBIC gains for both the PBS and ZEP7000 resists show roughly an order of magnitude increase as the beam current drops from 5nA to 0.5nA in the entire bias region. Based on equation (6.2) it shows that the carrier concentrations in both resists are the same regardless of the change of beam current. However, the gain for EBR900 resist shows approximately a factor of 2.5 increase of gain from high dose to low dose experiment, thus indicating a 4 times carrier concentration decrease from 5nA to 0.5nA.

Measurement of EBIC gain for the three resists produces results that agree with the trend in conductivity increase ratios in Table 5.2, where the EBR900 shows a highest conductivity increase of 2.4x and ZEP7000 shows a 1.3x increase as beam current increases by 10 folds. When a resist is under electron beam irradiation, the rate of electron-hole pair generation and the rate of carrier detrapping counter balance that of carrier trapping and recombination. These rates determine the variation of the carrier

concentration. Both the rates for electron-hole pair generation and carrier trapping should increase linearly as the dose rate increases since the electron-hole pair generation energy is a material constant and we assume that the polymer chain scission reaction in the irradiation volume provides the main trapping generation. The recombination and detrapping rates should only experience small changes as long as the applied field is fixed, however, they are strongly field strength dependent. I propose the change of trapping rate is probably the key contribution responsible for the variation of both carrier concentration and conductivity ratios. It is clear that both the PBS and ZEP7000 resists fall into a same category, which possesses higher trapping rate increase than that of the EBR900 in high dose rate experiment. I believe the explanation for this probably lays in the nature of the resist chemistry. The EBR900 resist consists of poly(2,2,2-trifluoroethyl- α -chloroacrylate), a linear aliphatic polymer from the acrylic family. The ZEP7000 resist is a copolymer of α -chloromethacrylate and α -methylstyrene, and it is also a derivative from the acrylic family. The PBS resist is a linear polymer of polybutenesulfone, a polymer from the poly(olefin sulfone) system. A definitive statement of the reasons for these changes cannot be made without knowing the electron-hole pair generation energy and the carrier transportation characteristic of these resists. In addition, the detrapping rate in EBR900 during irradiation is another factor that might possibly explain why it has the highest carrier concentration increase among the three resists as dose rate changes.

6.1.2 Long Term EBIC Characteristics

The steady state EBIC gain is sensitive to the dose rate for the resists other than PBS. From Figure 5.13 it is clear that the resists have higher EBIC gains at low beam current irradiation, except for PBS whose gain is insensitive in the whole dose range. The falling of EBIC gain at higher dose rate can be interpreted as the onset of the plasma formation in resists during electron beam irradiation, this is an effect which has been reported in some of the radiation studies regarding semiconductor materials[162-164]. As the beam current increases, the carrier generation rate rises to a point where the carrier density inside the interaction volume is high enough to form a conducting shield near the outer boundary of the interaction volume. The carriers generated inside the interaction volume therefore experience less influence from the applied field and result in decrease in EBIC effect, thus result in the decrease of EBIC gain.

The steady state trap level distribution of the resists is investigated by Fowler's power law (equation (3.1) and Figure 5.14), the result shows that PBS has the power law exponent of 1.02, which represents a uniform energy distribution of traps; EBR900 and ZEP7000 have the exponents of 0.7 and 0.67 respectively, which means an exponential energy distribution of traps. The uniform trap distribution and the dose rate insensitivity of PBS may be related to its decomposition chemistry. During electron beam irradiation only two types of fragments are generated; the CH_2CHR remains as solid residue for further depolymerization while SO_2 is a gas and it leaves the resist layer. CH_2CHR of different chain lengths probably contribute to form trapping sites of different levels if one assumes only one type of trapping site is available on the end of CH_2CHR . The length of

the polymer chain to which the site attached may influence the trap energy level and result in a distribution of trap in different energies. Since the scission reaction site is random, the energy levels are therefore uniform in distribution.

In contrast with PBS, both EBR900 and ZEP7000 follow the same type of depolymerization reaction introduced in Chapter 3.6.2. The double bond chain ends and radicals formed on the backbone and broken side groups are believed to serve as trapping sites with different energies. However, I believe the radicals, particularly the radicals from the broken side groups (in β fission) serve trapping levels in certain energy states since they are simple fragments and they don't have functional group variations. This explanation is believed to support the trapping level analysis that reveals trap energy distributions of EBR900 and ZEP7000 are not uniform.

The dose rate dependence of carrier mobility at steady state can be examined by the following derivation proposed by Gross[165]. The mobility concept from band theory can only be applied to polymer materials under the assumption that polymer materials have short range of order. Since there is no clear band structure in polymer materials, the trap modified mobility is therefore used in polymer material macroscopic carrier transportation analysis. Again it is needed to revisit the concept of trap modulated mobility introduced in Chapter 3.4 (equation (3.8)). I now consider electrons as the major carrier in the following discussion.

Under steady state condition, the carrier generation rate p should equal to that of recombination, therefore p is proportional to the free carrier concentration n_c times the density of recombination centers N that defined in equation (3.4). A trapped electron is

then lifted into the conduction band before it recombines with a hole. Under medium to high electron-hole pair generation, $n_c + n_t \cong n_c$ and equation (3.9) can be simplified as

$$p = \alpha \cdot n_c^2 \quad (6.3)$$

Since the conductivity g is in proportional to the free carrier concentration n_o , the above equation indicates that the conductivity will increase with respect to the square root of the dose rate. The equation (6.3) is also called the “bimolecular” recombination. The examination of the equation (6.3) to the three resists is shown in Figure 6.1 and relatively good agreement is observed.

The relationship between dose rate and trap-modulated mobility is discussed as followed, the detailed derivation is again proposed by Gross[165]. Combining the definition of μ in equation (3.8) and equation (3.9), one obtains

$$\mu = \mu_0 \cdot \alpha \cdot n_c^2 / p \quad (6.4)$$

The relationship between the carrier generation rate p and dose rate $\dot{D}$ is proposed as

$$p = c \cdot d \frac{\dot{D}}{E_{e-h}} \quad (6.5)$$

where c the dimensional factor; d the specimen specific mass; E_{e-h} the electron-hole pair generation energy. Combine equation (6.4), (6.5), and (3.1) one obtains

$$\mu = \left[(\alpha \cdot K^2 \cdot E_{e-h}) / (\mu_0 \cdot e^2 \cdot c \cdot d \cdot \dot{D}_0) \right] \left(\frac{\dot{D}}{\dot{D}_0} \right)^{2\Delta-1} = Const. \cdot \left(\frac{\dot{D}}{\dot{D}_0} \right)^{2\Delta-1} \quad (6.6)$$

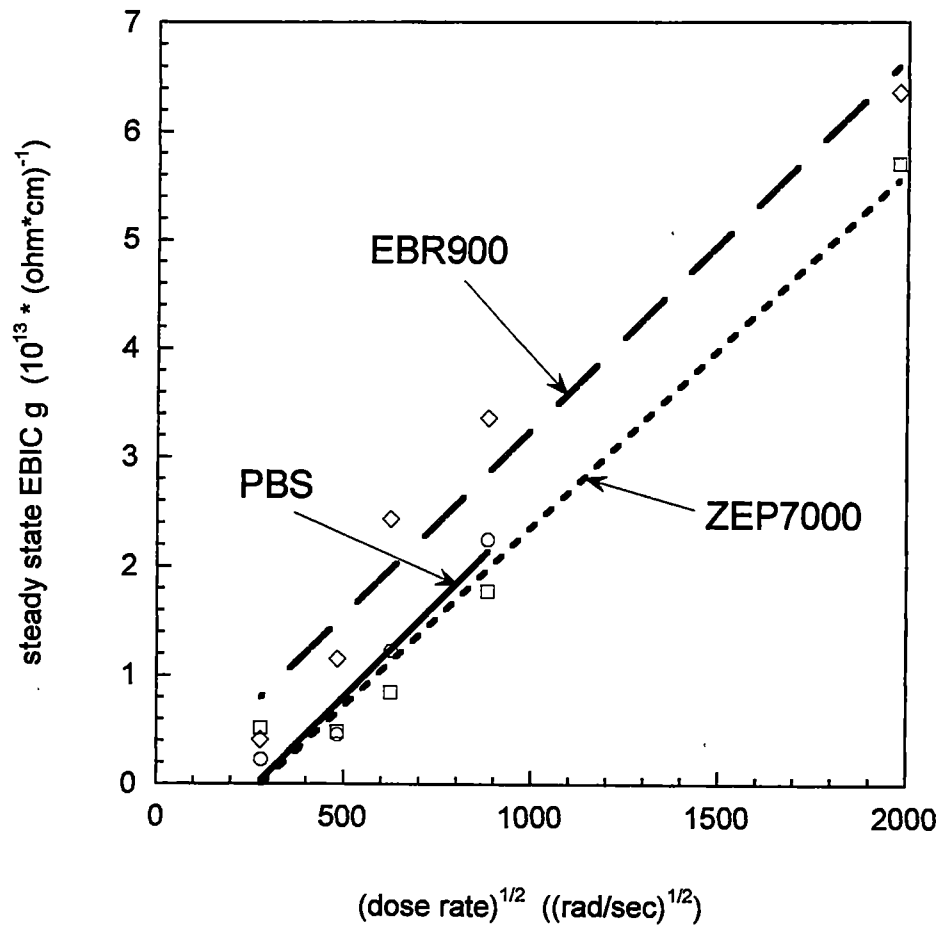


Figure 6.1. The steady state EBIC conductivity vs. $(\text{dose rate})^{1/2}$ for three resists.

It is clear that the exponent in equation (6.6) varies from 0 to 1 as the trap distribution from single energy level ($\Delta = 0.5$) to uniform distribution ($\Delta = 1$). From our steady state trapping level distribution study on the three resists the PBS will show the most dose rate dependent mobility over the dosage range, followed by the EBR900 resist, then by the ZEP7000 resist.

Figure 5.9, 5.11~5.13 reveal the transient characteristic of the electron beam induced conductivity over a period of recording time. The resists, particularly the EBR900, go through a maximum at about 14 minutes after irradiation and reach a steady state near the end of second hour. This long term conductivity variation on other polymers has been reported in literature for polymer electret studies [156, 157, 166-171]. The initial increase of conductivity, i.e. the build-up region of the conductivity curve, is believed to be the contribution from the steady carrier generation while the decay of the conductivity curve after its maximum is from the contribution of recombination and trapping. The rates of carrier generation, trapping, detrapping, and recombination are the factors that govern the conductivity variation during the electron beam irradiation experiment, it is these factors compete each other and result in the variation of conductivity over time.

Fowler's trapping model is not valid for considering the transient state of conductivity variation since all the assumptions in the model are made under the steady state condition. A later developed theory considering different rate factors was proposed in the '70s[166, 167] from the observation of the polymer film conductivity change in x-ray irradiation experiments and later generalized[166, 167, 171] for better explanation of

the transient period of conductivity change; however, the success in quantitative analysis is still limited since many parameters required for a precise calculation are usually uncertain for a given experimental condition. I shall discuss this model in a qualitative manner and consider the parameters that fit our photoresist system.

There are several assumptions for this rate theory. First, the charge transportation is assumed unipolar, the opposite polarity charge carriers are immediately captured by localized traps after carrier pair generation; the immobile carriers serve as the recombination centers in the later recombination process. Second, the rate of a transition is defined as the product of the corresponding rate constant to the concentration of the available site for that specific transition. This is the probability for the specific transition to happen per unit time. Third, the free carriers in the extended state can either be trapped into localized states and return to the extended state later by thermal re-emission or recombine with the opposite charge trapped in energetically deep traps. The carrier concentration is considered as the contribution from the rate of carrier generation, carrier trapping, carrier detrapping, and recombination of carriers of opposite polarity. For the free and trapped carrier concentrations, the equations are[166]

$$dn_c/dt = p(t) - \alpha_1 n_c (N_t - n_t) + \alpha_2 n_t (N_c - n_c) - \alpha_3 n_c (n_c + n_t) \quad (6.7)$$

for free carrier concentration n_c and

$$dn_t/dt = \alpha_1 n_c (N_t - n_t) - \alpha_2 n_t (N_c - n_c) \quad (6.8)$$

for trapped carrier concentration n_t . N_c and N_t are the degeneracy of the conduction band and the density of the trapping level; $p(t)$ is the carrier generation rate; α_1 , α_2 , α_3 are rate

constants for trapping, detrapping, and recombination respectively. The current flow across the dielectric film is again described by equation (6.1).

If the multiple trapping level is considered, the trapping and detrapping terms in equation (6.7) and (6.8) are replaced by

$$\begin{aligned}\alpha_{1,i} n_c (N_{t,i} - n_{t,i}) &= \alpha_{1,i} n_c N_{t,i} (1 - n_{t,i}/N_{t,i}) \\ &= \alpha_{1,i} R \cdot N \cdot N_{t,i} (1 - n_{t,i}/N_{t,i}) = N (1 - n_{t,i}/N_{t,i}) \cdot (1/\tau_{1,i})\end{aligned}\quad (6.9)$$

and

$$\begin{aligned}\alpha_{2,i} n_{t,i} (N_c - n_c) &= \alpha_{2,i} n_{t,i} N_c (1 - n_c/N_c) \\ &\cong \alpha_{2,i} n_{t,i} N_c = n_{t,i}/\tau_{2,i}\end{aligned}\quad (6.10)$$

where $\tau_{1,i}$ and $\tau_{2,i}$ are the time constants for trapping and detrapping respectively; R is a constant at the range of 10^{-6} to 10^{-10} since the concentration of trapped carrier will be several order of magnitude higher than that of the free carriers for a common dielectric material.

The recombination term is then arranged as follows:

$$\alpha_3 n_c (n_c + n_t) = \alpha_3 \cdot R \cdot N \cdot (n_c + n_s + \sum n_{t,i}) = \alpha_3 \cdot N \cdot N_d \quad (6.11)$$

where N_d is the density of deep-trapped electrons and n_s is the concentration of the shallow-trapped carriers.

The variation of conductivity g versus time is the numerical solution of the equation set from (6.7) to (6.11) with suitable parameters of p , α , and μ . The first problem one encounters is the estimation of the electron-hole pair generation energy in order to get carrier generation rate p . In literature estimations are proposed and the electron-hole pair generation energy of insulators are about three times of the band gap

for crystalline insulators and about the range of 10^2 to 10^4 eV for polymer materials[26, 73, 78, 172, 173]. Considering polymers' density as 2 g/cm^3 (PMMA), the carrier generation rate will be $10^{11} \sim 10^{12} \text{ cm}^{-3} \text{ sec}^{-1}$ per rad/s and thus in the range of $10^{18} \sim 10^{19} \text{ cm}^{-3} \text{ sec}^{-1}$ for our experiments. The trap density N_t is at least the range of 10^{18} cm^{-3} , and the density of the available states in the extended state is of the order of 10^{19} cm^{-3} .

The second step is the determination of rate constants $\alpha_1 \sim \alpha_3$ and assign their relative strength in order to have the calculated $g(t)$ fit the experimental data. This is a time consuming trial-and-error process since for a assigned set the g will be calculated and compared with the experimental data. There is little guideline one can rely on for the proper direction of guessing unless significant information about the carrier transport characteristics is revealed since the choice of α_2 with high (strong detrapping or shallow traps) or low (trap filling or deep trap level) values yield very similar conductivity versus time curves[166]. The system is even more complicated if multiple trapping level is applied, there may be more than one set of parameters that result in very similar conductivity curves, and they may all in the error range in comparison with the experimental data. In conclusion of the above discussion, this model is principally qualitative in explaining the transient behavior of conductivity over time.

6.1.3 Ramo's Theory Estimation

Electron beam irradiation of insulators creates a situation similar to the capacitor illustrated in Ramo's theory even if an external voltage source is absent. When an insulator is under electron beam irradiation, most secondary electrons generated near the

surface escape and a shallow depth of positively charged volume is formed. This positive charge helps forming a field inside the resist. The field will be maximized if the penetration depth of incoming beam is about the thickness of the specimen since most primary electrons will come to rest and constitute a negatively charged region near the rear surface of the sample. Carriers generated inside the specimen by the irradiation are driven with a drift velocity as a result of the existence of the field; and the conductivity of the specimen is consequently changed. The electric field and charge distribution induced in insulators by electron beam irradiation has been thoroughly discussed and modeled [41, 103, 104, 108, 113, 119]. The relationship between the secondary electron emissions from insulators and the resultant surface potential generated as a result of electron beam irradiation is also treated elsewhere [125].

In my experiment an external bias is applied. The initial state power consumption owing to carrier flow is determined by the product of the bias and the EBIC current determined in equation (4.1). From equation (3.12), considering the energy balance, we obtain

$$P = Q \cdot (V/L) \cdot v = e \cdot n \cdot \mu (V/L)^2 \quad (6.12)$$

where Q is the net free charge, V the applied voltage, v the drift velocity, e the electronic charge, n the carrier concentration, and μ the mobility. The power consumption will vary linearly with bias square, $(V)^2$, if the product of carrier concentration and mobility is independent of field strength.

Figure 6.2 and 6.3 show initial state power consumption plotted as a function of the bias squared for three resists at high and low dose rate irradiation. Under high dose

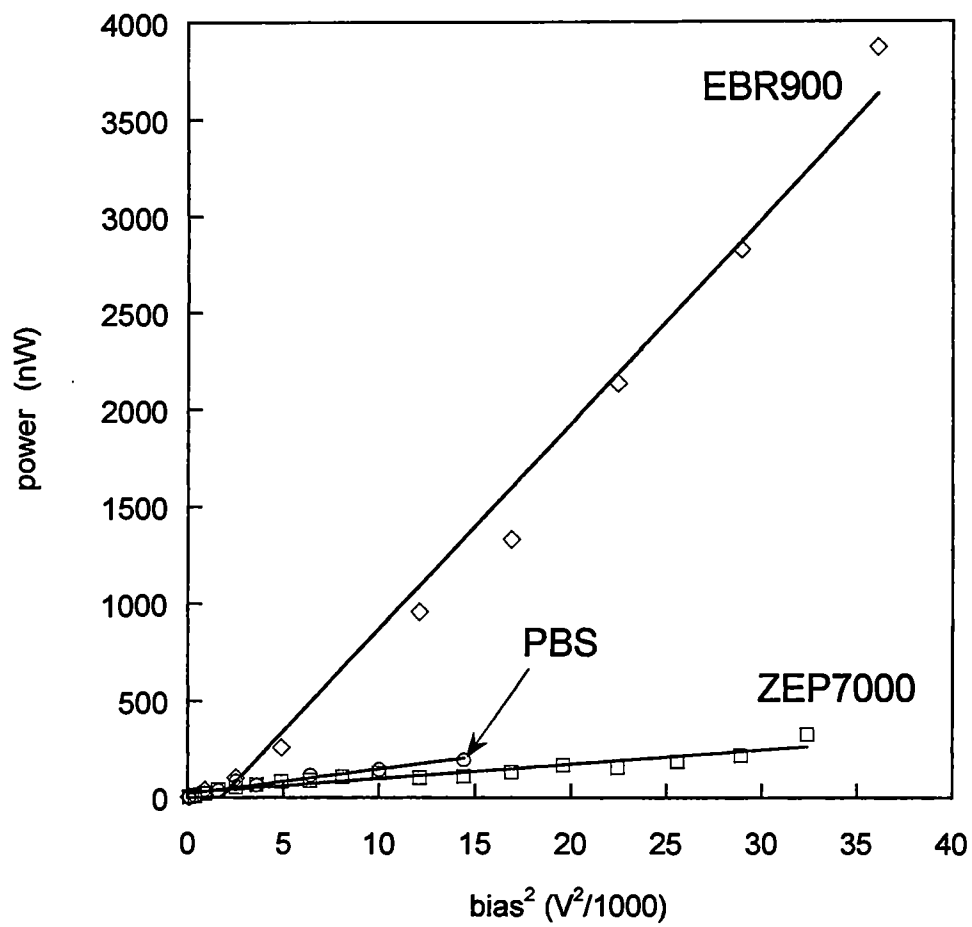


Figure 6.2. Initial state power consumption vs. $(\text{bias})^2$. High dose rate experiment.

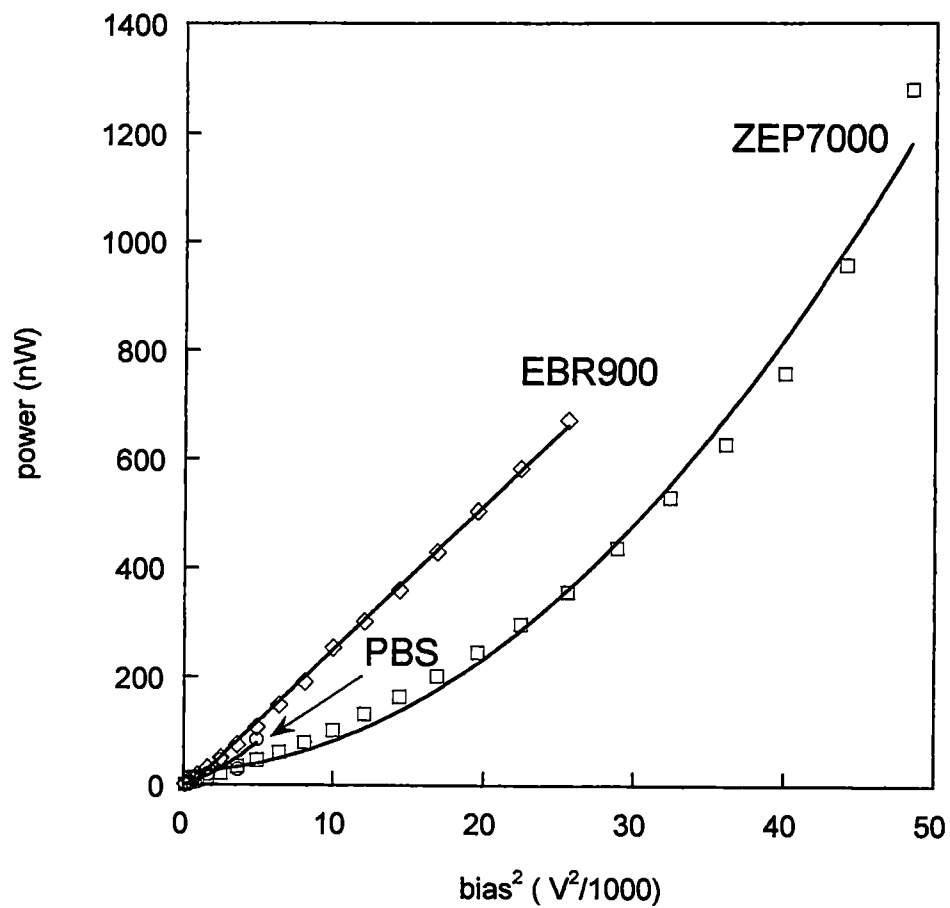


Figure 6.3. Initial state power consumption vs. $(\text{bias})^2$. Low dose rate experiment.

rate condition all resists show reasonably good linear trends with respect to the square bias variation while only the EBR900 resist remains linear behavior at low dose rates. In the low dose rate experiment the ZEP7000 resist shows a non-linear behavior, and for PBS resist the power consumption fluctuation reveals no dependence on the square bias variation. The three samples illustrate the field independent $n \cdot \mu$ argument applies only at high dose rate experiments. I therefore conclude the product of n and μ can be field dependent in certain dose rate ranges, in addition to be material dependent. In my experiments the applied field was up to 5 MV/cm at the bias of 200V, it is thus reasonable to assume that the carrier concentration is constant at a given dose rate at this moderate field. Based on this argument the mobility of the three resist samples at high dose rate experiment is constant throughout the bias range.

The slope of the profiles in Figure 6.2 provides an estimation of the $n \cdot \mu$ values for the resists, and these are listed in Table 6.1. Among the three the EBR900 resist has the highest value, which is roughly 2 orders of magnitude higher than the lowest value obtained from the ZEP7000 resist. The product of carrier concentration and mobility is an indication of the conductivity and the calculation shows that the EBR900 resist has the highest g , then followed by that from PBS resist and then from ZEP7000 resist. This is qualitatively in good agreement with the g value shown in Figure 5.2 where the same conductivity sequence is shown. Carrier mobility in different polymers is reported to be in the range of 10^{-6} cm²/V-sec [26, 73, 74] to 10^{-10} cm²/V-sec [174] from room temperature electron beam and x-ray excitation experiments. A simple estimation using these values yields two carrier concentration ranges, 10^{22} to 10^{24} cm⁻³ (PBS) and 10^{26} to

Table 6.1. ($n \cdot \mu$) values for the three resists at room temperature. High dose rate experiment.

resist	Bias range (V)	$n \cdot \mu$ (number/cm $\cdot$ V $\cdot$ sec)
EBR900	10~190	1.07×10^{18}
ZEP7000	10~180	7.47×10^{16}
PBS	10~120	1.30×10^{17}

10^{28} cm^{-3} (EBR900) respectively. Both of which are extremely high compared to semiconductors. Since the onset of plasma formation in semiconductors is reported in the range of 10^{19} cm^{-3} in charge collection scanning electron microscopy studies [162-164], if resist materials are treated as wide band gap semiconductors then these high carrier concentration will result in plasma formation within the electron beam interaction volume. The high concentration range suggests the trapping rate of the resists is also high during electron beam irradiation. Since positive resists are used in this work, we believe the trapping sites are generated from the resist chain scission reaction and other radiation damages, but further work is needed to determine the type of dominant carriers in the three resists before a precise judgement of a carrier concentration range can be made.

The EBR900 resist demonstrates the largest change in power consumption with different dose rates among the three, showing an increase by a factor of 5.7 from low to high dose rates. The ZEP7000 and PBS resists have roughly the same power consumption regardless of dose rate variation although for the EBR900 resist the product of carrier concentration and mobility is dose rate sensitive. Carrier mobility has been reported to show a field dependent [72, 175, 176] increase with applied field in transient space charge limited current experiments [136, 177]. This could be the reason why ZEP7000 and PBS show a non-linear trend at low dose rate experiments seen in Figure 6.3. The details of the dependence of the product of carrier concentration and mobility on dose rate is not clear although the mobility itself has been proposed as dose rate dependent in the previous discussion section.

6.1.4 Temperature Effect

Temperature also plays a role in EBIC behavior. Figure 5.8 shows initial state g values as a function of bias for EBR900 resists at 20°C and -30°C. It is clear that there is a conductivity decrease as the temperature drops; as g falls by a factor of 3.7 from 20°C to -30°C suggesting that it is likely that a reduction in carrier mobility is responsible. If the mobility is considered to be a function of temperature and the activation energy is assumed invariant in this temperature range, then a single trapping level approximation [71] with a value of 0.5eV as the activation energy [70] would give $\mu(20^\circ\text{C}) \approx 4\mu(-30^\circ\text{C})$. The temperature effect also contributes to the observed change in power consumption vs. bias² for the EBR900 resist (Figure 6.4). At -30°C the power consumption shows slightly curvy dependence on bias², and the power consumption at the same bias has dropped by a factor about 3.5 from the corresponding 20°C data. From the above discussion it is reasonable to say the mobility change contributes the drop of the power consumption at lower temperature, but more evidence is needed before a solid conclusion can be drawn since it is not known if the mobility is the dominant factor. From the steady state g analysis in Chapter 5.1.3 the EBR resist shows its power law dependence with an exponent of 0.7, which indicates an exponential trap distribution [61]. Since the single trap analysis gives a good agreement with the experimental observation, the trap distribution in EBR must display a very steep exponential decay.

The temperature dependence of electron-hole pair generation efficiency is not clear. The filled traps are less likely to release carriers at low temperature; this will also contribute the drop of power consumption seen in Figure 6.4. However, the

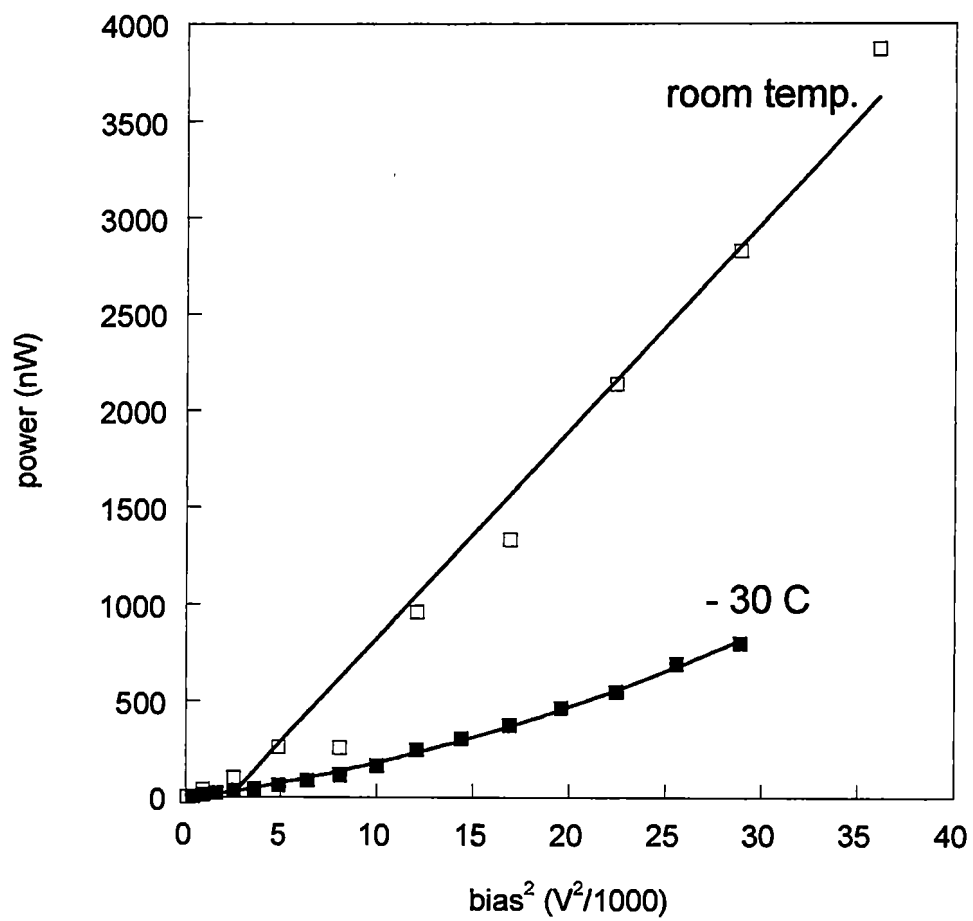


Figure 6.4. Initial state power consumption vs. $(\text{bias})^2$ for EBR 900 resist in two different temperatures.

primary single trapping level mobility estimation again coincides with the initial state g observation in Figure 5.8, which has a $3.7\times$ drop as the temperature drops from 20°C to -30°C .

6.2 Monte Carlo Simulations and the Double Layer Model

The Monte Carlo simulation was applied for the determination of positions of charging disks of opposite polarity, and the resist geometry was assigned as a bulk form in the simulation. From the dimension of interaction volume shown in Figure 5.15 it is clear that almost all the primary electrons traveled in the photoresist material in a distance more than $0.5\text{ }\mu\text{m}$. This implies that for a 400 nm resist film under 10 keV electron beam irradiation there will be negligible amount of negative charge deposited. The primary electrons will penetrate the resist layer and enter the chromium layer underneath. This in fact simplifies our double layer model since only the positive layer near the front surface needs to be considered. The chromium layer is grounded during electron beam irradiation. The primary electrons penetrating the photoresist layer deposit into the chromium layer and flow to the ground, thus lead no contribution in charging of the resist layer.

The positive charging disk resulting from the secondary electron emission is used for the spatial potential and field calculation for our following electron beam deflection simulation. As the secondary electron emission mechanism mention in Chapter 3.8 and 3.9.2, the lateral dimension of positive charged disk is larger than that of the beam diameter if a stationary beam is used to generate charging layers. The full width at half

maximum of SE_{II} signal is about 0.2 to 0.5 of the average electron range at a given beam energy[178]. For a 10 keV electron beam with the average penetration depth of $0.88\text{ }\mu\text{m}$ in photoresist (Figure 5.15), the SE_{II} signal will contribute the positive charging disk radius in the range of 0.09 to $0.22\text{ }\mu\text{m}$, or $0.155\text{ }\mu\text{m}$ if the average is taken. This implies that for a given writing pattern there is a boundary region outside its dimension that needs to be included for the lateral dimension consideration of the positive charging layer. However, in the charging induced deflection simulations the electron beam writing patterns are in the range of several micrometers. Since the amount of lateral dimensional increase by SE_{II} emission is only dependent on the incident beam energy, the use of large writing patterns results that the dimension of the positive charging disk approaches that of the electron beam writing as the assigned e-beam writing patterns are larger enough. The dimensional difference is about 31% for a $1\text{ }\mu\text{m}$ diameter circle but it significantly drops to roughly 10% for a $3\text{ }\mu\text{m}$ diameter circle and 6% for a $5\text{ }\mu\text{m}$ circle writing pattern. Consequently, the lateral dimension of the positive charging disk can further be approximated by the area to which the electron beam scans in the electron beam deflection simulations for larger writing pattern simulations.

6.3 Electron Beam Deflection Simulations

6.3.1 The Limitations of SIMION Tool

The charging patterns are simulated as electrodes with assigned potential values in SIMION. The non-irradiated surrounding area and pole piece along with the vacuum

chamber in which the resist sample is placed are assigned zero potential for the boundary conditions used in Laplace's equation calculation. The electrical potential and field calculation is confined in a 3-D space with finite dimensions in each direction and this is called a potential array in SIMION. The dimension of an array used for SIMION simulation is determined by the total grid points the array has along with the unit length of the grids; all points are equal distances from their nearest neighbor points in the array.

The choice of the array dimension is critical in SIMION computation since arrays are stored in computer memory and every grid point in an array requires 10 bytes of RAM. To make a compromise between the computation time and accuracy, a $0.1\text{ }\mu\text{m}$ grid unit length is used in 3-D potential arrays used for all SIMION calculations. In SIMION array the electron beam direction is defined to be the z direction and the charging area is in the x-y plane. The suitable dimension of an array for simulation has 501 points in z direction and 91 points in lateral dimensions; this constitutes the computational space which has $50\text{ }\mu\text{m}$ in z direction and $4.5\text{ }\mu\text{m}$ in radius for circular charging patterns, and $5\text{ }\mu\text{m}$ by $5\text{ }\mu\text{m}$ in both x and y directions for strip geometry calculations (Figure 6.5). One knows for regular e-beam tools the working distance is in the millimeter range, the $50\text{ }\mu\text{m}$ flight path the SIMION can calculate is a drawback since the electric field is limited in the vertical distance $50\text{ }\mu\text{m}$ above the charging surface. This implies that the beam deflection can be underestimated. The results from SIMION show the deflection in several nanometers over the surface charging ranging several tens to 100 volt. However, SIMION results serve as a first step indication for the relationship between the extent of beam deflection and surface potential of charging patterns.

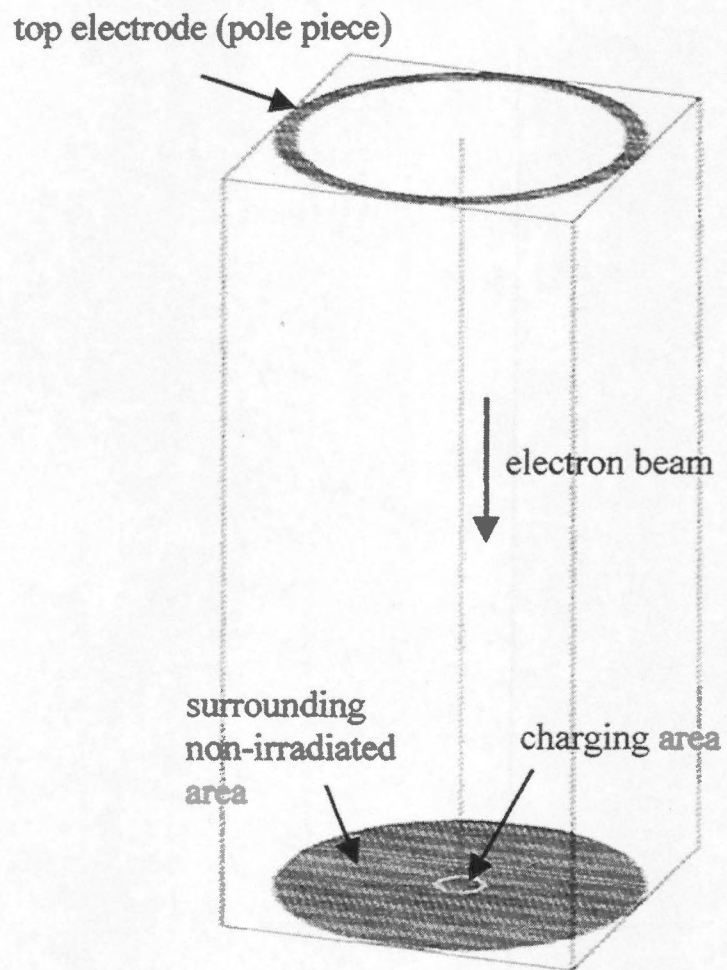


Figure 6.5. The illustration of a potential array used in SIMION simulation.

6.3.2 MATHEMATICA Simulations

The flexibility of MATHEMATICA programming provides a reasonable choice for computation dimension selection. The spatial electric potential is determined from equation (3.49) and the corresponding electric field components are determined from equation (3.50) using the built-in partial differential operational function in MATHEMATICA. In Figure 5.19 the field components in r and z directions are illustrated in the $100\text{ }\mu\text{m}$ distance above the edge of a $1\text{ }\mu\text{m}$ charging circle. The z field component decreases from $2.23 \times 10^5\text{ V/m}$ to 35.79 V/m from $5\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$ above the charging surface while the r field component decays from $3.11 \times 10^4\text{ V/m}$ to 0.27 V/m from $5\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$ respectively. Both the field components decay in 4 orders of magnitude in the first $100\text{ }\mu\text{m}$ from the surface. The z field component is always about 2 orders higher than that of the r field. From the information I conclude that the primary electrons flying along the z direction undergo a minor acceleration in z direction before they reach the final $100\text{ }\mu\text{m}$ distance from the charging surface, the contribution of r field on deflection doesn't emerge significantly until the electrons are in the final $100\text{ }\mu\text{m}$ flight path.

The 2-D field maps in Figure 5.20 show that the relative field strength changes drastically near the surface (Figure 5.20 (a) and (b)) and the patterns are indistinguishable above $100\text{ }\mu\text{m}$, this indicates as well that the field interference is not significant in the distance of $100\text{ }\mu\text{m}$ above the charging surface. Both 100 and $1000\text{ }\mu\text{m}$ flight paths were used in deflection simulation and less than 1 % discrepancy in results were found.

The 3-D potential illustration in Figure 5.21 also supports the field map

observation. The spatial potential decays from 57.748 to 0.620 V from the charging surface to 5 μm above for a 1 μm diameter charging circle. Surface potential is needed in both MATHEMATICA and SIMION simulations; however, the information of surface potential is a map in MATHEMATICA while it is a constant in SIMION, this is illustrated from the comparison between Figure 5.21 and Figure 5.16. The boundary condition from zero potential non-irradiated surrounding area in SIMION forces the equipotential lines to converge to the pattern edge and this may cause the distortion of potential lines and consequently introduce error in deflection.

The long-range effect of charging on deflection is illustrated in Figure 5.22. The beam deflection from a 1 μm charging circle shows 0.232 nm at the charging edge. The maximum deflection of 0.314 nm happens at 0.6 μm outside the circle edge; the deflection drops to 0.1 nm, about 31.8 % of the maximum deflection, at 7.5 μm away from the edge. If one considers the landing error close to the charging pattern at 0.1 μm away from the 1 μm charging circle edge, the deflection will cause 0.26 % to 0.52 % error with secondary electron yields of 0.1 and 0.2 respectively.

Dimensional effect is illustrated from Figure 5.23 to 5.27 for circles and squares with different dimensions and secondary electron yield emission yields. Figure 5.23 and 5.24 are for circles from 1 to 3 μm diameter while Figure 5.25 to 5.27 are for 1 $\times$ 1, 3 $\times$ 3, and 5 $\times$ 5 μm^2 square respectively. The secondary electron yield ranges from 0.1 to 0.2 in all the figures. The maximum deflections for circular patterns occur at 0.6 and 0.4 μm away from pattern edge for 1 and 3 μm diameter circles, and are at 0.6, 0.5, 0.5 μm away

from center point of square side for 1×1 , 3×3 , and $5 \times 5 \mu\text{m}^2$ square respectively. The deflection error at $0.1 \mu\text{m}$ away from the pattern for different pattern size is summarized in Table 6.2. The error exceeds 10 % for $5 \times 5 \mu\text{m}^2$ square with 0.2 as secondary electron yield. It is unlikely for a writing feature on a e-beam mask to have the dimension of $5 \times 5 \mu\text{m}^2$ range and cause the registration error to be around 10 %; however, the registration error caused by charging will become a more significant issue as the mask feature in e-beam lithography continues to shrink to close or below $0.1 \mu\text{m}$ in the near future.

The dimensional effect for circular and square patterns is considered and is defined as both the maximum deflection per surface potential and the maximum deflection per surface potential per unit area of charging and the results are in Table 6.3 and 6.4. From both tables it is clear that the dimensional effect results are not functions of secondary emission yield. Since the charge term contributes both the total generated positive charge (in equation (3.48)) and the extent of acceleration (in equation (3.52)) in the same order, the secondary emission yield independence discerned from both table demonstrates the validity of the MATHEMATICA programming algorithm. Larger pattern dimension contains more positive charge, the higher fields result in higher deflection contribution, therefore the maximum deflection per surface potential goes up as size of pattern increases.

The maximum deflection per surface potential per unit area from Table 6.4 can be served as an indication of “deflection efficiency” from the surface potential developed from charging. The uniform surface charge density was assumed in the programming

Table 6.2. The deflection error at 0.1 μm away from the charging patterns. It is 0.1 μm outside from a charging circle or 0.1 μm outside from the midpoint of a side from a charging square.

SE yield	1 μm circle	3 μm circle	1 $\times$ 1 μm^2	3 $\times$ 3 μm^2	5 $\times$ 5 μm^2
0.1	0.26 %	2.15 %	0.32 %	2.51 %	5.48 %
0.15	0.39 %	3.22 %	0.48 %	3.76 %	8.22 %
0.2	0.52 %	4.29 %	0.63 %	5.00 %	10.94 %

Table 6.3. The dimensional effect on electron beam deflection illustrated by maximum deflection (nm) per surface potential. MATHEMATICA results on squares.

SE yield	1 μm circle	3 μm circle	1 $\times$ 1 μm^2	3 $\times$ 3 μm^2	5 $\times$ 5 μm^2
0.1	5.44×10^{-3}	21.23×10^{-3}	5.99×10^{-3}	23.81×10^{-3}	45.36×10^{-3}
0.15	5.44×10^{-3}	21.22×10^{-3}	5.99×10^{-3}	23.80×10^{-3}	45.31×10^{-3}
0.2	5.44×10^{-3}	21.21×10^{-3}	5.99×10^{-3}	23.78×10^{-3}	45.27×10^{-3}

Table 6.4. The dimensional effect on electron beam deflection illustrated by maximum deflection (nm) per surface potential per unit area (μm^2). MATHEMATICA results on squares.

SE yield	1 μm circle	3 μm circle	1 $\times$ 1 μm^2	3 $\times$ 3 μm^2	5 $\times$ 5 μm^2
0.1	6.92×10^{-3}	3.00×10^{-3}	5.99×10^{-3}	2.65×10^{-3}	1.81×10^{-3}
0.15	6.92×10^{-3}	3.00×10^{-3}	5.99×10^{-3}	2.64×10^{-3}	1.81×10^{-3}
0.2	6.92×10^{-3}	3.00×10^{-3}	5.99×10^{-3}	2.64×10^{-3}	1.81×10^{-3}

algorithm, therefore the charge density at a given secondary emission yield would always be a constant regardless of pattern size. The field in the center of a pattern can be approached as a charging plane with constant surface charge density, consequently a large and small patterns will have the same z field strength close to the pattern center where the fringe field effect is at its minimum. It is by no doubt that a larger pattern creates a larger lateral field that results in higher deflection. The maximum deflection from a $5 \times 5 \mu\text{m}^2$ square is about 2.13 times from that of a $3 \times 3 \mu\text{m}^2$ square, which is then 6.68 times from that of a $1 \times 1 \mu\text{m}^2$ square. It is oversimplified to conclude that the deflection at a given distance away from a charging pattern edge would increase approximately linearly with respect to the pattern area by equation (3.48). The charge term q in equation (3.48) is in proportional to the pattern area under the assumption of constant charge density; however, the deflection calculation is carried out numerically and the deflection is the contribution of the relative strength of spatial z and r field components and the flight time needed for a given length of trajectory.

The position of the positive charging disk was set to be 15 nm below the resist surface for the consideration of the averaged escape depth of secondary electrons. The escape probability of secondary electrons generated at a distance z below a sample surface is dependent upon the depth z and it is assumed that the escape probability decreases with $\exp(-z/\lambda)$, where λ is the mean free path of secondary electrons. The secondary electron mean free path is in the range of 0.5 to 1.5 nm for metals and 10 to 20 nm for insulators. To simplify the calculation we took average of the mean free path

from insulators, consequently a positive charging layer 15 nm below the surface was used.

Secondary electron emission yield of 0.1 to 0.2 was chosen for the determination of charge in the positive charging disk in all the MATHEMATICA simulations.

6.3.3 Surface Potential Decay Simulations

Figure 5.28 and 5.29 show the simulation for the potential decay of EBR 900 resist with equation (5.2) in the first second after irradiation. A time increment of 1 ms was used for all charge flow calculations in equation (3.53). It is shown that the smaller pattern regardless of pattern geometry decays faster than its larger counterpart. The 1 μm diameter charging circle has surface potential of 0.366 V after first second, which is only 0.6 % of its initial value (57.75 V); the surface potential of the 1 $\times$ 1 μm^2 charging square decays from 65.64 V to 0.69 V, which is 1.1% of the initial potential. For the 3 μm diameter charging circle and the 3 $\times$ 3 μm^2 square, the remaining surface potentials after one second are 30.6% and 36.2% of their initial values respectively. It is reasonable to obtain slow potential decay from larger patterns since the constant charge density is assumed throughout the calculation. The total charge a pattern hold is in proportional with the square of its dimension, in the same time span both larger and smaller patterns flow roughly the same amount of charge owing to the EBIC effect and the amount of charge consequently poses less significance for larger patterns.

The reason that the potential decay simulation was done only one second is explained as follows. During the irradiation the conductivity is contributed by the free

carrier movement in the extended state. Right after the cease of irradiation a significant amount of conductivity may still persist owing to the thermal reemission of trapped carriers to the extended state; this detrapping of carriers is believed to be further enhanced by the electric field inside the resist layer formed during irradiation[161, 166]. The decay of conductivity after irradiation, based on Fowler's model, has time constant in the range of ~ 1 minute (equation (3.2))[61]. Since I didn't have suitable experimental setup to measure the decay conductivity, the alternative way is to assume the conductivity to be that during irradiation and then simulate the potential decay in a conservative manner. One second is therefore our choice. The simulation results for the $1\text{ }\mu\text{m}$ diameter circle and $1\times 1\text{ }\mu\text{m}^2$ square correlate well with reported experimental measurements[179]; however, larger patterns have higher surface potential values than expected. This deviation may be from the result of the constant surface charging density assumption. Larger patterns create higher field inside the resist layer, and the lateral diffusion of charge may need to be considered.

CHAPTER 7

CONCLUSION

The objective of this research is to investigate the EBIC behavior of different electron beam resists and derive a suitable charging model which incorporates the experimental data to perform feedforward electron beam deflection correction for electron beam pattern writing process. Three electron beam resists, PBS, EBR900, and ZEP7000 were used for the initial and long term EBIC studies. My experimental setup has proven to function for the direct EBIC calculation through the leakage current measurements during the electron beam irradiation; data from the three electron beam resists have been collected and analyzed. The characteristics of EBIC properties of the resist materials are consistent with semiconductor materials with wide band gaps. The initial state EBIC properties of the resists have been studied in consideration of their dependence on bias, dose rate, and temperature. The steady state EBIC results have been analyzed by the trapping level theory; the transition from initial to steady state has been explained qualitatively using the dynamic rate theory proposed in the literature.

The preliminary electron beam deflection simulation was done using SIMION6 and the results were found to agree with values reported in literature. In SIMION simulation only electrodes with different surface potential values were used to imitate charging patterns for the real case owing to the input parameter design of this simulation tool. The relationship between the amount of surface charging and the extent of electron beam deflection at different desired landing positions away from a charging pattern edge

was reported by SIMION. The deflection ranges obtained from SIMION agree with experimental observations found in literature. However, the heavy computer memory requirement during SIMION simulation limited its simulation up to 50 μm of electron trajectory and 5 μm in lateral diameter for charging area definition.

In this research the spatial distribution of electric field and potential were calculated and illustrated by programming in MATHEMATICA with classical electrostatics principles. The simulation model built in MATHEMATICA illustrated the flexibility of calculation range in electron beam trajectory up to millimeter working distance. The dimension of a charge pattern was firstly assigned with a suitable secondary electron emission coefficient, then the spatial potential and field were determined by Coulomb interaction from all the charging points on the pattern. The deflection of electron beam was finally calculated stepwise along the assigned trajectory. A 100 μm flight trajectory was used as the result of both appropriately covered the major decay of the spatial potential and field distribution and the reasonable computation time needed for a PC. Charging patterns of circles and squares of different dimensions were considered and the electron beam landing errors were found to be up to double digits in percentage landing error for large writing patterns. The surface potential decay after electron beam irradiation was also simulated by combining the initial state EBIC data and the MATHEMATICA programming; the results showed that the most significant potential decay happens in the first second after irradiation. The potential decay simulation correlated well with literature values.

This research showed the feasibility of combining a limited experimentation with simulation to model dynamic charging behavior of a particular electron beam resists. The algorithm proposed in this research also illustrated the idea of feedforward correction of writing errors during electron beam direct writing process. So far various experiments have been conducted to measure the deflection errors but none of them has developed a simulation model for predicting deflection error with confidence. The model proposed in this research therefore brings the research of charging problem in electron beam lithography into a new phase, which the prediction and correction of beam landing error can be evaluated.

CHAPTER 8

RECOMMENDATIONS FOR FUTURE RESEARCH

This research has been supported by the Semiconductor Research Corporation (SRC) since 1997 and this project is the first one that have focused on EBIC behavior and charging induced electron beam deflection simulation of electron beam resists in our group. The author wishes to suggest some relevant fields evolving from this research that post great academic values for further exploration.

- 1) The experimental estimation of the electron-hole pair generation energy: this term determines the carrier generation rate that is crucial in EBIC kinetics since the EBIC gain without trapping and recombination will be calculated by this information. The comparison of this ideal gain and the real gain measured in this research will lead to the further understanding about the trapping and recombination dynamics of a resist.
- 2) The experimental determination of carrier mobility of the electron beam resists: a sophisticated experimental setup with pulse electron beam of nanosecond range is needed. The current experimental setup for this research doesn't have the capability of generating a pulse electron beam owing to the fixed system design of the SEM used in this project. An electron beam source with shutter or quick scan raster coil design will be suitable to perform the task. The determination of carrier mobility value from experiments will serve better understand the carrier concentration of a resist; the carrier mean free path and the resultant charge transportation mechanism will also be further uncovered.

- 3) The relationship between the resist chemistry and the resultant EBIC behavior: the functional groups on polymer chain are believed to play some important but unclear roles to govern the EBIC behavior. Further research in this field can correlate the areas mentioned above to help resist development researcher in better developing and designing specific polymer resists with desirable EBIC and charging behavior.
- 4) The experimentation of measuring EBIC after electron beam irradiation of given dosage: this is very important for further improving the credibility of the electron beam deflection simulation model proposed from this research. Current model for surface potential decay simulation is constructed on the assumption of Poole-Frenkel effect is valid right after the stop of irradiation. The construction of EBIC behavior after irradiation with respect to time, temperature, bias, and dose rate by experiment can be applied with my prototype algorithm for potential decay behavior prediction beyond several time constants with confidence.

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