Chapter 8

General Considerations on the Radiation and Photochemistry of Resists

> Here the boundaries meet and all contradictions exist side by side.
>
> Fyodor Dostoevsky, *The Brothers Karamazov*

8.1 Interaction of Radiation with Resists

The interaction of exposure radiation with amorphous solid films of resists and their constituents leads to distinct photophysical and photochemical processes that in turn underlie the basis of the contrast between the exposed and the unexposed sections of the resist film. A short section of this chapter is therefore devoted to the rudiments of photochemistry and photophysics of amorphous solid resist films. We can only provide here the most basic information required for understanding the subject.[1]

It is necessary to introduce some terminology here. When the radiation-sensitive components of resists—the resins and components—are irradiated, they can absorb the energy and in turn get excited. It is the excited state form of the radiation-sensitive components of the resist that plays the central role in these processes. These excited states of the molecules are identified by their multiplicity (the overall spin of the electrons in that state), by their molecular orbital character (indicating the involvement of π, n, σ, or other orbitals in the excitation process), and by their energy in relation to the energy of the ground state. The relevant excited states of a molecule include the singlet S_1 and triplet T_1, and are typically

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[1]For a comprehensive treatment of the subject, the reader is referred to these excellent books: A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, Chapter 3, John Wiley & Sons, Hoboken, NJ (1989); N.J. Turro, *Modern Molecular Photochemistry*, Benjamin-Cummings, Menlo Park, CA (1978); J.A. Barltrop and J.D. Coyle, *Elements of Organic Photochemistry*, John Wiley & Sons, Hoboken, NJ (1975).

represented in a state diagram that shows their energy levels relative to the ground state singlet S_0.[2]

A good way to picture the singlet and triplet states is to consider the configuration of a pair of $1s$ orbital electrons in the ground state, represented as $1s^2$. When excited, one of these electrons may be promoted into a $2s$ orbital, giving the configuration $1s^1 2s^1$. The two electrons need not be paired since they occupy different orbitals. According to Hund's rule of maximum multiplicity,[3] the state of the atom or molecule in which the spins are parallel ($\uparrow\uparrow$) lies lower in energy than the state in which they are antiparallel or paired ($\uparrow\downarrow$). Both states are permissible, and can contribute to the photochemistry and photophysics of the atom or molecule.[4]

Electrons with parallel and antiparallel spins differ in their overall spin angular momentum. In the paired case, the two spin momenta cancel each other, resulting in zero net spin. The paired-spin arrangement is called a singlet. The triplet state is one in which the angular momenta of two parallel spins add together to give a nonzero total spin. In general, for states arising from the same configuration, the triplet state lies lower in energy than the singlet state. The origin of the energy difference between the singlet and triplet states arises from the effect of spin correlation[5] on the coulombic interactions between electrons.[6]

The generation of an excited singlet state S_1 of a molecule in a resist is either by direct absorption of a photon or by energy transfer from another excited molecule. Once excited, the fate of the excitation energy acquired by the molecule can follow quite a number of pathways. The excited singlet state S_1 may either emit fluorescence or it may be deactivated by a nonradiative transition to the ground state. When nonradiative transitions occur between states of the same multiplicity (i.e., singlet to singlet or triplet to triplet), they are called internal conversions. When the transitions occur between states of different multiplicity, they are termed intersystem crossings. Intersystem crossings are spin-forbidden transitions that are due to the intervention (in aromatic systems) of out-of-plane vibrations or by the state-mixing effects of heavy atoms. The fraction of S_1 that emits fluorescence is a function of the competition between the radiative fluorescence transition, the internal convervsion to ground state S_0, and the inter-system crossing to T_1. Furthermore, the excited triplet state may be deactivated by a radiative process (phosphorescence) and by nonradiative intersystem crossing to the ground state.[7]

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[2]A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, p. 65, John Wiley & Sons, Hoboken, NJ (1989).

[3]An atom in its ground state adopts a configuration with the greatest number of unpaired electrons.

[4]P.W. Atkins, *Physical Chemistry*, 5th ed., pp. 447–448, W.H. Freeman and Co., New York (1994).

[5]Spin correlation refers to the phenomenon in which electrons with parallel spins behave as if they have a tendency to stay well apart and hence repel each other less.

[6]P.W. Atkins, *Physical Chemistry*, 5th ed., pp. 447–448, W.H. Freeman and Co., New York (1994).

[7]A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, pp. 65–66, John Wiley & Sons, Hoboken, NJ (1989).

8.2 Excited State Complexes

In lithographic exposure sources and resist photopolymer systems, an important type of excited state is the excited state complex, which consists of excimers and exciplexes.

8.2.1 Excimers

Excimers[8] (excited dimers) are formed by pairs of molecules or atoms that do not significantly interact in the ground state, but are weakly bonded in the excited state. The bonding in the excimer takes place between an excited molecule and a ground state molecule of the same species. Its origin is in the change of orbital symmetry that accompanies excitation and leads to cooperative (positive) orbital overlap and hence to bonding between the two systems.[9] Examples in resist systems can be found in aromatic and heteroaromatic molecules used in photo-active compounds. Excimers were first observed by Forster and Kasper in 1954 when they observed two kinds of fluorescence in fairly concentrated solutions (10^{-3} M) of pyrene.[10]

Figure 8.1 shows a schematic of the potential energy diagram of an excimer-forming pair of molecules. Worthy of note is the red shift and the loss of vibrational structure in this figure, which can be understood from the shape of the potential energy surfaces of the two molecules as they approach each other. In the ground state, as the two molecules come within the distance of their van der Waals radii, they repel each other, indicated in the graph by the rise in the potential energy; however, in the excited state, the attractive force of positive orbital overlap creates a potential energy well that defines the excimer. The depth of this well is the excimer-binding energy B, which equals the amount of energy by which the excimer is stabilized relative to the energy of the excited state of an iso-lated (monomeric) molecule. Through fluorescence emission, the paired molecule is returned to the shoulder of the repulsive branch of the potential energy curve. The change in energy corresponding to the fluorescence transition from the excimer (excitation energy of the excimer), ΔE_{FD}, is smaller than the change in energy in the fluorescence of the monomer (excitation energy of the monomer), ΔE_{FM}, hence the red shift in the emission. Furthermore, this energy change covers a con-tinuous range of values and does not contain any vibrational fine structure of the molecular skeleton.[11]

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[8]A good example of the application of excimers is in lithographic exposure sources such as F_2-excimer lasers.

[9]A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, pp. 67–68, John Wiley & Sons, Hoboken, NJ (1989).

[10]T. Forster and K. Kasper, "Ein konzentrationsumschlag der fluoreszenz des pyrens," *Z. Phys. Chem. (N.F.)* **1**, 274 (1954).

[11]A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, p. 68, John Wiley & Sons, Hoboken, NJ (1989).
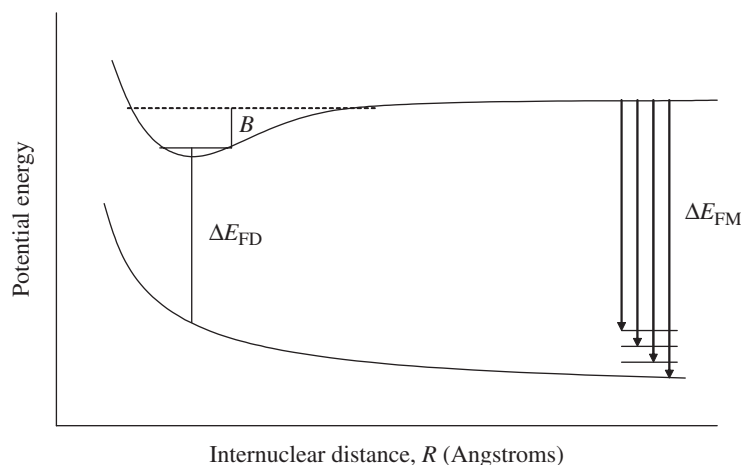
Figure 8.1 Schematic potential energy diagram of an excimer-forming pair of molecules. The lower curve shows both molecules in the ground state. The upper curve shows the excimer formation on the approach between an excited molecule and a molecule in the ground state. ΔE_{FM} is the excitation energy of the monomer, ΔE_{FD} is the excitation energy of the excimer, and B is the excimer-binding energy.

8.2.2 Exciplexes

The interaction on excitation of two similar molecules that do not have identical structures, for example, resist sensitizers such as anthracene and tetracene, can lead to the formation of heteroexcimers. If the two molecules differ significantly in their electron affinities such that one is an electron donor and the other an electron acceptor, the bonding process may be accompanied by a partial transfer of charge. Under this scenario, the interaction between the two molecules is stronger than in conventional excimers and the transient excited species formed as a result is termed an exciplex[12] (excited complex). Characteristically, exciplexes emit a structureless, red-shifted fluorescence, or phosphorescence, similar to that of an excimer.[13]

It should be pointed out that exciplexes are often stages in the complete transfer of an electron from one molecule to another, leading to the formation of radical ion pairs and finally of separated radical ions.[14] An illustrative example is the photoreaction of benzophenone (a common resist sensitizer) with tertiary amine (a common resist quencher), as illustrated in Scheme 8.1.[15]

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[12]Examples of the application of exciplexes in lithography include KrF and ArF exciplex laser light sources for 248 nm and 193 nm lithographies, respectively.

[13]A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, p. 70, John Wiley & Sons, Hoboken, NJ (1989).

[14]ibid., p. 70.

[15]R.F. Bartholomew, R.S. Davidson, P.F. Lambeth, J.F. McKellar, and P.H. Turner, "The photoreaction of aromatic carbonyl compounds with amines: evidence for electron transfer from tertiary aromatic amines to triplet benzophenone," *J. Chem. Soc. Perkin* **2**, 577 (1972).
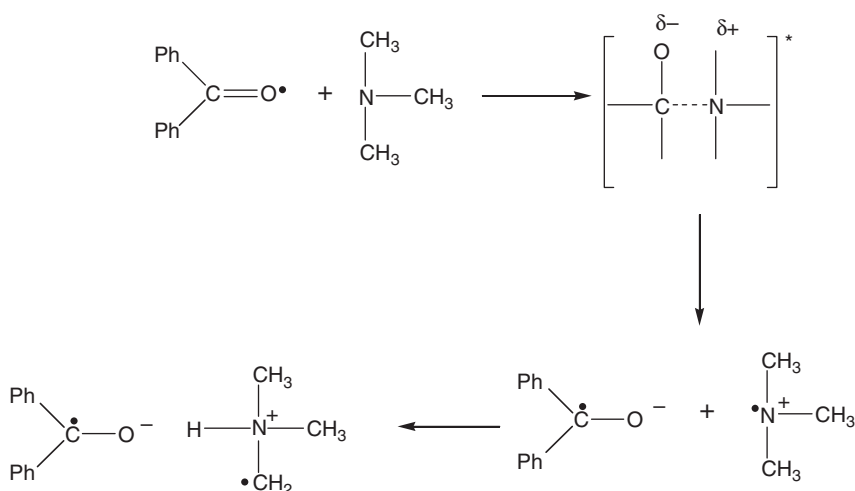
Scheme 8.1 Photoreaction of benzophenone and tertiary amine, illustrating electron transfer that leads to spatial transfer of charge typical of exciplexes.

8.3 Energy Transfer

Exposure-induced energy transfer in a resist matrix occurs not only between different states of a given radiation-sensitive resist molecule or component, but can also occur between such molecules or components when they are in close proximity to each other. It is customary to designate the molecule that carries the excitation energy as the donor (D) and the molecule that accepts the energy as the acceptor (A). The governing reaction is represented by Reaction [8.1]:

$$D^* + A \longrightarrow D + A^*. \qquad [8.1]$$

By nature, the energy transfer between molecules in resists is an electronic process, which is essentially adiabatic. Such a transfer will occur with reasonable probability only if the excitation energy of D^* is equal to or greater than that of A^*:[16]

$$E_{D^*} \geq E_{A^*}. \qquad (8.1)$$

At the point of transfer, donor and acceptor molecules are coupled and form a single quantum mechanical entity. The two distinct coupling mechanisms that have been recognized to mediate the transfer process[17] include coulombic or

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[16]Exceptions to this rule occur in reversible processes; see, for example, K. Sandros and H.L.J. Bäckstrom, "Transfer of triplet state energy in fluid solutions. II. Further studies of the quenching of biacetyl phosphorescence in solution," *Acta. Chem. Scand.* **16**, 958 (1962); "Transfer of triplet state energy in fluid solutions. III. Reversible energy transfer," *Acta. Chem. Scand.* **18**, 2355 (1964).

[17]For details on the experimental proof for various types of energy transfer, that is between singlet states, between triplet states, between and between singlet and triplet states, please see the following papers of Bennet, Kellog, and co-workers at Dupont: R.G. Bennet, "Radiationless intermolecular

dipolar interaction (proposed by Förster[18]) and electron exchange or orbital inter-
action (proposed by Dexter[19]).

8.3.1 Dipole resonance transfer

Energy transfer by coulombic interactions is a dipole resonance effect, which
according to Förster[20] may occur under favorable circumstances where the elec-
tronic transitions of two molecules may couple in a way similar to the coupling
of two oscillating dipoles, with energy being transmitted from one to the other.
For molecules in a resist, the rate of energy transfer for this kind of coupling is
given by the expression

$$k_{ET}(\text{coulombic}) = \frac{\mu_D^2 \mu_A^2}{R_{DA}^6}, \tag{8.2}$$

where k_{ET} is a rate constant $(\text{M}^{-1}\text{s}^{-1})$, μ_D and μ_A are transition dipole moments of
the fluorescence transition $(\text{D}^* - \text{D})$ and the absorption transition $(\text{A} - \text{A}^*)$,
respectively, and R_{DA} is the separation between the two molecular centers at the
moment of transition.

Expressing the transition moments in terms of measurable quantities allows the
Förster transfer rate to be written in the form[21]

$$k_{ET} = 8.8 \times 10^{-25} \frac{\kappa^2 \phi_F(D)}{n^4 R^6 \tau_D^0} \int f_D(\nu) \varepsilon_A(\nu) \frac{d\nu}{\nu^4}, \tag{8.3}$$

where n is the index of refraction of the medium, $\phi_F(D)$ is the quantum yield of
fluorescence of the donor, τ_D^0 is the fluorescence lifetime of the donor in the
absence of the acceptor, and κ^2 is a geometric factor, which in a solid resist film
medium has a value of approximately 0.457.[22] The factor $f_D(\nu)$ is the fluorescence
spectrum of the donor normalized to unity, while $\varepsilon_A(\nu)$ is the absorption spectrum

energy transfer. I. Singlet → singlet transfer," *J. Chem. Phys.* **41**, 3037 (1964); R.G. Bennet, R.P.
Schwenker, and R.E. Kellog, "Radiationless intermolecular energy transfer. II. Triplet → singlet
transfer," *J. Chem. Phys.* **41**, 3040 (1964); R.E. Kellog and R.G. Bennet, "Radiationless intermolecu-
lar energy transfer. III. Determination of phosphorescence efficiencies," *J. Chem. Phys.* **41**, 3042
(1964); R.E. Kellog, "Radiationless intermolecular energy transfer. IV. Triplet → triplet annihil-
ation," *J. Chem. Phys.* **41**, 3046 (1964); "Radiationless intermolecular energy transfer. V. Single-
t → triplet transfer," **41**, 3048 (1964).
[18]T. Förster, "Zwischenmolekulare Energiewanderung und Fluoreszenz," *Ann. Phys.* **2**, 55 (1948); "I.
Electron optical studies of imperfect crystals and their surfaces," *Discuss. Faraday Soc.* **27**, 7 (1959);
T. Förster, *Die Fluoreszenz Organischer Verbindungen*, Vanderhoek & Ruprecht, Gottingen (1951).
[19]D.L. Dexter, "A theory of sensitized luminescence in solids," *J. Chem. Phys.* **21**, p. 836 (1953).
[20]T. Förster, "Zwischenmolekulare Energiewanderung und Fluoreszenz," *Ann. Phys.* **2**, 55 (1948); "I.
Electron optical studies of imperfect crystals and their surfaces," *Discuss. Faraday Soc.* **27**, 7 (1959);
T. Förster, *Die Fluoreszenz Organischer Verbindungen*, Vanderhoek & Ruprecht, Gottingen (1951).
[21]M.Z. Maksimov and I.B. Rotman, "On energy transfer in solid solutions," *Opt. Spectrosc.* **12**, 337
(1962).
[22]ibid.