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# Mechanism of the Action of an Electron Beam on Organic Photoresists

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The litereature dealing with the decomposition of positive and negative photoresists by actinic light and by electron bombardment is reviewed, and the action of a stream of electrons on other organic materials, metals, and inorganic dielectrics is discussed. A mechanism producing internal irradiation of the resist is considered: the incident electrons excite the resist molecules into fluorescence and phosphorescence.
The influence of the (metallic or dielectric) substrate on the achievement of the required line widths is discussed. It is shown that the cross-linking of a negative photoresist under the influence of an electron beam occurs by free-radical polymerisation.
65 references.

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## I. INTRODUCTION

The basic components of integrated microcircuits (semiconductor diodes and transistors, capacitors, interconnections, and resistors) have simple geometric shapes of micron or sub-micron dimensions. The main requirement in the production of integrated circuits is the ability to reproduce a given pattern a large number of times and to register it very accurately on a pre-existing pattern. Even the production of discrete transistors requires the superposition of 4 or 5 patterns[1]. Photolithography is the only procedure by which this requirement can be met with acceptable yields.

The photolithographic process consists in coating the article with a layer of acid-resistant polymer, which protects the metal, dielectric, or semiconductor from the action of an etchant. The need for ever-greater miniaturisation of the components of microcircuits poses a number of difficult scientific and technological problems concerning the synthesis of improved photoresists and the development of new methods of exposure.

The resolving power of processes relying on exposure to light is, of course, limited by the wave length of the light. The smallest line widths so far reported[2] are of the order of 1 $\mu$m (0.65 $\mu$m windows and 0.35 $\mu$m stripes between windows). These dimensions coincide almost exactly with the theoretical limit of line width attainable by exposure to light of wave length 0.3–0.4 $\mu$m.

The use of an electron beam to produce lines and patterns of small dimensions is not subject to the same limitations. An electron beam can be focussed to a spot a few Ångstroms in diameter, and the effective wave length of the electrons can be decreased to one Ångstrom or less by using a sufficiently high accelerating voltage (see Table 1). This effect is of the utmost importance in minimising diffraction phenomena and increasing the resolving power.

The results achieved in practice by exposing photoresists with an electron beam fall very far short of theoretical predictions. Some data on the line widths obtained by irradiating photoresists with electrons are summarised in Table 2. Even the narrowest lines are wider than the electron beam by a large factor, whereas the most commonly reported results are orders of magnitude worse than the theoretical expectations.

Table 1. Relationship between electron wave $\lambda$ and accelerating voltage $U$.[3]

| $U$, V | 1 | 10 | 100 | 1000 | 10 000 | 30 000 | 40 000 | 50 000 |
|---|---|---|---|---|---|---|---|---|
| $\lambda$, A | 12.26 | 3.88 | 1.23 | 0.388 | 0.123 | 0.0698 | 0.0601 | 0.0530 |

Table 2. Electron beam irradiation of photoresists.

| Photoresist type | Accelerating voltage, kV | Charge, C cm$^{-2}$ | Beam diameter, A | Line width, A | Edge roughness, A | Substrate material | Layer thickness, A | Ref. |
|---|---|---|---|---|---|---|---|---|
| KPR, KMER, KOR, KTFR | 14, 20 | — | 10000 | — | — | Al | 1500—2500 | 4 |
| AZ-1350 | 7.5; 16; 30 | — | 2500 | 10000 | — | $SiO_2$ | 3600 | 5 |
| KTFR | 7.5; 16; 30 | — | 2500 | 10000 | — | $SiO_2$ | — | 5 |
| KTFR, KPR | 30 | | 3000 | 10000 | 500 | Al | 3000 | 6 |
| AZ-1350 | 30 | $7\cdot10^{-5}$ | 1000 | 10000 | — | $SiO_2$ | 3600 | 7 |
| KTFR | 30 | — | 1000 | 10000 | — | $SiO_2$ | — | 7 |
| AZ-1350 | 20—30 | $10^{-4}$ | — | 20000 | 500 | — | — | 8 |
| KTFR | 20—30— | $7\cdot10^{-6}$ | — | 20000 | 500 | — | 4500 | 8 |
| KTFR | 6 | $10^{-5}$ | — | — | — | $SiO_2$ | 3800 | 9 |
| — | — | — | 1000 | 10000 | — | Si | — | 10 |
| AZ-1350 | — | $10^{-5}$ | 5000 | 10000 | — | Si, $SiO_2$ | — | 11 |
| KPR | — | $10^{-6}$ | 5000 | 10000 | — | Si, $SiO_2$ | — | 11 |
| KPR | 25 | $5\cdot10^{-5}$ | 100 | 2500 | 700 | Au–Pt alloy | — | 12 |
| Siloxane SH-200 | — | — | 1000 | 4000 | — | Si | 3000 | 13 |
| KTFR | — | $5\cdot10^{-6}$ | — | 10000 | — | Cr | 2000 | 14 |
| KTFR | — | — | 5000 | 15000 | — | Ag | 10000 | 15 |

Note. KPR (Kodak Photo Resist, Eastman Kodak, USA) is the vinyl ester of cinnamic acid; KOR (Kodak Ortho Resist, Eastman Kodak, USA) is a type of KPR improved by the addition of a sensitiser; KMER (Kodak Metal Etch Resist, Eastman Kodak, USA) is a polymer of modified natural rubber, improved by a diazide sensitiser; KTFR (Kodak Thin Film Resist, Eastman Kodak, USA) is similar to KMER but needs to be decanted before use; AZ-1350 (Shipley, Azoplate, USA); SH-200 (Japan) is a polysiloxane containing methyl radicals.

This divergence between theory and practice is explained by various factors, including the lack of resists specially designed for electron beam exposure, complex interactions between the stream of electrons and the layer of resist (or the substrate), the lack of monochromaticity of the beam, etc. A working theory of the interaction between an electron beam and the resist is needed before any attempt can be made to formulate resists of the required composition and structure.

The most important parameters from the point of view of device fabrication are the line width and the unevenness of the edge. Hence, this review will deal specifically with the factors which influence the technologically accessible line widths.

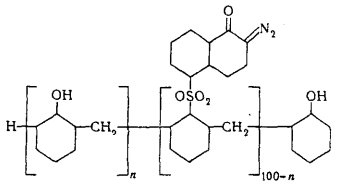
The interactions between high-energy electrons and polymers of various compositions have been discussed in detail by several workers (see, for example, Ref. 16, and the references quoted in the following Sections), particularly in the case of thin films [17,18].

Because of the complexity and multiplicity of the phenomena which accompany the passage of electrons through the photoresist and the substrate, a full discussion of the problem is not an easy matter. To facilitate the analysis, we shall deal first with the reactions accompanying the exposure of photoresists with light, the reactions induced by electron bambardment, and the interactions between a stream of electrons and the photoresist and substrate.

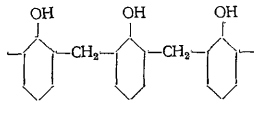
## 2. EXPOSURE OF RESIST BY A LIGHT BEAM

Positive resists are the most commonly used in the planar technology for the production of semiconductor devices [2]. Typical of this group of organic polymers are the compounds AZ-1350 (USA) and naphthoquinonediazide NKhDA (USSR). The two compounds have very similar compositions, differing only in some of the functional groups responsible for some specific properties.

The positive resist 1,2-naphthoquinonediazide(2)-5-sulphoester of novolak has the following structural formula [19]:

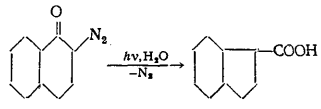


The photoresist also contains novolak resin as the film-forming component. Novolak consists of a complex mixture of products of different molecular weight, based on the polymer chain



When the resist is heated the photosensitive component decomposes with evolution of nitrogen. At first the thermoplastic film is converted into an insoluble compound which is very stable and adherent to the substrate. This reaction begins at 140–160°, i.e. below the temperature at which the novolak forms insoluble compounds. The reaction is assisted by the products of the decomposition of NKhDA. The most likely mechanism of this conversion is acylation of the hydroxy groups of the novolak by the ketens formed by thermal decomposition of the naphthoquinonediazido groups of the photoresist. Heating at temperatures above 250° is accompanied by heat evolution, characteristic of the condensation of the novolak units into a polymer of high molecular weight [20].

The application of NKhDA as a photoresist follows from the following change in the material under the influence of actinic light. Illumination with light of wave length shorter than 460–480 nm decomposes the NKhDA with evolution of nitrogen. The resulting indeneketen absorbs water present in the film, giving rise to indenecarboxylic acid which has hydrophilic properties and can dissolve in the aqueous developer. Addition of alkali to the developer helps to dissolve the exposed film. It should be noted that the novolak resin added to the resist is transparent to light of this wave length.



The quality and the sharpness of the image produced depend on a number of factors, including the completeness of the photochemical reaction and the avoidance of spurious polymerisation phenomena during the heating stage of the process.

One possible side reaction is acylation of the novolak by the ketens; other reactions include interaction of the ketens with the carbonium ions responsible for the photochemical reaction and decarboxylation of the decomposition products at high enough temperatures. The products of the side reactions are insoluble in organic solvents and in the alkaline developer. Tsirlin and coworkers [21] studied the effect of side reactions on the sharpness of the image obtained, and demonstrated the influence of resist composition and of the ratio of novolak to naphthoquinonediazide on the onset of negative resist behaviour.

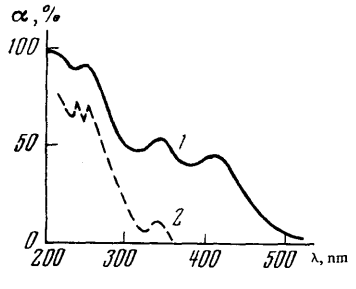



**Figure 1.** U.v. absorption spectra of (*1*) positive photoresist and (*2*) K-18 novolak resin [2].

Fig. 1 shows the absorption spectra of a layer of 1,2-naphthoquinonediazide(2)-5-sulphonate of novolak, and of the novolak resin K-18. The novolak resin absorbs at wave lengths below 370 nm.

The first and the second absorption band of phenol occur [22] at ~ 2780 Å and ~ 2380 Å respectively. The photolysis of phenol involves the series of reactions

$$ROH + h\nu \rightarrow ROH^* \overset{H_2O}{\rightleftarrows} RO^* + H_3O^* \rightarrow RO^- + h\nu' \overset{H_2O}{\rightleftarrows} ROH + OH^-.$$

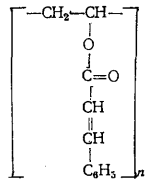
RO denotes a phenyl or a substituted aromatic system.

The most commonly used light source is a mercury lamp. The emission spectrum of the mercury lamp has a discrete line structure. The light of wave length 2537, 3650, 4050, and 4358 Å is active towards the photosensitive layers. The intensity distribution of these spectral lines in mercury lamps is 2:10:4:8. High-pressure lamps also emit a background radiation whose intensity amounts to 0.1–0.25 of the intensity of the main lines.

Negative photoresists, mostly based on poly(vinyl cinnamate), are known as PVTs in the USSR and KPR, KOR, etc. in the USA. These resists also are widely used in photolithographic processes for the production of electronic devices.

A very important feature of negative photoresists is their high stability—they are superior to positive resists in this respect.

PVTs is obtained by the etherification of poly(vinyl alcohol) and cinnamic acid, and has the following structural formula [2,23–25]:

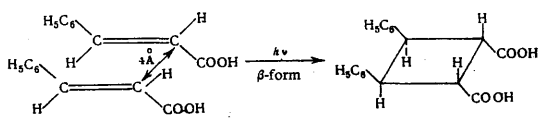


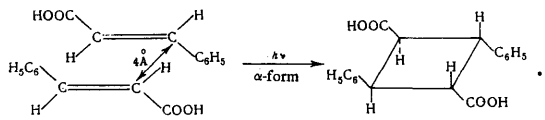
Irradiation of the resist with actinic light produces cross-linking of the molecules. Unsensitised PVTs has an absorption maximum at 270–320 nm and a long-wave absorption edge at 330 nm [26,27]. After irradiation, photoresist layers absorb more weakly in this region because of the decrease in the number of double bonds. Exposed resist contains up to 15% of three-dimensionally cross-linked groups [28]. The quantum yield of the cross-linking reaction can be as high as 50%.

The addition of a sensitiser shifts the absorption maximum to the region of 360–370 nm, and the absorption edge to 400–420 nm. Studies of absorption in the infrared region have shown [27] that the function of the sensitiser is to transmit to the double bonds of PVTs the energy of quanta of long-wave radiation. The quantum efficiency of the sensitiser (Michler's ketone) [29] does not exceed 0.76. This rather low efficiency is due to steric effects, which prevent intimate contact between the sensitiser and the PVTs molecules. The sensitiser is added in amounts of about 10% by weight. The loss of sensitiser is almost insignificant (0.04%): this is because the photon energy is insufficient to cause decomposition of the sensitiser.

According to Lyalikov and coworkers [27], the absorbed radiant energy is transmitted to the double bonds, which are converted into single bonds. The resulting biradicals interact to form cross-linkages, and the solubility of the photoresist in organic solvents decreases.

Robertson and coworkers [26] suggest that the cinnamoyl groups of PVTs form a four-membered ring. *Trans*-cinnamic acid is also believed [30] to form four-membered rings. It is known, from crystallographic studies, that effective photodimerisation is impossible unless the reacting centres are less than 4 Å apart. The dimer can be formed in two configurations, depending on the relative orientation of the constituent molecules:



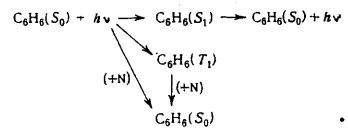




The probability of polymerisation increases when the molecules are excited to the triplet state. The sensitiser plays a special role in transmitting triplet–triplet energy to the PVTs molecules. Energy transfer is possible only when the triplet-state energy of the donor is greater than the triplet-state energy of the acceptor [31–33]. The height of the triplet level of the sensitiser affects the yield of the polymerisation products: for example, the efficiency of the dimerisation falls off steeply [30] when $E_T < 53$ kcal mole$^{-1}$. The triplet levels of some of the commonest sensitisers are listed below:

| | |
|---|---|
| acetophenone | 74 kcal mole$^{-1}$ |
| benzophenone | 69 kcal mole$^{-1}$ |
| Michler's ketone | 61 kcal mole$^{-1}$ |

Mention must also be made of the contribution of the benzene groups of the photoresist and of the sensitiser to the transfer of radiant energy.

High fluorescence yields are common [22] for aromatic hydrocarbons in solution at low concentration. Photodecomposition of aromatic molecules has a very low quantum efficiency in the first absorption band (0.01 to 0.0001 or less). In benzene, the primary processes induced by irradiation within the second or third absorption band (1849 Å) are very different from those induced by the first band (2537 Å). When benzene is excited to the $S_2$ and $S_3$ state, internal conversion to the $S_1$ state has a very low probability, but chemical reactions can occur very readily, including aromatic ring opening with formation of isomers and hydrogen:




The excitation of benzene groups is accompanied by the subsequent emission of light of greater wave length.

## 3. EXPOSURE OF RESIST BY AN ELECTRON BEAM

Thornley and Sun [4] exposed various kinds of photoresist to electron beams of 14 and 20 keV energy. In their view, electrons having these high energies must break all the chemical bonds in their path when they pass through a layer of resist: the resist molecules can then undergo a complete reorganisation. They found that 14 keV electrons are more effective than 20 keV electrons, and they ascribe this behaviour to the fact that the faster electrons can lose less energy than the slower electrons in collisions with resist molecules.

Matta [5] measured the dose needed for the exposure of negative and positive photoresists on a silicon substrate by electrons of various energies. The average current density required was found to be constant and independent of the thickness of the layer of resist. The optimum current densities are plotted in Fig. 2 as a function of accelerating voltage. A possible explanation of this phenomenon is that the exposure is due (at least partly) to the electrons reflected by the substrate). Matta also showed that the current density for optimum exposure with different depths of penetration of the primary electrons is

a function of the angular distribution of the electrons reflected by the silicon substrate. The positive resist required current densities 10 times greater than the negative resist.

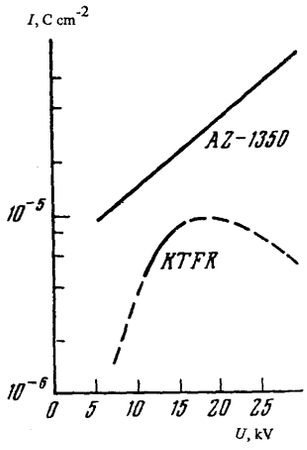



**Figure 2.** Variation of total charge needed with accelerating voltage.

Koichi and coworkers [6] studied the effect of an electron beam on negative resists. They concluded that the limitations on the obtainable line width are set by the reflection of electrons at the substrate interface and by the low sensitivity of photoresists to electrons. They considered the model for the interaction of the electron beam with the photoresist and the substrate shown in Fig. 3. The electrons, having passed through the resist, penetrate into the substrate material following a straight path up to a depth $x_d$ equal to the mean free path of the electrons in that material. Beyond this point they suffer diffuse scattering in all directions. Formulae for $x_r$ and $x_d$ are given:

$$x_r = \frac{I^2 A}{8\pi q^4 N \rho Z} \bar{E}_i \left\{ 2 \ln \frac{2E_p}{I} \right\}; \quad (1)$$

$$r_0 = \sqrt{x_r (x_r - 2x_d)}; \quad (2)$$

$$x_d = \frac{C \cdot x_r}{Z + 8}; \quad (3)$$

where $\bar{E}i$ is an exponential integral, $I$ is the mean excitation potential of the atom, $A$ is the atomic weight, $q$ is the electronic charge, $\rho$ is the density of the substrate material, $N$ is Avogadro's number, $Z$ is the atomic number, $E_p$ is the electron energy, and $C$ is a constant depending on the atomic number of the material ($C = 8-12$).

When a beam of electrons having energies in excess of 20 keV interacts with a layer of resist most of the chemical bonds are broken, and a complete redistribution of the molecular bonds can take place. Analogous effects occur in positive resist. It can be shown that the line width is a sensitive function of the thickness of the resist: lines cannot be narrower than the sum of the resist thickness and the beam diameter. For example, with a beam diameter of 0.3 μm and a layer thickness of 0.1–0.2 μm we can produce lines 0.3–0.5 μm wide. Furthermore, the line width depends also on the radius of the back-reflection $r_b$, which is determined by the properties of the substrate material. Experiments using aluminium and copper substrates gave minimum line widths in the ratio of 2 to 5. The raggedness of the line edges was of the order of 0.05 μm.

Studies of the exposure of different polymers have also been described [34]. Ordinary resists are shown to be insensitive to electron bombardment, and the need to develop special electron resists is pointed out. When the polymer is bombarded with electrons, instantaneous cross-linking of neighbouring side-chains is induced, but some significant breaking of the main chains also takes place. These effects influence the size of the molecules and the solubility of the polymer. Depending on the predominance of one or other of these processes, polymers may be classified into cross-linking types and degrading types. The following materials were examined in detail: poly(vinyl cinnamate) (degree of polymerisation 500–1000), polydimethylsiloxane (degree of polymerisation ~7000), and polydimethylsiloxane containing vinyl radicals (degree of polymerisation 5000–10 000).

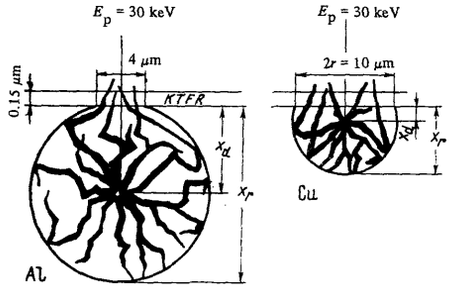



**Figure 3.** Schematic of the motion of electrons in a solid [6].

Miyauchi and coworkers [14,15] have published a study of the sensitivity to electron irradiation of several commercial grades of resist (KPR, KOR, AZ-1350, etc.). They obtained best exposures under the following beam conditions: beam voltage 10–30 kV, charge $5 \times 10^{-6}$–$10^{-4}$ C cm$^{-2}$.

The sensitivity of the resist is constant within the stated limits of accelerating voltage. The optimum exposure time depends on the thickness of the layer of resist. The width of the resulting stripe is greater than the beam diameter: this effect is due to scattering of the electrons in the material and reflection at the substrate interface. The minimum width obtained after development is equal to the sum of the thickness of the layer and the diameter of the beam. Broyde has described some experiments on the exposure of negative [35] (KPR, KTFR) and positive [36] (AZ-1350) resists. He explained the cross-linking processes in negative resists by radiation-chemical considerations. The cross-linking energy of the resists was determined experimentally ($2.5 \times 10^{20}$ eV cm$^{-3}$ for negative resists, $1.5 \times 10^{20}$ eV cm$^{-3}$ for positive resists). The cross-linking of KPR, in the presence of oxygen, is thought to be evidence for a free-radical polymerisation mechanism. The addition of sensitisers (benzotriazole, imidazole, indazole) to positive photoresist lowers the

threshold current of electrons by a large factor. Overexposure causes swelling in negative resists and loss of solubility in positive resists.

The main conclusions from this experimental study of the exposure of photoresists by an electron beam are: a) the exposure processes are influenced by the secondary electron emission characteristic of the substrate material; b) the use of terms such as "bond breaking" and "gel point" is quite inadequate as an explanation of the molecular restructuring produced by electron bombardment—Broyde's macroscopic explanation[35] in radiation-chemical terms is almost totally irrelevant to the mechanism of molecular conversion; c) there is no satisfactory explanation of the mechanism of the elementary polymerisation reactions in negative photoresist and of the degradation reactions in positive photoresists.

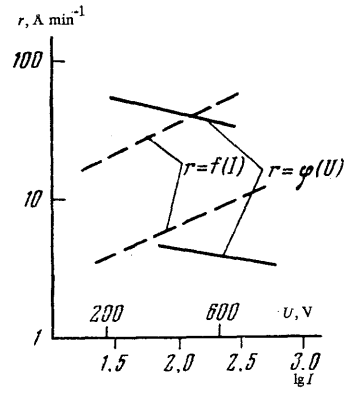



Figure 4. Rate of film growth against accelerating voltage and current density[39].

The molecular rearrangements induced by electron bombardment can be explained by using the results of work[17,18] on the deposition of polymer films from the gas phase. Workers are unanimous in their conclusion that film deposition occurs through the stages of adsorption of monomers by the solid surface, followed by electron-bombardment-induced polymerisation. Two mechanisms are considered: a) polymerisation by a radical mechanism[37], in which the radicals react with each other and with monomers; b) polymerisation by an ionic mechanism[38], in which the molecules dissociate into fragments which subsequently interact. The two polymerisation mechanisms lead to formally identical equations when detailed equilibrium [steady state condition (Ed. of Translation)] is assumed. The rate of growth of the film is

$$r = K_1 p \sqrt{I} \tag{4}$$

by the radical mechanism, and

$$r = K_2 p \sqrt{I}, \tag{5}$$

by the ionic mechanism, where $K_1$ and $K_2$ are constants, $p$ is the monomer concentration (butadiene) in the gas phase, $I$ is the current density. The form of the growth rate against current density relationship does not uniquely identify the polymerisation mechanism. Haller and White's experiments[38] with oxygen and hydrogen in the polymerisation vessel provide some evidence for an ionic mechanism of the polymerisation of butadiene.

Kolotyrkin and coworkers, after a critical assessment of a mass of published data, concluded that both polymerisation mechanisms may be operative in film formation, but one mechanism usually predominates, depending on the experimental conditions and on the nature of the starting material[17]. Tsapuk and coworkers[39] have described the deposition of polymers from the gas phase under the influence of electron bombardment. They find that the growth rate of the films decreases as the accelerating voltage increases, and increases with the power 0.5 of the current density. Plots of the growth rate of the polymer against accelerating voltage and current density are shown in Fig. 4. By solving simultaneously the equations $r = f(I)$ and $r = \varphi(U)$ we obtain a quadratic relationship between the current and the accelerating voltage:

$$I = -\alpha U^2 + \beta, \tag{6}$$

where $\alpha$ and $\beta$ are constants, and $I$ and $U$ are the current density and the accelerating voltage respectively.

We note a qualitative agreement between this equation and the observed current density–accelerating voltage relation for the negative photoresist KTFR (see Fig. 2). On the other hand, the $I = f(U)$ relationship for positive resist is entirely different.

## 4. INTERACTION OF AN ELECTRON BEAM WITH SOLIDS

Many studies have been made[41,42] of the passage of electrons through solids, the energy loss of electrons per unit length of absorber, the magnitude of the secondary electron emission, etc. (A recent review of the literature[40] contains 1035 references.) In order to discuss the interaction of an electron beam with a photoresist and the substrate material we need to know the range of the electrons in the materials, the energy loss, the secondary electron emission coefficient (SE), and the inelastic scattering coefficient of the electrons (IS).

According to Bethe[42], the energy losses of moving electrons due to inelastic collisions are described by the equation

$$\frac{dE}{dx} = \frac{2\pi \cdot q^4 NZ}{E} \ln \frac{2E}{J} \tag{7}$$

whence we can derive, by integration, the range of the electrons in the material:

$$R = \frac{J^3}{8\pi q^4 NZ} \left[E_i\left(2 \ln \frac{2E}{J}\right)\right] \tag{8}$$

where $R$ is the electron range, $T$, $q$, and $x$ are the energy, charge, and path length of the electron in the absorber, $NZ$ is the number of electrons per cm$^3$ of the absorber (for a photoresist we can take $NZ = 3 \times 10^{23}$), $J = \frac{8}{e} I$ is the energy needed to produce an ion pair in the absorber, $e$ is the base of natural logarithms, and $I = 26.4$ eV is assumed for gaseous ethylene irradiated with electrons. It is assumed that the value of $I$ does not differ very much for other hydrocarbons ($I = 24.8$–$27.1$ eV), and is independent of the state of aggregation; $[E_i(2 \ln \frac{2E}{J})$ is an exponential integral which can be expressed in the form

$$\left[\frac{e^{2 \ln \frac{2E}{J}}}{2 \ln \frac{2E}{J}}\right]\left(1 + \frac{1}{2 \ln \frac{2E}{J}} + \frac{2}{\left(2 \ln \frac{2E}{J}\right)^2}\right)$$

Calculations by Eqn. (8) agree well with experimental data on the passage of electrons through the negative resists KPR and KTFR [35] (see Table 3).

Table 3. Experimental ranges and ranges calculated by Eqn. (8).

| Electron energy, keV | Range, μm (exp.) | Range, μm (calc.) |
|---|---|---|
| 5 | 0.65 | 0.66 |
| 10 | 2—2.5 | 2.3 |
| 15 | — | 4.8 |
| 20 | — | 8.3 |

Broyde also points out[35] that calculations by the Thomson–Widdington equations gives low results (by a factor of five). His expression for the energy transferred by collisions is

$$\Delta E_p = \frac{2\pi q^4 NZT}{2E}\left(\ln\frac{2\pi q^4 NZT}{I(1-\beta^2)} - \beta^2 - 0.34\right) \qquad (9)$$

where, in addition to the symbols defined above, $T$ is the thickness of the layer of resist, and $\beta = v/c$ is the ratio of the electron velocity to the velocity of light.

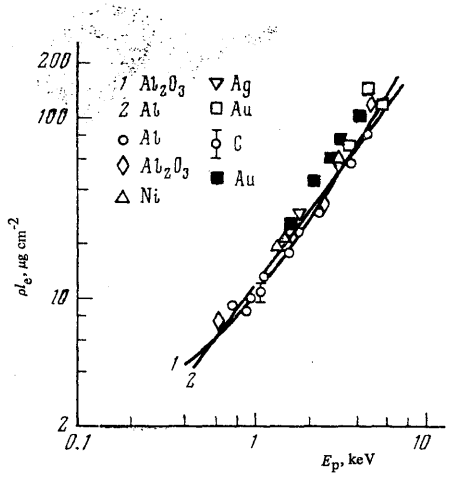



Figure 5. Depth of penetration against electron energy [43].

A great deal of experimental information on the transmission of electrons through matter is available in the literature. The most accurately measured quantity is usually the gravimetric depth of penetration (see Fig. 5), although the linear range is also quoted.

Plots of the secondary electron emission coefficient and the inelastic scattering coefficient for a number of materials are reproduced in Fig. 6.

The SE and the IS coefficient are related to the spectrum of secondary electrons (i.e. the relative proportions of fast and slow electrons). Fast electrons (energy > > 50 eV) include electrons emitted by the absorber and primary electrons reflected at 180°. The angular distribution of IS electrons for a massive metal target normal to the primary beam is closely approximated by the cosine law.

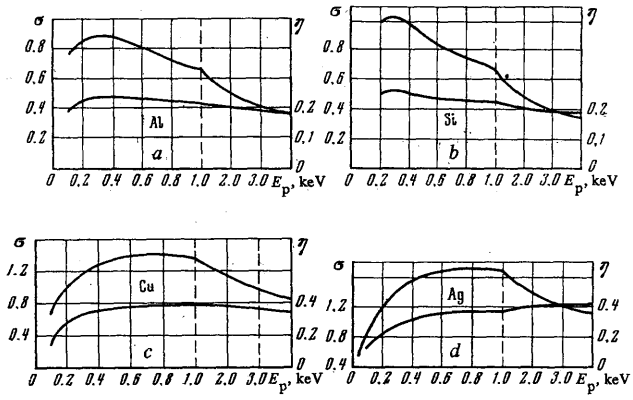



Figure 6. Secondary electron emission coefficients ($\sigma$) and inelastic scattering coefficients ($\eta$) for electrons in a number of materials [40].

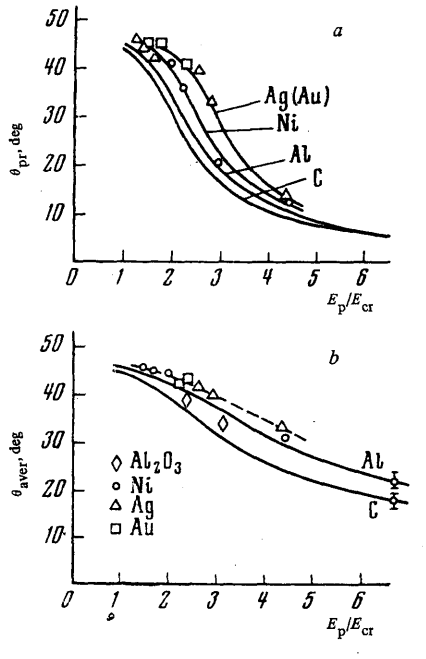



Figure 7. (*a*) Most probable and (*b*) average scattering angle of electrons [44].

Fig. 7 shows the most probable (*a*) and the mean (*b*) angle of scatter of electrons passing through films of various metals.

Irradiation of a solid by electrons is accompanied by a discrete energy absorption (called the characteristic

energy loss, CEL). Data on the CEL of various solids are summarised in Table 4.

The passage of electron beams through a carbon film and through films of various hydrocarbons [poly(vinyl formamide), poly(vinyl acetal), etc.] produces characteristic losses with very similar spectra[49]. The main difference noted[50] is that carbon has an additional absorption peak at 5.4 eV which is not found in poly(vinyl acetal).

Table 4. Characteristic energy losses of electrons in solids.

| Material | CEL, eV | | | | | Reference | Remarks |
|---|---|---|---|---|---|---|---|
| | level I | level II | level III | level IV | level V | | |
| Al | — | 7.2 | 14.6 | 20.5 | № | 45 | Arithmetic mean values |
| Cu | 3.5 | 6.8 | 11.9 | — | — | 45 | |
| Si | — | — | — | 3 | 34 | 46 | |
| C | — | — | — | 23.0 | 46.0 | 46 | Poly(vinyl acetate) films |
| Au | — | — | — | 24.0 | 47.0 | 46 | |
| $Al_2O_3$ | — | — | — | 23.0 | 46.0 | 46 | |
| MgO | — | 5.0 | 12.0 | 22.5 | 45.0 | 46 | |
| $SiO_2$ | — | 5.2 | — | 21.3 | — | 46 | |
| Ge | — | — | 16.5 | — | — | 47 | |
| Au | — | 6.6 | 15.5 | — | — | 48 | |
| C | — | 7.5 | — | — | — | 49 | Carbon films |
| C | — | 5.4 | — | — | — | 50 | |

The origin of the characteristic energy losses of the electrons can be explained by two mutually exclusive hypotheses: one-electron interactions and collective interactions.

According to Sternglas[51], the CEL are associated with electron transitions from the inner shells to the uppermost levels, ultimately leading to escape from the atom. This suggestion is confirmed by the good agreement between the magnitude of the characteristic losses and the fine structure of the X-ray absorption edge.

A CEL mechanism involving the excitation of plasma waves in the metal cannot be excluded. This hypothesis was put forward by Watanabe[47].

The secondary electron emission of metals and semiconductors varies between relatively narrow limits (from 0.5 to 1.8 eV). Narrow-gap semiconductors (Ge, Si, and others) have secondary emission properties similar to those of metals. The most probable energy of slow secondary electrons in these materials is ~1.5–3.5 eV, and is almost independent of the primary beam energy above ~200 eV.

In dielectrics, the secondary electron emission coefficient and the secondary electron energy are quite different from the corresponding values for metals. For example, the number of secondary electrons decreases as the energy of the incident electrons increases, and the escape depth of secondary electrons is greater in dielectrics. In metals the internal secondary electrons interact strongly with the conduction band electrons, and therefore their energy is insufficient to overcome the surface barrier after a few collisions. Conversely, the internal secondary electrons in dielectrics are located in the conduction band with an energy less than 10 eV, which they cannot transfer to electrons in the filled band.

The secondary electron emission from glass and fused quartz[40,41] has a value of 2–3; values reported for paraffin oil and for diffusion pump oil are 3–4.8 and 2.8–2 respectively.

The anomalous secondary emission given by metallic emitters covered with a layer of dielectric consists in a large secondary emission coefficient coupled with an unusually high emitted electron energy. It follows from the above arguments that electron bombardment of such an emitter must result in the appearance of positive charge in the dielectric, due to the large difference in secondary emission coefficient between the metal and the dielectric.

By exploiting the analogy with a maintained gas discharge, Jacob (quoted in Ref. 40) analysed experimental data on the emission from magnesium oxide and showed that the average electron energy was 10–20 eV, with a field strength of $10^6$ V cm$^{-1}$ in the dielectric.

According to Fridrikhov and coworkers[52], these parameters have the values 11 eV and $5 \times 10^5$ V cm$^{-1}$ in sodium chloride. Goetze[53] finds that the energy of secondary electrons emitted from potassium chloride reaches 4 eV. The calculations assume that the enhanced secondary emission and secondary electron energy in dielectrics is due to the positive space charge in the dielectric, and also to the presence of pores. In dense dielectrics the anomalous secondary emission parameters are not observed[40].

Polymers (including photoresists) may also contain gas-filled pores: experimental evidence for this assumption is given by Karasev[54].

## 5. MECHANISM OF INTERNAL IRRADIATION OF A POSITIVE PHOTORESIST

The essential facts concerning positive photoresists can be summarised as follows:

1. The changes in positive photoresist due to irradiation with light occur by two competing reaction paths: a) decomposition of the light-sensitive component and conversion of the resist into a water-soluble component (this reaction occurs when the resist is exposed to light of wave length shorter than 4600–4800, i.e. to a photon energy of 2.6 to 2.7 eV); b) deacylation of the NKhDA by ketens with formation of insoluble compounds (this reaction is observed when the resist is heated). Because the commonly used lamps do not emit radiation of wave length shorter than 3700 Å, and the photoresist layers are usually cooled during exposure, we may assume that the role of the novolak resin is an entirely passive one (film-forming ingredient).

2. The reaction products are the same after irradiation with electrons and with light. The exponential relationship between accelerating voltage and current suggests that the molecular rearrangement following electron bombardment involves neither a free-radical nor an ionic mechanism.

3. The electrons passing through a layer of photoresist lose fairly substantial amounts of energy. Calculations by Eqns. (8) and (9) indicate the following losses:

| Energy of incident electrons, keV | Thickness of resist, Å | Energy loss, keV |
|---|---|---|
| 15 | 3600 | 1.2 |
| 15 | 6000 | 2.4 |
| 15 | 12000 | 5.1 |
| 20 | 6000 | 1.6 |

The energy take-up by secondary electrons is relatively small (a few per cent). The large characteristic energy losses of electrons passing through organic compounds suggest electronic excitation of the molecules.

4. The secondary electron emission from a solid includes two characteristic groups of electrons: a) slow electrons, having an energy of a few electron-volts, and b) fast electrons, with energies higher than 60 eV. The energy of the fast electrons is high enough to cause excitation and ionisation of hydrocarbon molecules. The passage of fast electrons through a dielectric causes the appearance of positive space charge. The dielectric–metal combination of materials offers an enhanced secondary electron emission coefficient and slow-electron energy (up to 4, 10, or 20 eV).

Inelastic collisions between electrons and atoms or molecules lead to excitation and ionisation of the latter. An electron can excite a molecule provided that its energy exceeds that of the excited level of the molecule.

Electrons can excite different groups in the NKhDA molecule during their passage through a layer of resist: a) excitation of naphthyl groups causes decomposition of the photosensitive component, followed by typical photolytic changes in the NKhDA molecule; b) excitation of the electrons in the novolak and in the phenolic groups of NKhDA is accompanied by fluorescence, inter-state transition to the triplet state, and partial phosphorescence.

The photon energy of the phosphorescence is probably close to the u.v. absorption edge of the novolak (typically, 3.3–4 eV).

Lastly, the recombination of ion-molecules produced by electron impact can produce similar effects (i.e. fluorescence and phosphorescence). A rough estimate of the number of resulting ions from the measured secondary emission suggests that their role in the balance of internal radiation is very limited (a few per cent).

We shall now consider in detail the conditions which obtain when a photoresist is irradiated by a stream of electrons, the effect of the substrate material on the width of the resulting line and the sharpness of its edges, and lastly the optimisation of the resist composition from the standpoint of further miniaturisation of electronic devices.

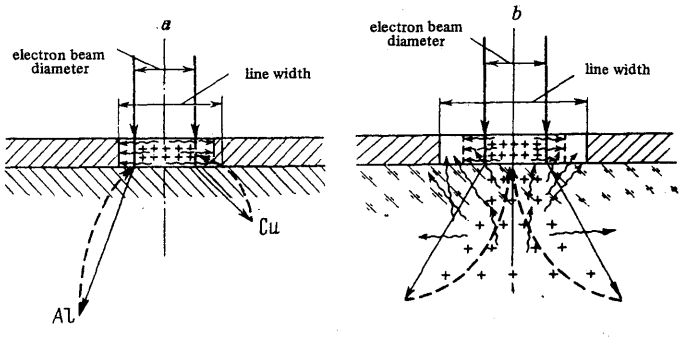



**Figure 8.** Passage of electrons through a layer of resist into a solid, and resulting diffuse irradiation: *a*) metallic substrate; *b*) dielectric substrate.

1. Irradiation of a positive photoresist on a metal substrate (Fig. 8*a*). We assume negligible divergence of the beam in the resist. The left-hand side of Fig. 8*a* depicts the penetration of the electrons into a light-metal substrate (Al), the right-hand side applies to a heavy-metal substrate (Cu). As a result of secondary electron emission, positive charges appear in the photoresist along the path of the primary electrons. The passage of the electron beam through the photoresist causes excitation and ionisation of the molecules. Both the NKhDA and the novolak resin molecules are excited.

The instability of electronically excited naphthyl groups in the NKhDA molecules results in decomposition by a reaction path indicative of excitation by photons of 2.7 to 2.8 eV energy.

The phosphorescence of the phenolic groups of the NKhDA molecule, of the novolak resin, and of the recombining ion-molecules gives rise to radiation in all directions (including the horizontal). This radiation is the main reason for the large difference between the line widths obtained in practice and the width of the electron beam.

The presence of positive space charge in the resist produces, on the one hand, an acceleration of the slow secondary electrons to energies at which they become able to excite molecules, and on the other hand it deflects the trajectories of inelastically scattered electrons, which therefore suffer a drift in the direction of the positive charge. Because of the shallower escape depth of the inelastically scattered electrons in heavy metals, and of their greater concentration, their interaction with the charge is less marked in heavy metals, and therefore the lines are broader (the comparison between copper and aluminium was given by Koichi and coworkers [6]).

The electrons which have passed through the resist are gradually slowed down, and they transfer their energy to the substrate. The temperature rise of the substrate favours competing reactions like the deacylation of the naphthyl groups by ketens and the condensation of the novolak resin. It is interesting to note that the roughness of the edges obtained in practice is of the same order as the grain size of thin metal films thermally evaporated in a vacuum. (The edge roughness is given [6] as 0.05 μm, the grain size [55–57] is 500–1000 Å.)

2. Irradiation of a positive photoresist on a dielectric substrate (Fig. 8*b*). The internal irradiation of the photoresist is similar to the case of a metal substrate, but there are some important differences. Because of the finite dielectric constant of the substrate material, the secondary and the inelastically scattered electrons suffer more marked interactions with the space charge (which now appears in the substrate as well as in the resist). Their trajectories will be drawn towards those of the primary electrons, and as a result the line width should be less dependent on the density of the substrate material.

However, if the substrate material is transparent to u.v. light (e.g., silicon dioxide) the radiation produced in the bulk of the substrate is propagated in all directions and can irradiate the resist from below. This effect also influences the line width which can be obtained, as compared with a metallic substrate (see Table 2). Many workers [4,6,14] have deposited metallic films on the transparent dielectric substrate in order to attenuate the u.v. light emerging from the substrate: the metal film acts as a screen to short-wave radiation. However, the use of a u.v. screen produces undesirable side effects, discussed above.

These variants include the whole range of experimental conditions quoted in the literature. It is evident from the above discussion that there are a number of reasons why the very narrowest lines cannot be obtained. The most important are: internal irradiation of the resist, bombardment of the resist by reflected and accelerated secondary electrons in the case of a metallic substrate, and irradiation from the substrate in the case of a dielectric substrate transparent to actinic light.

In spite of their different origin, all these effects lead to the same undesirable result: a broadening of the line. Procedures to localise phenomena conducive to line broadening have been suggested.

a) The use of photoresists containing ions and atoms which absorb light of 480 nm wave length and below ($Cr^{6+}$, $V^{5+}$, Cu, Au, etc.) minimises internal irradiation and prevents its lateral propagation from the exposed areas.

b) The use of thin screens of light metals protects the photoresist from the radiation emitted by the dielectric substrate.

c) The stream of short-wave radiation emerging from the dielectric substrate can be attenuated by providing a screen of glass containing heavy-metal ions and atoms ($Cr^{6+}$, $V^{5+}$, Cu, Au, etc.). The low thermal conductivity of glass and its high secondary electron emission coefficient should favour the production of narrow lines.

## 6. COURSE OF POLYMERISATION REACTIONS UNDER ELECTRON BOMBARDMENT

The internal irradiation phenomena observed in positive photoresists occur also in negative resists, for the following reasons: a) the presence of benzene rings, excited to the first singlet level by the beam of primary electrons, produces efficient fluorescence and phosphorescence effects—the excitation and deactivation of the sensitiser is accompanied by similar phenomena; b) inelastically scattered electrons are able to excite resist molecules; c) the generation of positive space charge in the bulk of the resist by the anomalous secondary electron emission results in the excitation of the resist molecules by secondary electrons which are accelerated to sufficiently high energies.

The deactivation of the resist molecules which are excited by primary electrons, by inelastically scattered electrons, and by accelerated secondary electrons is accompanied by radiation which is propagated into the bulk of the resist.

The procedures used to localise the radiation in positive resists (by adding absorbing ions) are applicable, in general, also to negative resists.

The excitation and the deactivation of the cinnamoyl groups in the photoresist molecules, and their subsequent polymerisation (both in the irradiated and in the adjacent areas), are the exact counterpart of the reactions which occur in the photoresist under the influence of light (i.e. biradical polymerisation). The energy of u.v. light is insufficient to extract electrons from the molecules.

The polymerisation mechanism involving excitation of the double bonds of the cinnamoyl groups is not the only one available to the resist. Electron irradiation produces, in addition to excitation, substantial ionisation of the molecules (up to 50% of the irradiated molecules): in other words, this form of irradiation gives rise to a greater number of primary processes than does irradiation with light. The subsequent deactivation and recombination of the molecules can take place by a great variety of possible reaction paths.

Thus, electron bombardment can activate other groups in the PVTs molecule, whilst also forming free radicals and ions. Hence, polymerisation reactions involving other groups of the PVTs molecule and of the sensitiser are possible, for example: a) bond formation between benzene ring, between a benzene ring and a linear chain, etc.; b) free-radical polymerisation; c) ion–molecule reactions.

Deactivation of the benzene rings, and also of radicals and ions, is accompanied by fluorescence and phosphorescence effects. The energy of transitions from the excited levels to the ground state is fairly high: in benzene, for example, it corresponds to the edge of the first absorption band, i.e. ~ 2537 Å. Light quanta of this energy can excite the cinnamoyl groups of the photoresist molecules, the sensitiser, etc. This stepwise utilisation of the energy of the electron beam partly explains the well known fact that the exposure of a negative photoresist with an electron beam requires less energy than exposure with light.

Several workers [27,35,58] have found that the energy needed to polymerise a poly(vinyl cinnamate) photoresist such as PVTs or KPR with an electron beam is smaller by a factor of 3 than the energy needed for exposure with light.

It must be stressed that electron irradiation can also lead to polymer degradation. According to Pshezhetskii, irradiation of poly(vinyl alcohol) causes evolution of hydrogen (95%), methane, carbon dioxide, and other radiolysis products [16]. The yield of gaseous products can be as high as 1.7 molecules per 100 eV of energy absorbed and increases with the dose of radiation. The optimum dose for the production of high-molecular products varies between 0.5 and 5 Mrad for different substances [59]. Negative photoresists have been irradiated with doses as high as 4.65 Mrad [35], 3.9 Mrad [11], 23 Mrad [6], 46 Mrad [12], etc.

As stated above, the irradiation of poly(vinyl alcohol) with high-energy electrons is accompanied by polymer degradation and gas evolution. Poly(vinyl esters) are also readily degraded by penetrating radiation [60]. PVTs is obviously an exception to this rule, at least within the range of electron energies and radiation doses of relevance to this review.

The polymerisation produced by electron bombardment is largely determined by the nature of the target molecules [61] and by the specific features of the reactions induced by the radiation.

Because of the difficulty of isolating individual products, and of defining conditions for the unambiguous identification of the polymerisation mechanism, contradictory results are often obtained. In spite of the generally adopted working hypothesis that radiation-induced polymerisation involves free radicals, the polymerisation is often accompanied by interactions between ions and molecules.

Irradiation with an electron beam can initiate a large number of reactions in a photoresist. None of the published papers deals specifically with the polymerisation mechanism of poly(vinyl cinnamate) resists: this is unfortunate, because a knowledge of the predominant reaction could be of great help in the choice of the best resist composition and of the best exposure energy. The cross-linking of separate molecules into blocks undoubtedly influences the resolution of the photolithographic process.

Press [2] has shown that the energy needed for exposure with light, assuming excitation of the double bonds in PVTs, obeys an exponential law. Even allowing for the stepwise, repeated utilisation of the energy of the primary electrons, transmitted through fluorescence and phosphorescence phenomena, this energy is insufficient to cause cross-linking of the resist. The ion–molecule reaction mechanism, or the free-radical mechanism, seems to be more economical in energy.

The system in which a film of resist on a metallic layer is irradiated by scanning a beam of accelerated

electrons in a vacuum behaves as a complex emitter. Electron bombardment of this two-layer structure (dielectric–metal) is accompanied by anomalous secondary electron emission. The appearance of positive space charge in the bulk of the resist can be treated as the addition of a large number of ions with a sufficiently long life time. These ions are not usually carbonium ions, though they may give rise to carbonium ions (possibly as intermediate products) during subsequent decomposition.

In the gas phase these ionic particles can be formed only at sufficiently low pressures, because the breaking of a covalent bond to give a carbonium ion requires a greater expenditure of energy than does the formation of radicals. It must also be remembered that the ions formed as a result of excitation have a life time of the order of $10^{-5}$ s, followed by decomposition. Ionisation with formation of carbonium ions is possible only when the required ionisation energy is compensated by solvation of the resulting ion in solution or by coulombic interaction in an ion pair (either in solution or in the gas phase) [62].

In the solid phase the course of the reaction is affected by heterogeneities, defects, etc., which enable the electrons to be captured and retained by the crystal lattice. This effect is responsible for the high stability of cations in solids.

Although the possibility of an ionic–molecular polymerisation mechanism is not entirely excluded, the most likely mechanism for the polymerisation of poly(vinyl cinnamate) photoresists under electron bombardment is a mechanism involving free radicals, for the following reasons:

1. Irradiation of PVTs with u.v. light gives rise to cross-linking even though the quantum energy of the light is insufficient to cause ionisation.

2. Addition of oxygen to the chamber in which KPR is irradiated with electrons does not affect the polymerisation [35]. Oxygen is the strongest known inhibitor of cationic polymerisation.

3. The fact that irradiation with a beam of 14 keV electrons is more effective than irradiation with 20 keV electrons [1] also suggests a free radical polymerisation mechanism. The beam of 14 keV electrons suffers considerably greater losses in the layer of resist, which is therefore heated to a higher temperature.

The cross-linking of negative photoresists by a free-radical polymerisation mechanism explains a number of previously surprising features of electron-beam exposure. The most important are: a) the energy needed for the cross-linking reaction becomes lower; b) the spatial resolution of the resist depends on the tendency of free-radical reactions to initiate chain growth, which can propagate sideways from the point of initiation; c) the roughness of the edge of the polymerised stripe depends both on the propagation of free-radical chains and on the properties of the substrate (thermal conductivity, thermal diffusivity, thickness, grain size, etc.).

## 7. DISCUSSION AND CONCLUSIONS

The many and complicated phenomena which accompany the passage of an electron beam through a photoresist have not yet been fully investigated. This is the main reason for the inconsistent results reported by different workers and for the contradictory explanations advanced to account for them.

Although some encouraging results have been obtained in attempts to decrease the size of the microcircuit elements, and in defining the optimum accelerating voltage, charge, and other technological parameters, many outstanding problems still stand in the way of a more general application of electron-beam exposure of photoresist. Some of these are: a) the inconstancy between theoretically expected and practically accessible dimensions of the microcircuit elements [6,11,13,63]; b) the low operating efficiency, due to the slow scanning speed of the beam—according to Thornley and coworkers [64], electron beam exposure can be profitable only if projection or multiple-beam apparatus is used; c) the difficulty of obtaining a spot of sufficiently small diameter.

Although the above problems have separate identities, they are by no means unconnected: a decrease in beam diameter is accompanied by a decrease in the flux of electrons, which makes the permissible scanning speed even slower and therefore lowers the operating efficiency of the process. The discrepancy between the calculated and the experimentally obtained line widths is explained by the lack of monochromaticity of the beam, by the lack of resists specially designed for exposure by electrons, and by the influence of the substrate material. The low productive capacity, and the difficulty of producing patterns of prescribed dimensions, stem from the use in electron lighography of materials which were designed as photoresists, although other materials could be used to better effect [13,64,65].

Detailed analysis of the problems is complicated by the large numer of commercial resists and by the wide variety of their properties [23].

The reactions considered in this review (changes in positive photoresist based on naphthoquinonediazide and changes in negative photoresist based on PVTs) are a convincing illustration of the problems underlying the use of an electron beam for exposure. We have deliberately chosen the most familiar and widely used resists, though many other types and grades are available. For the grades considered here, the following parameters of the layer of resist can be calculated with quite good accuracy: energy balance, resolving power of the beam, edge roughness of the resulting pattern, thickness of resist, and accelerating voltage. With other types of polymer (of both the cross-linking and the degrading type), based on different compounds, the phenomena and the rules discussed above should be applied with care, taking due notice of the structure and composition of the starting materials and of their reactions under electron irradiation.

The sequence of reactions in the polymers should be investigated in accordance with the nature of the chosen material: a) primary excitation and ionisation reactions; b) secondary reactions involving deactivation and recombination of the molecules.

It is important to consider first of all the physical processes associated with fluorescence, phosphorescence, triplet–triplet energy transfer, and secondary electron emission. The subsequent chemical reactions (intramolecular decomposition, degradation, or polymerisation) are critically dependent on the properties of the starting compound. In addition to the reactions of the main component of the resist, we must consider also the role of the various additives.

The main conclusion to be made from the present review is that the widespread penetration of electron-beam exposure into industrial practice must await the solution of the following problems:

1. The influence of the substrate material on the exposure and on the development of the film of resist (including the effect of secondary electron emission).

2. The effect of the radicals and ions formed by electron bombardment on the course of chemical reactions in photoresists.

3. Minimising the energy required for the exposure of the resists. Special interest attaches to the use of an electron beam for exposing negative photoresists, for the following important reasons: a) the energy required for exposure is lower by a factor of 6 as compared with positive photoresists; b) the energy required is lower by a factor of 3 as compared with exposure by light; c) negative resists are more stable towards etchants than positive resists.

The use of sensitisers to decrease the energy required for the exposure of positive photoresist has been convincingly demonstrated by Broyde[36].

4. The synthesis of new resists, more sensitive towards electron irradiation, and free from internal irradiation effects. The latter requirement is essential to the achievement of even smaller dimensions in microelectronic circuits.

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