Silver Clusters of Photographic Interest (2): A New Model for R and P Centers

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Reduction sensitization with various sensitizers, silver digestion, and hydrogen hypersensitization were applied to octahedral and cubic silver bromide emulsion grains to form P centers, identified by the observation of sensitivity increase and photoconductivity decrease caused by the centers, and absorption band characteristic of the centers. It was found that P centers decreased the ionic conductivity of the grains, which was proportional to the concentration of interstitial silver ions. By taking into account the fact that silver ions at kink sites are in equilibrium with interstitial silver ions, we propose that a P center was formed adjacent to a silver ion at a kink site and prevented it from going into an interstitial position in an emulsion grain. It is further proposed that a P center of a silver ion as successfully applied to the explanation of the formation, property, and behavior of silver clusters of photographic interest.

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Introduction

Silver clusters on silver halide grains play essential roles in photographic sensitivity.¹ Spencer and coworkers clearly demonstrated two types of silver clusters on silver bromide grains.² One was an image center, which appeared and grew by capturing a photoelectron during exposure, and the other a reduction sensitization center, which disappeared by capturing a positive hole during exposure. The present author³ and Takada⁴ showed that even among reduction sensitization centers electron-trapping as well as hole-trapping centers exist. The present author proposed that an electron-trapping center and a hole-trapping center were silver clusters at a positively charged kink site and at a neutral site on the grain surface, respectively.³ Hamilton and Baetzold supported the above-stated proposal by constructing a model for dimers of silver atoms on a positively charged kink site and on a neutral site and calculating the electronic structure by a molecular orbital method.⁵ They called the electron-trapping and hole-trapping centers P and R centers, respectively, because they believed the P center was formed photolytically, and the R center by reduction sensitization. However, note that P centers also could be formed by reduction sensitization as stated by the literature in the past and in this article and that P centers formed by reduction sensitization are considered to be the same as photolytically formed ones.^{1,3,4}

Tani and Murofushi obtained evidence for the abovestated model by analyzing reduction sensitization centers on fine silver bromide grains.⁶ On these grains, they ob-

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served two kinds of reduction sensitization centers, as already seen in previous studies.^{3,4} One increased sensitivity and did not decrease photoconductivity of emulsion grains, and the other increased sensitivity and decreased photoconductivity. The one that did not decrease photoconductivity and the one that did were assigned to R and P centers, respectively. The authors could observe the effects of R and P centers selectively by gradually increasing the amount of sensitizers for reduction sensitization. They observed for the first time the absorption bands of P centers and fog centers at 474 and 540 nm, respectively, and obtained evidence for the hypothesis that a P center is composed of a dimer of silver atoms. By measuring the oxidation potential of R and P centers on the emulsion grains, the authors estimated the electronic energy levels of the reduction sensitization centers. According to these estimates the highest occupied molecular orbital (HOMO) of the P centers was lower by about 0.4 eV than that of R centers, which supported the model that P and R centers acted as electron and hole traps, respectively.

These results thus verified the above-stated model for R and P centers. However, the present author is concerned that the difference in charge between R and P centers, which is only one half of one electronic charge, is not sufficient for the experimentally observed large difference between them. Electric charge does not have such a large influence on the electronic energy level of a center in silver halide with a large dielectric constant.⁷ It seems important to study the nature of the interaction of R and P centers with the surface of emulsion grains.

It is known that the charge carriers of ionic conductivity of silver bromide emulsion grains are interstitial silver ions in equilibrium with silver ions at kink sites and that compounds preventing silver ions at kink sites from moving into interstitial positions by stabilizing them decrease the ionic conductivity of emulsion grains.⁷ It is, therefore, considered that the interaction of R and P centers with the grain surface can be studied by measuring the effect of those centers on the ionic conductivity of emulsion grains.

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Figure 1. Photographic sensitivity, fog density, and ionic conductivity of octahedral silver bromide emulsion grains as functions of the amount of DMAB used for their reduction sensitization. Sensitivities of the emulsion layers, which had been chemically unsensitized and were hydrogen-hypersensitized at 40°C for 4 h and 50°C for 4 h, are denoted by arrows A and B. respectively. The hydrogen-hypersensitized emulsion layers gave no fog density.

This study was undertaken to examine and revise the model for R and P centers by studying the effect of those centers on the ionic conductivity of the fine silver bromide emulsion grains under the same conditions as that of Tani and Murofushi in the previous investigation⁶ and to compare the new results with the results which they obtained.

Experimental

The emulsions used were the same as those in the previous paper,⁶ which were composed of octahedral and cubic silver bromide grains with equivalent circular diameters of $0.2 \,\mu m$ suspended in inert and deionized gelatin. The emulsions were prepared at 70°C by a controlled double-jet method,^{8,9} and the pH of the reaction solutions were kept at 2 during precipitation.

Reduction sensitization centers were formed on the above-stated emulsion grains by various methods.¹⁰ One was to digest the above emulsions at 60°C for 60 min in the presence of DMAB, thiourea dioxide, or stannous chloride. Silver digestion¹¹ of octahedral and cubic silver bromide emulsions was carried out by digesting them at 60°C for 60 min after their silver potential was adjusted at 400 mV and their pH was fixed at various values. The silver potential and pH of the digested emulsions were readjusted to the values of the corresponding undigested emulsions before coating. Reduction-sensitized and silver-digested emulsions were coated on TAC film bases after pH and pAg of the emulsions were adjusted to be the same for all the emulsions. Coated and dried emulsion layers were used as samples for sensitometry and photoconductivity measurements. Hydrogen hypersensitization¹² was carried out for coated samples of unsensitized emulsions by evacuating and then keeping them in hydrogen gas at 40°C and 50°C for 4 h (Conditions A and B. respectively).

The coated samples were exposed to a tungsten lamp (color temperature of 2854 K) for 10 s through a continuous wedge. The exposed samples were developed at 20° C for 10 min by use of a surface developer MAA-1. The optical densities of the developed and fixed film samples were measured by use of a Fuji HPD densitometer. Sensitivity was given by the reciprocal of the exposure, which gave the optical density of 0.1 above fog for each film sample.

The formation of P centers on the emulsion grains was confirmed by two methods. One was to observe the decrease in photoconductivity of the grains due to the capture of photoelectrons by P centers. Photoconductivity of the emulsion grains was measured at -100° C by means of a microwave photoconductivity method.^{13,14} The photoconductivity of a film sample was given by the peak height of its microwave photoconductivity signal. The other method was to observe the absorption band of P centers at 474 nm in the diffuse reflection spectra of thick emulsion layers.⁶ The ionic conductivity of the above-stated emulsion grains were measured at room temperature and at lower temperatures for some emulsion grains by the dielectric loss method^{15,16} on evacuated thick layers of the emulsions.

Results and Discussions

Figure 1 shows the sensitivity and fog density of the octahedral silver bromide emulsion, which was reductionsensitized with DMAB as a sensitizer. As described in the previous article,⁶ sensitivity increased through two steps and then fog appeared with increasing amounts of DMAB. Although the sensitivity increase in the first step was not associated with the change in the photoconductivity of the grains, the sensitivity increase in the second step was associated with the decrease in photoconductivity. It was confirmed from the correspondence of this result with those described in the previous article that the former was brought about by R centers, while the latter by P centers. As shown in Fig. 2, the appearance of the absorption band at 474 nm also indicated the formation of P centers in the second step consistent with the previous results.⁶

Figure 1 also shows the change in the ionic conductivity of the reduction-sensitized octahedral silver bromide grains along with their sensitivity and fog density as a function of the amount of DMAB. It was found that the first step of the sensitivity increase was not associated with any change in the ionic conductivity, while the decrease in the ionic conductivity was observed in the second step and in the region with fog formation. Thus, it



Figure 2. Diffuse reflectance spectra of octahedral silver bromide emulsions, which were reduction- sensitized with DMAB of (a) $3.5\times10^{\text{-5}}$ and (b) $8.8\times10^{\text{-5}}$

Figure 3. Temperature dependence of dielectric loss curves of thick layers of octahedral silver bromide emulsions, which were unsensitized (solid curves) and reduction-sensitized with DMAB of 3.5×10^{-5} mol/mol AgBr (broken curves).

appeared that P centers and fog centers decreased the ionic conductivity, while R centers did not.

Diffuse reflectance (%)

Figures 3 and 4 show the dielectric loss curves of the emulsion grains in the regions with the formation of P centers and fog centers at various temperatures. It is noted

that there were two peaks in each curve. The ionic conductivity with interstitial silver ions as carriers was given by the frequency that gave the peak in the lower frequency side according to the studies by Takada,¹⁶ and Ohzeki, Urabe, and Tani.¹⁷ Note also that the ionic conductivity,



Figure 4. Temperature dependence of dielectric loss curves of thick layers of octahedral silver bromide emulsions, which were unsensitized (solid curves) and reduction-sensitized with 8.8×10^{-5} (broken curves) and 3.5×10^{-4} mol/mol AgBr (dashed lines).

which was given by the higher frequency peak and ascribed to mobile silver ions on the grain surface according to Ohzeki, Urabe, and Tani,¹⁷ was also decreased on formation of P centers and fog centers. The temperature coefficients of the ionic conductivities owing to both interstitial and surface silver ions also increased on formation of P centers. It is known that the temperature coefficient of the ionic conductivity with interstitial silver ions as carriers is composed of the formation energy of interstitial silver ions and the activation energy of their migration.⁷ Because the activation energy should be constant among silver bromide grains, the increase in the temperature coefficient indicates increase in the formation energy of interstitial silver ions.

Figure 5 shows the sensitivity, fog density, and ionic conductivity of the cubic silver bromide grains, which were reduction-sensitized with DMAB as a sensitizer. In a similar fashion to the case of octahedral silver bromide grains, sensitivity increased through two steps with increasing the amount of DMAB. The sensitivity increase in the first step was associated neither with the decrease in the photoconductivity of the grains nor with the appearance of the absorption band of P centers at 474 nm, while the sensitivity increase in the second step was associated both with the decrease in the photoconductivity and with the appearance of the band of P centers at 474 nm. These results made it clear that the sensitivity increases in the first and second steps were brought about by R and P centers, respectively.

Figure 5 also shows the ionic conductivity along with the sensitivity of the grains as a function of the amount of DMAB. It was inferred from these results that P centers decreased the ionic conductivity of cubic silver bromide grains. Figure 6 shows the dielectric loss curves of the unsensitized and reduction-sensitized grains and the temperature dependence of the ionic conductivity of the grains. As seen here, P centers decreased the ionic conductivity and increased its temperature coefficient. As discussed in the case of the octahedral grains, the increase in the temperature coefficient of the ionic conductivity indicated increase in the formation energy of interstitial silver ions at kink sites.

Figure 7 shows the sensitivities and fog densities of octahedral silver bromide emulsions, which were reduction-



Figure 5. Photographic sensitivity, fog density, and ionic conductivity of cubic silver bromide emulsion grains as functions of the amount of DMAB used for their reduction sensitization. Sensitivities of the emulsion layers chemically unsensitized and hydrogen-hypersensitized at 40° C for 4 h and at 50° C for 4 h, are denoted by arrows A and B, respectively.



Figure 6. Temperature dependence of dielectric loss curves of cubic silver bromide emulsion grains, which were unsensitized (solid curves) and reduction-sensitized with DMAB of 8.8×10^{-6} mol/ mol AgBr (broken curves).



Figure 7. Photographic sensitivity and fog density of octahedral silver bromide emulsions as functions of the amounts of stannous chloride (a) and thiourea dioxide (b) used for their reduction sensitization.



Figure 8. (a) Dielectric loss curves of octahedral silver bromide emulsion grains, which were unsensitized (solid curve) and reduction-sensitized with stannous chloride of 1.3×10^{-4} (broken curve) and 2.2×10^{-4} mol/mol AgBr (dashed curve). (b) Dielectric loss curves of octahedral silver bromide emulsion grains, which were unsensitized (solid curve) and reduction-sensitized with thiourea dioxide of 8.8×10^{-4} (broken curve) and 1.4×10^{-3} mol/mol AgBr (dotted curve).

sensitized with stannous chloride and thiourea dioxide as sensitizers. The formation of P centers on the emulsion grains was confirmed at the sensitizer concentration indicated by the arrows in this figure on the basis of decrease in photoconductivity of the emulsion grains and the appearance of the absorption band of P centers at 474 nm. Figure 8 shows the dielectric loss curves of these reduction- sensitized grains. The frequencies corresponding to the dielectric loss peaks of the grains on which P centers were formed were lower than those of unsensitized grains, indicating that formation of P centers decreased the ionic conductivity of the grains.

Figure 9 shows the sensitivity and fog density of the silver-digested emulsions. The silver digestion increased the sensitivity and caused fog formation depending on pH. Figure 10 shows the sensitivities of the emulsions silver-digested at pH 9 as functions of silver potential of the emulsions. The redox potential of a corresponding gelatin solution at pH 9 is also indicated by a broken line a. Significant increase in sensitivity was achieved by silver digestion for an emulsion at silver potential of the corresponding gelatin solution. This result indicated that reduction sensitization centers were formed as a result of the reduction of silver ions by gelatin.



Figure 9. (a) Photographic sensitivity, fog density, and ionic conductivity of octahedral silver bromide grains in emulsions, which were silver-digested at 60° C for 60 min at silver potential of 400 mV at pH denoted in the abscissa. (b) The same as Fig. 9(a), except cubic silver bromide grains.

The emulsions digested at pH 8, 9, 10, and 11 gave the absorption bands of P centers at 474 nm, and the emulsions digested at pH 10 and 11 gave the absorption bands of fog centers at 540 nm in their diffuse reflection spectra. It was judged that many P centers were formed on the emulsion grains digested at pH of 8 and 9, while fog centers were scarcely formed.

Figure 9 also shows the ionic conductivity of the digested emulsions along with the sensitivity of the emulsions as a function of the pH at which the emulsions were silver-digested. The ionic conductivities of the emulsion grains digested at pH 8 and 9 were lower than those of the corresponding undigested grains, which correlated with formation of P centers under these conditions and indicated that P centers formed by silver digestion decreased the ionic conductivities of both octahedral and cubic silver bromide grains.

The sensitivities of hydrogen-hypersensitized octahedral and cubic silver bromide emulsions are indicated in Figs. 1 and 5, respectively. Note that the sensitivities of the hydrogen-hypersensitized emulsions were markedly larger than those achieved by R centers of reduction



sensitization, suggesting formation of P centers in addition to R centers. Figure 11 shows the diffuse reflectance spectra of the thick emulsion layers, which were hydrogen-hypersensitized, indicating the formation of P centers as evidenced by the appearance of the absorption band at 474 nm. Figure 12 shows the dielectric loss curves of the hydrogen-unsensitized and hydrogen-hypersensitized emulsions, indicating that hydrogen hypersensitization decreased the ionic conductivities of the grains. The above-stated results indicate that P centers formed by hydrogen hypersensitization decreased the concentration of interstitial silver ions in the grains.

Proposal of New Model for R and P centers

In this study, silver clusters were formed on octahedral and cubic silver bromide emulsion grains by various methods including reduction sensitization with a variety of sensitizers, by silver digestion, and by hydrogen hypersensitization. The formation of P centers was confirmed by observing the sensitivity increase associated with the decrease of the microwave photoconductivity of the emulsion grains, which we attribute to the capture of photoelectrons by P centers and with the appearance of the absorption band of P centers at 474 nm in the diffuse reflectance spectra of the emulsions. In all the cases, it was found that P centers decreased the ionic conductivity of the emulsion grains studied.

It is known that carriers of ionic conductivity of silver bromide emulsion grains are interstitial silver ions, which are in equilibrium with silver ions at kink sites on the grain surface, as described in Fig. 13 and by the following equation.

$$Ag^{+}(kink) = Ag^{+}(interstitial) + Br^{-}(kink),$$
 (1)

where Ag⁺(kink) and Ag⁺(interstitial) are silver ions at a kink site and at an interstitial position, respectively, and Br⁻(kink) is a bromide ion at a kink site. Although Eq. 1 does not look balanced, it expresses the above-stated equilibrium by accounting for the fact that the jump of a silver ion at a kink site into an interstitial position leaves a bromide ion at a kink site. It has been reported that ionic conductivity proportional to the concentration of interstitial Figure 10. Photographic sensitivities of octahedral and cubic silver bromide emulsions, which were silver-digested at pH 9 and at silver potential denoted in the abscissa. The redox potential of an aqueous gelatin solution, which simulated the above-stated emulsions by using the same kind of gelatin and adjusting the concentration and pH to the values which were the same as those of the emulsions, was indicated by an "a".



Figure 11. (a) The diffuse reflectance spectra of thick layers of chemically unsensitized cubic silver bromide emulsions, which were not hydrogen-hypersensitized (solid curve) and hydrogen-hypersensitized at 40°C for 4 h (a broken line) and at 50°C for 4 h (a dashed line). The thickness of the emulsion layers was around 100 μ m. (b) The same as Fig. 11(a) except octahedral silver bromide emulsions.



Figure 12. (a) Dielectric loss curves of thick layers of chemically unsensitized cubic silver bromide emulsions, which were not hydrogen-hypersensitized (solid line), hydrogen-hypersensitized at 40°C for 4 h (broken line) and at 50°C for 4 h (a dashed line). The thickness of the emulsion layers was around 100 μ m. (b) The same as Fig. 12(a), except octahedral silver bromide emulsions.

silver ions was decreased by compounds such as 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI) and 1-phenyl-5-mercaptotetrazole (PMT). These compounds combined with silver ions at kink sites and prevented the silver ions from jumping into interstitial positions.^{15,16} But compounds such as cyanine dyes increase the concentration of interstitial silver ions by destabilizing and promoting silver ions at kink sites to jump into interstitial positions.¹⁸

It was found for the first time in the present work that P centers decreased the concentration of interstitial silver ions in silver bromide emulsion grains. From this result and the above-stated knowledge,^{15,16,18} it appears that P centers stabilize and prevent silver ions at kink sites from jumping into interstitial positions of silver bromide grains, as shown in Fig. 13. Specifically, we believe the interaction of a P center with a silver ion at a kink site is not merely physical, but chemical, and that a P center, which is Ag₂ adjacent to Ag⁺ at a kink site, combines with it to form Ag₃⁺ at a negatively charged kink site, as illustrated in Figs. 13 and 14.

Figure 14 illustrates the electronic structures of an R and a P center, based on the conventional model,^{5,6} and that of a P center on the new model proposed in this study. The electronic structures were given by the calculation with the Hueckel-approximation molecular orbital (HMO) method. Note that the electronic structure of Ag₂, which



Figure 13. (a) Illustration showing the equilibrium between silver ions at surface kink sites and interstitial silver ions in silver bromide. (b) Illustration showing the effect of a P center on the above-described equilibrium between a silver ion at a kink site and an interstitial silver ion on the basis of the ionic conductivity of reduction-sensitized silver bromide emulsion grains.

forms R and P centers according to the conventional model, is quite different from that of Ag_3^+ which forms a P center according to the new model. Namely, the HOMO and LUMO of a P center are much lower in principle than those of a R center according to the new model. According to this result, the new model is much more appropriate than the conventional one for the explanation of why on a silver bromide grain, an R center and a P center are a positive hole trap and an electron trap, respectively.

The old model predicts that both R and P centers are composed of dimers of silver atoms and have their absorption maxima at the same wavelength. But the new model predicts that the wavelength of the absorption maximum of P centers is longer than that of R centers, because the energy gap between the LUMO and HOMO of the former, which is inversely proportional to the wavelength of its absorption maximum, is much smaller than that of the latter. It is probable that the new model gives the explanation for the reason why the wavelength of the absorption maximum of P centers in Fig. 2 was longer than that of the absorption maximum of Ag₂ in rare gas matrix, which was reported to be 412 nm by Ozin et al.¹⁹

Figure 15 illustrates the electronic structures of R and P centers with variation of size on the basis of the new model proposed in this study. They were given by applying the HMO method to silver clusters in linear structure. Regardless of size, the electronic structures of the HOMO and LUMO of a P center are much lower than those of an R center, indicating that the former is an electron trap and the latter is a positive hole trap.



Figure 14. Illustration showing the conventional model and the new model proposed in this study for R and P centers on the basis of the electronic structures of linear silver clusters calculated by the HMO method.



Figure 15. Illustration showing the electronic structures of R and P centers with variation of the number of silver atoms (n) on the basis of the new model proposed in this study. The electronic energy levels of these centers were estimated by means of the HMO method under the assumption that these centers were linear in structure. An open circle indicates the lowest unoccupied level in each center.

In Figs. 14 and 15, the electronic energy levels of R and P centers were estimated by applying the HMO method to silver clusters,^{1,20} under the assumption that they were linear in structure. For isolated clusters in the uncharged, negatively charged, and positively charged states, Baetzold²¹ has concluded on the basis of calculation with extended Hueckel and CNDO methods that the minimum energy configuration occurs for linear arrays of silver nuclei when the number of atoms in the array is less than 30. Although the HMO calculation was simple and neglected the interaction of the silver clusters with the AgBr, it was rather useful to express clearly the difference in the electronic structure between the P centers on the conventional model and on the new one. Moreover, the difference between them was big enough to be explained by the simple method.

Figure 16 illustrates the growth of a P center (i.e., a latent subimage center) in the presence of R centers under illumination according to the new model. Absorption of a photon by a silver halide grain advances the growth

efficiently by inducing two parallel processes originating from a photoelectron and a positive hole, respectively. Each is composed of electronic and ionic processes. A photoelectron is captured by a P center (i.e., an electronic process) and then combines with an interstitial silver ion to add a silver atom to the center (i.e., an ionic process). A positive hole reacts with an R center to give a Ag_2^+ (i.e., an electronic process), which then dissociates to give a silver atom and an interstitial silver ion (i.e., an ionic process). Then, a silver atom dissociates to give an interstitial silver ion and a free electron (i.e., a Lowe's electron¹), which is available for the growth of an image center.

Discussion on the Formation and Properties of R and P Centers on the New Model

After Spencer and coworkers demonstrated the presence of two types of silver clusters on silver halide grains,² the present author proposed on the basis of several experimental results that the type with the ability to



Figure 16. Illustration showing the growth of a P center (i.e., a latent subimage center) in the presence of R centers. The growth is based on two parallel processes, each of which is initiated by absorption of a photon by silver halide and is composed of an electronic process followed by an ionic process. One of them is the capture of a free electron by a P center (Ag₃^{+1/2}) to give Ag₃^{-1/2} (an electronic process), which then combines with an interstitial silver ion to give Ag₄^{+1/2} (an ionic process). The other is the capture of a positive hole by an R center (Ag₂) to give Ag₂⁺ (an electronic process), which then releases an interstitial silver ion to give Ag (an electronic process). A single silver atom thus formed dissociates to give an interstitial silver ion and a free electron (i.e., Lowe's electron), which is available for the growth of an image center.

capture an electron was a silver cluster formed at a positively charged kink site (i.e., a P center) and the type with the ability to capture a positive hole was a silver cluster at a neutral site (i.e., an R center).³ Spencer proposed that an R center was a silver cluster formed at a negatively charged kink site.²² Moisar, Granzer, and coworkers proposed that a small silver cluster was a hole-trapping center while a large cluster was an electron-trapping center.²³

It seems that Moisar, Granzer, and coworkers made much of the size of silver clusters and underestimated the effect of surface sites where the centers were formed. It now should be accepted that the properties of R and P centers cannot be explained without accounting for the effect of surface sites where the centers were formed. As described in the previous article⁶ and here, reduction sensitization may produce sensitization centers composed of diners of silver atoms, estimated to be as many as 2800/ mµ² of the grain surface and 600/grain in the case of octahedral silver bromide grains (Fig. 1) under the assumption that each DMAB molecule gave six electrons to a grain and formed three sensitization centers on it. Although those centers were composed of dimers of silver atoms, they could be discriminated into positive hole traps and electron traps according to their effects on sensitivity and photoconductivity. These results indicated that the difference between R and P centers could be explained not by the difference in size, but by the difference in the site where they were formed.

According to the mechanism of latent image formation as illustrated in Fig. 16, a silver cluster at a positively charged kink site is stable, while a silver cluster at a negatively charged kink site is unstable. Because the charge of a kink site is one half of one electronic charge, a silver cluster at a positively charged kink site $(Ag_n^{+1/2})$ is in equilibrium with a silver cluster at a negatively charged kink site $(Ag_n^{-1/2})$ through an ionic process or an electronic process as described below.

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$$Ag_n^{+1/2} = Ag_{n-1}^{-1/2} + Ag^{+}(interstitial),$$
 (2)

$$\operatorname{Ag}_{n}^{+1/2} + e^{-} \to \operatorname{Ag}_{n}^{-1/2}, \qquad (3)$$

$$\operatorname{Ag}_{n}^{-1/2} + \mathbf{h}^{+} \to \operatorname{Ag}_{n}^{+1/2}, \tag{4}$$

where silver clusters Ag_n at positively and negatively charged kink sites are expressed by $Ag_n^{+1/2}$ and $Ag_n^{-1/2}$, respectively, and an interstitial silver ion by Ag^+ (interstitial). The mechanism illustrated in Fig. 16 is based on the assumption that a silver cluster at a positively charged kink site is much more stable than a silver cluster at a negatively charged kink site under the equilibrium described in Eq. 2.

According to Eq. 3, a P center that captures an electron would become a silver cluster at a negatively charged kink site, which is unstable and rapidly combines with an interstitial silver ion to form a silver cluster at a positively charged kink site. Otherwise, a P center that captured an electron should be subject to recombination by capturing a positive hole. Accordingly, a silver cluster at a negatively charged kink site, which Spencer considered as an R center, should not be stable from the viewpoint of the process originating from a photoelectron in Fig. 16.

If a silver cluster at a negatively charged kink site were stable, it would capture a positive hole to form a silver cluster at a positively charged kink site, which is a P center according to Eq. 4 and should be subjected to recombination by capturing an electron. Accordingly, a silver cluster at a negatively charged kink site should not be stable from the viewpoint of the process originating from a positive hole in Fig. 16.

The above-stated considerations eliminate a silver cluster at a negatively charged kink site as an R center and indicate that the mechanism of latent image formation as illustrated in Fig. 16 is based on the idea that only silver clusters at neutral sites and positively charged kink sites are stable and play important roles as R and P centers, respectively. It is understandable that a neutral silver cluster (Ag_n) is stable at a neutral site, and that Ag_n captures a positive hole to give Ag_n⁺, which is unstable owing to its electric charge of +1 at a neutral site and rapidly dissociates to give Ag_{n-1} at a neutral site and an interstitial silver ion. The idea that a silver cluster at a positively charged kink site is much more stable than a silver cluster at a negatively charged site is supported by the following proposal: Namely, a silver cluster at a positively charged site is stabilized by its chemical interaction with a silver ion at the kink site, while a silver cluster at a negatively charged kink site is not so stabilized.

Several articles have reported on the theoretical calculation of the stability of isolated silver clusters in the uncharged, negatively charged, and positively charged states.^{21,24} According to the theoretical calculation, Mitchell has concluded that Ag_3^+ is unstable, and Ag_4^+ is stable in silver halide.²⁴ It is however considered from the above-stated discussions that the stability of silver clusters depends on the sites where they are formed. Namely, neither Ag_3^+ nor Ag_4^+ should be stable at electrically neutral sites, because they were R centers that captured positive holes. But the decrease in ionic conductivity of silver bromide caused by P centers indicates that the Ag_3^+ at a negatively charged kink site is stable.

As shown in the previous article⁶ and in Fig. 1, the formation of R centers preceded the formation of P centers with increasing amount of reduction sensitizers. This result indicates that an R center is more stable and therefore more liable to be formed than a P center. Moreover, a silver cluster adjacent to a negatively charged kink site is unstable. The situation of an electrically neutral silver cluster adjacent to a neutral kink site is stable from the viewpoint of the neutralization of electric charge for the stabilization of the cluster and its surroundings. However, the situation of a neutral silver cluster adjacent to a positively charged kink site is not stable, and a negatively charged ion should be situated adjacent to a positively charged kink site for the stabilization of the cluster and its surroundings from this viewpoint. The situation of a neutral silver cluster adjacent to a negatively charged kink site is also unstable from the same viewpoint. The combination of a neutral silver cluster with a silver ion at a kink site results in the fact that a silver cluster adjacent to a positively charged kink site (i.e., P center) is more stable than a silver cluster adjacent to a negatively charged kink site.

The above-stated idea is also supported by the electronic states of an R center and a P center in the new model as examined by the HMO method. The electronic energy level of the HOMO of an R center of Ag_2 is -1β , and the binding energy is 2β /center and 1β /atom. But the electronic level of the HOMO of a P center of Ag_3^+ is 1.4β , and the binding energy is 2.8β /center and 0.9β /atom. Thus, it is judged from the binding energy/atom that less energy is required to form an R center than a P center.

However, note that from the energy of the HOMO, an R center is more likely to be oxidized than a P center.

It is inferred from the results shown in Fig. 1 and in the previous article⁶ that reduction sensitization could form many sensitization centers composed of dimers of silver atoms without forming larger silver clusters. Under the assumption that a DMAB molecule gave six electrons to an emulsion grain and formed three centers of dimers of silver atoms on it, reduction sensitization produces as many as 2800 silver dimers/ μ m² of the grain surface before it produced fog centers composed of larger silver clusters. Namely, it is considered that, although many dimers are formed, it is difficult for a dimer to grow to a trimer during the digestion for reduction sensitization if a dimer is much more stable than a trimer. This idea is supported by the molecular orbital theory,^{1,20} as depicted in Figs. 14

and 15 and also by the shell model for metal clusters.^{1,25–27} According to this model, each cluster is spherical in shape and has discrete electronic energy levels, such as the 1s, 1p, and 1d shells. One of the most important and experimentally confirmed characteristics of metal clusters is the magic number, which is the number of valence electrons at the closed shell configurations. Thus, the clusters with a closed shell, such as Ag_2 with a closed 1s shell, and Ag_8 with closed 1s and 1p shells, are more stable and liable to be formed than clusters with an open shell. Note that both which may function as an R center (Ag_2) and a P center (Ag_3^+) have the magic number of two, since the magic number is not the number of the atoms, but the number of valence electrons at the closed shell configurations.²⁷

Moisar, Granzer, and coworkers put P centers into the interior of emulsion grains, and observed the increase in both surface and internal sensitivities, which should be ascribed to the effect of hole trapping by the centers in the interior.²³ They considered that silver clusters acted as electron traps under some condition and as positive hole traps under others.²³ Hamilton gave a more plausible explanation, according to which a P center on the grain surface should be an R center in the interior.⁵ This explanation is also valid for the new model of a P center as illustrated in Fig. 14. According to the new model as illustrated in Fig. 14, the interaction of a P center with the grain surface is stronger than that of an R center, implying that P centers are more likely to be put into the interior than R centers.

Conclusion

- (1) It was found that P centers, which were produced on octahedral and cubic silver bromide emulsion grains by reduction sensitization with various sensitizers, silver digestion, and hydrogen hypersensitization, decreased the concentration of interstitial silver ion in the grains. This result indicated that P centers combined with silver ions at kink sites and prevented them from jumping into interstitial positions in the grains according to the equilibrium as expressed in Eq. 1.
- (2) It was proposed from the above-stated result that a P center based on a silver dimer is not merely Ag_2 adjacent to Ag^+ at a kink site, but Ag_3^+ at a negatively charged kink site (i.e., $Ag_3^{+1/2}$)
- This new model can explain the properties and be-(3)havior of silver clusters of photographic interest more successfully than the conventional one. The model explains the large difference in properties and behavior between R and P centers, the identification of an R center as a silver cluster at a neutral site, the sequence of the formation of R and P centers during the digestion for reduction sensitization, the reason for the formation of many silver dimers (i.e., reduction sensitization centers) without the formation of larger silver clusters (i.e., fog centers) by reduction sensitization, and the conversion of surface reduction-sensitization centers into internal ones.

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