Comprehensive Model for Sulfur Sensitization III: Sulfur-Plus-Gold Sensitization

Tadaaki Tani▲ and Yuji Yoshida

Ashigara Research Laboratories, Fuji Photo Film Co., Ltd., Minami-Ashigara, Kanagawa, Japan

We propose a model for a sulfur-plus-gold sensitization center, which is derived by replacing one of two interstitial silver ions with a monovalent gold ion in a model for sulfur sensitization center proposed in this series of papers, and predict that (a) the incorporation of gold ions into silver halide grains is enhanced by the presence of sulfur sensitization centers owing to stronger bond formation of sulfide ions with gold ions relative to that with silver ions, and that (b) an electron trap for a sulfur-plus-gold sensitization center is shallower and has larger cross section than that fur a sulfur sensitization center, since a gold ion is larger than a silver ion. The prediction (a) was supported by the measurement of the amount of gold ions incorporated into AgBr grains by means of an isotopic tracer technique with a gold sensitizer labeled with ^{198}Au. The prediction (b) was supported by the measurements of the activation energy and frequency factor of the rate of development of developer fog, which resulted from the electron transfer from a developer to sensitization centers.

Journal of Imaging Science and Technology 44: 242–249 (2000)

Introduction

From the time that sulfur sensitization was discovered by Sheppard in 1925,[1] it has always been indispensable for the development of highly sensitive silver halide photographic emulsions. Many groups of investigators have ever been involved in the study of the mechanism of sulfur sensitization.[2]

In this series of articles,[3,4] the present author proposed the comprehensive model for sulfur sensitization, according to which sensitization centers are composed of dimers of substitutional sulfide ions on silver halide grains, and fog centers are composed of clusters of silver sulfide on the grains. The merit of the proposed model is its applicability to sensitization centers with wide variety. In this article, the proposed model has been extended to characterize sulfur-plus-gold sensitization centers.

Gold sensitization was discovered in 1936 by Koslowsky in collaboration with Mueller,[5] and has also been indispensable for development of highly sensitive silver halide emulsions. Gold sensitization is usually used in combination with sulfur sensitization to achieve sulfur-plus-gold sensitization.

One of the functions of sulfur-plus-gold sensitization is to decrease the size of the smallest latent image center by incorporating a gold atom into a latent image center. It is known that the smallest latent image center formed in a sulfur-plus-gold-sensitized emulsion is smaller than that in sulfur-sensitized emulsions,[6–10] being in accord with the facts that the electron affinity of gold is larger than that of silver,[11] and that the oxidation potential of latent image centers formed in a sulfur-plus-gold-sensitized emulsion was more positive than that of latent image centers in a sulfur-sensitized emulsion.[12]

Another function of sulfur-plus-gold sensitization is to modify sulfur sensitization centers as the sites for latent image formation. This proposal has been discussed for many years,[2] and have been recently supported by the experimental results to indicate that the trap depth of a sulfur-plus-gold sensitization center was shallower than that of a sulfur sensitization center.[13,14]

The present study was undertaken to propose a model for a sulfur-plus-gold sensitization center on the basis of the model for a sulfur sensitization center proposed in this series of studies, and to testify the model by characterizing sulfur-plus-gold sensitization centers.

Proposal of a Model for a Sulfur-Plus-Gold Sensitization Center

As illustrated in Fig. 1, the present author proposed in this series of papers the comprehensive model for sulfur sensitization,[3,4] according to which sensitization centers are composed of dimers of substitutional sulfide ions on silver halide grains, and fog centers are composed of clusters of silver sulfide on the grains. Because a sulfide ion at a lattice position of silver halide possesses a net negative charge, it is accompanied with an interstitial silver ion for the compensation of the negative charge in the lattice. Each interstitial silver ion accompanies a hydrogen-like orbital, which can bound a photoelectron only loosely. Each sulfur sensitization center has two interstitial silver ions with the hydrogen-like orbitals, which are forced to be close to each other. The two hydrogen-like orbitals thus interact with each other to give a bonding orbital and an anti-bonding one. The

Original manuscript received May 17, 1999

▲ IS&T Fellow

©2000, IS&T—The Society for Imaging Science and Technology

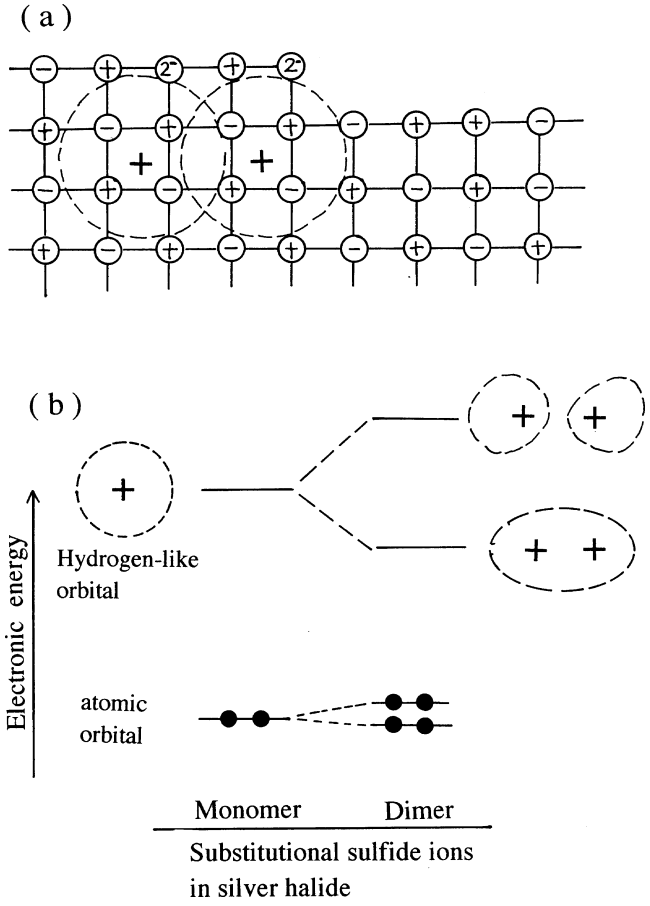

Figure 1. Illustration showing the model for a sulfur sensitization center proposed in this series of papers. (a) The structures of a sulfur sensitization center composed of a dimer of substitutional sulfide ions in a silver halide grain, where circles with +, –, and 2– are silver ion, bromide ion, and substitutional sulfide ion, respectively, in a silver bromide grain. Two signs + at interstitial positions in the lattice represents interstitial silver ions for the compensation of excess negative charges at the sulfide ions, and are placed at probable positions under the condition thet their positions are not certain at the present. Two broken circles centered at the interstitial silver ions represent hydrogen-like orbitals accompanying the interstitial ions. (b) The electronic energy levels of a monomer and a dimer of substitutional silver ions in s silver halide grain, where + is an interstitial silver ion.

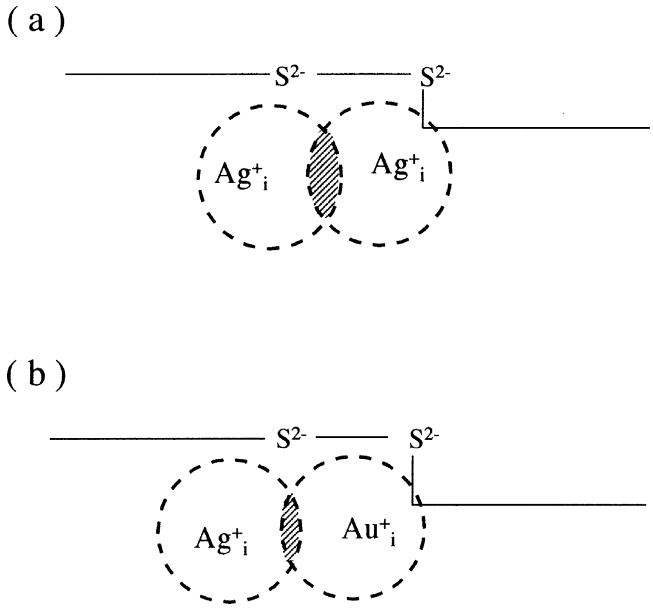

Figure 2. Illustration showing the model for a sulfur sensitization center (a) and a sulfur-plus-gold sensitization center (b) proposed in this series of papers, where Ag^{+}_{i} and Au^{+}_{i} are an interstitial silver ion and an interstitial gold ion, respectively, circles with broken lines represent hydrogen-like orbitals, which loosely bound photoelectrons.

bonding orbital, which can bound a photoelectron more strongly than a single hydrogen-like orbital, provides an electron trap suitable for the enhancement of the formation of a latent image center (i.e., a sulfur sensitization center).

Taking into account the fact that gold sensitization is especially effective when it is used in combination with sulfur sensitization, a model as illustrated in Fig. 2 is proposed for a sulfur-plus-gold sensitization center. Because the bond formation of sulfide ions with gold ions is stronger than that with silver ions as judged from the solubility products of Ag_2S[15] and Au_2S,[16] the replacement of one of the two interstitial silver ions with a gold ion takes place in a sulfur sensitization center to give a sulfur-plus-gold sensitization center, in which a gold ion and a silver ion at interstitial positions have hydrogen-like orbitals, which interact with each other to form a bonding orbital and an anti-bonding one. The sizes of monovalent silver and gold ions are 1.26 and 1.37 Å, respectively.[17] Because a gold ion is larger than a silver ion, the degree of the interaction between the two hydrogen-like orbitals is smaller, and therefore the electronic energy level of the bonding orbital is shallower, and its cross section is larger for a sulfur-plus-gold sensitization center than for a sulfur sensitization center. This prediction was partly proved by the experimental result which indicated that the trap depth of a sulfur-plus-gold sensitization center was shallower than that of a sulfur sensitization center for photoelectrons.[13,14]

The above-stated model gives the following predictions for the formation and property of sulfur-plus-gold sensitization centers.

(1) The incorporation of gold ions into silver halide grains is enhanced by the presence of sulfur sensitization centers on the grain surface owing to stronger bond formation of sulfide ions with gold ions relative to that with silver ions.
(2) A sulfur-plus-gold sensitization center provides an electron trap, which is shallower in depth and larger in cross section than a sulfur sensitization center.

In this article, several experiments have been designed and carried out to testify the proposed model by examining the adequacy of the above-stated predictions.

It is known that there are two kinds of fog; emulsion fog and developer fog.[18,19] In the case of emulsion fog, fog centers are present at the beginning of development, and are formed during digestion for chemical sensitization as a result of some excessive reaction taking place on some of emulsion grains owing to lack of uniformity of the formation of chemical sensitization centers among the grains. It is therefore expected that the development of emulsion fog starts rapidly.[18,19] In the case of sulfur sensitization, a sensitization center is a dimer of substitutional sulfide ions, while a fog center is a cluster of silver sulfide, which is large enough to be observed by

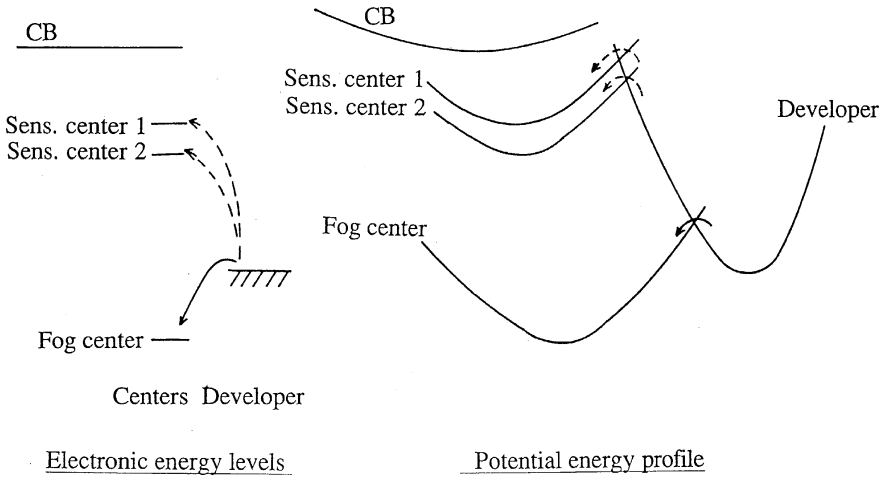

Figure 3. Illustration showing the electronic energy levels and potential energy profile for developer fog, which is ascribed to the electron transfer from a developer to sensitization centers.

electron microscopy.[3,4] In the case of reduction sensitization, a sensitization center is a dimer of silver atoms, while a fog center is a large silver cluster, which is mostly observable by electron microscopy.[20]

In the case of developer fog, fog centers are absent at the beginning of development and are formed during development as a result of the electron transfer from a developer to emulsion grains. It is therefore considered that developer fog centers are large silver clusters and are formed as a result of the electron transfer from a developer to sensitization centers on sulfur-sensitized and sulfur-plus-gold-sensitized grains. Thus, it is known that these sensitization centers are abundant on a grain and provide electron-trapping sites suitable for the formation of silver clusters. It is expected that the development of developer fog starts slowly and proceeds with increasing rate.[18,19] No clusters were observed by electron microscopy on any of octahedral AgBr grains with average diameter of 0.2 μm in optimally sulfur-sensitized and sulfur-plus-gold-sensitized emulsions, for which the rate of development of developer fog was measured in order to get the information of the knowledge of the depth and cross section of the electron traps provided by sulfur and sulfur-plus-gold sensitization centers. It is therefore considered that the developer fog and emulsion fog in this study could be distinguished from each other and that the former resulted from Ag cluster formation as a result of the electron transfer from a developer to the sensitization centers as shown in Fig. 3.

It is therefore considered that the activation energy of the rate of the formation of developer fog centers decreases with increasing the trap depth of sensitization centers, and that the frequency factor increases with increasing the cross section of the centers. Namely, the proposed model for a sulfur-plus-gold sensitization is proved by confirming that both activation energy and frequency factor of the rate of the formation of developer fog are larger for sulfur-plus-gold-sensitized emulsions than for sulfur-sensitized emulsions.

Experiments

In this study, we used mostly the emulsions with octahedral AgBr grains (average equivalent diameters of 0.2 and 0.8 μm), and the one with cubic AgBr grains (0.2 μm) for the phenomenon which needed it. The above-stated emulsions were prepared by means of a controlled double jet method.[21,22] The pH value of the reaction solutions during the formation of all the above-stated grains was 2.0, and the silver potential values of the solutions during the formation of the octahedral and cubic grains were –30 mV and +50 mV versus SCE, respectively. Sulfur sensitization was carried out by digesting at 60°C for 60 min the octahedral AgBr grains with $Na_2S_2O_3$ as a sulfur sensitizer, and the cubic AgBr emulsion with triethylthiourea as a sulfur sensitizer. Sulfur-plus-gold sensitization was carried out by digesting at 60°C for 60 min the octahedral AgBr emulsions, to which aqueous solutions of a gold sensitizer (KAuCl4 and KSCN) were added.

The thin layers of the above-stated emulsions were prepared by coating and drying them on triacetate cellulose film bases and were used as samples for sensitometric measurements. Each film sample was exposed for 10 s to a tungsten lamp (color temperature: 2854 K) through a continuous wedge and subjected to surface development at 20°C for 10 min by use of a developer MAA-A.[23] The optical density of a developed film was measured by use of a Fuji densitometer. Photographic sensitivity of an emulsion was given by the reciprocal of the exposure that gave the middle point between the maximum and minimum densities in its characteristic curve.

The change in optical density of a film sample during development was measured at the wavelength of 1090 nm by use of an apparatus developed by Ohzeki.[24] The light scattering by emulsion grains with equivalent circular diameter of 0.2 μm in a film sample at 1090 nm was not so large as to disturb the measurement of the rate of development initiated by fog centers and latent image centers.

The amounts of Ag_2S formed and Au^+ incorporated into emulsion grains from the above-stated sensitizers during digestion for sensitizations were measured by means of an isotopic tracer technique.[25,26] Namely, an emulsion, to which a labeled sensitizer was added, was digested for sensitization, and subjected to a centrifuge to separate AgBr grains from an aqueous gelatin solution. The obtained AgBr grains were dissolved, and subjected to the measurement of their radioactivity. In order to get the amount of Ag_2S, sulfur sensitizers, that remained on the grains after the digestion, were desorbed by treating the grains with an aqueous solution of 0.1

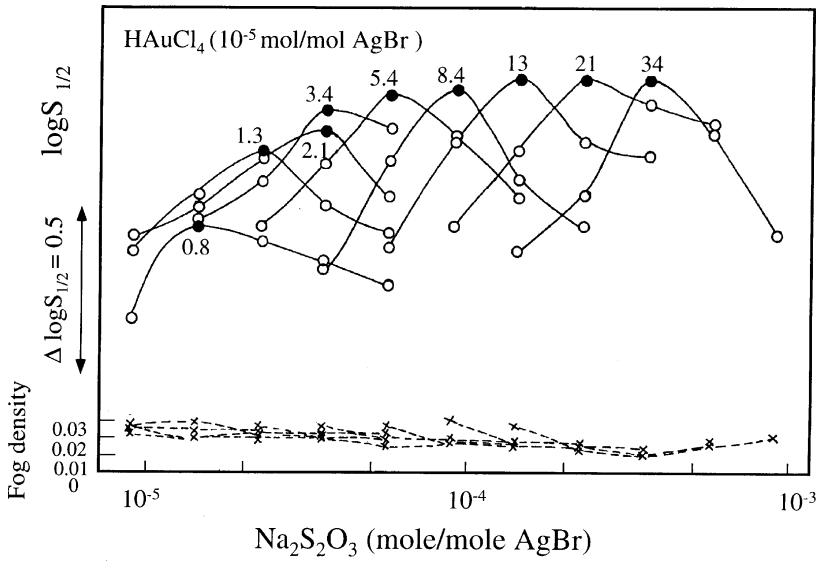

Figure 4. Sensitivity and fog density of sulfur-plus-gold-sensitized octahedral AgBr emulsions as functions of the amount of a sulfur sensitizer ($Na_2S_2O_3$) and a gold sensitizer ($HAuCl_4$). Emulsions were digested for 60 min at 60°C.

N KBr. An aqueous solution of KCN was used to remove Au^+ from the grains according to the procedure described by Spencer.[27] The above-stated experiments were carried out by use of sulfur sensitizers labeled with ^{35}S and a gold sensitizer labeled with ^{198}Au. The latter was prepared by exposing powder of $HAuCl_4 \bullet 4H_2O$ to neutron irradiation in the nuclear reactor TRIGA-2 in the Institute for Atomic Energy, Rikkyo University.

Results and Discussion

Figure 4 shows the sensitivity and fog density of sulfur-plus-gold-sensitized octahedral AgBr grains with average equivalant diameter of 0.2 μm in emulsions as functions of amounts of a sulfur sensitizer (i.e., $Na_2S_2O_3$) and a gold sensitizer (i.e., $HAuCl_4$). As seen in this figure, sensitivity increases, reaches the maximum, and decreases with increasing the amount of $Na_2S_2O_3$ for each branch with a fixed amount of $HAuCl_4$. The amount of $Na_2S_2O_3$ which gave the sensitivity maximum in each branch, increased with increasing the amount of $HAuCl_4$ in the corresponding branch. As shown in Fig. 5, the amount of $Na_2S_2O_3$ for the maximum sensitivity and the amount of $HAuCl_4$ in each branch were proportional to each other. This result indicates that the incorporation of gold sensitization centers (i.e., Au^+) into emulsion grains was enhanced by sulfur sensitization centers on the grain surface.

An emulsion composed of octahedral silver bromide grains with average equivalent circular diameter of 0.8 μm was digested for 60 min at 60°C for sulfur sensitization with $Na_2S_2O_3$ (10 μmole/mole of AgBr) as a sensitizer. Then, the sulfur-sensitized emulsion and corresponding unsensitized one were digested for 10 min at 40°C in the presence of a labeled gold sensitizer, $H^{198}AuCl_4$. The amounts of Au^+ incorporated into the unsensitized grains and sulfur-sensitized ones were measured by means of an isotopic tracer technique, and found to be 1.4 and 5.2 μmole/mole AgBr, respectively. This result indicates that the presence of sulfur sensitization centers markedly enhanced the incorporation of Au^+ into the emulsion grains.

Figure 6 shows the sensitivity and fraction of triethylthiourea which was decomposed to give Ag_2S on

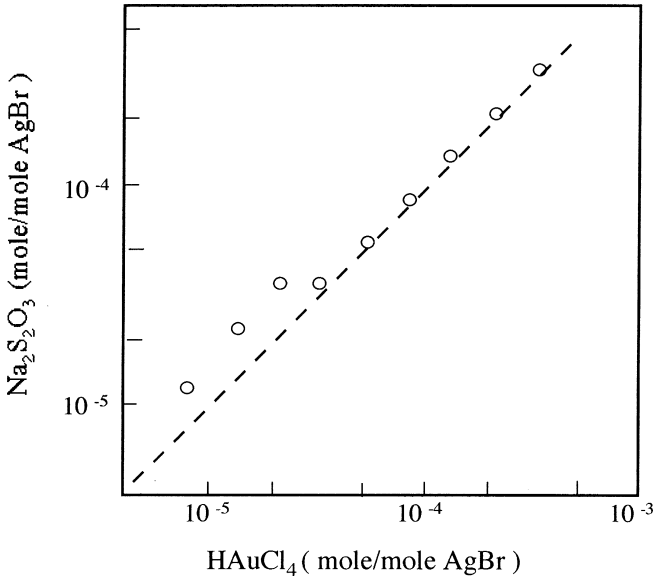

Figure 5. Relation between the amount of a sulfur sensitizer ($Na_2S_2O_3$) which gave the maximum sensitivity for octahedral AgBr emulsions, which were sulfur-plus-gold-sensitized in the presence of a gold sensitizer ($HAuCl_4$) with amount shown in the abscissa.

cubic AgBr grains in emulsions as a function of the digestion time for the sulfur sensitization of the emulsions. As seen in this figure, all the triethylthiourea added to the emulsions was decomposed to give Ag_2S after the emulsions were digested for 20 min, while the sensitivity continued to increase, reach its maximum, and then decrease with prolonging the digestion time after the completion of the formation of Ag_2S. This phenomenon, which could isolate the process of coagulation of Ag_2S to form sulfur sensitization centers from the process of Ag_2S formation, was observed only for cubic AgBr emulsions with triethylthiourea. This was studied by Kanzaki and Tadakuma on the basis of the measurements of their sensitivity, the amount of Ag_2S by means of an isotopic tracer technique, and the amount

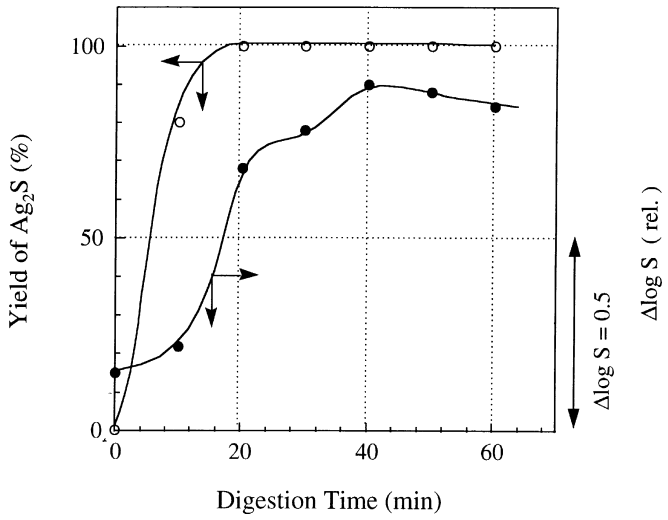

Figure 6. Quantum yield of silver sulfide formation (O) and photographic sensitivity (●) in a cubic AgBr emulsion as functions of the digestion time at 60°C in the presence of triethylthiourea for its sulfur sensitization.

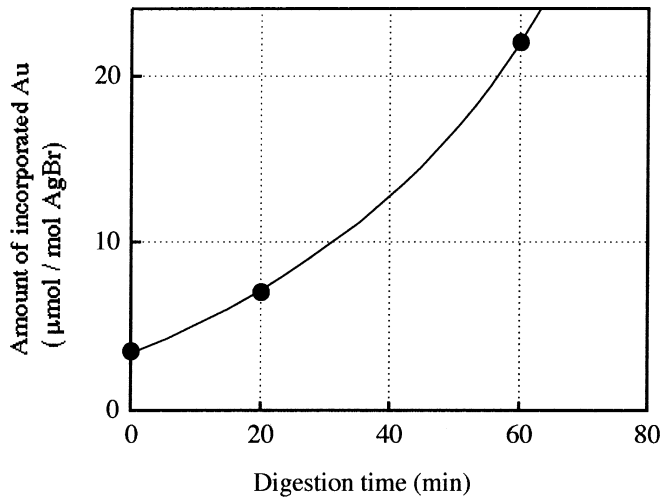

Figure 7. Amount of gold incorporated into cubic AgBr grains in an emulsion, which was digested at 60°C for the time designated in the abscissa in the presence of triethylthiourea of 32 μmole/mole AgBr, and was then treated at 40°C with $HAuCl_4$ of 32 μmole/mole AgBr.

of sulfur sensitization centers by means of a fluorescence modulation method.[28] It was found that sulfur sensitization centers acting as electron traps were composed of dimers of Ag_2S, and were formed as a result of coagulation of monomers of Ag_2S during digestion of emulsions for sulfur sensitization. It is therefore considered that the coagulation of Ag_2S monomers to dimers proceeded during the digestion after the completion of the reaction for the formation of Ag_2S.

Then, an aqueous solution of a gold sensitizer, $HAuClO_4$, was added to each of the emulsions described in Fig. 6. The amount of Au^+ incorporated into emulsion grains was measured by means of an isotopic tracer technique with $H^{198}AuClO_4$, and plotted in Fig. 7 as a function of the digestion time for the sulfur sensitization. As seen in this figure, the amount of incorporated Au^+ into the grains increased with increasing the digestion time, indicating that the incorporation of Au^+ into the grains was increased by the formation of Ag_2S on the grains, and was further accelerated by the coagulation of Ag_2S.

The coated layers of sulfur-sensitized and sulfur-plus-gold- sensitized octahedral AgBr emulsions were bathed in aqueous solutions of KCN, washed, dried, and subjected to sensitometry. The sensitivities thus obtained were plotted against the concentration of the KCN solutions in Fig. 8. As seen in this figure, the sensitivity of a sulfur-sensitized emulsion layer was hardly influenced by bathing it in a KCN solution, while the sensitivity of a sulfur-plus-gold-sensitized emulsion layer was decreased by bathing it in a KCN solution, and finally became to be nearly the same as that of a sulfur-sensitized emulsion layer. It is known that CN^- acts as a strong ligand to Au^+, forming a water-soluble complex ion, $Au(CN)_2^-$, and that Au^+ in emulsion grains is thus extracted by an aqueous solution of KCN.[27] The result shown in Fig. 8 therefore indicates that the extraction of Au^+ from a sulfur-plus-gold sensitization center gave a sulfur sensitization center, supporting the model for the sulfur-plus-gold sensitization proposed in this article.

Figures 9 and 10 show the optical densities at 1090 nm of layers of sulfur-sensitized and sulfur-plus-gold-sensitized emulsions with octahedral AgBr grains with

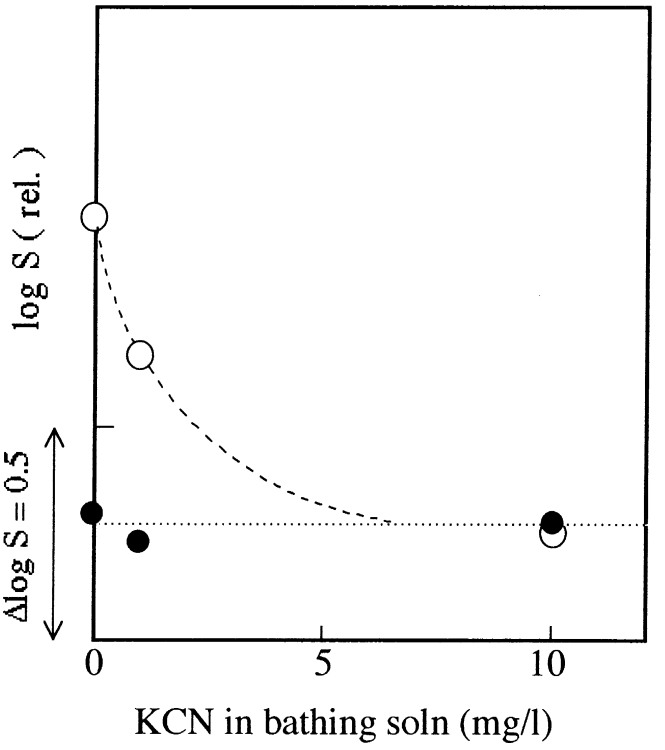

Figure 8. Photographic sensitivity of sulfur-sensitized (●) and sulfur-plus-gold-sensitized (O) octahedral AgBr emulsion layers, which were treated by aqueous solutions of KCN with concentration shown in the abscissa according to the procedure described by Spencer.

average equivalent circular diameter of 0.2 μm as functions of the time and temperature of development. In each case, the density started to increase slowly, and the rate of increase in density increased with time of development until the density approached its maximum. This behavior is consistent with that of developer fog,

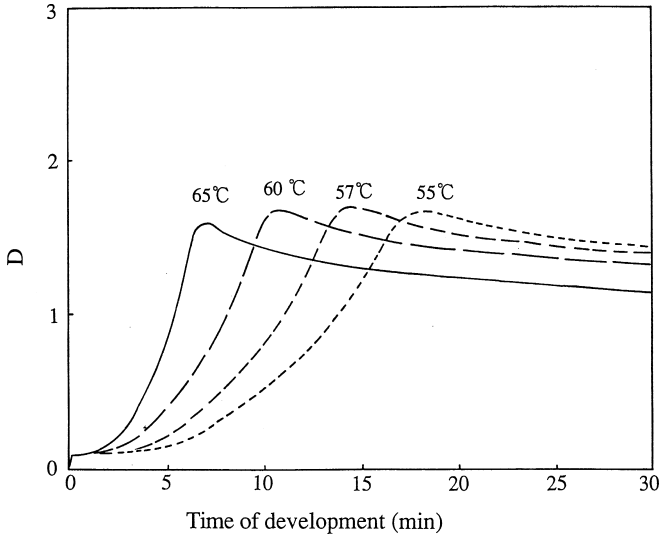

Figure 9. Optical density of sulfur-sensitized octahedral AgBr emulsion layers after they were immersed in a surface developer MAA-1 at the temperature designated in this figure for the time shown in the abscissa.

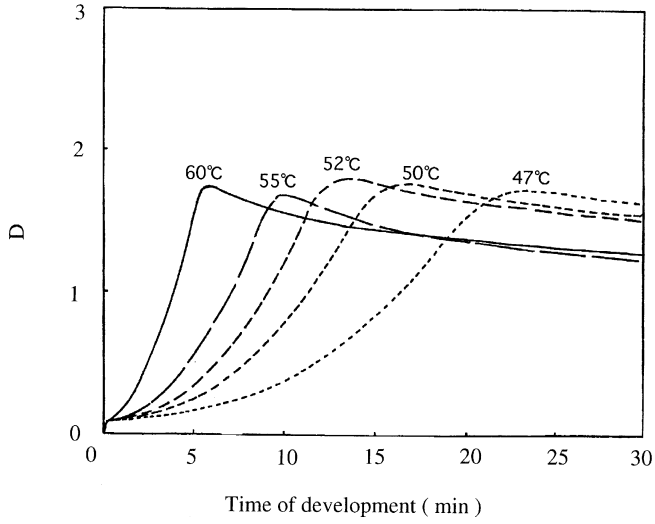

Figure 10. As Fig. 9, except sulfur-plus-gold-sensitized octahedral AgBr emulsion layers.

for which fog centers are absent at the beginning of development, and are formed during the development in these emulsion layers. In addition, the formation of the fog centers was enhanced by sulfur sensitization and sulfur-plus-gold sensitization centers. It is therefore considered that the fog centers were large Ag clusters, and were formed as a result of the electron transfer from the developer to those sensitization centers during the development, giving the developer fog of these emulsion layers.

The rate of the development of the above-stated developer fog was determined by the development time to give the middle point between the minimum and maximum densities in the curves in Figs. 9 and 10, and plotted against the reciprocal of the temperature of the developer in Fig. 11. As seen in this figure, the rate of the development of the developer fog of sulfur-plus-gold sensitized emulsion layers was larger than that of sulfur-sensitized emulsion layers.

The activation energy $\Delta H^{\ddagger}$ and the frequency factor A of the development of the developer fog, which were regarded as $\Delta H^{\ddagger}$ and A of the electron transfer from the developer to sensitization centers, were given by applying the Arrhenius equation to the straight lines in Fig. 11 and are plotted as functions of the amount of $Na_2S_2O_3$ in Fig. 12. It was found from the result in this figure that both $\Delta H^{\ddagger}$ and A of sulfur-plus-gold-sensitized emulsions were larger than those of sulfur-sensitized ones. The larger activation energy observed for the former would not lead to a higher rate of development than for the latter. Only the larger pre-exponential factor A can be responsible for the higher rate of development of developer fog in the sulfur-plus-gold sensitization relative to the sulfur sensitization.

As shown in Fig. 12, the amount of $Na_2S_2O_3$ which gave the maximum sensitivity in sulfur-plus-gold-sensitized emulsions was slightly less than that in sulfur-sensitized emulsions. On the basis of the models for sulfur sensitization and sulfur-plus-gold sensitization centers proposed in this series of papers, it is therefore considered that the concentration of sulfur-plus-gold sensitization centers for the maximum sensitization was

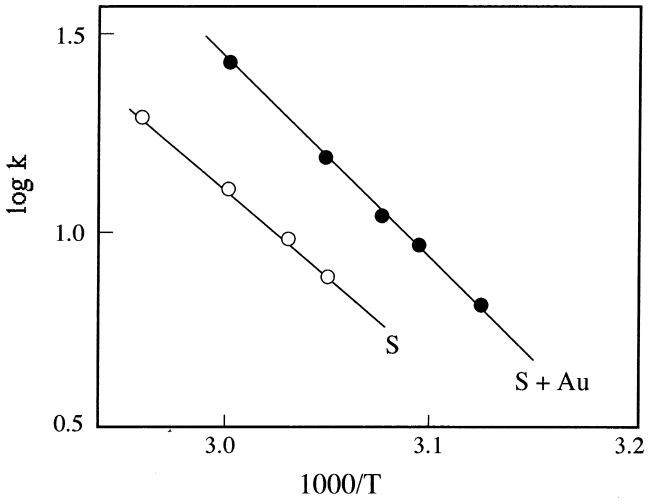

Figure 11. Arhenius plots of the rate of development of developer fog of sulfur-sensitized (O) and sulfur-plus-gold-sensitized (●) octahedral AgBr emulsion layers by a surface developer MAA-1.

not more than that of sulfur sensitization centers, and that the frequency factor for each sulfur-plus-gold sensitization center to receive an electron was larger than that for each sulfur sensitization center.

It was found that $\Delta H^{\ddagger}$ was lower for emulsions with lower sulfur sensitizer level as well as for an unsensitized one than for the emulsion with the optimal sulfur sensitizer level. This result indicates that some deeper electron traps with lower concentration and/or smaller cross section relative to sulfur sensitization centers are responsible for the formation of developer fog centers on unsensitized AgBr grains. It is obvious that they are less effective for latent image formation than sulfur sensitization centers, although they could not be identified in this study. It is considered that the contribution of sulfur sensitization centers to the

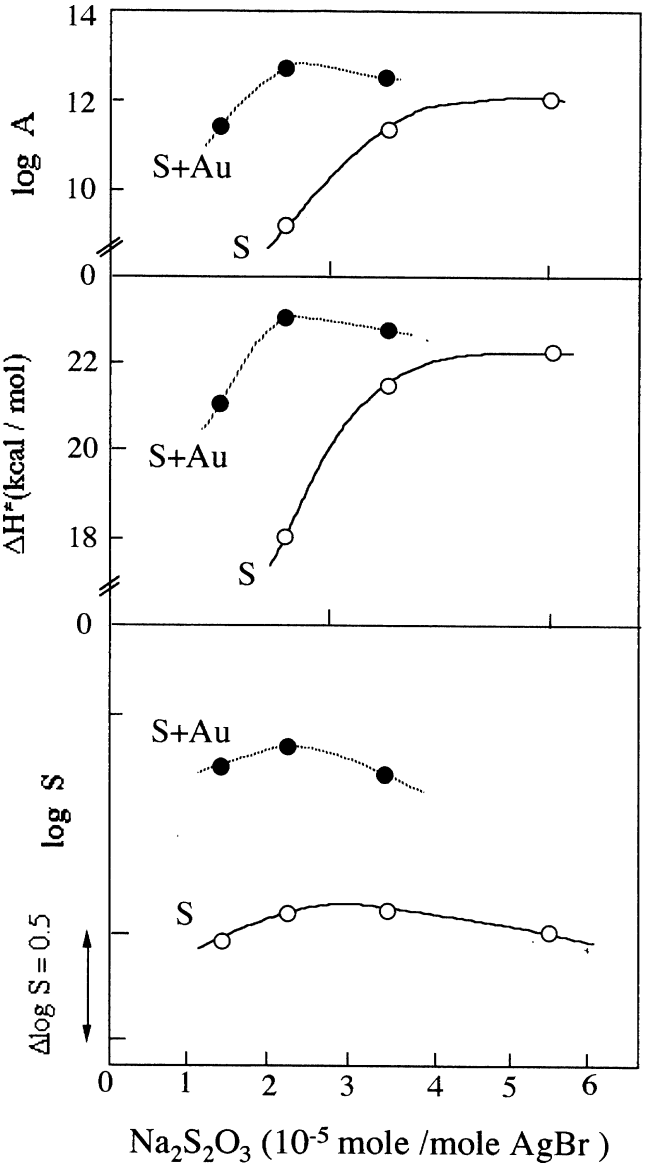

Figure 12. Photographic sensitivity, the activation energy and frequency factor of developer fog by a surface developer MAA-1 of sulfur-sensitized (O) and sulfur-plus-gold-sensitized (●) octahedral AgBr emulsion layers as a function of the amount of $Na_2S_2O_3$ used for their sulfur sensitization.

formation of developer fog centers increased with increasing sulfur sensitizer level, and became to be dominant at the optimal sensitizer level.

Discussion on Model for Sulfur-Plus-Gold Sensitization Centers

The model for a sulfur-plus-gold sensitization center was proposed in this article[3,4] as shown in Fig. 2, and made two predictions. One of them is given by its structure, which is derived by replacing one of the two interstitial silver ions with a gold ion in a sulfur sensitization center owing to stronger bond formation of sulfide ions with gold ions relative to that with silver ions. Namely, sulfide ions on the grain surface enhances the incorporation of gold ions into emulsion grains, and vice versa. The enhancement of the incorporation of gold ions into emulsion grains by the formation of sulfur-plus-gold sensitization centers was proved by the following experimental results in this study.

(1) As shown in Figs. 4 and 5, the amount of a gold sensitizer was proportional to that of a sulfur sensitizer for achieving the maximum sensitivity by sulfur-plus-gold sensitization.
(2) The amount of Au^+ incorporated into emulsion grains was greatly increased by the formation of sulfur sensitization centers on the grain surface.
(3) The coagulation of silver sulfide on emulsion grains enhanced the incorporation of gold ions into the grains.
(4) The sensitivity of a sulfur-plus-gold-sensitized emulsion decreased and became to be nearly the same as that of a sulfur-sensitized one when gold ions were eliminated from the emulsion grains.

The prediction of the enhancement of the incorporation of sulfide ions into emulsion grains by the formation of sulfur-plus-gold sensitization centers is in accord with the result obtained by the studies of the interaction between sulfur sensitization and gold sensitization.[29]

It is also predicted that the stabilization of dimers of substitutional sulfide ions (i.e., sulfur sensitization centers) by their incorporation of gold ions prevent substitutional sulfide ions from taking part in the formation of large Ag_2S clusters (i.e., fog centers of sulfur sensitization according to the model proposed in this series of papers). This prediction is in accord with the fact that gold sensitization depressed the formation of fog centers of sulfur sensitization.[30,28]

It is considered that the interstitial gold ion in the center is photolytically reduced and incorporated into a latent image center as a gold atom. Under the light of the fact that the electron affinity of gold is larger than that of silver,[31] the above-stated prediction is therefore consistent with the fact that the oxidation potential of latent image centers formed in sulfur-plus-gold-sensitized emulsions was always more positive than that of latent image centers formed in sulfur-sensitized emulsions.[12]

The present model also predicts that, as an electron trap, a sulfur-plus-gold sensitization center should be shallower in depth and larger in cross section than a sulfur sensitization. It was already reported that the former provided a shallower electron trap than the latter. By taking into account the consideration in the former section, this prediction was also supported by the result in this paper that the activation energy of and frequency factor of the rate of development of developer fog in a sulfur-plus-gold-sensitized emulsion were larger than those in a sulfur-sensitized emulsion.

Although the explanation of the cross section of a sulfur-plus-gold sensitization center with respect to that of a sulfur sensitization center in terms of the difference in size between silver and gold ions, which is one of the most important characteristics of the present model, was experimentally supported, it should be subjected to further examinations by means of more sophisticated and quantitative experiments and calculation.

References

1. (a) S. E. Sheppard, *Photogr. J.* **65,** 380 (1925), (b) S. E. Sheppard, *Photogr. J.* **66,** 399 (1926).
2. T. Tani, Photographic Sensitivity: Theory and Mechanisms, Oxford University Press, New York, 1995, Chapter 6.
3. T. Tani, *J. Imaging Sci. Technol.* **39,** 386 (1995).
4. T. Tani, *J. Imaging Sci. Technol.* **42,** 135 (1998).

5. (a) R. Koslowski, *Z. Wiss. Photogr.* **46,** 65 (1951), (b) F. W. Muller, *J. Opt. Soc. Am.* **39,** 494 (1949), (c) F. W. Mueller, *Photogr. Sci. Eng.* **10,** 338 (1966).
6. T. Tani, *Photographic Sensitivity: Theory and Mechanisms*, Oxford University Press, 1995, Chapter 4.
7. E. T. Larson, *PSA J. Photogr. Sci. Technol.* **17B**, 19 (1951).
8. J. F. Hamilton and P. C. Logel, *Photogr. Sci. Eng.* **18,** 507 (1974).
9. (a) J. W. Mitchell, *Photogr. Sci. Eng.* **22,** 1 (1978), (b) J. W. Mitchell, *Photogr. Sci. Eng.* **22,** 249 (1978).
10. R. K. Hailstone, J. F. Hamilton, *J. Imaging Sci.* **29,** 125 (1985).
11. P. A. Faelens, in *The Photographic Image, Formation and Structure*, S. Kikuchi, Ed., Focal Press, London, 1970, p.72.
12. (a) P. J. Hillson, *J. Photogr. Sci.* **6,** 97 (1958), (b) J. Bourdon and A. Bonnerot, *Sci. Ind. Photogr.* **30,** 205 (1959), (c) J. Bourdon and A. Bonnerot, *Sci. Ind. Photogr.* **32,** 369 (1961), (d) T. Tani, *Photogr. Sci. Eng.* **27,** 75 (1983), (e) T. Tani and M. Murofushi, *J. Imaging Sci. Technol.* **38,** 1 (1994).
13. J. F. Hamilton, J. M. Harbison and D. L. Jeanmaire, *J. Imaging Sci.* **32,** 17 (1988).
14. L. M. Kellogg and J. Hodes, The Measurement of Electron Trap Depths for Sulfur and Sulfur-plus-Gold Centers in AgBr Emulsions Using Thermally Stimulated Current (TSC) Techniques, in *Preprint Book of the 40th Annual Conference of SPSE*, SPSE, Washington, D.C.,1987.
15. J. Pouradier, A. Pailliotet and C. R. Berry, in *The Theory of the Photographic Process*, 4th ed., T. H. James, Ed., Macmillan, New York, 1977, p.9.
16. A. de Cugnac-Pailliotet and J. Pouradier, *C. R. Seances Acad. Sci.* **C275,** 551 (1972).
17. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, New York, 1960, p. 514.
18. T. Tani, *Photographic Sensitivity: Theory and Mechanisms*, Oxford University Press, 1995, Chap. 7.
19. R. W. Swenson, *Photogr. Sci. Eng.* **1,** 119 (1958).
20. T. Tani, T. Tasaka, M. Murofushi, K. Hosoi, and A. Hirano, *Imaging Sci. J.* **47,** 1 (1999).
21. C. R. Berry and D. C. Skillman, *Photogr. Sci. Eng.* **6,** 159 (1962).
22. (a) E. Klein and E. Moisar, *Photogr. Wiss.* **11,** 3 (1962), (b) E. Moisar, *J. Soc. Photogr. Sci. Technol. Jpn.* **54,** 273 (1991).
23. T. H. James, W. Vanselow and R. F. Quirk, *Photogr. Sci. Technol.* **19B,** 170 (1953).
24. K. Ohzeki, *J. Imaging Sci. Technol.* **40,** 594 (1996).
25. H. Frieser and E. Ranz, *Ber. Bunsenges. Physik. Chem.* **68,** 389 (1964).
26. Y. Yoshida, H. Mifune and T. Tani, *J. Soc. Photogr. Sci. Technol. Jpn.* **59,** 541 (1996).
27. H. E. Spencer, *J. Imaging Sci.* **32,** 28(1988).
28. H. Kanzaki and Y. Tadakuma, *J. Phys. Chem. Solids* **55,** 631 (1994).
29. D. A. Pitt, M. L. Rachu and M. R. V. Sahyun, *Photogr. Sci. Eng.* **25,** 57 (1981).
30. H. Hirsch, *J. Photogr. Sci.* **20,** 187 (1972).
31. P. A. Faelens, in *The Photographic Image, Formation and Structure*, S. Kikuchi, Ed., Focal Press, London, 1970, p.72.
32. P. J. Hillson, *J. Photogr. Sci.* **6,** 97 (1958).
33. J. Bourdon and A. Bonnerot, *Sci. Ind. Photogr.* **(2)30,** 205 (1959).
34. J. Bourdon and A. Bonnerot, *Sci. Ind. Photogr.* **(2)32,** 369 (1961).
35. T. Tani, *Photogr. Sci. Eng.* **27,** 75 (1983).
36. T. Tani, *J. Imaging Sci. Technol.* **38,** 1 (1994).