JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY® • Volume 48, Number 3, May/June 2004

A Review of the Mechanism of Photographic Sensitivity and Roles of Silver Clusters

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Recent progress in the mechanism of latent image formation and roles of silver clusters in photographic sensitivity is reviewed with respect to classification of silver clusters: comparison between light and reduction clusters; preferential formation of reduction sensitization R centers to P centers; difference between latent sub-image centers and P centers; characterization of R and P centers by photoconductivity measurements; utility of R centers with two electron sensitization; and direct observation of latent image and fog centers.

Journal of Imaging Science and Technology 48: 278–284 (2004)

Introduction

The mechanism of photographic sensitivity is one of the most important subjects in silver halide photography, and has continuously progressed owing to extensive studies by many groups of investigators over many years.[1] There are however many subjects in the mechanism of photographic sensitivity which should be solved from the quantitative viewpoint. They were recently discussed at international scientific meetings and in journals. On the basis of this progress and discussion, this review is undertaken to summarize our present understanding of the mechanism of photographic sensitivity and roles of silver clusters in photographic process.

Current Understanding of Mechanism of Photographic Sensitivity

The historical description of the mechanism of photographic sensitivity has been provided elsewhere.[2] The outline of the mechanism of photographic sensitivity of silver halide grains,[1] as currently accepted by many photographic scientists and engineers, is described below. Many silver ions are displaced from kink sites on the grain surface to interstitial positions in the interior, and are mobile in a silver halide grain.[3] By use of chemical reactions, electron trapping chemical sensitization centers are formed on the grain surface.[3] There are as many as 1000 – 3000/μm^2 on the grain surface.[4–8] It has been proposed that each center is composed of a dimer of silver sulfide,[4–9] more specifically a dimer of substitutional sulfide ions,[7] which substitute halide ions at lattice positions and are accompanied by two interstitial silver ions for charge conpensation. It has been also proposed that the replacement of one of these two interstitial silver ions by a gold ion gives a sulfur-plus-gold sensitization center.[10]

A silver halide grain absorbs blue light to generate free electrons, i.e., photoelectrons, and positive holes. Photoelectrons take part in the formation of latent image centers. Green and red light are absorbed by sensitizing dye molecules adsorbed on the surface of a silver halide grain. Photoexcited dye molecules inject electrons into the conduction band of a grain, leaving positive holes in the dye phase, i.e., dye positive holes. Injected electrons take part in latent image formation.

A photoelectron migrates in a grain, being repeatedly trapped and detrapped by chemical sensitization centers. This is called the electronic process. While a photoelectron is trapped by one of chemical sensitization centers, an interstitial silver ion nearby may migrate and reach the center. As a result, a silver atom is formed there, and the electron trapping ability of the center is thus reset. This is called the ionic process. Repetition of electronic and ionic processes at the same center leads to the formation and growth of a silver cluster. A cluster which becomes large enough to initiate photographic development is called a latent image center. The latent image formation is thus the result of the concentration principle, according to which the effect of the absorption of photons taking place at various places in a grain is concentrated into one place.

A latent image center is a deep electron trap, and can accept an electron from a developing agent in a developer. A center, which has accepted an electron from a developer, attracts an interstitial silver ion and reacts with it to form a silver atom. The repetition of these processes converts an entire silver halide grain into a silver grain. The formation of silver grains gives a negative working black-and-white image. The formation of dyes by the reactions of oxidized developing agents with color couplers gives a negative working color image.

Original manuscript received July 7, 2003

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The size of the smallest latent image center is very important information for understanding photographic sensitivity, and has been evaluated by many groups of investigators.[11–16] It is now generally accepted that the smallest latent image center is composed of three and four atoms in the presence and absence of gold sensitization, respectively. The efficiency of latent image formation is usually expressed in terms of quantum sensitivity, which is defined as the number of absorbed photons per grain needed to render half the existing emulsion grains developable. It was reported that less than three absorbed photons were needed to form a latent image center on a sulfur-plus-gold-sensitized and hydrogen-hypersensitized silver bromide grain with size of less than 0.5 μm.[13,17] Recently, the quantum sensitivity of a highly sensitive silver halide emulsion used for color reversal film was reported to be 5 absorbed photons per grain.[18]

Two Kinds of Silver Clusters

As stated above, silver clusters play central roles in photographic sensitivity. The exposure of a silver halide grain to light leads to the formation and growth of a silver cluster, i.e., a light cluster. On the other hand, the reduction of a silver halide grain also leads to the formation of silver clusters, i.e., reduction clusters. Moderate reduction of silver halide grains leads to the formation of silver clusters which cause the increase in sensitivity without initiating photographic development, and are called reduction sensitization centers. On the other hand, excessive reduction of silver halide grains causes the formation of silver clusters which initiate development by themselves, and are fog centers.[1]

By use of an elegant experiment, Spencer, Brady, and Hamilton indicated that light clusters appeared and grew under illumination, while reduction clusters, i.e., reduction sensitization centers, disappeared under illumination.[19] It was thus experimentally made clear that there are two kinds of silver clusters; clusters growing under illumination by trapping electrons and those disappearing under illumination by trapping positive holes.

Several ideas have been proposed to explain the reason for the presence of two kinds of silver clusters. On the basis of thermodynamic study of silver clusters, Moisar et al. proposed an idea that a smaller cluster trapped a positive hole, while a larger one trapped a photoelectron.[20] This idea was however not in accord with the mechanism of photographic sensitivity, according to which an image center should grow by trapping a photoelectron even when it was small. Spencer proposed an idea that a silver speck acting as a positive hole trap was formed in adjacent to a negatively charged site.[21] However, a silver speck in adjacent to negatively charged site should not be present for efficient formation of latent image centers, since it should act as a recombination center. When a silver cluster at negatively charged site traps a positive hole, it becomes to be a positively charged silver speck in adjacent to a negatively charged site, which is stable and can capture a photoelectron.

Tani also attributed the difference in behavior between two kinds of silver clusters to the difference in the electric charge of the sites where they were formed.[22] However, silver clusters formed at neutral sites in stead of negatively charged sites were considered hole trapping centers, while silver clusters formed at positively charged sites were considered electron trapping centers.[22] Following Tani's proposal, Hamilton and Baetzold constructed the models for two kinds of silver dimers on {100} face of silver bromide, and verified Tani's proposal by a molecular orbital calculation. According to their calculation, the electronic energy level of LUMO (the lowest unoccupied molecular orbital) of a silver dimer at a positively charged kink site was lower than the bottom of the conduction band of silver bromide, and that of HOMO (the highest occupied molecular orbital) of a silver dimer at a neutral kink site was higher than the top of the valence band. The former and the latter were named P and R centers, respectively, since it was considered that they were formed by photolysis and reduction of silver bromide, respectively.[23]

Tani and Murofushi applied reduction sensitization to a simple model emulsion composed of monodispersed fine silver bromide grains. With increasing amount of a reduction sensitizer, sensitivity increased in two steps, indicating the formation of two kinds of reduction sensitization centers. The centers responsible for the first step of sensitivity increase decreased radiowave photoconductivity of silver bromide grains with positive holes as carriers,[26] and the centers responsible for the second step of sensitivity increase decreased the microwave photoconductivity with photoelectrons as carriers (Fig. 1).[24,26] This result could indicate that the former and the latter were R and P centers of reduction sensitization, respectively, and seemed to be in accord with Spencer's observation that latent image centers were not formed at reduction sensitization centers when his emulsion was moderately reduction sensitized, while they were formed at reduction sensitization centers when his emulsion was intensely reduction sensitized.[21(a)] In accord with the above results, formation of electron trapping silver clusters, without ability to initiate development by reduction of silver bromide grains, could be further experimentally confirmed by Tani and others with various experiments,[27] by Marchetti and others with the analysis of the luminescence of clusters,[28] and by Baetzold with theoretical calculations.[29]

The idea that reduction sensitization centers are composed of dimers of silver atoms (more precisely, silver clusters with two valence electrons) is now accepted by many photographic scientists and engineers. The present author considers the reason for it to be as follows. According to the evaluation of the size of the smallest latent image center,[11–16] an electron trapping cluster composed of four or more of silver atoms initiates development. The reduction of a silver bromide grain leads to the formation of many electron trapping centers without developability, i.e., reduction sensitization P centers, before it leads to the formation of centers with developability. When reduction sensitization P centers are much more stable than larger clusters, the additional reduction of a grain leads to the formation of new P centers, rather than the growth of P centers which are already present. According to cluster science, this phenomenon can be realized when a P center contains a magic number of valence electrons.[30,31] The magic number indicates the number of electrons for completing the closed shell in a metal cluster. The smallest magic number is two for filling a 1s orbital with electrons, and the next smallest is eight for filling both 1s and 1p orbitals with electrons. Since an electron trapping cluster with eight valence electrons should initiate development, a P center should contain two valence electrons.

We note that the magic number is not the number of atoms in a cluster with a closed shells of electrons, but the number of valence electrons to complete the closed shells of electrons in a cluster according to cluster science.[31] The present author has proposed and proved that a silver dimer combines with a silver ion at a kink site,

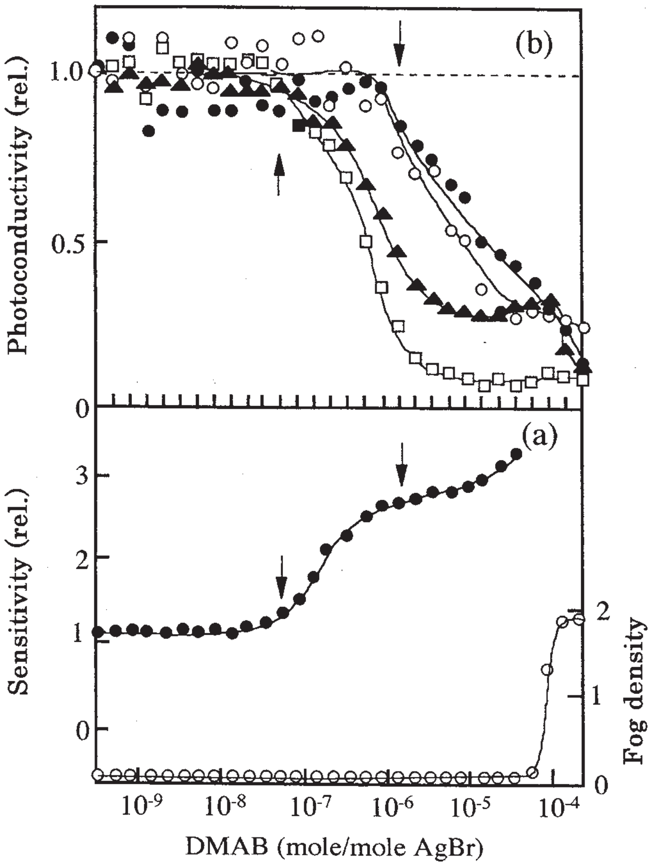

Figure. 1. (a) Sensitivity and fog density, and (b) photoconductivity of reduction sensitized octahedral silver bromide emulsion grains (0.2 μm) as a function of the amount of dimethylamine borane (DMAB) used for the reduction sensitization of the grains. The photoconductivity measurements were made by using four methods [9 GHz microwave photoconductivity at –150°C (●), 35 GHz microwave photoconductivity at room temperature (○), and radio wave photoconducrivity at room temperature with and without addition of an electron trapping dye (Pinakriptol Yellow: 1.1 mmol/mol AgBr) to emulsion layers (□ and ▲, respectively)].[26] *(Courtesy of Imaging Sci. J.)*

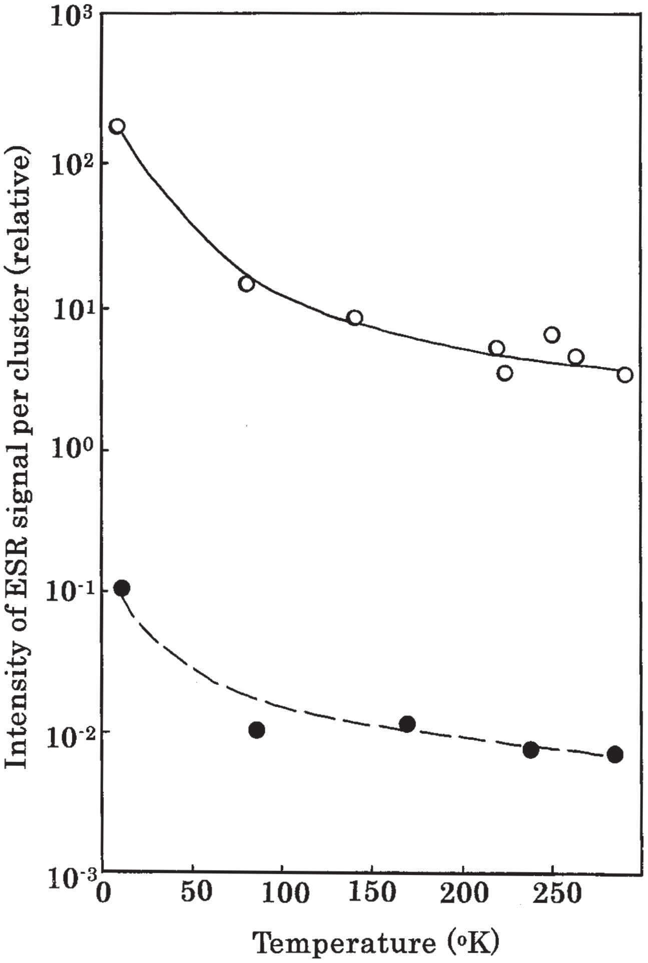

Figure 2. Temperature dependence of intensity of ESR signals of light clusters (○) and reduction (●) of silver atoms on cubic AgBr grains with edge length of 0.18 μm. The average sizes of the light and reduction were 5.3 and 5.5 nm, respectively. The ESR signals of the light clusters and reduction ones were structureless, and appeared at the g values of 2.005 and 2.003, respectively.[32]

TABLE I. Sizes and Energies of Silver Clusters

Diameter (nm)	No. of Ag atoms*	E_A (eV)†	Δ (eV)‡
2	240	1.0	1.8×10^{-2}
5	3,800	0.4	1.1×10^{-3}
10	31,000	0.2	1.4×10^{-4}

* Calculated values under the assumption that silver clusters are crystalline with the same lattice constant as bulk silver.

† $E_A = e^2/2\pi\varepsilon_0 d$, where ε_0 was the dielectric constant of the medium of the silver clusters.

‡ $\Delta = E_F/n$, where E_F is the Fermi energy of silver, i.e., 4.3 eV, and n is the number of silver atoms in a cluster.

and that a reduction sensitization P center is Ag$_3^+$ in adjacent to a negatively charged kink site rather than Ag$_2$ adjacent to a positively charged kink site.[27(a)] Both an Ag$_3^+$ as well as an Ag$_2$ species contains two valence electrons to complete the closed 1s shell, and may be regarded as dimers of silver atoms.

Excessive reduction of silver halide grains causes formation of nanoclusters, which are observable by an electron microscope.[26] Tani made a comparison in formation and properties between light and reduction nanoclusters with the same number and size distribution.[32] The formation of only one light nanocluster per grain was distinct from the formation of many reduction nanoclusters per grain,[26,32] as already observed with an arrested development technique by Spencer et al.[19,21(a)] Although formation of a single light cluster per grain is the result of the concentration principle, formation of many reduction clusters per grain is not, and therefore involves neither a free electron nor a single silver atom.

It was also found from the electron spin resonance (ESR) measurement of the light and reduction nanoclusters on fine silver bromide grains that the magnetic susceptibility of each reduction nanocluster was as small as less than 1/1000 of that of each light nanocluster.[32] This result was analyzed by applying Kubo theory[33] to nanoclusters with average, smallest, and largest sizes in the above study, as shown in Table I. The difference in electriconic energy between a cluster and a cluster with one excess charge (E$_A$) was evaluated to be fairly large as also shown in Table I, especially for a cluster with average or smallest size to exchange

TABLE II. Characterization of Silver Clusters (Agn) on Silver Halides

Preparation	Function	Even/odd valence electrons	Presence	Number per grain	Roles of clusters with n valence electrons in photographic processes
By light	Electron trap	Even	Present	1	$n > 2 \sim 3$: Latent sub-image center
		Odd	Present	1	$n \geqq 4$: Latent image center
	Positive hole trap	Even	Absent		
		Odd	Absent		
By reduction	Electron trap	Even	Present	Many	$n = 2$: Reduction sensitization P center $n >> 2$: Fog center
		Odd	Absent		
	Positive hole trap	Even	Present	Many	$n = 2$: Reduction sensitization R center
		Odd	Absent		

an electron with its surroundings on storage after formation. The spacing of the adjacent electronic energy levels in a cluster (Δ) was evaluated to be much larger than the Zeeman energy splitting of the spin-up and spin-down states at the X-band frequency used for ESR measurements. It was therefore likely that a silver nanocluster in the above study neither exchanged an electron with its surroundings nor changed the direction of electron spins in it after it was formed. Therefore low temperature odd and even silver nanoclusters should exhibit Curie law paramagnetism and diamagnetism, respectively, and that ESR signals should only be observed from the odd clusters in the sample at low temperature. The above result of the ESR experiment therefore indicated that all the reduction nanoclusters were even clusters and formed as the result of the coagulation of silver dimers to saturate the surface kink sites of the grains.[32]

Classification of Silver Clusters Formed on Silver Halide Grains

By light or reduction, silver clusters which vary in size and properties are formed on the surfaces of silver halide grains. Owing to the complicated process of advance in photographic sensitivity, there may be some confusion regarding concepts and technical terminology in relation to silver clusters on silver halide grains. The present author has tried to summarize the knowledge of silver clusters formed on silver halide grains in Table II.

Clusters formed on the grains by light and reduction are called light and reduction clusters, respectively. Clusters composed of even and odd numbers of valence electrons are called even and odd clusters, respectively. While a light cluster is always an electron trap, a reduction cluster may be an electron trap or a positive hole trap. Owing to the concentration principle, only one light cluster is formed on a fine grain, and may be either an even cluster or an odd cluster. Since the smallest latent image center is composed of four silver atoms (more precisely, four valence electrons) on a silver bromide grain in the absence of gold sensitization,[12,14,15] a latent sub-image center is composed of either two or three silver atoms, i.e., valence electrons, and a latent image center is composed of four or more silver atoms, i.e., valence electrons.

While reduction clusters may be either positive hole traps or electron traps, they are always even clusters.[32] On the contrary to the case of light clusters, many reduction clusters are formed on a grain, and dimers (more precisely, clusters with two valence electrons) are stabilized at surface kink sites to act as reduction sensitization centers. By observing and analyzing phenomena as a function of the amount of reduction sensitizer, it was confirmed that the formation of R centers of reduction sensitization precedes the formation of P centers.[24] This result indicated that the formation of R centers were more likely than P centers. We infer that R centers are more stable than P centers,[24,27] and/or that the concentration of neutral kink sites for R centers is greater than that of positively charged kink sites for P centers.[29] When the number of silver dimers exceeded the number of available surface kink sites, the rest of the dimers coagulate to form nanoclusters which act as fog centers.

Hamilton and Baetzold considered that electron trapping and hole trapping clusters would be formed by photolysis and reduction, respectively, and named them P and R centers, respectively.[23] Since it was found that electron trapping silver clusters could also be formed on reduction,[24,26] the nomenclature, P and R centers, is now confusing. In this paper, electron trapping and hole trapping reduction sensitization centers are named reduction sensitization P and R centers, respectively, since they are the same in structure as P and R centers in the model of Hamilton and Baetzold.[23]

Preferential Formation of Reduction Sensitization R Centers to P Centers

Tani et al. demonstrated that electron trapping silver clusters were also formed on silver halide grains by reduction.[24,27] This observation was confirmed by Spencer and others,[21(a)] Marchetti and others,[28] Kawasaki and Oku,[34] Baetzold,[29] and Guo and Hailstone.[35]

Tani and Murofushi also demonstrated the preferential formation of reduction sensitization R centers to P centers by showing that formation of R centers preceded formation of P centers as the amount of a reduction sensitizer increased.[24] This result was confirmed by Baetzold by theoretical calculation.[29] With increasing amount of a reduction sensitizer, R centers are at first formed at neutral kink sites, and P centers are then formed at positively charged kink sites after neutral kink sites have been saturated with dimers.

The observation of this phenomenon was successful when experimental conditions of uniform samples and accurate measurement of photographic sensitivity could be realized. Since only one latent image center was formed on a grain in the emulsion they used, the emulsion suffered neither from latent image dispersion nor competition between surface and interior of the grains. Moreover, the change in the sensitivity of the emulsion with changing the amount of reduction sensitizers was measured with careful control of experimental condition and high reproducibility.[24] It should be especially noted that mild and controllable reducing agents were used as reduction sensitizers, and that many experimental points were obtained with fairly good reproducibility in comparison with others.[25]

Is a Reduction Sensitization P center the Same as a Latent Sub-Image Center?

A latent sub-image center, which is formed by imagewise exposure, is stable and lacks ability to initiate photographic development. It seems that a reduction sensitization P center may be the same as a latent sub-image center, since both of them are stable, lack of ability to initiate development and capture photoelectrons to grow under illumination. Accordingly, much discussion has been made if a reduction sensitization P center were the same as a latent sub-image center.

Table II reveals the difference between a reduction sensitization P center and a latent sub-image center. A reduction sensitization P center is a dimer of silver atoms (more precisely, a cluster with two valence electrons), while a latent sub-image center may be either a dimer or a trimer of silver atoms. While a dimer captures an electron at its LUMO, a trimer captures an electron at its SOMO (the singly occupied molecular orbital). The height of SOMO of an odd cluster is generally lower in electronic energy than that of LUMO of an even cluster with similar size. It is therefore considered that the electron trapping activity of a trimer is much larger than that of a dimer, and causes it to act a concentration center for the growth of an image center. Of course, a reduction sensitization P center is the same as one of the two kinds of latent sub-image centers, whose electron trapping ability is much smaller than the other. The idea that the electron trapping ability of reduction sensitization P centers should exceed that of sulfur sensitization centers[35–37] is not therefore appropriate.

Discussion has taken place regarding usefulness of P centers for efficient formation of latent image centers. Leubner proposed that a latent image center can be formed by one absorbed photon per grain in the presence of both reduction R and P centers.[38] Namely, one absorbed photon generates a photoelectron and a positive hole. A photoelectron is captured by one of reduction sensitization P centers. A captured electron attracts an interstitial silver ion and combines with it to form a trimer of silver atoms. According to Lowe's mechanism,[1] a positive hole reacts with one of R centers to generate a free electron, which is captured by the trimer and combines with an interstitial silver ion to form a tetramer of silver atoms. Thus, one absorbed photon renders a grain developable if a tetramer can act as a latent image center.

This idea does not, however, correspond with the fact that the quantum sensitivity of an optimally reduction sensitized fine silver bromide emulsion was found to be ~30 absorbed photons per grain,[24,27] and reduction sensitization does not, therefore, seem to be as effective as expected by Leubner. Moreover, grains with P centers are easily rendered developable by gold ions, while R centers are not.[27(d)] By taking into account the fact that gold sensitization is indispensable to highly sensitive emulsions, reduction sensitization P centers are not useful for highly sensitive silver halide emulsions, since they can not coexist with gold sensitization centers without causing fog formation.

While the preparation of clusters formed by light contains many odd clusters, all the reduction clusters are even clusters.[32] It is therefore important to understand the difference between even and odd clusters. The even-odd distinction of image centers was theoretically pointed out by Baetzold,[39] and experimentally confirmed by Kawasaki, Tsujimura, and Hada.[40] Namely, the electron trapping orbital of an even cluster is its LUMO, while that of an odd cluster is its SOMO. It has therefore been proposed that the electron trapping levels of odd clusters should generally be deeper than those of even clusters. Although Tani proposed an idea that the degree of the difference in trap depth between odd clusters and even clusters would decrease by their interaction with silver ions at surface kink sites,[27(a)] he could still observe that the developability, i.e., ability to accept an electron from a developer, of odd nanoclusters was larger than that of even nanoclusters.[32] This tendency should be enhanced as the size of clusters decreases.

Characterization of Reduction Sensitization Centers by Photoconductivity

The electron trapping ability of reduction sensitization P centers was proved by observing the decrease in time resolved photoconductivity of silver halide grains when such centers were introduced onto the grains.[24,26] A 35 GHz microwave photoconductivity apparatus with a light pulse of 10 ns was used to observe the change in the concentration of photoelectrons with time. The exposure of the light pulse for the photoconductivity was comparable to that for the latent image formation on fine silver halide grains.[41] Since it was reported by Serpone, Lawless, and Sahyun that laser flash photolysis (35 ps pulse, 355 nm) of sub-μm cubic silver bromide emulsion grains led to reversible formation of light absorbing transients assigned to silver clusters,[42] it was anticipated that electron trapping silver clusters formed during photoconductivity measurement by themselves decreased the photoconductivity. However, this expectation was not realized, since the photoconductivity of a sample as measured by the first exposure was equal to that of the same sample by the second exposure within experimental error.

The above result could be explained as follows. Since the light pulses for the laser flash photolysis[42] and the photoconductivity measurement[24,26] were 35 ps and 10 ns in half width, respectively, the number of photons per second of the former pulse should be much larger than that of the latter. Futhermore, the intensity of the light pulse used for the photoconductivity measurement was in the ordinary photographic regime, i.e., it was comparable to that for latent image formation on fine silver halide emulsion grains.[41] On ordinary exposure, only one cluster was usually formed on a fine silver bromide grain.[26,32] Under illumination, an electron trapping cluster grows by capturing a photoelectron and an interstitial silver ion sequentially. It takes around a microsecond for an interstitial silver ion to reach and reset a trap, which captures an electron.[3,42] It is not therefore likely that electron trapping clusters form during the photoconductivity measurement and thereby decrease the photoconductivity.

Hailstone pointed out the following possibility.[36] After a reduction sensitization R center captures a positive hole to form Ag_2^+ during photoconductivity measurement, Ag_2^+ should capture a subsequent photoelectron to decrease photoconductivity. On the other hand, Tani and others observed that the dependence of sensitivity on the amount of reduction sensitizer indicated two kinds of reduction sensitization centers. The first one of them decreased radiowave photoconductivity with positive holes as carriers without decreasing 35 GHz microwave photoconductivity with photoelectrons as carriers, and was ascribed to a reduction sensitization R center.[26] The second one decreased 35 GHz microwave photophotoconductivity with photoelectrons as carriers, and was ascribed to a reduction sensitization P center.[26] This result could exclude the possibility pointed out by Hailstone, since R centers, as approved by radiowave photoconductivity measurement, could not decrease the photoconductivity with photoelectrons as carriers. While positive holes survived for more than several microseconds, photoelectrons disappeared by 20 nanoseconds in fine silver bromide grains.[26] It was thus found that most photoelectrons already disappeared when many Ag_2^+ were formed as the result of the capture of positive holes by R centers. If R centers would act as recombination centers, they should not increase photographic sensitivity.

Hailstone also pointed out[36] that Hirano observed the capture of positive holes by reduction sensitization centers by radiowave photoconductivity measurement.[43] However, the reproducibility and accuracy of the apparatus used by Hirano was not good enough to distinguish between R centers and P centers, and needed considerable improvement in sensitivity to be useful for that purpose.[44,26] In addition, it does not appear that silver iodobromide grains of 0.5 μm size as used by Hirano were sufficiently uniform for preferential formation of R centers over P centers.

Usefulness of R Centers and Two Electron Sensitization

For many years, it was understood that reduction sensitization R centers increase photographic sensitivity by irreversibly trapping positive holes and preventing them from recombining with photoelectrons. Lowe expected more than that for reduction sensitization by proposing the following processes[45]: An R center captures a positive hole to give Ag_2^+, which then undergoes to ionic relaxation. Namely, Ag_2^+ dissociates to give a silver atom and an interstitial silver ion. Then, a silver atom dissociates to give an interstitial silver ion and a free electron. In total, one absorbed photon generates two free electrons in the presence of reduction sensitization R centers. This is a proposal of so-called two electron sensitization based on reduction sensitization centers.

Lowe's proposal for two electron sensitization with reduction sensitization centers was experimentally demonstrated by Tani[46] and Hailstone.[17] Lowe's process of two electron sensitization could explain the observation that less than three absorbed photons were needed to form a latent image center on a fine silver bromide grain in a sulfur-plus-gold-sensitized and hydrogen-hypersensitized emulsion in spite of the fact that the smallest latent image center contained three atoms (more precisely, three valence electrons). It was therefore made clear that two electron sensitization was useful for designing highly sensitive silver halide emulsions.[13,17] It is considered that the rate determining step of Lowe's process is the dissociation of a silver atom, and therefore needs several seconds.[47] In addition, the quantum yield of Lowe's process was evaluated to be about 50%.[48] Therefore there is considerable room for improvement in the capability of reduction sensitization, from the viewpoint of two electron sensitization.

Recently, different two kinds of two electron sensitization were proposed and discussed. On the basis of the current doubling effect with formate in electrophotochemistry,[49] a new proposal was made by Belloni and others for two electron sensitization with formate ion doped into silver halide grains,[50] although it does not appear to have been extended by themselves or others in the open literature up to the present time. On the basis of one photon-two electron photoreduction reactions in photochemistry,[51] another new proposal was made by Muenter et al. for two electron sensitization, and demonstrated by themselves.[52] Two electron sensitization attracts the current interest of many photographic scientists and engineers, and has been actively discussed at international meetings.

Observation of Latent Image Centers

As indicated by many discussions in this article, the knowledge of the size, structure, number, and location of latent image centers on silver halide grains is very important to make clear the mechanism of photographic sensitivity, and this need has driven many photographic scientists to try to observe latent image centers on the grains. However, photographic scientists have found it difficult to observe latent image centers on silver halide grains by electron microscopy, since the smallest latent image center comprises a cluster as small as 3 – 4 atoms. Although such new methods as STM and AFM have been developed, STM is not applicable for the observation of the surface of silver halide. While AFM is suitable for observation of the lattice on the surface of silver halide, it is not capable of observation of small centers on the surface owing to the limitations of its resolution. An arrested development method has usually been used as an expedient method to determine the number and location of latent image centers,[53] but it cannot provide knowledge of the size and structure of latent image centers.

Tasaka, Murofushi, and Tani found that latent image centers formed at the shoulder of the characteristic curve are large enough to be observable by electron microscopy. They observed latent image centers formed at the shoulders of characteristic curves of fine silver bromide emulsions, and obtained the direct and quantitative information of the size distribution and number of the centers without using a development procedure.[54] It is expected that future progress in surface analysis will make it possible to observe smaller latent image centers on silver halide grains.

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