Comprehensive Model for Sulfur Sensitization

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Abstract

The present author has proposed a comprehensive model for sulfur sensitization, according to which monomers and diners of substitutional sulfide ions on silver halides are sulfur sensitization centers acting as positive hole traps and electron traps, respectively, while silver sulfide clusters are fog centers. The difference in oxidation potential and absorption spectrum between sulfur sensitization centers and fog centers supported the proposed model. As many as 500 silver sulfide clusters (i.e., fog centers) /grain (i.e., 2400/mμ^2) were observed by an electron microscope in slightly fogged emulsions, indicating that the developability of each silver sulfide cluster was very low. The concentration of fog centers were independent of the amount of silver sulfide formed among variously fogged emulsions, suggesting that sulfur sensitization centers as well as fog centers were formed at surface sites, where sulfide ions were stable and liable to be coagulated. It is considered that low developability of silver sulfide clusters makes it possible to achieve high sensitivity and stability without fog formation in sulfur-sensitized emulsions. The model was successfully extended to sulfur-plus-gold sensitization centers.

Introduction

Sulfur sensitization is one of the most important and popular technologies to increase photographic sensitivity, and has ever been studied since its birth[1] by many investigators.[2] Recently, remarkable progress has been made on the knowledge of the structure and property of sulfur sensitization centers. Keevert and Gokhale[3] analyzed the rearrangement process of silver sulfide on silver halide emulsion grains on the basis of Smoluchouski's equation and concluded that sulfur sensitization centers were dimers of silver sulfide, which were as many as 1000/mμ^2 on the grain surface. Kanzaki and Tadakuma studied the property and structure of sulfur sensitization centers acting as electron traps by means of luminescence modulation spectroscopy and concluded that sulfur sensitization centers were dimers of silver sulfide, since the relative number of sulfur sensitization centers was proportional to the squared amount of silver sulfide formed.[4]

The above-stated progresses were desired to expand over wider area including roles of monomers, diners, and clusters of silver sulfide in order to get a comprehensive model for sulfur sensitization.

Proposal of a Comprehensive Model for Sulfur Sensitization

The present author selectively formed and characterized monomers, dimers, and clusters of silver sulfide on fine octahedral silver bromide grains in emulsions by digesting them in the presence of sodium thiosulfate under conventional condition and also in the presence of uniformly distributed sodium sulfide at the digestion temperature which was too low for silver sulfide molecules to coagulate on the grain surfaced.[5] He observed the increase in sensitivity through two steps with increasing the amount of sodium sulfide, and considered that the sensitivity increases in the first and second steps were brought about by monomers and dimers of silver sulfide, respectively. On the basis of the observation that the sensitivity increase in the first step was not associated with any change in the photoconductivity of the grains, it was considered that isolated silver sulfide molecules on the grain surface acted as positive hole traps. On the other hand, dimers of silver sulfide acted as electron traps, causing the sensitivity increase in the second step and the decrease in the photoconductivity.

He observed by an electron microscope silver sulfide clusters on the grains in emulsions, which were excessively sulfur-sensitized.[5] He also measured the oxidation potentials of sulfur sensitization centers and fog centers, which were formed on moderately and excessively sulfur-sensitized emulsion grains, respectively, and found that the former was more negative than that of the latter.

According to the above-stated results, he has proposed a comprehensive model for sulfur sensitizations according to which monomers and dimers of sulfide ions which substitute halide ions at the lattice positions on silver halides are sensitization centers acting as positive hole traps and electron traps, respectively, and silver sulfide clusters are fog centers. It is considered that the distinct difference in electron-trapping ability between the monomers and dimers requires the condition for sulfide ions to substitute halide ions at the lattice positions of silver halides. Namely, an substitutional sulfide ion is associated with an interstitial silver ion for the compensation of its excess electric charge in the lattice of silver halide. An interstitial silver ion carries a hydrogen-like orbital, which loosely binds an electron. A dimer of substitutional sulfide ions carries two interstitial silver ions and thus two hydrogen-like orbital which interact with each other to form an anti-bonding and bonding orbital It is considered that the bonding orbital provides an electron trap as a sulfur sensitization center. Since the amount of silver sulfide which gave fog was by two orders of magnitude larger than that of silver sulfide which gave the maximum sensitivity, it is reasonable to consider that fog centers were composed of clusters of silver sulfide itself.

Many groups of investigators studied the structure and property of silver sulfide crystal and specks in relation to sulfur sensitization centers under the assumption that sulfur sensitization centers had the structure and property which were similar to those of silver sulfide crystal.[1,2,6-14] The above-stated assumption differs from the compre-hensive model proposed in the previous paper[5], according to which fog centers have the property characteristic of silver sulfide, while sulfur sensitization centers have not. It is therefore important to make clear the difference in structure and property between sulfur sensitization centers and fog centers in relation to the structure and property of silver sulfide.

Verification of a Proposed Model

Further efforts have thus been made to characterize sulfur sensitization centers and fog centers to examine the proposed comprehensive model for sulfur sensitization.

The diffuse reflectance spectra of sulfur-sensitized octahedral silver bromide emulsions without fog centers gave the absorption band, which was centered at 500 nm and vanished at wavelength shorter than 760 nm. This band is thus ascribed to sulfur sensitization centers. As Morimura and Mifune found for the first time,[15] the absorption band, which was distinctive in the region with wavelength longer than 760 nm, was observed for the emulsions, which gave fog density, and was ascribed to fog centers according to their proposal. Namely, it was confirmed that the absorption bands of sulfur sensitization centers and fog centers differed from each other. Since silver sulfide grains are black, it seems that the absorption spectrum of fog centers is similar to that of silver sulfide, while the absorption spectrum of sulfur sensitization centers differed from it.

The oxidation potentials of sulfur sensitization centers and fog centers formed on octahedral and cubic silver bromide emulsion grains were measured under the assumption that the oxidation potential was in linear relationship with the highest occupied electronic energy level of a cluster.[5] The marked difference in property between sulfur sensitization centers and fog centers was revealed by the result that the oxidation potential of the latter was much more positive than that of the former, and more positive than 400 mV. Since the oxidation potential of silver sulfide grains was also more positive than 400 mV,[16] it is consid-ered that fog centers of sulfur sensitization possessed the property of silver sulfide, while sulfur sensitization centers did not.

The above-stated results indicated that the difference between sulfur sensitization centers and fog centers arose not merely from the difference in size, but also from the difference in the state of sulfide ions. The results supported the proposed comprehensive model,[5] and did not support the model on the basis of the assumption that sulfur sensitization centers had the structure and property which were similar to those of silver sulfide crystals.[1,2,6-14]

The oxidation potential of sulfur sensitization centers acting as positive hole traps was more positive than that of R centers of reduction sensitization centers.[2,17] This result is consistent with the fact that R centers are more effective for increasing photographic sensitivity than sulfur sensitization centers acting as positive hole traps.[5] It is considered that sulfur sensitization centers acting as electron traps are more important than those acting as positive hole traps. From this viewpoint, the result and consideration in this study are consistent with the proposal by Keevert and Gokhale[3] and by Kanzaki and Tadakuma[4] in that sulfur sensitization centers are composed of timers of silver sulfide.

With increasing the amount of sodium thiosulfate, the sensitivity of octahedral silver bromide grains with equivalent circular diameter of 0.2 μm increased and decreased after passing its maximum, and then fog appeared with sodium thiosulfate, amount of which was nearly two orders of magnitude larger than that of sodium thiosulfate which gave the maximum sensitivity. Many silver sulfide clusters per grain were observed in the electron micrographs of the gelatinate shells of even slightly fogged grains as well as of heavily fogged grains, while any silver sulfide cluster was not observed in the gelatinate shells of unsensitized grains. It was noted that the number of silver sulfide clusters observed was as many as 500 per grain (i.e., $2400/\mu m^2$) and independent of the amount of sodium thiosulfate (i.e., the amount of silver sulfide formed). The average size of silver sulfide clusters were several tens A, and increased with increasing the amount of sodium thiosulfate.

It is considered from this result that fog centers were formed at surface sites, concentration of which was fixed. Although the surface sites, where fog centers were formed, could not be identified in this study, they should be the place, where sulfide ions were stable and liable to be coagulated. It seems reasonable to assume that sulfur sensitization centers were formed at the same sites with $2400/m\mu^2$. It is interesting to note that the concentration of the centers observed was similar to those predicted for sulfur sensitization centers by Keevert and Gokhale[3] and by Kanzaki and Tadakuma.[4]

It was confirmed that the rate of development of fog centers was very slow and much slower than that of latent image centers, increasing with increasing the size of the centers. This result indicates that silver sulfide clusters, which were large enough to be observed by an electron microscope, had very low developability. The fact that those silver sulfide clusters could initiate development means that the bottom of the conduction band of the silver sulfide clusters was lower than the bottom of the conduction band of silver bromide grains, becoming to be lower with increasing the size of the clusters. The fact that the developability of the silver sulfide clusters was markedly smaller than that of latent image centers composed of silver cluster indicated that the bottom of the conduction band of the silver sulfide clusters was higher than the Fermi level or the electron-accepting level of silver clusters.

As stated above, the discrimination between sensitivity increase and fog formation by sulfur sensitization of octahedral silver bromide emulsions was significant in terms of the amount of sulfur sensitizer and silver sulfide formed, making it possible to achieve high sensitivity and stability without fog formation in the sulfur-sensitized emulsions. It is considered that the above-stated discrimination was given by low developability of silver sulfide clusters.

Proposal of a Model for Sulfur-plus-Gold Sensitization Centers

The adequacy of the above-stated model should be proved if it could be applied to sulfur-plus-gold sensitization centers According to the model for sulfur sensitization centers, it is proposed that a sulfur-plus-gold sensitization center is composed of a dimer of substitutional sulfide ions on silver halide, which is associated with a interstitial silver ion and a interstitial gold ion for the compensation of excess electric charges of sulfide ions in the lattice of silver halide.

The above-stated model for sulfur-plus-gold sensitization centers is characterized by (a) the replacement of an interstitial silver ion by a gold ion in a sulfur sensitization center, and (b) the increase in the distance between the two hydrogen-like electronbinding orbitals in the dimer due to its incorporation of a gold ion, which is larger than a silver ion. It is considered that the character (b) causes the decrease in the trap depth and the increase in the cross section of the center for an electron.

The above-stated model should be therefore proved by (a) the observations of the enhancement of incorpor-ation of gold ions into silver halide emulsion grains by preformed sulfur sensitization centers, (b) the confirma-tion of the fact that sulfur-plus-gold sensitization centers are associated with shallower trap depth and larger cross section as compared with sulfur sensitization centers. It was already reported by Hamilton, Harbison, and Jeanmaire[18] and Kellogg and Hodes[19] that the trap depth of sulfur-plus-gold sensitization centers for electrons was shallower than that of sulfur sensitization centers.

Yoshida, Mifune, and Tani[20] observed by use of ^{198}Au-labelled hydrogen tetrachloro aerate (III) as a gold sensitizer and ^{35}S-labelled sodium thiosulfate and triethyl thiourea as sulfur sensitizers that the incorporation of gold ions into silver bromide emulsion grains could be markedly enhanced by pre-formed sulfur sensitization centers.

Tani, Ohzeki, and Tsukada analyzed developer fog of sulfur-sensitized and sulfur-plus-gold-sensitized silver bromide emulsions under the assumption that the developer fog was initiated by the electron transfer from a developer to sulfur sensitization centers and sulfur-plus-gold sensitization centers on the emulsion grains, respectively.[21] It is therefore considered that the activation energy of the rate of development of developer fog increases with decreasing the trap depth of the centers, and that the frequency factor of the rate increases with increasing the cross section of the centers. He could get the evidence for the proposed model of sulfur-plus-gold sensitization centers by observing that the activation energy of the rate of development of developer fog of sulfur-plus-gold-sensitized silver bromide emulsions was larger than that of the corresponding sulfur-sensitized emulsions, and that the frequency factor of the rate of sulfur-plus-gold-sensitized emulsions was larger than that of the corresponding sulfur-sensitized emulsions.

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