On the Role of Sulfide Molecules in Photographic Sensitivity

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Models and mechanisms which have been proposed for silver sulfide and silver–gold sulfide sensitization are reviewed. These sulfides are not involved in the primary photochemical processes of the direct photolysis theories of Sheppard, Gurney and Mott, Hamilton, Kanzaki and Tadakuma, and Tani. In these theories, photoelectrons and positive holes are created in pairs and the role of sulfide sensitization in trapping photoelectrons is emphasized. With a chemically sensitized silver halide emulsion grain, there are, however, a large number of equivalent sites at which electron trapping can occur and the theories provide no process for the efficient formation of a development center by the separation of a small number of silver and gold atoms at one particular site. According to the photoaggregation theory, chemical sensitization results in the formation of small monolayer islands of Ag_2S and (Ag,Au)S molecules at surface sites with Ag_2 molecules adsorbed around their edges. These sensitizing molecules are dissociated by the annihilation of energy quanta with creation of photoelectrons and release of Ag_0^+ or Au_0^+ interstitial ions. A development center is formed at an Ag_2 latent image growth nucleus precursor by two effective events. In the first event, a photoelectron and interstitial ion combine with an Ag_2 molecule to form a Ag_3 or $AuAg_2$ molecule that adsorbs a Ag^+ ion to give an Ag_4^+ or $AuAg_3^+$ latent image growth nucleus. In the second event, this positively charged nucleus attracts and traps a photoelectron and the positive charge is restored by the effective adsorption of an Ag_0^+ ion giving an Ag_5^+ or $AuAg_4^+$ development center of minimum size, adsorbed to a sulfide monolayer island. This center grows by the repetition of these electronic and ionic events and this provides an efficient concentration process.

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Introduction

Sensitive gelatin silver bromide emulsions were first made by Wortley[1] in 1876 and by Bennett[2] in 1878. In subsequent work it was found that when gelled, washed, and remelted emulsions were digested, there was a progressive change from increased sensitivity to fog. Eder reported in 1881 that both the sensitization and the fog were removed by treating gelatin silver bromide plates with solutions of potassium ferricyanide containing potassium bromide or with dilute solutions of chromic acid also containing potassium bromide.[3] He proposed that the sensitization resulted from the formation of silver by the reducing action of gelatin on the silver bromide and that fog arose when the optimum amount of silver was exceeded. The effect of oxidizing agents on chemical sensitization and the latent image was studied by Lüppo-Cramer[4] and many others over the next 45 years and silver sensitization came to be accepted.

A significant observation was made by Clark[5] in 1923. He found that a fraction of the chemical sensitization in an unexposed silver bromide plate was attacked only at a very slow rate by a dilute solution of chromic acid. The resistant sensitization was rapidly removed by this treatment after exposure. This suggested that two types of sensitization resulted from digestion, one of which, probably a form of silver, was rapidly oxidized by a dilute solution of chromic acid and the other of which was resistant before exposure.

In a major advance in 1925, Sheppard and his coworkers discovered that (what would prove to be) the oxidation resistant form appeared during the digestion of gelatin silver bromide emulsions with sulfur compounds having a labile sulfur atom such as allyl thiourea or sodium thiosulfate.[6,7] He concluded that specks of silver sulfide were formed on the surfaces of the crystals and introduced his concentration speck theory of latent image formation.[8–10] He believed that the silver sulfide specks were photochemically inert during exposure and served only to concentrate

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liberated silver atoms. The significance of Clark's observation was not appreciated at this time.[11]

The next important advance was made by Koslowsky in 1936.[12,13] He found that sensitivity was increased when complexed salts of monovalent gold were present during silver sulfide sensitization. Complexed thiocyanates such as $KAu(SCN)_2$ were particularly effective. The work of Faelens and his coworkers showed that (Ag,Au)S molecules were probably formed in association with the Ag_2S molecules.[14–16] Bourdon and Bonnerot,[17,18] and Spracklen[19] then showed that latent image specks with silver and gold atoms were formed during exposure with these silver–gold sulfide-sensitized emulsions.

Since 1938 the Gurney–Mott theory has been applied to the formation of the latent image in silver sulfide and silver–gold sulfide-sensitized emulsions.[20] According to this theory, the uncharged sulfide specks provide the deepest traps for electrons in silver halide emulsion grains. The negatively charged speck attracts an interstitial silver ion and forms a silver atom and the latent image grows by a succession of these processes.

The purpose of this paper is to discuss properties of sulfide sensitization and some of the models and mechanisms proposed for its function in latent image formation. Adsorbed Ag_2S and (Ag,Au)S molecules have three main roles: (1) they provide donor centers which are dissociated by the annihilation of photons or of excitons of polarization waves and excited dye molecules, giving photoelectrons and Ag_0^+ or Au_0^+ interstitial ions; (2) they form small two-dimensional islands, strongly adsorbed to the surface of a silver halide crystal, which themselves adsorb Ag atoms, Ag_2 molecules, and larger latent image clusters; and (3) they provide trapping centers for positive holes giving positively charged Ag_2S^+ or $(Ag,Au)S^+$ centers. These rapidly dissociate releasing Ag_0^+ or Au_0^+ ions which may combine with photo electrons at sites at the surface and along internal dislocation lines.

Sensitization of Silver Bromide Crystals with Ag_2S and (Ag,Au)S

The interface between a silver bromide crystal and the medium is the site of chemical sensitization. There are many undefined variables at this interface in photographic emulsions with silver bromide microcrystals suspended in gelatin.

For this reason, thin sheet crystals of silver bromide with near {001} surfaces were used to study sulfur sensitization in the absence of gelatin.[21,22] Crystals of high purity are insensitive and form neither a surface nor internal developable latent image on exposure. They may be sensitized with Ag_2O and with Ag_2 molecules derived from Ag_2O and then form a surface latent image, which solarizes rapidly, and a subsurface internal latent image. As prepared, the crystals have a high density of dislocations terminating at the surfaces. The sites of termination are sites of enhanced surface reactivity at which chemical sensitization and chemical development tend to be initiated. An internal latent image and particles of photolytic silver form along the dislocation lines. The dislocations were reduced in density and eliminated within large subgrains by recrystallization and the crystals then had a low level of sensitivity. Lightly annealed crystals with a high density of surface-terminating dislocations were used for most of the work.[23]

The crystals were sensitized with an adsorbed layer of Ag_2O by washing with water at pH = 8. They then had low sensitivity for the formation of a surface latent image which rapidly solarized. This was converted to an adsorbed sensitizing layer of Ag_2S, which resisted oxidation with a dilute chromic acid solution, by treatment with a dilute solution of $Na_2S_2O_3$. The most reliable method for Ag_2S sensitization involved two stages following the methods of James and Vanselow[24,25] and of Dickinson.[26,27] In the first stage, an adsorbed monolayer of allyl thiourea or of thiosulfate ions was formed by immersion in a dilute solution of the reagent. The crystal was then immersed in a buffer at pH = 8 and 40°C and washed and dried. This meth-od gave uniform fog-free Ag_2S sensitization. The crystals were sensitized[21,22] with Ag_2S and (Ag,Au)S by immersion in a solution of 10 to 20 mg liter^{-1} of $Na_3Au(S_2O_3)_2$ at 40°C. Uniform fog-free sensitization occurred and the maximum was reached very rapidly. The overall reaction is represented by the following equation:

$$Na_3Au(S_2O_3)_2 + 3AgBr + 2OH^- \rightarrow Ag_2S, (Ag,Au)S + 3NaBr + 2HSO_4^-.$$

Surface singularities, surface terraces, and sites of termination of dislocations were locally sensitized with Ag_2S using the two-stage method and brief immersion in dilute solutions of allyl thiourea or $Na_2S_2O_3$.

The same observations were made when the thin sheet crystals were sensitized in the presence of one-half percent inert gelatin solutions.[21,22] There have been many sensitometric studies of sulfur and sulfur-plus-gold sensitization of gelatin silver halide emulsions by Carroll and Hubbard,[28] Dickinson,[26,27] Faelens,[14–16] Moisar,[29] Cash,[30–32] Corbin et al.,[33] Kanzaki and Tadakuma,[34,35] Tani,[36–38] and others. They show that sensitization with Ag_2S appears to occur in at least two stages. In the first, the sulfur sensitizer is adsorbed and reacted to give a distribution of adsorbed Ag_2S molecules and a lower level of sensitization. In the second, which does not occur in the presence of azaindene stabilizers,[33] sensitivity increases to a maximum through aggregation with the possible formation of dimers and monolayer islands[26] and then falls with the onset of fog. Maximum sensitization is reached more rapidly with sulfur-plus-gold sensitization. In this article, it will be assumed that the adsorbed Ag_2S or (Ag,Au)S covalent molecule is the effective photochemical unit of sulfur sensitization whatever the state of two-dimensional aggregation.

Properties of Ag_2S and (Ag,Au)S Sensitized Crystals

When the thin sheet crystal methods were used, the formation of discrete specks of the sulfides was never observed with the optical microscope or with the cardioid ultramicroscope at limiting resolutions with optimum illumination. The sensitization was produced by reactions involving an adsorbed monolayer of the reagents. With the small enthalpy of formation and large heat of adsorption of Ag_2S and (Ag,Au)S, the free energy should be lower in the adsorbed state and small monolayer islands should be formed rather than specks or three-dimensional clusters. The removal of Ag_2S fog by treatment with a complex salt of monovalent gold depends on this property.[39] At 25°C, the ionic solubility product of Ag_2S, $K = [Ag^+]^2 [S^{2-}]$ is 6.31×10^{-50} mol^3 liter^{-3} (Ref. 40). At 25°C and pH 7, the solubility of Ag_2S, mainly in the form of complex $[Ag(SH)_2]^-$ ions, is 5.78×10^{-15} mol liter^{-1} (Refs. 41 and 42). There will thus be a kinetic mechanism for the dissolution and surface adsorption of molecules from small specks of sulfides.

The reaction of an adsorbed $Au(S_2O_3)_2^{3-}$ ion may give an Ag_2S,(Ag,Au)S dimer. The complex thiosulfate ion, $Ag(S_2O_3)_2^{3-}$ is present[43] in solutions in contact with AgBr. Its adsorption and reaction could also give Ag_2S dimers.[44] These could provide nuclei for the growth of small monolayer islands.

Sulfide-sensitized thin sheet crystals washed at pH 7.5 and pAg 6.5 before drying had a low level of low intensity sensitivity. They formed a developable latent image when exposed to a high-intensity short-duration argon flash tube or to a high-pressure mercury vapor lamp.[21,22]

Ag_2S and (Ag,Au)S Molecules as Donor Centers

High-purity AgBr crystals are insensitive in the visible wavelength range between 400 and 720 nm. They are sensitized[45] by the adsorption of Ag_2S and (Ag,Au)S molecules which extends the optical absorption to 800 to 900 nm. The first role of these sulfide sensitizers is to introduce occupied levels in the energy gap so that they act as electron donor centers.[46,47] In the primary photochemical process, they are dissociated with the ejection of electrons by the annihilation of photons or of the excitons of polarization waves or excited dye molecules. The resulting Ag_2S^+ or $(Ag,Au)S^+$ centers then rapidly dissociate with liberation of Ag_0^+ or Au_0^+ ions. Photoelectrons and these interstitial ions are thus made available for the processes of latent image formation.[48,49]

The sulfide molecules do not have an initial chemically inert role during exposure as in the theories of latent image formation of Sheppard, Gurney and Mott, Hamilton, and Tani. Their photochemical involvement was demonstrated with thin sheet crystals sensitized with Ag_2S or with Ag_2S and (Ag,Au)S molecules.[50] When these were exposed through a narrow slit and developed, a black image of the slit appeared, the contrast of which increased with the duration of exposure. When a similarly exposed crystal was treated with a dilute solution of chromic acid, washed, dried, uniformly re-exposed and developed, a reversed image of the slit appeared against a black background, the contrast of which again increased with the duration of the first exposure. The chromic acid solution did not attack unexposed sulfide sensitization and the reversal was not influenced by the presence of non-reducing halogen acceptors during the first slit exposure. These observations confirmed the work of Clark who showed in 1923 that oxidation-resistant chemical sensitization was removed by treatment with a dilute chromic acid solution after exposure.[5]

Further evidence for the active role of sulfide molecules in the photochemical process is provided by the observations of the incorporation of gold atoms in latent image specks during exposure provided by the work of Bourdon and Bonnerot[17,18] and Spracklen.[19]

Adhesion of Ag_2S and (Ag,Au)S Molecules to the Surface of AgBr Crystals

Ag_2S and (Ag,Au)S molecules are strongly adsorbed and cannot be stripped from the surfaces of thin sheet AgBr crystals. Thin films of silver, vacuum deposited from an atomic beam or produced by reduction sensitization can be readily stripped from the surfaces. The Ag atoms of the vacuum-deposited films are mobile. They dissociate into Ag_0^+ ions and electrons, diffuse, and combine to form a distribution of Ag_2 molecules on the surface and on the internal dislocation lines. This provides a model for reduction sensitization.[51]

These thin films of silver, formed on sulfide-sensitized crystals, cannot be stripped from the surfaces. The silver is strongly adsorbed to the sulfide films which are themselves strongly adsorbed to the AgBr crystal. A thin film of Ag_2S or Ag_2S, (Ag,Au)S molecules prevents the diffusion of vacuum-deposited Ag atoms from the surface to internal sites.[51] This is the second role of sulfide sensitization in photographic sensitivity. It promotes the adhesion of Ag atoms, sensitizing Ag_2 molecules and larger clusters to the surfaces of AgBr crystals.

Sensitization of AgBr Crystals with Ag_2S, (Ag,Au)S, and Ag_2 Molecules

The sensitivity of sulfide-sensitized thin sheet AgBr crystals, particularly low-intensity sensitivity, is increased by the deposition of thin films of silver from an atomic beam. The increased sensitivity is eliminated by treatment with a dilute solution of chromic acid which leaves the sulfide sensitization unaffected.

The same behavior is observed when Ag_2S-sensitized sheet crystals are immersed in a one-half percent gelatin solution at 40°C and pH 8. The initial increase in sensitivity is followed by the appearance of fog. Both are removed by treatment with a dilute solution of chromic acid. Under the conditions of reduction sensitization with silver bromide emulsion grains, low concentrations of Ag_2O molecules are adsorbed around the edges of the sulfide monolayer islands. These are reduced to Ag_2 molecules, adsorbed and stabilized at shallow positive potential wells at these edges, by reducing groups associated with gelatin molecules or by added reducing agents.[47] The resulting Ag_2 *sensitization centers* are further stabilized by the preferential adsorption at the sulfide surface of molecules of azaindene and heterocyclic mercapto compounds, the accompanying adsorption of which to the silver halide surface reduces the concentration of Ag_0^+ ions and increases the sensitivity.

Reduction sensitization of gelatin AgBr emulsions following Ag_2S sensitization was demon strated in 1950 by Lowe, Jones, and Roberts who used a solution of potassium ferricyanide to oxidize the silver without attacking the silver sulfide.[52] With sulfur-plus-gold sensitized emulsions, the complexed aurous ions must be exhausted by incorporation in (Ag,Au)S molecules before the initiation of reduction sensitization to avoid unacceptable fog levels.[53]

Formation of Latent Image Acceptor and Development Centers

The adsorbed Ag_2 molecules introduce donor centers and latent image growth nucleus precursors. They allow Ag_4^+ and $AuAg_3^+$ latent image growth nuclei adsorbed to sulfide monolayer islands to be formed by one effective photochemical event. These are transformed into Ag_5^+ and $AuAg_4^+$ development centers of minimum size by a second effective event. These positively charged clusters strongly adsorbed to the sulfide islands attract conduction electrons in the associated Coulomb fields and provide deep traps for them. They are responsible for the site-directing properties attributed to products of sulfide sensitization.[29,47,49]

Formation and Trapping of Positive Holes

Positive holes are created by the annihilation of photons, excitons of polarization waves, or of excited dye molecules at Ag_n^+ or $AuAg_n^+$ latent image acceptor centers. They may also be generated by the same processes at polyvalent cationic acceptor centers.[47,49,54] The third role of Ag_2S and (Ag,Au)S donor centers, which is to trap positive holes, is now brought into play. The resulting positively charged Ag_2S^+ and $(Ag,Au)S^+$ centers dissociate rapidly with creation of Ag_0^+ or Au_0^+ ions and the Au_0^+ ions may be incorporated in latent image centers. The positive charge is restored to the Ag_n or $AuAg_n$ centers by the effective adsorption of an Ag_0^+ ion and the space charge is eliminated by the drift of an Ag_0^+ ion. It has to be emphasized that adsorbed Ag_2 molecules trap positive holes with higher probability than Ag_2S or (Ag,Au)S molecules so this third role of sulfide molecules may not have a high efficiency.[50]

Direct Photolysis Theories of Latent Image Formation in Sulfur-Sensitized AgBr Crystals

The Sheppard and Gurney–Mott Concentration Speck Theories. It is difficult to reconcile the conflicting hypotheses that provide the basis for the theories proposed for sulfide sensitivity centers and their role in the processes of latent image formation. According to Sheppard, a chemically inert silver sulfide speck provides a concentration center for Ag atoms liberated together with bromine molecules during exposure. A small number of sensitizing specks is formed on an AgBr emulsion grain.[6–10]

Gurney and Mott presented a theory of the concentration process in 1938. They proposed that the sulfide speck provides a deep trap for a photoelectron charging it negatively. The speck then attracts an Ag_0^+ ion in the Coulomb field which combines with the electron to form an Ag atom. Development centers are produced by a succession of these events.[20,55]

In the Sheppard and Gurney–Mott theories, it is assumed that a bromine atom, equivalent to the silver atom, is formed at a surface site. After a second event, a bromine molecule is produced which escapes from the surface. In 1956, Mitchell proposed that the positive hole, which is liberated with the electron in the primary electronic process of these theories, would be trapped by a sensitizing Ag_2 or Ag_2S molecule and that the resulting Ag_2^+ or Ag_2S^+ center would rapidly dissociate with release of an Ag_0^+ ion.[56] This would prevent recombination with the electron. According to Mitchell, deep traps for electrons are provided not by uncharged chemically-produced Ag_2S specks but by photochemically-produced, positively charged Ag_4^+, $AuAg_3^+$, and larger latent image acceptor centers.[57]

The Hamilton Nucleation and Growth Theory. Soon after this, Hamilton abandoned the sulfide concentration speck and introduced his nucleation and growth theory.[58–60] He used an ideal ionic model for an AgBr crystal in which the Ag^+ and Br^- ions carry unit positive and negative charges and ions on kink sites along terraces on {001} surfaces, effective half-unit charges. In this direct photolysis theory, the annihilation of a photon or exciton in the crystal creates a photoelectron and a positive hole. These are attracted to and trapped by Ag^+ and Br^- ions on kink sites forming Ag atoms and Br atoms and leaving the kink sites with half-unit charges of opposite sign. The traps are then reset by the displacement of Ag_0^+ ions to and from these sites in the resulting Coulomb fields. The atomic species are unstable and dissociate after a certain lifetime. The nucleation and growth process depends on a statistical sequence of successive reversible cycles of formation, dissociation, and recombination of atomic species in which both electrons and positive holes participate. In this theory the uncharged clusters of Ag atoms of the latent image are formed by successive events at a large number of equivalent sites and bromine molecules are formed and escape from the surface. Sulfide sensitization has an inert primary photochemical role and is believed only to cause a small increase in the depth of shallow traps provided by adjacent Ag^+ ions on kink sites. There is no concentration process and the latent image has a distribution of particle sizes, the largest of which are able to initiate development.

The Ionic Model for Sulfide Sensitivity Centers. Recently in their comprehensive model for sulfur sensitization, Kanzaki and Tadakuma,[34,35] and Tani[36–38] have proposed an ionic model for sensitizing Ag_2S and (Ag,Au)S molecules. They believe that a sulfide dimer is formed in which two S^{2-} ions occupy a pair of adjacent surface anionic lattice sites. The excess negative charges are compensated by two Ag_0^+ ions or by an Ag_0^+ ion and an Au_0^+ ion on adjacent nearest subsurface interstitial sites. It is further suggested that the two interstitial ions introduce a bonding orbital that provides a deep trap for a photoelectron. Trapping results in the creation of a center with the symmetry of an Ag_2^+ or $(Au,Ag)^+$ molecule. The dimer then has a unit negative charge. An Ag_0^+ ion is attracted in the Coulomb field giving an uncharged latent image center with three interstitial ions on neighboring sites and one trapped electron. The latent image grows by a succession of these electronic and ionic Gurney–Mott processes.[36–38] The $(S^{2-} - Ag_0^+)$ monomer provides a hole trap but not an electron trap.

Stability of ionic models is a problem for silver sulfide or silver–gold sulfide molecules adsorbed at the surface of an ionic AgBr crystal. The electron affinity of an S atom is[61] 2.08 eV. The S^- ion has a negative affinity for a second electron and the S^{2-} ion is not stable in the gas phase.[62–65] In an ionic solid, a large positive Madelung potential at the anionic site is needed to stabilize the S^{2-} state as in the CaS, SrS, and BaS alkaline earth sulfides. With the Born–Mayer ionic model, Mayer and Maltbie found a mean value of -6 ± 2 eV for the electron affinity for the second electron of S^{2-} in the alkaline earth sulfides.[62] The ionization potential of Ag is 7.57 eV and of Au is[66] 9.22 eV. With these values for the electron affinity and ionization potentials, it seems unlikely that an ionic model with S^{2-} ions and adjacent subsurface Ag_0^+ and Au_0^+ interstitial ions could be valid for Ag_2S or (Ag,Au)S at the surface of an ideal ionic AgBr crystal. If this model represented the state of Ag_2S or (Ag,Au)S molecules adsorbed at the surface of an AgBr crystal, it would be surprising if they were not rapidly oxidized by a dilute chromic acid solution whereas these molecules resist oxidation before exposure.

It is evident that these direct photolysis theories have not yet provided one accepted mechanism for the role of sulfur sensitization in latent image formation that accounts for the formation of very few development centers on an exposed silver halide emulsion grain.

The Photoaggregation Theory

In this theory, the AgBr crystal has partial covalent bonding with fractional ionic charges. Because of reduced Madelung potentials, these are smaller at the surface than in the interior.[67] Covalent Ag_2S and (Ag,Au)S molecules are initially adsorbed at surface kink and terrace sites and provide nuclei for the formation of small discrete monolayer islands of sulfide molecules. After sulfide sensitization, Ag_2 molecules are formed by the reduction of Ag_2O molecules and adsorbed at shallow positive potential wells around the edges of the sulfide islands.

The Gurney–Mott, Hamilton, and Tani theories are all based on a primary photoelectronic process in which the absorption of energy by the AgBr grain produces an independently diffusing electron and positive hole. In the Hamilton theory, the holes are needed for the initial stage of the nucleation and growth mechanism and the sensitizing Ag_2, Ag_2S, or (Ag,Au)S molecules have no primary role. This is not consistent with the observations that AgBr crystals of high purity have negligible photoconductivity and no sensitivity with normal photographic exposures in the visible wavelength range between 400 and 720 nm. For both photoconductivity and photosensitivity, the crystals have to be sensitized with electron donor centers which are involved in the primary photoelectronic process. These include Ag_2, Ag_2O, Ag_2S, and (Ag,Au)S molecules which are photodissociated by energy quanta within this wavelength range.[47,49]

In the Mitchell photoaggregation theory, the latent image is formed, not by the primary photolysis of the AgBr, but by the photoaggregation of Ag or Au atoms chemically equivalent to the Ag_2, Ag_2O, Ag_2S, and (Ag,Au)S donor center products of sensitization. These molecules are photodissociated by smaller energy quanta than are required for the formation of Ag and Br atoms from AgBr. They are dissociated in the primary process through the annihilation by Auger processes of the excitons of polarization waves or excited dye molecules with the creation of photoelectrons and of Ag_0^+ or Au_0^+ ions.[48,49,54] In the absence of polyvalent cationic acceptor centers, positive holes are not created in the primary process:

$$\begin{gathered}Ag_2 + h\nu \text{ or } E^* \rightarrow Ag_2^+ + n^- \rightarrow Ag + Ag_0^+ + n^- \\ \rightarrow Ag^+ + n^- + Ag^+ + n^-, \\ Ag_2S + h\nu \text{ or } E^* \rightarrow Ag_2S^+ + n^- \rightarrow AgS + Ag_0^+ + n^-, \\ (Ag, Au)S + h\nu \text{ or } E^* \rightarrow (Ag, Au)S^+ + n^- \rightarrow AgS + Au_0^+ + n^-.\end{gathered}$$

A latent image center is produced by the photoaggregation of Ag and Au atoms equivalent to those of the donor centers. Sites within and around the edges of sulfide monolayer islands provide shallow positive potential wells for photoelectrons which are ineffective for trapping at room temperature. An Ag or Au atom is formed when an electron and an Ag_0^+ or Au_0^+ ion approach the well together, with the electron cloud screening the mutual repulsion, as with the bonding orbital of the H_2^+ molecule ion.[49] The interstitial ion is attracted to the well and combines with the electron to give an Ag or Au atom on the surface. The Ag atoms dissociate again after a lifetime of about 1 s whereas the Au atoms are stable. These are loss processes because there is a large number of shallow traps and the probability for the occurrence of a second event at the same site is extremely small.

The photoelectrons are efficiently trapped at shallow positive potential wells around the edges of sulfide monolayer islands associated with adsorbed Ag_2 molecules that introduce latent image growth nucleus precursors. They are strongly adsorbed to the sulfide monolayer islands which are strongly adsorbed to the AgBr surface. In the first effective event, a latent image growth nucleus is formed from an Ag_2 molecule as an Ag_4^+ or $AuAg_3^+$ center by the trapping process just discussed followed by the adsorption of an Ag_0^+ ion.[49]

$$\begin{gathered}Ag_2 + n^- + Ag_0^+ \rightarrow Ag_3 \qquad Ag_3 + Ag_0^+ \rightarrow Ag_4^+ \\ Ag_2 + n^- + Au_0^+ \rightarrow AuAg_2 \quad AuAg_2 + Ag_0^+ \rightarrow AuAg_3^+.\end{gathered}$$

For the following second effective event, this center provides a Coulomb field in which a conduction electron is attracted and trapped, the positive charge being restored by the adsorption of an Ag_0^+ ion with the formation of an Ag_5^+ or $AuAg_4^+$ development center of minimum size:

$$Ag_4^+ + n^- + Ag_0^+ \rightarrow Ag_5^+ \qquad AuAg_3^+ + n^- + Ag_0^+ \rightarrow AuAg_4^+.$$

Space charges are eliminated by the displacement of Ag_o^+ ions. The adsorbed positively charged centers are responsible for the apparent deep trapping of electrons by products of sulfur sensitization. After trapping an electron, the positive charge is restored and the trap reset by the adsorption of an Ag_0^+ ion. The theory provides an efficient concentration process for the further growth of the first surface development center. A photoelectron is now trapped by this surface center with higher probability than by a shallow surface or internal trap and the efficiency for surface latent image formation is increased. The quantitative theory of the action of the positively charged concentration center has been presented in a number of papers.[39,46,68,69]

The Concentration Process in Latent Image Formation

Tani has recognized the need for an effective concentration process in his recent publication on photographic sensitivity:

> "Thus, one latent image center must be formed on a grain in the presence of a large number of sensitization centers acting as electron traps. Thus, once the nucleation of an image center is achieved, only the growth of the image center should proceed, preventing the occurrence of further nucleation. Although these sensitization centers acting as electron traps are necessary for nucleation of the formation of an image center, they tend to disturb the growth of an image center, since they further enhance nucleation by decreasing the mobility and diffusion length of photoelectrons, which should reach the growing image centers. It is therefore important to look for the optimum condition for electron trapping of these sensitization centers to meet the demand for high efficiency in latent image formation."[37]

The model of the comprehensive theory for sulfur sensitization does not satisfy these requirements.[34–38] With this model, there are a large number (2800/μm^2, Ref. 37, p. 232) of sensitizing sulfide dimers which provide deep electron traps on the surface of an emulsion grain and there is no mechanism for the selective successive trapping of electrons at one of them. A dispersed latent image must be produced.

A model that does satisfy the requirements was first proposed in the 1950s and refined in subsequent publications.[51,56,57] It is consistent with fundamental physical principles and has been incorporated in the photoaggregation theory. The problem is to provide a mechanism for the efficient trapping of liberated photoelectrons at one site on the surface of a silver halide emulsion grain.[39,46,68,69]

A photoelectron at its instant of creation has maximum free energy and minimum entropy. It diffuses away from its site of creation by a constrained radial three-dimensional random walk diffusion process. As the spherical volume accessible to the electron increases, the entropy increases and the free energy decreases. At any time, the electron may be located anywhere within a spherical volume with a radius equal to the diffusion distance but the probability for finding it within any particular small element of this volume is extremely small. The entropy increases and the free energy decreases with increasing diffusion radius until the diffusion range of the electron is reached at the end of its lifetime.[68,69]

The entropy would be decreased by the localization of the electron within a small volume, as in the Gurney–Mott trapping process with an uncharged sulfide speck and with this the free energy would be increased. With random walk diffusion, there is a very small probability for the localization of the electron at any particular site and a negligible probability for the occurrence of successive events at the same site when there are many equivalent sites.

The localization of the photoelectron at a particular site requires a process that will decrease the potential energy term of the free energy as the electron approaches the site. For this to occur, the site must carry a positive charge with an associated Coulomb field. The drift of the electron to the site in the Coulomb field then further reduces the free energy of the diffusing electron. In these circumstances, the diffusion force and the Coulomb force are additively superimposed and the electron drifts toward the positively charged site and is trapped.[68,69] The occurrence of successive events at a particular site with any reasonable probability requires that the site carry a positive charge and that the positive charge is restored after the trapping of the electron. These are essential elements of an efficient concentration process when there is initially three-dimensional random walk displacement of photoelectrons.

A microcrystal of a high-speed negative emulsion may have many active surface sites including sites of termination of dislocations at which products of chemical sensitization are formed. There may also be a high surface density of small monolayer islands of $\mathrm{Ag_2S}$ and (Ag,Au)S molecules associated with these sites and with other surface sites. These islands may have $\mathrm{Ag_2}$ molecules adsorbed around their edges acting as donor centers, latent image growth nucleus precursors, and positive hole traps. There is evidently a very large number of equivalent $\mathrm{Ag_2}$ *sensitization centers* on the surface of an emulsion grain at which a silver atom might be formed during exposure. How is it possible for one site to become preferred over all the others following one effective event so that subsequent silver atoms separate at this site? From the reasoning presented, this first event must create a positively charged entity at the site that can attract and trap subsequently liberated photoelectrons and the positive charge must be restored after each event.

Covalent $\mathrm{Ag_2S}$ and (Ag,Au)S molecules are formed and strongly adsorbed[67] to the surfaces of partially covalent silver halide crystals as small monolayer islands. The reduction of $\mathrm{Ag_2O}$ molecules around the edges of the islands gives $\mathrm{Ag_2}$ molecules adsorbed at shallow positive potential wells. All these sensitizing molecules provide donor centers which are dissociated by the annihilation of an energy quantum in the primary photoelectronic process with the creation of a photoelectron and an $\mathrm{Ag_0^+}$ or $\mathrm{Au_0^+}$ interstitial ion. A photoelectron may combine with an interstitial ion at a shallow positive potential well to give an isolated Ag or Au atom. This is, however, a loss process. With random walk diffusion of an electron and the very large number of shallow trapping sites on the surface of a crystal, the probability for the occurrence of a second event at one particular site is extremely small.

An efficient latent image growth process becomes possible when a photoelectron and an interstitial ion diffuse to a $\mathrm{Ag_2}$ latent image growth nucleus precursor adsorbed at a shallow positive potential well at the edge of a sulfide monolayer island. In this first effective event, they combine with the $\mathrm{Ag_2}$ molecule to give an $\mathrm{Ag_3}$ or $\mathrm{AuAg_2}$ cluster that adsorbs a $\mathrm{Ag_0^+}$ ion to give a $\mathrm{Ag_4^+}$ or $\mathrm{AuAg_3^+}$ latent image growth nucleus. This positively charged nucleus introduces a site-directing Coulomb field and a deep electron trap or latent subimage center in the dry system.[55,70] One efficient latent image growth nucleus is thus produced, adsorbed to a sulfide monolayer island.

For the second effective event, the latent image growth nucleus attracts and traps a photoelectron, liberated within the drift range, and the positive charge is restored by the adsorption of an $\mathrm{Ag_0^+}$ ion resetting the trap and giving an $\mathrm{Ag_5^+}$ or $\mathrm{AuAg_4^+}$ development center of minimum size for the aqueous medium. This center grows by the repetition of these processses. The deep trap renders the shallow electron traps ineffective, including the remaining $\mathrm{Ag_2}$ latent image growth nucleus precursors. These also suffer photodissociation or hole trapping. This gives a very efficient concentration process. Continued exposure results in the formation or only a small number of development centers on an emulsion grain.

This process provides a solution to the problem of dispersion of latent image centers raised by Tani but not resolved in his discussion of future prospects for improvement of efficiency of latent image formation with individual silver halide grains.[37] It shows how one $\mathrm{Ag_4^+}$ or $\mathrm{AuAg_3^+}$ latent image center can be formed on a grain in the presence of a large number of equivalent $\mathrm{Ag_2}$ sensitization centers at shallow electron traps.[49,70,71] This center provides a positively charged deep electron trap which desensitizes remaining $\mathrm{Ag_2}$ molecules at shallow trapping centers. Hamilton has rejected this approach as untenable[60,69] and Tani has not discussed it.[37]

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