encapsulation of IC devices to protect them against particulate and environmental contamination. They have also found applications as interlayer dielectric materials in IC devices.

4.3.1.2 Crosslinking imaging mechanism from radiation-generated reactive species

In a number of negative-resist systems, crosslinks are formed by the reaction of radiation-generated reactive species. When these reactive species mediate, at most, one crosslinking event per each unit of radiation received, the reaction is termed a non–chemical amplification reaction, and the resists thus formed are called non–chemically amplified crosslinking resists. Examples include: (1) dichromate resists in which crosslinks of the resin are formed by the coordinative bonding of Cr^{3+} ions generated from the dichromate PAC with the amide groups of the protein resin; (2) metal oxide sulfate resists based on $HfSO_x$ and $ZrSO_x$, in which radiation-induced decomposition of peroxo bridges creates reactive metal centers with unsatisfied coordination numbers that form crosslinks via metal–oxo bridges; (3) azide resists in which crosslinks are formed from thermal reactions of photogenerated nitrenes (electron-deficient species) with the poly(*cis*-isoprene) rubber resin, or with polyimide resin; (4) acylsilane resists in which siloxycarbenes mediate the grafting of acylsilyl groups onto suitable polymers such as poly(vinyl alcohol) and poly(vinyl pyridine), causing the crosslinking of these polymers; and (5) functionalized polystyrene-based resists where radicals are coupled to form crosslinks.

When the reactive species mediate multiple crosslinking events per unit of radiation, the reaction is termed chemically amplified, and the resists thus formed are termed chemically amplified crosslinking resists. Examples of such chemical amplification reactions employed in negative-resist design include pinacol rearrangement, intramolecular dehydration, condensation/intermolecular dehydration, esterification, and cationic polymerization of polymers with polymerizable pendant groups or crosslinking agents added to the resist resin. Briefly described below are some resists based on the above class of reactions used in the design of negative resists.

4.3.1.2.1 Crosslinking imaging mechanisms from radiation-generated reactive species in non–chemical amplification mode

4.3.1.2.1.1 Dichromate resists based on crosslinking by chromium (III) ions

Dichromate resists based on solution of ammonium dichromate gelatin casts fine films from water and, after exposure, can be developed with water. When exposed to visible light, the exposed area of the film is hardened and remains on the substrate, while the unexposed area is washed off with warm water. The hardening of the exposed area is based on the light-induced

crosslinking between adjacent chains of protein molecules in the gelatin.[120] After drying, the gelatin image becomes hydrophobic and can accept printing ink.

Biltz and Eggert[121] established that the mechanism that underlies the crosslinking of the dichromated coatings process involves the photoreduction of Cr(VI) to Cr(III) as shown in this reaction:

$$Cr_2O_7^{2+} + 14H^+ + 10e^- \rightarrow 2Cr^{3+} + 7H_2O. \qquad [4.16]$$
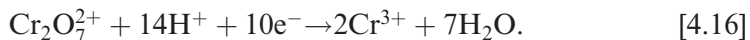
Datta and Sollern[122] established that the detailed fate of the Cr(VI) depends somewhat on the colloidal medium, but that the final stage of the photoprocess always yields Cr^{3+} ions. Given that trivalent chromium is a well-known, powerful coordination center, it was thought that crosslinks may be formed by the coordinative bonding of Cr^{3+} with the amide groups of the protein. This view is incidentally supported by the fact that all polymers that have been used as gelatin substitutes, such as other proteins, starch, poly(vinyl alcohol), poly(vinyl pyrrolidone), and poly(vinyl butyral), carry ligands capable of forming complexes with Cr(III). In fact, Duncalf and Dunn's studies on coordinative bonding of gelatin to Cr(III) revealed that crosslinking occurs only in dry coatings of dichromated gelatin, but not in concentrated aqueous solutions where Cr^{3+} preferentially coordinates water to form $Cr(Cl)_3.6H_2O$ and does not interact with the protein.[123]

4.3.1.2.1.2 Condensation imaging mechanism of metal oxide sulfate resists based on hafnium and zirconium oxide sulfates

These resists are metal oxide sulfates such as $HfSO_x$ and $ZrSO_x$, which are complexed with a peroxo complexing agent that caps the inorganic clusters and inhibits crosslinking or network formation during spin coating and post-applied bake processing steps of the resist. Upon exposure, the interaction of this resist complex with EUV photons or an electron beam leads to the generation of secondary electrons that decompose the polymerization inhibitor,

120. C. G. Willson, R. A. Dammel, and A. Reiser, "Photoresist materials: A historical perspective," *Proc. SPIE* **3050**, 38–51 (1997).

121. M. Biltz and J. Eggert, *Wiss. Veroeff.* AGFA **3**, p. 294 (1928) [cited in A. Reiser, *Photoactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, p. 24 (1989)].

122. P. Datta and B. R. Sollern, *18th SPSE Fall Symp.*, Nov. 1978 [cited in A. Reiser, *Photoactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, p. 23 (1989)].

123. B. Duncalf and A. S. Dunn, *Print. Technol.* **14**(3), 125 (1970) [cited in A. Reiser, *Photoactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, pp. 22–24 (1989)].
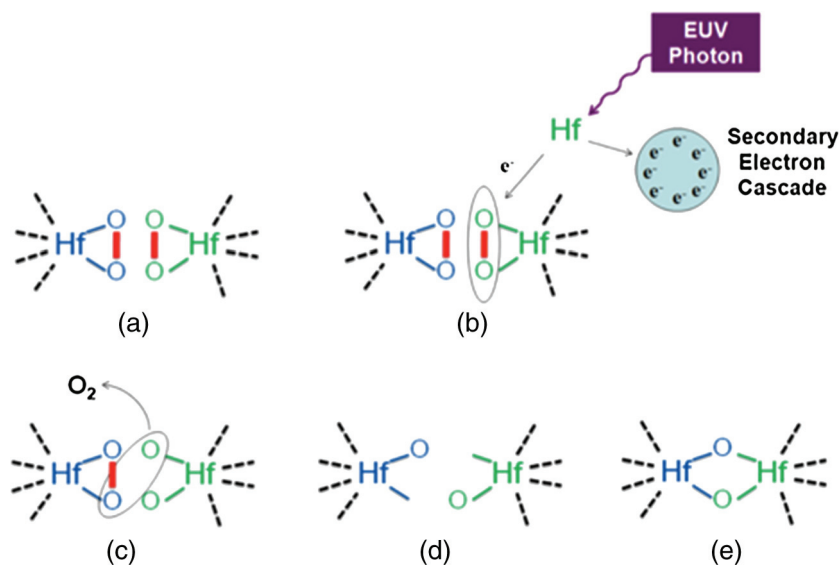
Figure 4.12 Illustration of the exposure mechanism of metal oxide sulfate resists, e.g., $HfSO_x$. (a) During spin coating, polymerization-inhibiting peroxo groups prevent network formation. (b) Upon exposure, an EUV photon generates a photoelectron, which induces a secondary electron cascade, some of which decompose the peroxo groups. (c) An oxygen radical is generated from each peroxo group, which when combined with another oxygen atom from a neighboring peroxo group, leaves the film as an oxygen molecule and (d) creates metal centers with unsatisfied coordination numbers and vacant coordination sites. (e) Crosslinking of the metal–oxo bridges results in a three-dimensional network, satisfying the coordination number of the metal. (Reprinted from Stowers et al.[124] with permission.)

leading to the formation of active metal sites. The active metal sites react with each other via condensation, resulting in the crosslinking of metal–oxo bridges and the production of three-dimensional network structures (Fig. 4.12). These three-dimensional network structures produce the differential solubility between unexposed and exposed regions of the resist.[125]

It should be pointed out that this resist does not contain organic components, either as ligands, or as photoinitiators, or as solvents. The resist is developed in 25% w/w tetramethyl ammonium hydroxide. The resists form atomically smooth, dense and pin-hole free amorphous films.[126]

124. K. Stowers, A. Telecky, M. Kocsis, B. L. Clark, D. A. Keszler, A. Grenville, C. N. Anderson, and P. Naulleau, "Directly patterned inorganic hardmask for EUV lithography," *Proc. SPIE* **7969** 796915-1 (2011).

125. J. Stowers and D. A. Keszler, "High resolution, high sensitivity inorganic resists," *Microelectronic Engineering* **86** 730–733 (2009).

126. K. Stowers, A. Telecky, M. Kocsis, B. L. Clark, D. A. Keszler, A. Grenville, C. N. Anderson, and P. Naulleau, "Directly patterned inorganic hardmask for EUV lithography," *Proc. SPIE* **7969** 796915-1 (2011).

4.3.1.2.1.3 Azide resist systems based on crosslinking of isoprenoids by nitrenes

The introduction of azide groups in a polymeric system offers another possibility of effecting photo- and radiation-induced crosslinking imaging mechanisms in resist systems. This method has been successfully employed with organic bis-azides, which photodecompose into reactive species called nitrenes (electron-deficient nitrogen species analogous to carbenes), and, which, under application of heat, mediate the crosslink formation between chains of cyclized poly(isoprene) rubber.[127]

The bis-azide 2,6-bis(4-azidobenzal)-4-methylcyclohexanone (**IX**) (see Scheme 4.5) is the most popular azide resist system, as it was used in the formulation of Kodak thin film resist (KTFR),[128] a resist that was the workhorse of the semiconductor industry from 1957 until about 1972, when the critical dimensions of IC devices reached about 2 μm, the resolution limit of KTFR.[129]
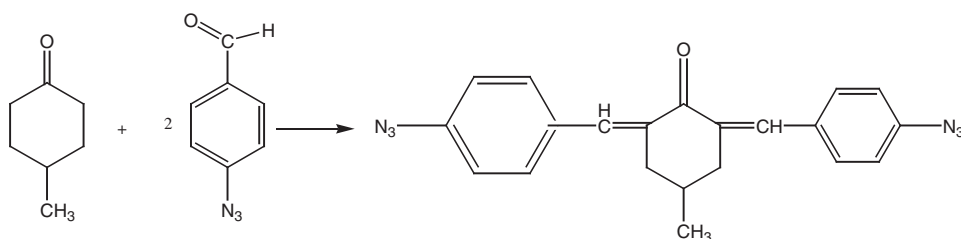
Scheme 4.5 Synthetic scheme of 2,6-bis(4-azidobenzal)-4methylcyclohexanone (**IX**) (Hans Wagner's bis-arylazide that was the basis of Kodak's KTFR resist system).
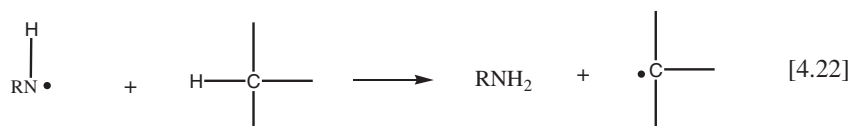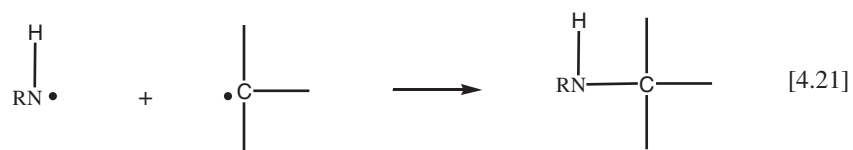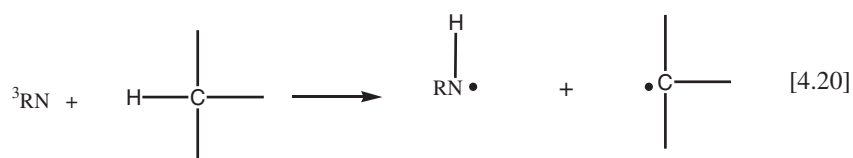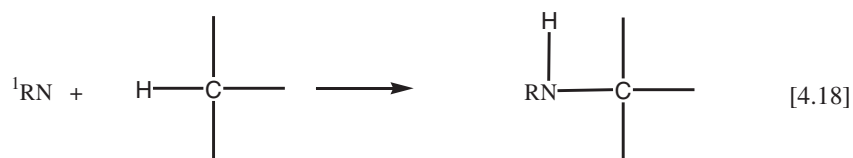
The mechanism of the crosslinking reaction of cyclized rubber by photogenerated-nitrenes, in other words, the photoprocess and the subsequent thermal reactions of azide photolysis in a polymeric substrate, are described by the following reactions (Scheme 4.6):[130]

127. M. Hepher and H. M. Wagner, British Patent No. 762,285 (1954); A. Reiser and H. M. Wagner, in *The Chemistry of the Azido Group*, S. Patai, Ed., p. 461, Wiley Interscience, New York (1971).
128. M. Hepher and H. M. Wagner, British Patent No. 762,285 (1954).
129. R. K. Agnihotri, D. L. Falcon, F. P. Hood, L. G. Lesoine, C. D. Needham, and J. A. Offenbach, "Structure and behavior of cyclized rubber photoresist," *Photogr. Sci. Eng.* **16**(6), 443 (1972).
130. A. Reiser, *Photoactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, p. 33 (1989).

$$RN_3 \xrightarrow{\ h\nu\ } {}^1RN + N_2 \qquad\qquad [4.17]$$

$$[4.18]$$

$$^1RN \longrightarrow {}^3RN \qquad\qquad [4.19]$$

$$[4.20]$$

$$[4.21]$$

$$[4.22]$$

Scheme 4.6 Reaction mechanism of the crosslinking reaction of cyclized rubber by photogenerated nitrenes.

The main reason for this chemistry according to Reiser[131] lies in the fact that nitrenes have a triplet ground state. The first step in this reaction mechanism (Reaction [4.16]) involves the photoinduced loss of nitrogen by the azido group, transforming the azido group into a (singlet) nitrene. This is the only photoreaction in the reaction mechanism. Readily, the singlet nitrene inserts into H–C bonds of the poly(*cis*-isoprene) rubber and forms, in a single step

131. ibid.