Silver Molecules and Photographic Sensitivity

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Abstract

Ag_2 molecules in silver halide crystals have three functions in the mechanisms of photographic sensitivity. (1) They introduce donor centers which are dissociated into Ag_o^+ ions and electrons by the annihilation of photons or of excitons of polarization waves and excited dye molecules. (2) They provide latent image growth nucleus precursors at which Ag_o^+ ions and conduction electrons combine to give Ag_3 clusters. These adsorb a silver ion from an adjacent site to give Ag_4^+ latent image growth nuclei. Positive holes are created by the annihilation of photons and excitons at these and larger Ag_n^+ acceptor centers. (3) The Ag_2 molecules then provide effective traps for positive holes giving Ag_2^+ centers which dissociate. The silver atoms released in both (1) and (3) have a lifetime of about 1 sec at room temperature before dissociation.

Introduction

The Ag_2 silver molecule was introduced in the theory of photographic sensitivity as the latent subimage speck by Katz[1,2] and Webb[3,4] in their analysis of the mechanism of reciprocity failure. The latent subimage as an intermediate stage in latent image formation had been studied by Berg and Burton[5-8] who concluded that it was converted into a stable latent image capable of rapidly initiating the reduction of a silver halide grain by one further photochemical event. In all this work, the first stage in the formation of a stable latent image was the combination of an Ag_o^+ interstitial silver ion with a conduction electron at a surface or internal site to give an Ag atom. The isolated Ag atom was unstable and after a certain lifetime, dissociated with thermal activation θ, into a conduction electron and an Ag_o^+ ion.

$$Ag + \theta \rightarrow Ag_o^+ + n^- \tag{1}$$
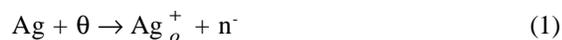
The activation energy for this thermal dissociation was determined by Webb from his study of the temperature dependence of high intensity reciprocity failure and found to be 0.69 eV.[9] This dissociation energy was confirmed by later calculations.[10] With a vibration period of 10^{-12} sec for the essentially ionic process, this gives a lifetime at room temperature for an Ag atom at the surface of an AgBr crystal

of about 1 sec.[11] For the formation of a more stable Ag_2 molecule or latent subimage speck, a second Ag atom had to be formed at the site within this period. These properties of Ag atoms and Ag_2 molecules were established before 1952 during the course of studies on the application of the Gurney-Mott theory to the interpretation of latent image phenomena.[12]

From the beginning of silver halide photography, it has been recognized that silver halide grains suspended in gelatin are first sensitized and then fogged by digestion.[13] In 1881, Eder[14] suggested that AgBr is reduced by digestion with gelatin and that the resulting traces of silver are responsible for the increase in sensitivity. In 1925 Sheppard[15,16] introduced the Ag_2S surface concentration speck and, twenty five years later, Lowe, Jones and Roberts[17] established the independent occurrence of reduction sensitization and the additivity of reduction and Ag_2S sensitization. When it was believed that a stable latent image was formed by the separation of three Ag atoms at a surface site and that isolated Ag atoms were mobile and had a lifetime of about 1 sec at a particular site, there could be nothing but the Ag_2 molecule, adsorbed on the surface or incorporated in the crystal, as the elementary product of reduction sensitization. This possibility was not introduced, however, in 1950.[17] The latent subimage speck was then believed to be an Ag_2 molecule which was converted to a stable latent image development center by one further photochemical event.[12]

Thin Sheet Crystals of Silver Bromide

Thin sheet AgBr crystals of high purity and perfection have vanishingly small photoconductivity and photosensitivity.[18] After a normal photographic exposure, they form neither a surface nor an internal latent image which can be developed in standard developers.[19,20]

These crystals were sensitized with very thin films of silver with an average surface atomic density of 10^{14} atoms per cm^2 deposited upon their surfaces from an atomic beam in highly evacuated apparatus.[18,21,22] On exposure, a surface latent image was formed which could be both chemically and physically developed. After the deposition of a thin film of silver with an average surface atomic density not greater than 10^{15} atoms per cm^2, the crystals were reduced even without previous exposure when they were immersed in the developer. It is difficult to imagine that any process could have occurred during exposure in films with an average density of 10^{14} Ag atoms per cm^2 other than the

photochemical aggregation of Ag atoms to form particles with the same dimensions as those in the films with an average density of not more than 10^{15} atoms per cm^2. [21]

The experimental work provided the first direct evidence for the instability and mobility of Ag atoms on the surfaces and within AgBr crystals.[22] The properties of thin sheet AgBr crystals sensitized by the deposition of 10^{14} Ag atoms per cm^2 as determined by treatment with solutions of KAu(SCN)$_2$ or of oxidizing agents such as K$_3$Fe(CN)$_6$[17] or dilute chromic acid solutions before and after exposure and after initial development, very closely matched those of reduction sensitized AgBr sheet crystals[22] and of emulsion grains with a latent subimage produced by a high intensity exposure. Matrix isolation work has shown that Ag$_2$ molecules and Ag atoms would have reached the surface from the atomic beam.[23,24] The Ag$_2$ molecules would remain at the site of impact. The Ag atoms would dissociate, diffuse into the crystal as Ag$_o^+$ ions and electrons, and separate along the dislocation segments of sub-boundaries. The impact of two Ag$_2$ molecules at a site would produce an Ag$_4$ cluster and after adsorption of an Ag$^+$ ion an Ag$_5^+$ fog center.[20] The sensitized thin sheet crystal system thus gave a sound model for a reduction sensitized crystal of AgBr and provided the first direct experimental evidence to suggest that Ag$_2$ molecules are probably produced by reduction sensitization. The thin sheet crystals were sensitized with a low concentration of Ag$_2$O molecules together with Ag$_2$ molecules produced by their thermal decomposition.[18] Emulsion grains were similarly sensitized with Ag$_2$O molecules and Ag$_2$ molecules produced by their reduction in the gelatin medium.[20]

It seemed that the conclusion that the Ag$_2$ molecule was the elementary product of reduction sensitization drawn from the experimental work with the thin sheet crystal system could not be applied to reduction sensitized AgBr emulsion microcrystals at that time because Berg and Burton had concluded that the Ag$_2$ molecules of the latent subimage were unstable and dissociated after a lifetime of a day. Our conclusion appeared, however, to be soundly based. The uncertainty was resolved when the dissociation energy of the Ag$_2$ molecule was found to be 1.74 eV.[10,20]

During reduction sensitization, Ag$_2$ molecules are produced at the interface between the AgBr crystal and the aqueous medium. They are formed by the reduction of an Ag$_2$O molecule by a reducing molecule which has no oxidized form in reversible equilibrium with the reduced form.[20,22,25] This results in the formation of Ag$_2$ molecules which are incorporated in the crystals by overgrowth or formed on the final surface. Ag$_2$ molecules are also formed in the dry system by the reduction of Ag$_2$O molecules at the crystal interface by hydrogen.[20,26,27]

Silver Molecules as Electron Donor Centers

In a crystal with Ag$_2$ molecules as donor centers,[19,20] produced by a high intensity pre-exposure of an Ag$_2$S sensitized emulsion or by reduction sensitization, an effective latent image is formed by the photoaggregation of Ag atoms chemically equivalent to the Ag$_2$ molecules. There are two mechanisms for the primary process. As in the Herschel effect, Ag$_2$ molecules are dissociated by the absorption of infrared photons with a wavelength of about 800 nm (1,54 eV) with the production of conduction electrons and Ag$_2^+$ centers.[3,4,28-30]

$$Ag_2 + h\nu \rightarrow Ag_2^+ + n^- \qquad (2)$$
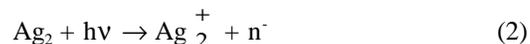
In a second mechanism, the Ag$_2$ donor centers are dissociated by an Auger process involving the annihilation of an exciton of a polarization wave near the surface or within the crystal or of an excited state of a sensitizing dye adsorbed on the surface.[29-35]

$$Ag_2 + E^* \rightarrow Ag_2^+ + n^- \qquad (3)$$
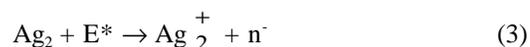
With both mechanisms, the Ag$_2^+$ center dissociates rapidly with the passage of a silver ion into an interstitial position and the formation of an Ag atom.

$$Ag_2^+ \rightarrow Ag + Ag_o^+ \qquad (4)$$

The Ag atom has a lifetime of about 1 sec at room temperature before thermal dissociation with the formation of a conduction electron and an Ag$_o^+$ ion.[10]

$$Ag + \theta \rightarrow Ag_o^+ + n^- \qquad (1)$$

The overall result of the optical excitation is thus the formation of two Ag$_o^+$ ions and two conduction electrons.[29]

$$Ag_2 + h\nu \text{ or } E^* \rightarrow Ag^+ + n^- + Ag^+ + n^- \qquad (5)$$
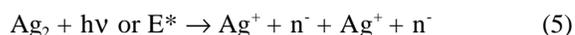
This is the first function of Ag$_2$ molecules in the photoaggregation process. These donor centers are photodissociated to provide the Ag$_o^+$ ions and conduction electrons which combine to form the initial clusters of Ag atoms of the latent image. The photodissociation mechanism was proposed for the first time in papers published in 1957.[11,29,32,33] It provides the primary process for the formation of clusters by the photoaggregation of the Ag atoms of a distribution of Ag$_2$ molecules at wavelengths longer then 400 nm.

Silver Molecules as Latent Image Growth Nucleus Precursors

Growth nuclei for these clusters are formed by the combination of Ag$_o^+$ ions and conduction electrons at Ag$_2$ latent image growth nucleus precursors to give Ag$_3$ clusters

which adsorb an Ag^+ ion from an adjacent lattice site to give an Ag_4^+ latent image growth nucleus. [20,29,34,36]

$$Ag_2 + n^- + Ag_o^+ \rightarrow Ag_3 \qquad (6)$$

$$Ag_3 + Ag_{SL} \rightarrow Ag_4^+ + Ag_{VL}^- \qquad (7)$$

$$Ag_{VL}^- + Ag_o^+ \rightarrow Ag_{SL} \qquad (8)$$

$$Ag_3 + Ag_o^+ \rightarrow Ag_4^+ \qquad (9)$$
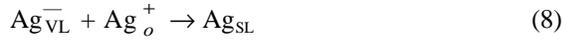
Ag_{SL} is an adjacent lattice site and Ag_{VL}^- an adjacent vacant lattice site. The Ag *ion* at a surface lattice site has a small fractional charge.[37] Its transfer to an interstitial position as an Ag_o^+ ion with a unit positive charge leaves a unit negative charge at the site.

This is the second function of Ag_2 molecules in the photoaggregation process. They provide latent image growth nucleus precursors.[29,31,34] The Ag_4^+ clusters grow by a process in which they trap conduction electrons and then adsorb Ag_o^+ ions thereby adding Ag atoms to the clusters.

$$Ag_n^+ + n^- \rightarrow Ag_n \qquad (10)$$

$$Ag_n + Ag_{SL} \rightarrow Ag_n^+ + 1 + Ag_{VL}^- \qquad (11)$$

$$Ag_{VL}^- + Ag_o^+ \rightarrow Ag_{SL} \qquad (12)$$

$$Ag_n + Ag_o^+ \rightarrow Ag_n^+ \qquad (13)$$
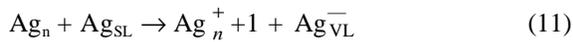
Ag_o^+ ions and electrons are thus effectively transferred from Ag_2 donor centres to Ag_n^+ acceptor centers. Ag_o^+ ions and conduction electrons created by the thermal dissociation of Ag atoms are similarly transferred. These are the elementary processes of the photoaggregation theory.[38]

Silver Molecules as Positive Hole Traps

With the formation of the Ag_4^+ acceptor centers, a second photoelectronic process becomes possible. Positive holes may be created by the transfer of electrons from the valence band to the Ag_4^+ acceptor centers following the absorption of infrared photons.[11,30]

$$Ag_4^+ + h\nu \rightarrow Ag_4 + p^+ \qquad (14)$$

At wavelengths longer than 400 nm, they may also be created by the annihilation of intrinsic or dye excitons at the Ag_4^+ acceptor centers by Auger processes.[20,30,38]

$$Ag_4^+ + E^* \rightarrow Ag_4 + p^+ \qquad (15)$$

The positive charge is restored to the Ag_4 cluster by the adsorption of an Ag^+ ion.

$$Ag_4 + Ag_{SL} \rightarrow Ag_5^+ + Ag_{VL}^- \qquad (16)$$

$$Ag_{VL}^- + Ag_o^+ \rightarrow Ag_{SL} \qquad (17)$$

$$Ag_4 + Ag_o^+ \rightarrow Ag_5^+ \qquad (18)$$
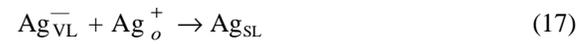
Creation of holes by the same two processes occurs at these and larger Ag_n^+ acceptor centers and is responsible for the Becquerel effect.[11] Positive holes may also be created by the annihilation of intrinsic or dye excitons at Ir^{3+} acceptor centers.[25,39]

The third function of Ag_2 molecules in the photoaggregation processes of latent image formation is now brought into play. An Ag_2 molecule provides a deep trap for a positive hole giving an Ag_2^+ center.[11,29,32]

$$Ag_2 + p^+ \rightarrow Ag_2^+ \qquad (19)$$

This center dissociates rapidly at room temperature giving an Ag_o^+ ion and an Ag atom.

$$Ag_2^+ \rightarrow Ag_o^+ + Ag \qquad (4)$$

The Ag atom then dissociates after a lifetime of about 1 sec giving an interstitial silver ion and a conduction electron.

$$Ag + \theta \rightarrow Ag_o^+ + n^- \qquad (1)$$

The overall result of the trapping of a hole by the Ag_2 molecule is therefore

$$Ag_2 + p^+ \rightarrow Ag_o^+ + n^- + Ag_o^+ \qquad (20)$$

An Ag_2^+ center is created at an Ag_2 molecule by the ejection of an electron by the absorption of an infrared photon, by the annihilation of an exciton of a polarization wave, or of a dye exciton, by the trapping of a positive hole, or by an oxidation process.[40,41] In all these cases, an Ag atom is liberated by the rapid decay of the center as in (4).

Discussion

Electron Donor Centers

Adsorbed or incorporated Ag_2 molecules, together with Ag_2O and Ag_2S donor centrer have no direct photoelectronic role in the direct photolysis theories of latent image formation of Hamilton[20,34,42] and Tani.[43-46] In the primary electronic process of these theories, the absorption of an intrinsic photon produces a pair of electronic carriers, a conduction electron and a positive hole. In the theory of spectral sensitization of Tani,[46] the absorption of a photon transfers an electron from the dye molecule to the conduction band leaving a "dye hole" which is then released to the full band as a positive hole, returning the dye molecule to its ground state.

These primary photoelectronic processes are not consistent with experimental observations with thin sheet crystals of AgBr of high purity and perfection. These crystals show neither photoconductivity nor photosensitivity, whether dye sensitized or not, at wavelengths beyond 400 nm (3.1 eV). For this, they have to be chemically sensitized by the adsorption of Ag_2, Ag_2O or Ag_2S donor centers and these centers are actively involved in the photochemical processes.[20]

Latent Image Growth Nucleus Precursors

In the Hamilton nucleation and growth theory, latent image formation begins with the formation of a thermally unstable Ag atom at a surface or internal site by the combination of a conduction electron with an Ag_o^+ ion. A stable Ag_2 molecule is formed by the occurrence of a second event at the site within the lifetime of the Ag atom. The uncharged Ag_n cluster then grows by a succession of electronic and ionic events in a strict Gurney-Mott sequence. Hamilton rejects any role of chemically produced Ag_2 molecules as latent image growth nucleus precursors and any concentration process in latent image formation in his nucleation and growth theory. This leads to the paradox of Hamilton and Baetzold[47,48] and the dilemma of Moisar and Granzer[49] which are resolved by the photoaggregation theory.[34]

Positive Hole Traps

Only the third role of Ag_2 molecules, that of providing effective traps for positive holes has been accepted by Hamilton and Tani. In the primary electronic stage of the direct photolysis theories, conduction electrons and positive holes are created in pairs by the absorption of intrinsic photons, and conduction electrons and dye holes are created by photon absorption by dye molecules. There was a problem for efficient latent image formation with the direct photolysis theories because the positive holes could be trapped by the uncharged latent image clusters of Ag atoms and cause regression. This problem was resolved and the increase in sensitivity on reduction sensitization understood with the introduction in 1957 of the mechanism for efficient hole trapping by Ag_2 molecules.[11,29,32]

Summary and Conclusions

Silver halide crystals of ultrahigh purity have an extremely low level of photoconductivity and photosensitivity. The first function of adsorbed or incorporated Ag_2 molecules is to provide donor centres which are dissociated by the annihilation of energy quanta to give two conduction electrons and two Ag_o^+ ions:[29]

$$Ag_2 + h\nu \rightarrow Ag_o^+ + n^- + Ag_o^+ + n^- \qquad (5)$$
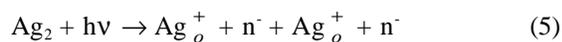
Dissociation occurs in stages represented by Equations (2) or (3), (4), and (1) and is responsible for photoconductivity. In the wavelength range between 400 and 720 nm, dissociation by the annihilation of photons near the surface or of excitons of polarization waves and excited dye molecules by Auger processes is the most important process for the photocatalyzed aggregation of a distribution of Ag_2 molecules produced by reduction sensitization.

The second function of Ag_2 molecules is to provide latent image growth nucleus precursors at which conduction electrons and Ag_o^+ ions, equivalent to those released by the processes of Equations (4) and (1), can efficiently combine to form Ag_3 clusters which adsorb an Ag^+ ion from an adjacent site as in Equations (6) to (9) to give Ag_4^+ latent image growth nuclei. These and larger Ag_n^+ clusters formed by growth as in Equations (10) - (13) introduce electron acceptor centers with unoccupied levels in the energy gap.[20]

In crystals which were previously without electron acceptor centers, the third function of Ag_2 molecules is now brought into play. Positive holes are created by the annihilation of energy quanta at the $Ag_n^\top$ acceptor centers as in Equations (14) or (15). They are deeply trapped by the Ag_2 molecules as in Equation (19) to give $Ag_2^\top$ centers which dissociate in the same two stages represented by Equations (4) and (1) as in the operation of the first function of the Ag_2 donor centers. The overall reaction is represented by:

$$Ag_2 + p^+ \rightarrow Ag_o^+ + n^- + Ag_o^+ \qquad (20)$$

This leads to a second photoaggregation process for a distribution of Ag_2 molecules.[20,35,38] All three functions of Ag_2 molecules are thus operative in the processes of the photoaggregation theory.

The adhesion of Ag_2 molecules to the surface of an AgBr crystal has to be discussed. These molecules are weakly adsorbed to a thin sheet crystal of AgBr. Thin sensitizing and fogging films of silver produced by vacuum deposition or reduction sensitization may be readily stripped from the surfaces of the crystals. Sensitizing films of Ag_2S cannot be stripped and it is evident that Ag_2S is strongly adsorbed. Neither can a thin film of silver produced on an Ag_2S film by vacuum deposition or reduction sensitization be stripped. The thin film of Ag_2S provides an interfacial layer between the silver film and the crystal ensuring the strong adhesion of the silver film. In the photographic system, the Ag_2 molecules which are most effective as surface latent image growth nucleus precursors are adsorbed around the edges of small monolayer islands of sulfide molecules.[20,34,41] Ag_2 molecules are stabilized against environmental rections by adsorption to clusters of Ag_2S molecules.

A density of Ag_2O and Ag_2 molecules, sufficient for the nucleation and initial growth of the surface latent image in a

negative emulsion, is incorporated in AgBr microcrystals and adsorbed on the final surfaces during growth and digestion in a mildly reducing natural gelatin medium at a pH > 7. Higher densities are introduced by growth and digestion in the presence of reducing agents such as ascorbic acid.[25] These donor centers are removed with loss of sensitivity by treating the emulsion, before or after coating, with a dilute chromic acid solution which does not attack Ag_2S. AgBr microcrystals grown in a gelatin medium at a pH < 5.5 under mild oxidizing conditions have a very low sensitivity. The need for a minimum density of Ag_2 molecules in the models for the theory of the processes of latent image formation has not been fully appreciated. This arises because it is not recognized that Ag_2 molecules are usually present within and on emulsion grains. It is difficult to completely desensitize AgBr microcrystals grown, in a gelatin medium, with bromine and other oxidizing agents, to remove excess oxidizing agents without resensitization, and to maintain the desensitized state until exposure and development.[20]

In the direct photolysis theories of latent image formation of Hamilton and Tani, the absorption of a quantum by the silver halide crystal or by an adsorbed dye molecule results in the creation of an electron and a positive hole in the primary electronic process:

$$AgBr + h\nu \rightarrow AgBr + n^- + p^+ \qquad (21)$$
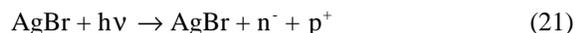
Ag_2 molecules do not participate in the primary process in reduction sensitized crystals according to these theories so that the first function of Ag_2 molecules is inoperative. The second role as a latent image growth nucleus precursor has been rejected.[34,48] The third role, that of acting as an effective positive hole trap has been accepted by Hamilton and his coworkers and by Tani with emphasis on the "Lowe reaction", the "Lowe electron" and the "extra electron" Other essential features of the photoaggregation theory (as, for example, the concept of the Ag_4^+ positively charged latent image growth nucleus) have been rejected as untenable by Hamilton.[36,42,50,51]

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