# Photoconductivity and Latent Image Formation in Silver Halide Grains on Nanoseconds Exposure

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## Abstract

By means of time-resolved photoconductivity apparatuses, a method was developed to get characteristic curves for both photographic performance and photoconductivity of silver halide on exposure to light pulses of several nanoseconds. This method provided the knowledge of photographic performance of silver halide emulsions on exposure to very high intensity light, and made it possible to compare between photographic performance and photoconductivity on the same exposure condition for several nanoseconds.

## Introduction

The physical aspect of the photoelectric effect in silver halide emulsions has been examined by the measurement of the time-resolved photoconductivity of the emulsion grains with a microwave photoconductivity method, for which a laser pulse of several nanoseconds is used as a light source[1-4]. It is noted that the exposure condition for the measurement of the microwave photoconductivity of silver halide grains is quite different from that for the measurement of photographic performance, for which each sample is exposed to light for ten seconds in the series of this study[1,4]. It is therefore difficult to compare the result of the microwave photoconductivity measurement with that of the photographic performance, since both photoconductivity and photographic performance strongly depend on the light intensity for the measurements[1].

In this study, an experiment was designed and carried out to compare between the results of the photoconductivity and photographic performance under the same exposure condition with exposure time of nanoseconds in order to solve the above-stated problem. It is expected that this experiment will also provide the knowledge of photographic performance on exposure to a very intense light pulse for such a short time as several nanoseconds.

This study was undertaken to make clear the mechanism of latent image formation by applying the above-stated experiment to silver bromide and silver chloride emulsion grains, both of which are essentially important for photographic materials.

## Materials and Experiments

The emulsions used in this study were composed of octahedral and cubic silver bromide grains, and cubic silver chloride grains. The average size of all these grains was 0.2μm. Each emulsion was coated and dried on a TAC film base and used as a sample.

Time-resolved photoconductivity measurements of each sample were carried out by means of a 35GHz microwave photoconductivity method with a light pulse of several nanoseconds as a light source and a 100MHz radio wave photoconductivity method with a light pulse of several microseconds as a light source[1-4]. Each sample was exposed to a light source through a neutral density filter with variation of optical density. Thus, the photoconductivity of each sample as given by the intensity of the signal peak was plotted as a function of the exposure (i.e., light intensity) to give a characteristic curve for the photoconductivity of a sample. The dominant process for the decay of photoelectrons in each sample was analyzed and ascribed either to the electron-trapping process or the recombination process on the basis of the shape of the characteristic curve and the dependence of the photoconductivity on light intensity (I). It was judged that the photoconductivity was proportional to the light intensity when the electron-trapping process was dominant, and that the photoconductivity was proportional to the square root of the light intensity when the recombination process was dominant. The dark conductivity (i.e., ionic conductivity) of each grain was measured at room temperature by means of a dielectric loss method[1].

In order to get photographic performances of a sample, each sample was exposed for 10 seconds to a tungsten lamp (Color temperature of 2856K) through a continuous wedge, developed at 20°C for 10 min by use of a surface developer MAA-1[5]. The optical density of a developed film was measured by a densitometer and plotted as a function of exposure to give a characteristic curve for photographic performance. On the other hand, film strips of each sample, which were exposed to light pulses for the measurement of time-resolved photoconductivity, were developed under the same development condition, and subjected to the measurement of optical density by a micro densitometer. Then, the optical density was plotted as a function of exposure to give a characteristic curve of photographic performance under the same exposure condition as that for the time-resolved photoconductivity measurement.

## Photoconductivity and Latent Image Formation in AgBr Grains

By means of the above-stated method, the following results were obtained on photoconductivity and latent image formation in AgBr emulsion grains.

(1) It was confirmed from the measurement of the ionic conductivities of the above-stated grains by means of a dielectric loss method that the concentration of interstitial silver ions was several times higher in octahedral AgBr grains than in cubic ones. It was therefore estimated that the ionic relaxation time (i.e., the time for an interstitial silver ion to reach and react with a trapped electron) is shorter in octahedral grains than in cubic ones.

(2) It was found from the microwave photoconductivity measurement that photoelectrons almost disappeared within 20 ns in AgBr grains[4]. According to the light intensity dependence of the photoconductivity with photoelectrons as carriers, it was judged that the decay of photoelectrons in octahedral AgBr grains was determined by electron-trapping processes on exposure to light of relatively low intensity, while it was determined by recombination processes of trapped electrons with positive holes on exposure to light of relatively high intensity. On the other hand, the decay of photoelectrons in cubic AgBr grains was determined by the recombination processes regardless of light intensity. It was considered that the rate of the recombination of a trapped electron with a positive hole was higher in a cubic AgBr grain than in an octahedral one, since the rate of the ionic relaxation to prevent the recombination is slower in the former than in the latter.

(3) The photographic sensitivity on exposure for several nanoseconds was much higher in an octahedral AgBr emulsion than in a cubic one, while the photographic sensitivity on exposure for 10 seconds was lower in the former than in the latter. This result also indicates that the rate of the recombination on short and high-intensity exposure was slower in octahedral AgBr grains than in cubic ones, since the rate of the ionic relaxation to prevent the recombination was much higher in the former than in the latter.

(4) Although reduction sensitization R centers brings about significant increase in the photographic sensitivities of AgBr emulsions on their exposure for 10 seconds, they brought about only slight increase in the sensitivities on exposure for several nanoseconds, and hardly influenced the photoconductivities of the grains on exposure for several nanoseconds. These results indicate that positive holes could be hardly captured by R centers until photoelectrons almost disappeared about 20 nanoseconds after the exposure of the grains to a light pulse. Namely, R centers could cause, neither the enhancement of the recombination of positive holes trapped by themselves with free electrons owing to the delay of the ionic relaxation, nor the depression of the recombination of trapped electrons with positive holes during the above-stated period of time.

(5) On the contrary to reduction sensitization R centers, P centers significantly increased the photographic senseitivities of AgBr emulsions on exposure for several nanoseconds. In accord with this result, P centers decreased the photoconductivity of the emulsion grains under the same exposure condition, and increased the intensity of light, at which the predominant process for the decay of photoelectrons changed from electron-trapping to recombination as the light intensity increased.

## Photoconductivity and Latent Image Formation in AgCl Grains

By means of the above-stated method, the following results were obtained on photoconductivity and latent image formation in AgCl emulsion grains.

(1) It was confirmed from the dielectric loss measurement of silver halide emulsion grains that the concentration of interstitial silver ions in AgCl grains was two or three orders of magnitude lower than that in AgBr grains. Accordingly, the ionic relaxation time in AgCl grains was two or three orders of magnitude longer than that in AgBr grains. This result indicates that, on high-intensity exposure of an AgCl grains, trapped electrons are inclined, not to react with interstitial silver ions, but to recombine with positive holes, and that photographic performance on exposure to high-intensity light is therefore deteriorated more intensely in an AgCl emulsion than in an AgBr emulsion[6,1]. Taking into account the fact that interstitial silver ions come from kink sited on the grain surface[1], the above result indicates that the concentration of silver ions at surface kink sites, which are capable of trapping photoelectrons, is higher on the surfaces of AgCl grains than on the surfaces of AgBr grains.

(2) Microwave photoconductivity measurement indicated that photoelectrons can survive for more than several microseconds in AgCl grains on the contrary to those in AgBr grains[4]. In addition, a radio-wave photoconductivity method could detect photoelectrons for more than several tens microseconds in AgCl grains after their exposure to a light pulse. These results are consistent with the result described in (1) that the ionic relaxation in AgCl grains is very slow as compared with that in AgBr grains.

(3) On exposure to a relatively weak light pulse for several microseconds, the photoconductivity with photoelectrons as carriers increased in proportion to light intensity, indicating that the decay of photoelectrons was determined by their trapping. On exposure to a relatively strong light, the photoconductivity however increased in proportion to the square root of the light intensity, indicating that the decay of photoelectrons was determined by their recombination with positive holes. The photoconductivity on exposure to a light pulse for several nanoseconds increased in proportion to the squared root of light intensity regardless of light

intensity, indicating that the decay of photoelectrons was determined by their recombination with positive holes regardless of light intensity. These results clearly indicated that trapped electrons in AgCl grains are inclined to recombine with positive holes as the light intensity increased.

(4) Although reduction sensitization itself was not effective for an AgCl emulsion[7], hydrogen hypersesitization was effective. The increase in sensitivity by hydrogen hypersensitization was remarkable on exposure for 10 seconds, weak on exposure for 1 milliseconds, and remarkable again on exposure for several nanoseconds. While remarkable sensitivity increase on 10 seconds exposure was mostly caused by R centers[7], it was considered that remarkable sensitivity increase on nanoseconds exposure was mostly caused by P centers, since P centers decreased the photoconductivity on the same exposure.

## Discussions

**Table Comparison in photoconductivity and photographic performance between AgBr and AgCl grains.**

| | AgBr grains | AgCl grains |
|---|---|---|
| Ionic conductivity (ohm-1cm-1) | <Oct>~$2\times10^{-5}$<br><Cub>~$5\times10^{-6}$ | ~$5\times10^{-8}$ |
| Ionic relaxation time | <Oct>~50 ns<br><Cub>~200 ns | ~100 μs |
| Cause for decay of photoelectrons in microseconds | (No detectable photoelectrons) | •Low I: electron-trapping<br>•High I: recombination |
| Cause for decay of photoelectrons in nanoseconds | <Oct><br>Low I:e-trapping<br>Medium~high I:recombination<br><Cub><br>Recombination | Recombination regardless of light intensity |
| Effect of $H_2$-hypersens. on the above photoconductivity | <Oct><br>Low~medium I: electron-trapping<br>High L:recombination | Low I: electron-trapping<br>High I: Recombination |
| HIRF | No HIRF | Finite HIRF |
| Sensitization by R centers | Remarkable for 10 s exposure<br>Slight for ns exp. | Remarkable for 10 s exposure<br>Slight for ns exp. |
| Sensitization by P centers | Weak for 10 s exposure<br>Remarkable for ns exposure | Weak for 10 s exposure<br>Remarkable for ns exposure |

Photoconductivities and photographic performances of AgBr and AgCl emulsion grains thus obtained are summarized and compared with each other in the above table.

The physical properties of silver halide emulsion grains have revealed that the reaction of trapped electrons with interstitial silver ions, which should result in latent image formation, is in severe competition with the recombination of trapped electrons with positive holes, depending on the concentrations of interstitial silver ions and positive holes. The probability of the recombination was thus larger in AgCl grains than in AgBr ones, and increased with increasing the intensity of light pulses for the photoconductivity measurements. It was also indicated that photoelectrons disappeared within ~20 ns in AgBr grains, while it survived more than several tens μs in AgCl grains.

The measurement of photographic performances on exposure for several nanoseconds in this study was useful to understand the mechanism of latent image formation on exposure to light of very high intensity, and to confirm that physical properties and photographic performance of silver halide grains corresponded well with each other.

Although effective positive hole traps such as R centers of reduction sensitization centers and hydrogen hypersensitization centers brought about remarkable sensitization on exposure for 10 seconds, they exhibited only slight sensitization and hardly influenced the photoconductivity of photoelectrons in emulsion grains on exposure for several nanoseconds. It was therefore considered that R centers could not capture positive holes effectively in such a short period of time in silver halide grains. On the other hand, P centers were effective for the sensitization and decreased the photoconductivity of photoelectrons on exposure for several nanosdeconds.

## Conclusion

By means of time-resolved photoconductivity apparatuses, a method was developed to get characteristic curves for both photographic performance and photoconductivity of silver halide emulsion grains under the same exposure condition with light pulses of several nanoseconds. This method provided the knowledge of photographic performance of silver halide emulsions on exposure to light of very high intensity for very short time, and made it possible to compare between photographic performance and photoconductivity. It has been indicated by this method that, on both AgBr and AgCl emulsion grains, the reaction of trapped electrons with interstitial silver ions leading to the formation of latent image centers is under severe competition with the recombination of the trapped electrons with positive holes on exposure to light for ultra-high intensity. However, R centers of reduction sensitization and hydrogen hypersensitization hardly capture positive holes before photoelectrons disappeared, and therefore exhibited only slight sensitization on exposure to light pulses for several nanoseconds.

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## Biography

Tadaaki Tani received his B.S. degree in Synthetic Chemistry from the University of Tokyo in 1963 and a Ph.D. in Applied Chemistry from the same University in 1968. Since 1968 he has worked in Research Laboratories in Ashigara, Fuji Photo Film Co., Ltd. His work has been primarily focused on the mechanisms of photographic processes including latent image formation, physical properties of silver halide grains, chemical and spectral sensitizations. He is a member of the SPSTJ, IS&T, RPS.