Scanning Electron Microscopy

Volume 1982
Number 1 *1982*

Article 29

1982

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Jacob Pacansky
IBM Research Laboratory

Adolfo Gutierrez
IBM Research Laboratory

Richard Kroeker
IBM Research Laboratory

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Pacansky, Jacob; Gutierrez, Adolfo; and Kroeker, Richard (1982) "Electron Beam Induced Chemistry of Lithographic Materials," *Scanning Electron Microscopy*: Vol. 1982 : No. 1 , Article 29.
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Electron Beam Interactions With Solids (Pp. 343-348)
SEM, Inc., AMF O'Hare (Chicago), IL 60666, U.S.A.

ELECTRON BEAM INDUCED CHEMISTRY OF LITHOGRAPHIC MATERIALS

JACOB PACANSKY,* ADOLFO GUTIERREZ AND RICHARD KROEKER
IBM Research Laboratory
K34/281
5600 Cottle Road
San Jose, California 95193

*Phone: (408) 256-6073

ABSTRACT

Experimental apparatus has been designed to study the solid state electron beam chemistry of lithographic materials. Thin organic films are simultaneously analyzed in situ with several different spectroscopic tools throughout the electron beam exposure. The equipment has enabled us to determine, in situ, the reaction paths for product formation when organic films are irradiated with high energy (25 keV) electron beams. In addition, cross sections for the electron beam chemistry are defined by monitoring the changes in optical absorption for a molecular species as a function of incident electron beam dose; these are very useful for providing a direction for synthesis of new materials. Studies using the methods described above are presented for an important lithographic system, AZ-type resists which contain diazo ketones as sensitizers.

Keywords: Electron beam chemistry, electron beam lithography, AZ-resists.

INTRODUCTION

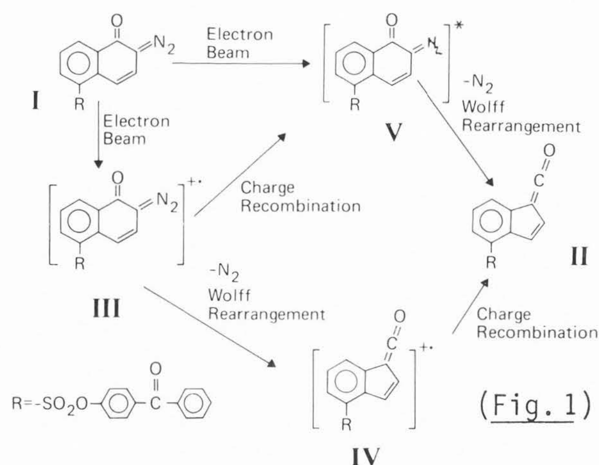
The understanding of electron beam induced chemistry of organic materials in the solid state is very important for the fabrication of microcircuits. As the quest for smaller and smaller solid state electronic circuits continues, the demand for suitable organic materials has increased stridently. One technique, electron beam lithography, designed to produce devices at the micron-sized level, utilizes organic materials called resists to create the complicated multilayered circuitry. In principle, the role of the resist is quite simple: an electron beam draws a pattern across a silicon wafer coated with the resist (≈ 1 μm thick), and in doing so creates a chemical change which either makes the resist more soluble (positive resist) or less soluble (negative resist) in a developer. Since the total pattern for the circuit is sequentially written by the electron beam, then it is paramount to have resists in which the electron beam chemistry is optimized for the developer. If this is the case, the electron beam can write a pattern more rapidly and thus permit the whole process to be economically feasible. Consequently, a knowledge of the chemistry induced in the resist by a beam of high energy (25 keV) electrons is not only important but vital for the technology.

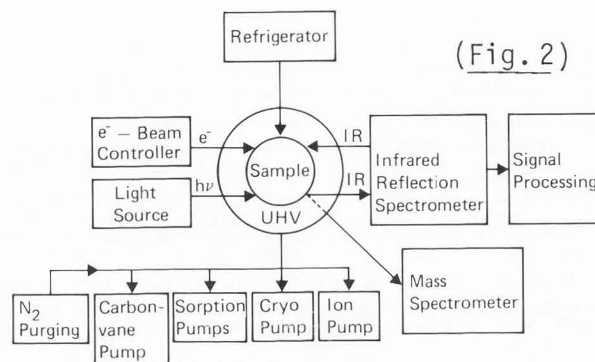
A generalization that seems to emerge on the radiation chemistry induced in organic materials is that a large number of physical and chemical processes are generated by the electron beam; concomitant with this is the belief that a large number of chemical products are produced. Indeed, this is true, when very large doses of electrons are used. However, in all of the cases studied thus far in our laboratory, by carefully following the progress of an electron beam induced chemical reaction with low doses of electrons, very selective and clean chemistry was observed. This was rather surprising, and is best illustrated by citing an example summarized in Fig. 1: the photochemistry (Pacansky and Coufal (1979)) of a thin film of the diazo-ketone *I* proceeds quantitatively via the Wolff Rearrangement to the ketene *II* (Pacansky and Lyerla (1980), Pacansky (1980)). Exposure of *I* to a 10 keV electron beam also produces *II*, presumably also by way of the Wolff Rearrangement; consequently, both UV and electron beam processes produce the same product with identical yields—at least to the sensitivity of our infrared spectroscopic techniques.

In this report, we demonstrate that reaction mechanisms

Fig. 1. A summary of the possible mechanisms for the solid state electron beam induced chemistry of the diazoketone (I).

Fig. 2. A block diagram of the experimental apparatus used to study solid state electron beam chemistry.





for formation of products, via electron beam exposure in the solid state, may be revealed and also quantified. This is developed by showing results for an important lithographic system; a diazo-ketone sensitizer mixed in a phenolic resin.

EXPERIMENTAL

A block diagram for the experimental apparatus is shown in Fig. 2. A thin film ($\sim 1\ \mu$m) of the sample is enclosed in an ultra-high vacuum system (UHV) constructed of stainless steel and fitted with con flat flanges with copper gaskets. The system is capable of operation down to pressures of 10^{-10} mm Hg. The system is pumped down from atmospheric pressure using sequentially a carbon vane pump, sorption pumps, and a cryopump with several ion pumps. This sequence permitted the system to be free of contamination from pump oil and routinely allowed the system to be operated at pressures in the 10^{-9} mm Hg range.

The sample may be exposed to either a beam of electrons with energy from 0-30 keV or UV light from deep UV to the infrared (IR). The electron beam or UV induced reaction mechanism may be examined in more detail by lowering the temperature of the sample to ~ 10°K with a closed-cycle refrigerator. The progress of a reaction is followed using a reflection type infrared spectrometer, the details of which were previously reported by Pacansky et al. (1977). In effect, a transmission type IR spectrum is obtained of the thin film by reflecting infrared light from a gold plated quartz disc onto which the sample was coated. Additional information about the reaction mechanism was obtained using a quadrupole mass spectrometer; this analytical tool was used to determine whether volatile fragments were being released from the thin film by the radiation.

In Fig. 3, a schematic diagram of the apparatus is shown illustrating the system in more detail. The reflectance infrared spectrometer is designed to operate with a double beam to cancel out atmospheric absorptions. Two choppers, f_h, a high frequency chopper, and f_ℓ, a low frequency chopper, are used to modulate the infrared beam; f_ℓ, in addition, alternatively directs the IR beam to the reflectance sample, RS, or to the reflectance reference, RR, and so is directly responsible for the double beam design. The IR radiation is dispersed by a ¾ meter monchromator. The electron beam gun, E, is constructed of stainless steel. The electron beam is focussed and deflected by a magnetic lens coil, and a magnetic deflection coil, respectively. Two ion pumps are used to maintain a suitable vacuum in the electron beam gun column. A Faraday cup F_c is used to measure the incident current of the electron beam; this is essential for quantitative studies.

LIST OF SYMBOLS

D_s	=	Smallest incident dose required to develop an image with no thickness loss in the unexposed areas of a resist.
I	=	Current in the incident electron beam.
I′	=	Current in the backscattered electron beam.
I_T	=	Sum of I and I′.
f(D)	=	A function that describes the action of a developer on a resist.
f(R)	=	A function that describes the extent of the chemistry induced in a resist by radiation.
N	=	The number of molecules or functional groups after a dose D of electrons.
N_0	=	The number of molecules at D=0.
N_t	=	The normalized thickness of a resist.
M_w	=	Molecular weight.
P(GMA/EA)	=	Poly(glycidylmethacrylate/ethylacrylate).
PMMA	=	Poly(methylmethacrylate).
Q	=	Probability of a chemical event after excitation by an electron.
S	=	Sensitivity of a resist.
t	=	Time.
T	=	Film thickness.
σ	=	Chemical cross section at the energy of the incident electron beam.
σ_i	=	Cross section for inelastic scattering of an electron.

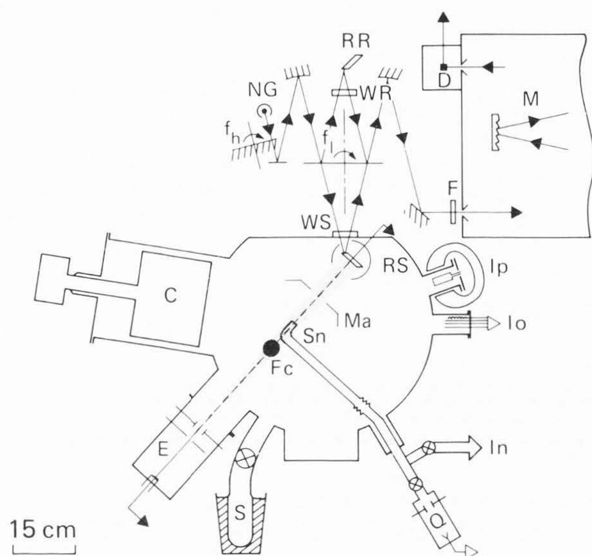


Fig. 3. A schematic diagram of the apparatus for studying electron beam induced chemistry of organic thin films. System description: NG = Nernst glower; f_h = high frequency chopper; f_ℓ = low frequency butterfly mirror; WR = window reference; WS = window sample; RR = reflectance reference; RS = reflectance sample; F = order sorting filter; M = monochromator; C = cryopump; D = detector; E = electron beam gun; S = sorption pump; Q = quadrupole mass spectromer; In = inlet for gas mixture; Io = ionization gauge; Ip = ion pump; Sn = spray nozzle (for gas deposition); Fc = Faraday cup; Ma = mask.

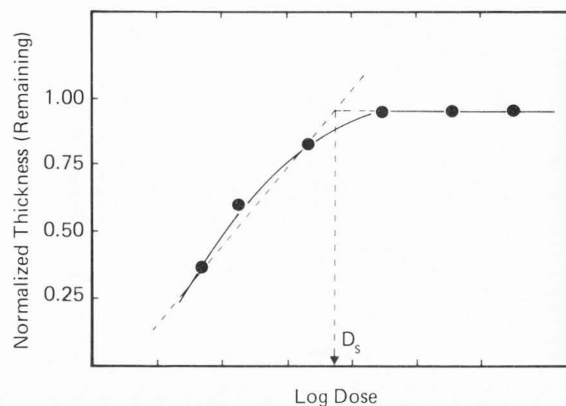


Fig. 4. A plot of N_t, the normalized thickness remaining in the unexposed areas of a resist after development, versus the log of the incident electron beam dose. The sensitivity of a resist is usually defined by the slope of the curve or by the minimum dose D_s at which no thinning of the resist is found.

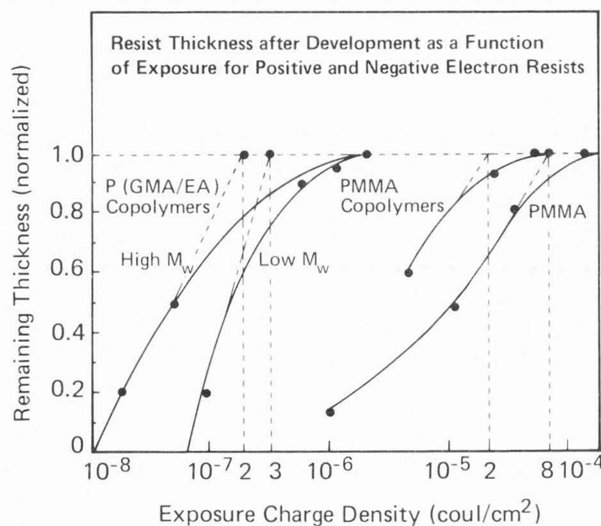


Fig. 5. Plots for normalized thickness loss versus log dose for several representative resists.

RESULTS AND DISCUSSION

Lithographic Sensitivity of Electron Beam Resists

To decipher the role of electron chemistry in the lithographic process, a little reflection on methods used to quantitatively describe the sensitivity of a resist is in order. In Fig. 4, a plot is shown for N_t, the normalized thickness remaining in the unexposed region of a resist, versus the log of the dose in the incident electron beam. The sensitivity of the resist is usually described in two ways using plots of this type as, for example, shown by Shaw and Hatzakis (1978). One way is to obtain the slope of the line as indicated in Fig. 4; the other way is the extrapolated dose, D_s. This latter quantity is probably used more frequently because it describes the smallest incident dose that can be used to develop an image with no thickness loss in the unexposed regions of the resist. Some representative values of D_s for commonly used positive and negative electron beam resists are shown in Fig. 5. Negative electron beam resists generally have a higher inherent sensitivity (lower D_s than positive electron beam resists).

The lithographic development process involves two steps, the electron beam exposure followed by a treatment with a developer. Hence, the lithographic sensitivity may be formulated as the convolution of two terms as shown below:

$$S = f(R) \cdot f(D) \qquad 1$$

where S is the lithographic sensitivity using either the slope or D_s definition shown in Fig. 4, f(R) is a function that describes the extent of the pertinent radiation chemistry and f(D) is a function that quantifies the action of the developer on the resist, that is, the dissolution process. A knowledge for the functional form of either f(R) or f(D) should give insight into the extent to which each contributes to the ultimate sensitivity. We choose to study f(R) because it is much easier to understand from a fundamental point of view, and, most of all because a quantitative comparison between D_s values and the efficiency of the electron beam chemistry has not been attempted.

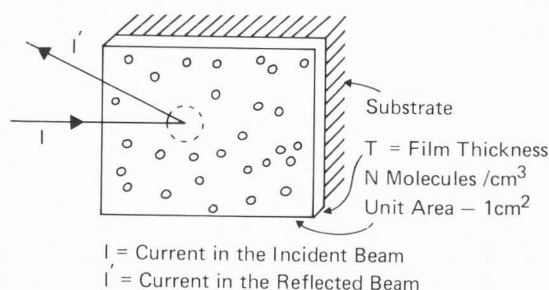


Fig. 6. An illustration for a thin film on a substrate undergoing electron beam irradiation.

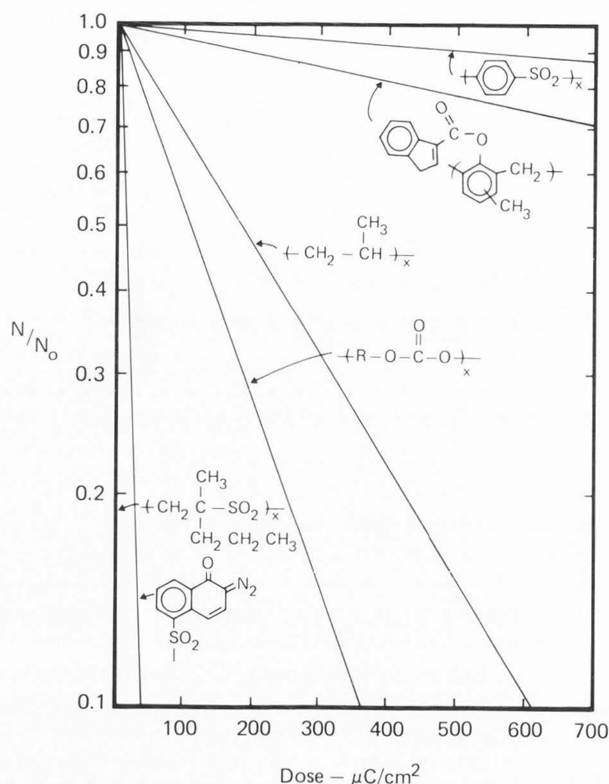


Fig. 7. A semilog plot for N/N_0 versus dose ($\mu C/cm^2$) for several systems chosen to display the rather large variation in solid state electron beam chemistry of organic materials. All of the resists were obtained using the apparatus described in Fig. 3.

Cross Sections for Solid State Electron Beam Chemistry

In the previous section, it was stated that the lithographic sensitivity consists of a radiation chemistry (exposure) and subsequent developer step. The extent of the pertinent chemistry involved in the radiation chemistry may be quantified by introducing a cross section for the chemistry. For example, Fig. 6 shows a schematic of the exposure process in an electron beam lithographic tool, or electron microscope, etc. A thin film on a substrate (gold in our case) is exposed with a beam of 25 keV electrons whose current is measured accurately. The number of molecules N that are chemically transformed in a given time t is given by the following:

$$-\frac{dN}{dt} = Q\sigma_i I_T N \qquad 2$$

where I_T is the current in the incident plus reflected beam σ_i is the cross section for total inelastic scattering of an electron and Q is the probability for a chemical event when an electron is inelastically scattered. In essence, the photochemical analogy of Q is the quantum yield. After rearranging Equation 2, the following expression is obtained:

$$\int_{N_0}^{N} \frac{dN}{N} = -Q\sigma_i I_T \int_0^t dt \qquad 3$$

where at $t = 0$, N_0 is the initial number of molecules. After integration, the simple exponential expression which results is:

$$\frac{N}{N_0} = e^{-(Q\sigma_i)(I_T t)} \qquad 4$$

Let $I_T t$ = Dose D in units of μC (μ Coulombs)/cm^2 and $\sigma = Q\sigma_i$, the cross section for the chemical events that lead to a decrease in a molecular species or organic functional group described by N. Thus, the cross section σ may be obtained using the relation

$$N/N_0 = e^{-\sigma D} \qquad 5$$

and by measuring the changes in optical density for a particular optical absorption (to define N/N_0) as a function of incident electron beam dose. The slope of a semilog plot of N/N_0 versus D yields σ. When the dose D is in units of $\mu C/cm^2$ the units of σ are $cm^2/\mu C$.

The benefit of obtaining cross sections defined in this manner is that the sensitivities of materials to electron beam may easily be compared, thus establishing a sound course for the synthesis of new materials for lithography. In addition, plots of N/N_0 versus dose D are very useful to an electron microscopist who wants to minimize electron beam chemistry, or for electron beam polymerization or curing of materials where very selective, rapid chemistry is required.

It is pertinent at this point to introduce Fig. 7 which is a semilog plot of N/N_0 versus dose D for a wide range of materials whose cross sections have been determined in our laboratory. This will be discussed in another section, however, it is important now to stress the very broad range of cross sections for the materials graphically illustrated. Note that even within a particular class of materials, e.g., the polysulfones, the value N/N_0 for a particular dose D can vary significantly.

Solid State Electron Beam Chemistry of Positive Electron Beam Resists

The positive electron beam resists discussed here are formulated from two ingredients – an acidic polymer (phenolic resin *VII*, see Fig. 8) that dissolves in an inorganic aqueous base, and a radiation sensitive inhibitor. The exposure either converts the inhibitor to a material that is soluble in a basic developer or simply destroys the inhibitor. In either case, the action of radiation on the exposed areas renders the resist more soluble to the basic developer than the unexposed areas; hence, an image may be formed.

Diazo-Ketone Sensitizers

An example of a sensitizer that is known to photochemically convert to a base soluble organic acid is the diazoketone *VI* shown in Fig. 8; the formulation consisting of *VI* and the phenolic resin *VII* is known as the AZ-1350J resist in the electronics industry and has a sensitivity $D_s \approx 30\ \mu C/cm^2$ (Shaw and Hatzakis (1978)). Broyde (1970) reported a rather interesting result for the AZ-1350J resist. He observed that the sensitivity of the resist increased by about a factor of two when heterocyclic bases like imidazole were added to the resist.

The AZ-1350J resist is an excellent material in which to study the relative importance of the electron beam chemistry and developer on the sensitivity of the resist. A knowledge of the cross section for the electron beam induced chemistry reveals some interesting lithographic features. The cross section for disappearance of the diazo-ketone *VI* in the resist (25% of *VI* by weight in the resin) was determined by monitoring the decrease in absorption of the $C = N = N$ stretching frequency as a function dose. The result shown in Fig. 9 indicates that a semilog plot of N/N_0 versus dose gives a straight line with $\sigma = 0.051\ cm^2/\mu C$. The immediate conclusion grasped from the plot in Fig. 9 is that when $D_s = 30\ \mu C/cm^2$, N/N_0 0.2, i.e., about 80% of the diazo groups have been destroyed. The electron beam chemistry, therefore, accounts for almost all, or possibly, all of the sensitivity of the resist. A rationale for the rather low electron beam sensitivity of the diazo-type resists may be that very little, if any, amplification of the electron beam chemistry by the developer can be found. Also shown in Fig. 9 is the cross section obtained when imidazole is incorporated as an additive (25% diazoketone *VI* and 1% imidazole in phenolic resin by weight; this insures that each diazo group may complex with at least one molecule of imidazole). In this case, the cross section increases from 0.051 to 0.077 $cm^2/\mu C$, and hence provides a convenient explanation and verification of Broyde's (1970) observations for the increase in sensitivity of the resist. As

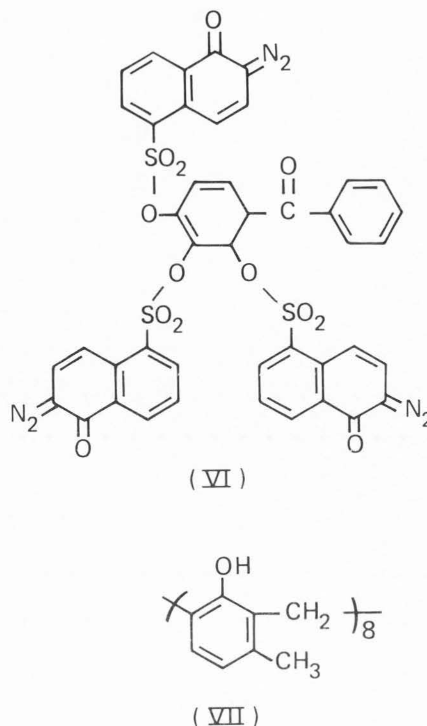


Fig. 8. **A typical formulation for the AZ-type photoresists. The formulations usually vary, for the most part, in the structure of the diazo-ketone (VI) which is incorporated in the phenolic resin (VII).**

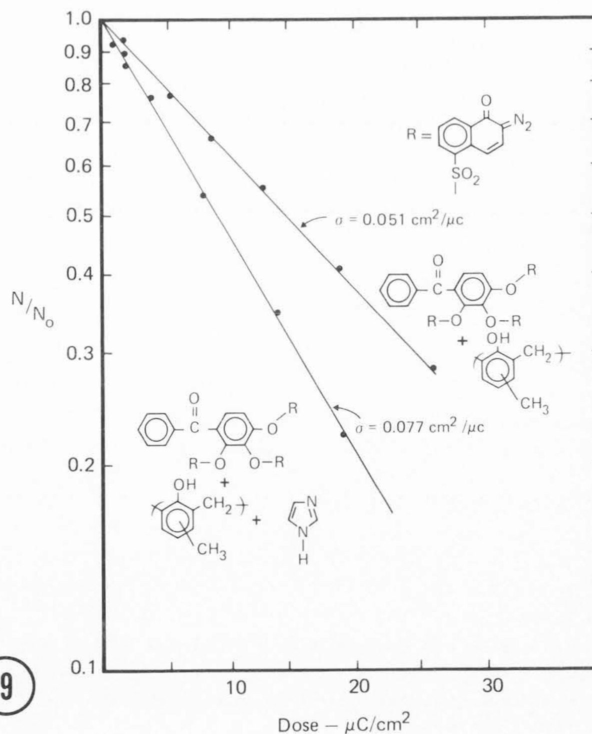


Fig. 9. **The plot for N/N_0 versus dose (upper line) for the diazo-ketone (VI) mixed in the phenolic resin (VII). The mixture was 25% (VI) in (VII) by weight to simulate AZ-type resist formulations. The plot for N/N_0 versus dose (lower line) for the mixture of (VI) in (VII) used to obtain the upper line with the addition of 1% imidazole by weight. The results clearly show that the fraction of diazo groups N/N_0 that survives a dose D is significantly reduced by the incorporation of imidazole in the resist.**

stated above, when $D_s \approx 30\mu C/cm^2$, N/N_0 is 0.2. The dose needed to get the same value for N/N_0 when imidazole is added to the resist is $\sim 19\ \mu C/cm^2$. If $D_s = 19\ \mu C/cm^2$ for the resist with imidazole, then again the electron beam chemistry alone may explain the factor of ~2 increase in sensitivity of the resist.

A Comparison of Cross Sections for Organic Materials

A plot for N/N_0 versus dose D for a variety of polymeric systems containing organic functional groups is shown in Fig. 7. The ratio N/N_0 was obtained by following the decrease in absorption of the sulfone $-SO_2-$, diazo C=N=N, carbonate -O-C(=O)-O, CH bonds, and ester -C(=O)-O functional groups, respectively. Not all of the systems produced linear plots whose cross sections could be defined. However, all of the results shown in Fig. 7 are presented in linear form to illustrate the rather broad radiation sensitivity displayed by the organic systems. For example, the semilog plot for poly (2-methyl-1-pentene) sulfone cannot be distinguished from the vertical axis. This very high sensitivity is in striking contrast to the very small cross section for poly(phenylene sulfone).

The large decrease in cross section exhibited by poly (phenylene)sulfone is most likely a result of excitation energy going into radiative channels for decay rather than nonradiative channels because when this material is irradiated with high energy electrons (25 keV) a large amount of fluorescent is observed.

Cross sections may be obtained from linear plots for diazo ketones, esters and polymeric hydrocarbons like polypropylene; these values are nominally above 0.02, 0.0006 and 0.006 $cm^2/\mu C$ respectively. Thus far, the cross sections for the particular systems studied have not varied much from these values, but since only a few have been examined it is anticipated that a broader range may be found within each class.

Some of the cross section plots for polycarbonates exhibit a slight convex curvature. Presently, our explanation for this is based on the following mechanism

$$A \underset{\Delta}{\overset{e^-}{\rightarrow}} B \overset{e^-}{\rightarrow} C \qquad 10$$

where the polycarbonate A forms a thermally unstable intermediate B that rapidly reforms the carbonate for a low dose, but forms C when the electron dose is relatively large. Of course, at low temperatures B should be quite stable and thus, the N/N_0 versus dose plots should be linear. These experiments are in progress.

The experimental data displayed in the form shown in Fig. 7 are very useful in a number of areas. First of all, they are a guide for synthetic chemists whose task is to tailor materials for applications in electron beam technology. One such application, lithography, was discussed in this report. Other applications are electron curing, polymerization processes, radiation biology, and radiation damage in an SEM. The N/N_0 versus dose plots are useful in those areas because when the incident electron beam current is known, the fraction of material surviving (N/N_0) for a particular dose is quantitatively obtained.

CONCLUSION

Experimental equipment has been constructed to study solid state electron beam chemistry. In general, the results obtained thus far indicate that the product distribution for solid state electron beam induced chemistry is similar to photochemical product distributions. However, one should acknowledge that the electron beam is like a white light source and hence those photochemical reactions requiring wavelengths not accessible from conventional light sources will be observed. These, of course, will depend on the cross sections for the particular reaction and so will be dose-dependent.

A useful way to display cross sections is in the form of the N/N_0 versus electron dose plots. These are valuable aids for synthetic chemists who need to know the sensitivities of various organic functional groups to high energy radiation, and also are of intense interest in the areas of lithography, radiation curing and polymerization of materials.

ACKNOWLEDGMENT

We gratefully appreciate the many conversations and materials support that Mr. Edward Gipstein gave us on the polysulfone project.

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