Dispersion of Latent Image Specks at Reduction-Sensitized Emulsions

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Abstract

Dispersion of latent image specks (LIS) on reduction-sensitized octahedral (Oct) and cubic (Cub) grain emulsions was studied. The number of developed small silver clusters in a grain was counted and the distribution was observed. At 1 sec exposure only the highly sensitized Oct emulsion indicated the wide Poisson distribution and the other emulsions indicated the narrow one-cluster-per-grain distribution. At 10^{-4} sec exposure all the sensitized emulsions indicated the Poisson distribution. The microwave photoconductivity was also measured and the decay lifetime was almost same at every sensitized level for the both emulsions. The P-centers where LIS was formed were more easily formed on the {111} surface than on the {100} surface. They acted as an electron trap but did not affect the decay lifetime as the number of them in a grain was not so large.

Introduction

Properties of reduction sensitization center were discussed by many authors. Hamilton and Baetzold proposed two kinds of centers, P-centers and R-centers.[1] They suggested that the former was formed on a positively charged kink site and acted as an electron trap (e-trap), and the latter was formed on a neutral kink site and acted as a hole trap (h-trap). This ingenious consideration was referred to the centers formed on {100} surface. If the {111} surface was regarded as an accumulation of negative kink site, there would be no P-centers on the {111} surface.

Difference of photographic sensitivity between the {100} and {111} surfaces was also discussed by many authors, but effects of the difference to the reduction sensitization was not discussed so much. Tani and Takada compared photographic sensitivity, fog density and photoconductivity between octahedral grain (Oct) emulsion and cubic grain (Cub) emulsion, and proposed that the centers which acted as the electron trap were formed more on the Oct emulsion than on the Cub emulsion.[2]

It was considered that the density of e-traps in a grain affected the dispersion of latent image specks (LIS). When there were many P-centers, several numbers of LIS would be formed and the dispersion would be enhanced. The arrested development technique is one of the effective method to examine the dispersion of LIS. Spencer observed the distribution of the number of LIS in a grain at the reduction sensitized emulsions.[3] However, he used only the Oct emulsion. Comparison between the Oct and the Cub emulsions by this technique has not been done. We compared the dispersion of LIS by this technique and the decay lifetime of photoelectrons by the microwave photoconductivity technique. Then, we considered the property of reduction sensitization centers in the Oct and the Cub emulsions.

Experimental

Two photographic emulsions were used. Both were pure silver bromide monodisperse grains, and one consisted of octahedral grains of 0.44 μm diameter and the other consisted of cubic grains of 0.43 μm edge length.

DMAB was used as a sensitizer. Amounts of the sensitizer were 0.1, 0.4 and 1 mg per AgBr mol for the Oct emulsion and 0.05, 0.07 and 0.1 mg per AgBr mol for the Cub emulsion. We will represent them as Cub(0.1 R) or Oct(1 R), etc. These emulsions were coated on a polyester base to make the maximum density to ca. 1.

They were exposed through step wedge for 1 sec with JIS III sensitometer or for 10^{-4} sec with Edgerton mark VII sensitometer.

The arrested developer used here was an *p*-phenylene-diamine developer and it's formula was shown in Table I. This developer was a little different from the one previously reported[4] as this did not contain a quaternary ammonium salt as a restrainer. This developer did not dissolve the grains and so the grains kept clear shapes after development. Development time was adjusted to make a suitable size of silver speck. For the sensitometry we used the modified M-AA-1 developer where the amount of sodium metaborate was doubled.

We observed carbon replicas of the developed grains with the electron microscope and counted the number of small developed silver clusters on a grain. The comparison was made at the exposure value of the fraction of developed grains between 0.5 and 0.7. The following values were obtained for evaluation.

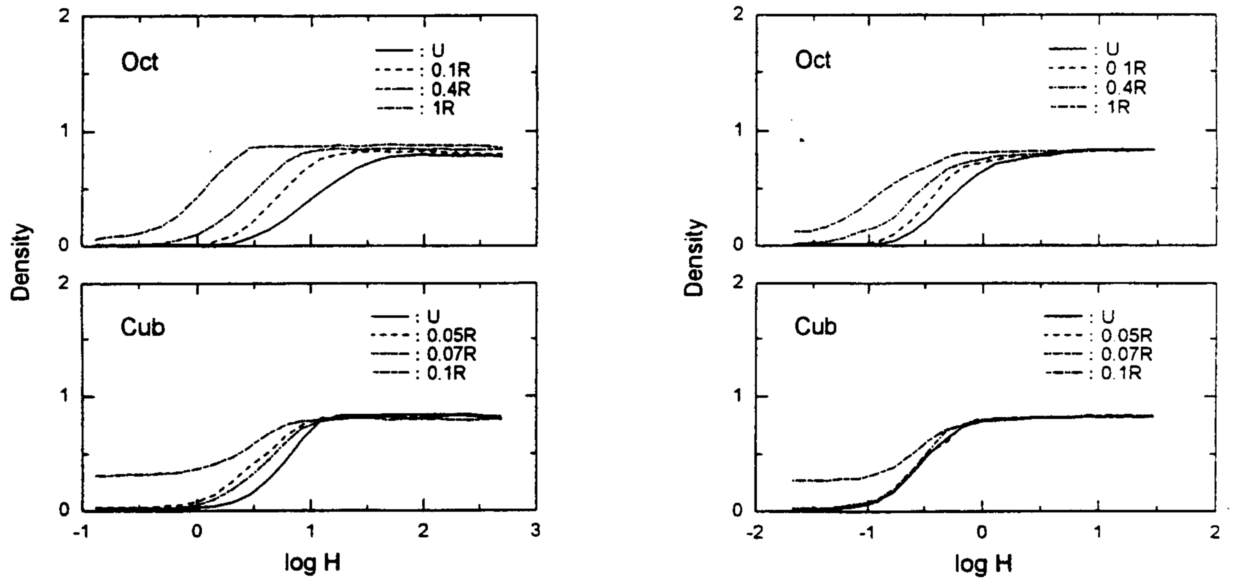


Figure 1. Characteristic curves of reduction-sensitized emulsions. Top: Octahedral grain emulsion. Bottom: Cubic grain emulsion. (a) 1 sec exposure, (b) 10^{-4} sec exposure.

f(n) = fraction of grains, having n developed clusters per grain
v = average number of developed clusters per grain
s = standard deviation of the distribution of f(n)
p(n) = Poisson distribution (presence probability of grains each having n developed clusters)
= $e^{-v} \bullet v^n / n!$

The highly sensitive microwave spectrometer was used to measure the photoconductivity.[5] The light source used was a nitrogen laser having a wavelength of 337 nm with a pulse half-width of 3 nsec.

Every exposure and measurement was carried out at room temperature in room air.

Table I. Formula for the arrested developer

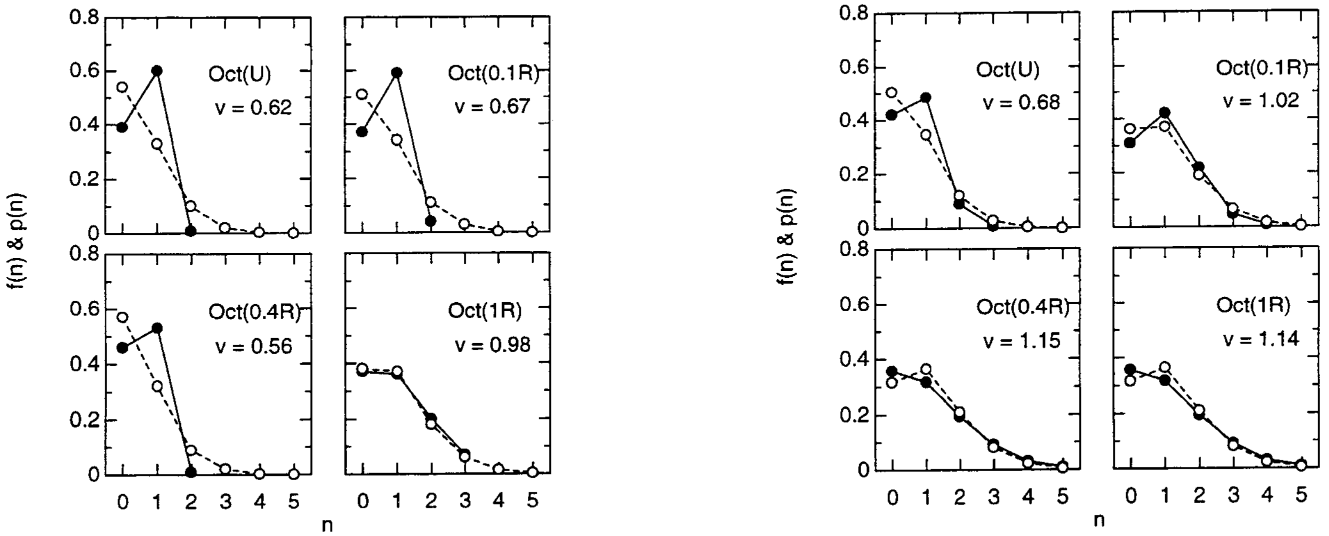
Na_2SO_3	2.0 g
p-Phenylendiamine sulfate	0.3 g
H_3BO_3	12.4 g
NaCl	2.9 g
$Na_2B_4O_7 \bullet 10H_2O$	19.1 g
water to make	1 l
adjust pH with HCl to	7.5

Experimental Results

Characteristic curves of the emulsions used here are shown in Fig. 1(a) for 1 sec exposure and Fig.1(b) for 10^{-4} sec exposure. The sensitivity increased with the sensitization level at the Oct emulsion, while it slightly or hardly increased at the Cub emulsion. However, as fog appeared at the highest sensitization level, the sensitization was saturated at that level.

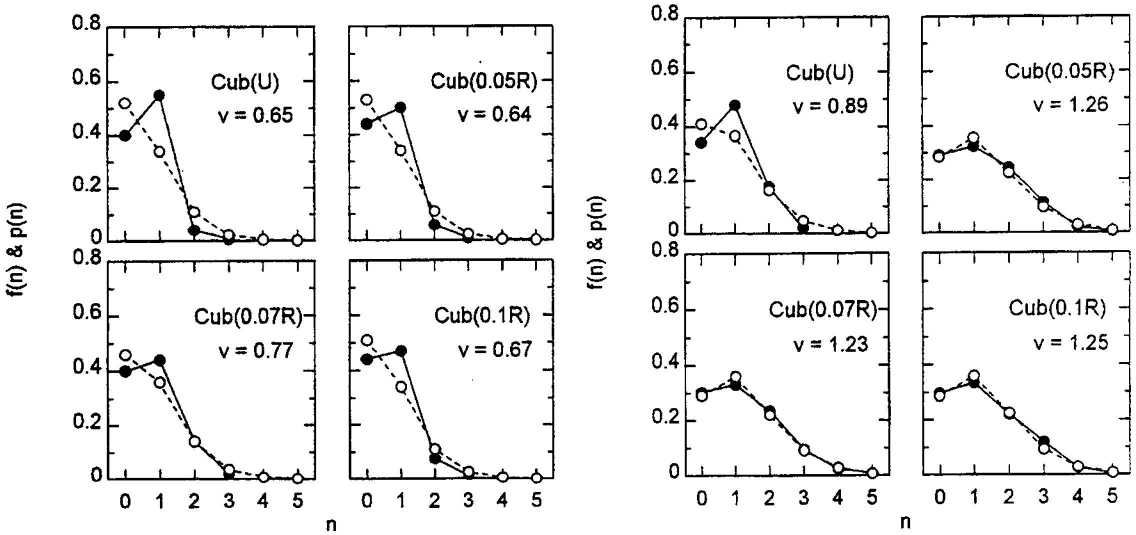
The relationships of f(n) and p(n) to the number of developed silver clusters for 1 sec exposure are shown in Fig. 2(a) for the Oct emulsions and Fig. 2(c) for the Cub emulsions. Closed circles with solid line represent f(n) and open circles with dashed line represent p(n). At the unsensitized and weakly-sensitized samples of both Oct and Cub emulsions the distribution was very narrow one and had a large f(1) value. The distribution of f(n) and p(n) did not overlap, and f(n) indicated a one-cluster-per-grain distribution. At the highest sensitization level only the Oct(1R) sample indicated the broader distribution of f(n) where f(n) overlapped p(n), and f(n) altered to obey the Poisson distribution law.

The relationships for 10^{-4} sec exposure are shown in Fig. 2(b) for the Oct emulsions and Fig. 2(d) for the Cub emulsions. The results were a little different from those for 1 sec exposure. The distribution was wider, especially at the sensitized samples and the distribution of f(n) approached p(n). The dispersion of LIS enhanced at the high intensity exposure.



(a) 1 sec exposure

(b) 10^{-4}sec exposure



(c) 1 sec exposure

(d) 10^{-4} sec exposure

Fig.2. Distribution of the number of small developed silver clusters per grain for reduction-sensitized emulsions. Closed circles with solid line : f(n) = experimental results. Open circles with dashed line : p(n) = expected values from Poisson distribution law. v : average number of developed clusters per grain. (a) Oct emulsions, 1 sec exposure, (b) Oct emulsions, 10^{-4} sec exposure, (c) Cub emulsions, 1 sec exposure, (d) Cub emulsions, 10^{-4} sec exposure

In order to compare the degree of dispersion we evaluated s^2/v value and χ^2 test. Plottings of s^2/v value to the amount of sensitizer M are shown in Fig. 3(a) for the Oct emulsions and Fig. 3(b) for the Cub emulsions. Open circles with solid line represent the results for 1 sec exposure and closed circles with dashed line represent for 10^{-4} sec exposure. This plotting by Hailstone[6] was convenient to compare the distribution of f(n) with p(n). As the value s^2/v is equal to unity at the Poisson distribution and is smaller than unity at the one-cluster-per-grain distribution, this value is one of the index whether f(n) obeys to the Poisson distribution or not.

We also used the χ^2 test to judge whether f(n) obeys to the Poisson distribution. Large circles in those figures represent the results when f(n) obeyed to the Poisson distribution.

At the low intensity 1 sec exposure s^2/v for the Oct sample increased with the sensitization level and approached to unity at the highest level. The χ^2 test also indicated that only the Oct(1R) obeyed the Poisson distribution. None of the Cub samples obeyed the Poisson distribution even at the highest level.

At the high intensity 10^{-4} sec exposure f(n) of the Oct(U) and Cub(U) samples did not obey the Poisson distribution, while all the sensitized ones had large s^2/v value near unity and obeyed the Poisson distribution.

Plottings of decay lifetime of the photoconductivity to M are shown in Fig 4(a) for the Oct emulsion and Fig 4(b) for the Cub emulsion. The lifetime was almost same each other regardless of the sensitization level for the Oct and Cub emulsions.

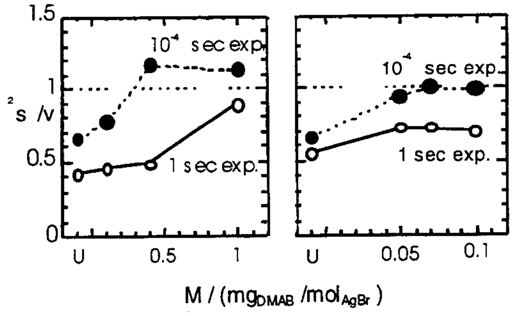
Discussion

The reduction sensitization was accompanied at both emulsions, as the sensitivity increased with the level and the fog appeared at the highest level. Hence, there were some reduction-sensitization centers, P-centers or R-centers, on those emulsion grains. The R-centers may be formed on every sensitized emulsion and they increased the sensitivity.

At the low intensity exposure only the Oct (1R) sample showed the wide Poisson distribution. This indicated that there were some e-traps on which LSI would be formed. Therefore, the P-centers existed on the Oct (1R) emulsion but not on the other emulsions. Tani and Takada suggested that the P-centers were formed more easily on the octahedral grain emulsions.[2] This result agreed with their observation.

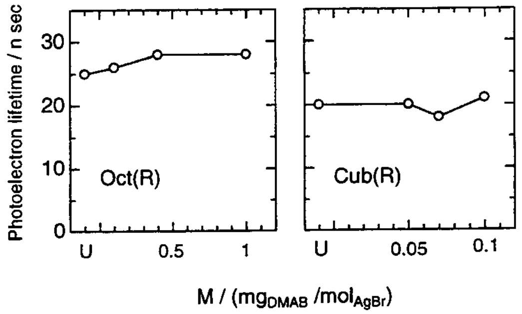
On the other hand, at the high intensity exposure all the sensitized emulsions indicated the Poisson distribution while both unsensitized samples did not. However, this result did not mean that the P-centers existed on every sensitized emulsion, but suggested that the dispersion of LIS would take place at the high intensity exposure regardless of the P-centers when there were enough R-centers. This may be due to the decrease of recombination or the increase of total lifetime of photoelectrons. At the low intensity exposure the dispersion did not take place as the electron density was not so large, and took place only when the P-centers existed at the high level of sensitization.

The decay lifetimes of photoconductivity were almost same regardless of the sensitization level, even at the highest one. This seems to suggest that there was no e-trap in the reduction-sensitized emulsion, let alone the P-center. However, if the number of P-centers were not so many, those few centers would not affect the electron lifetime when there were more electrons. The dispersion of LIS was affected enough by such few centers as the number of LIS formed was only a few.



(a) Oct(R) (b) Cub(R)

Fig. 3. Width of distribution of the number of latent image specks per grain represented by s^2/v to the amount of sensitizer added. Large circles represent the results which were judged that f(n) obeyed the Poisson distribution law. (a) octahedral grain emulsion, (b) cubic grain emulsion.



(a) (b)

Fig. 4. Relationship between decay lifetime of microwave photoconductivity and the amount of sensitizer added. (a) octahedral grain emulsion, (b) cubic grain emulsion.

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