Photoelectric and Photographic Processes in AgCl, AgBr, and AgI Grains

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Abstract

By means of the microwave and radio wave photoconductivity apparatuses, the measurement and analysis of time-resolved photoconductivity and photographic process with the same exposure condition were carried out for AgCl, AgBr, and AgI grains in emulsions in order to properly characterize photographic phenomena in the emulsions. The obtained results are useful for understanding the photographic phenomena on exposure for several nanoseconds and comparative studies of the physical properties and photographic processes of AgCl, AgBr, and AgI grains.

Introduction

The physical aspect of the photoelectric effect in silver halide (AgX) 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 AgX grains is quite different from that for the measurement of their 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 the studies of this series, 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 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 AgBr and AgCl emulsion grains, both of which are essentially important for photographic materials, and to AgI grains, which have been recently introduced into photothermographic materials[5].

Materials and Experiments

The emulsions used in this study were composed of octahedral and cubic AgBr grains, cubic AgCl grains, and AgI grains. The average sizes of AgBr and AgCl grains were 0.2µm, and that of AgI grains was 0.14µm. 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 20ºC for 10 min by use of a surface developer MAA-1[6] in the case of an AgBr and AgCl emulsion, and at 38• for 60 min by use of a developer with pyrogaroll as a developing agent in the case of an AgI emulsion[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 on AgBr Grains

By means of the above-stated method, the following results were obtained on photoconductivity and latent image formation in AgBr emulsion grains, as summarized in Table 1.

It was confirmed 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.

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.

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.

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.

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, as summarized in Table 1.

It was confirmed 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 exposure of AgCl grains for a short time, trapped electrons are inclined, not

to react with interstitial silver ions, but to recombine with positive holes, and that photographic performance on exposure for a short time is therefore deteriorated more intensely in an AgCl emulsion than in an AgBr emulsion[7,1]. 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.

Microwave photoconductivity measurement indicated that photoelectrons 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 observations 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.

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 intense 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.

Although reduction sensitization itself was not effective for an AgCl emulsion[8], 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.

Iodide ions (~1 mole %), which were adsorbed to the AgCl grains, formed epitaxial AgI microcrystals on the grain, and recrystalized with host AgCl to form AgClI phase on the grain, significantly increase both the ionic conductivity (by two orders of magnitudes) and sensitivity of the grains.

Electron-trapping process, which is diffusion-limited in AgCl grains, became to be reaction-limited and suitable for electrons to be preferably trapped by sulfur sensitization centers owing to the presence of iodide ions (~1 mole %)

Photoconductivity and latent image formation in AgI grains

It has been recently found that AgI grains are useful for photothermographic materials, since they are sensitive particularly in the atmosphere of the materials with high concentration of silver ions and are fixed during thermal

development. Then, the author has been involved in the study of physical properties of AgI grains and planning to report at this congress its results as summarized in Table 1.

The ionic conductivity and ionic relaxation time in AgI grains are middle points between the corresponding values of octahedral and cubic AgBr grains. However, it is estimated that the concentration of interstitial silver ions is much higher in AgI grains than in AgBr grains, since the formation energy of interstitial silver ions from surface kink sites is much smaller, and the activation energy for their migration is much larger in the former than in the latter.

The concentration of photoelectrons as given by the peak height of the 35GHz microwave photoconductivity was considerably lower in AgI grains than in AgBr grains in spite of the fact that the absorbance of the probe light pulse by the former is about one order of magnitude larger than that by the latter. It has been considered from the result (1) that the concentration of photoelectrons is much smaller in AgI grains than in AgBr grains owing to the fact that the capture of photoelectrons by interstitial silver ions is much faster in the former than in the latter. It seems to be also probable that the efficiency of the dissociation of an exciton to give a free electron and a positive hole is smaller in the former than in the latter.

Comparison among AgCl, AgBr, and AgI grains

The physical properties and photographic performance of AgCl, AgBr, and AgI grains are summarized in Table 1, and make it possible for the first time to compare in performance among all three silver halide grains available for photographic materials.

The ionicity is in the order of AgCl, AgBr, and AgI, and seems to reflect the facts that the formation energy of interstitial silver ions from surface kink sites is in the same order, and that the activation energy for the migration of interstitial silver ions is in the reverse order. This brings about the facts that the concentration of interstitial silver ions acting as electron traps is higher and the photoconductivity in terms of the concentration of photoelectrons is much lower in AgI grains than those in AgCl and AgBr grains.

It is considered from the following reasons that the activity of positive holes is in the order of AgI, AgBr, and AgCl grains. Owing to the differences in ionicity and solubility among silver halides, the solubility of impurity ions acting as positive hole traps should be in the order of AgCl, AgBr, and AgI grains. Since the height of the top of the valence band is in the order of AgI, AgBr, and AgCl, the probability for impurity ions to act as positive hole traps is in the order of AgCl, AgBr, and AgI grains.

It is probable that the above-stated low activity of photoelectrons and high activity of positive holes in AgI grains makes primitive AgI grains less sensitive than AgCl and AgBr grains. It is expected that the sensitivity of AgI grains will be improved by several methods to meet their physical properties.

Table 1. Comparisons in physical properties and photographic performance among AgCl, AgBr, and AgI grains.

	AgCl grains	AgBr grains	AgI grains
Ionic conductivity (ohm-1cm-1)	$\sim 5\times10^{-8}$	\<Oct\> $\sim 2\times10^{-5}$ \<Cub\> $\sim 5\times10^{-6}$	$\sim 1\times10^{-5}$
Ionic relaxation time	~ 100 µs	\<Oct\> ~ 50 ns \<Cub\> ~ 200 ns	~ 100 ns
Activatn. energy for ionic conductivity	0.53 eV	\<Oct\> 0.34 eV \<Cub\> 0.39 eV	0.45 eV
Activation energy for Ag_i^+ migration	0.018 eV	0.042 eV	0.62 eV (c∥) 0.29 eV (c⊥) 0.45 eV (average)
Formation energy of Ag_i^+ from surface kink sites	0.51 eV	\<Oct\> 0.31 eV \<Cub\> 0.35 eV	~ 0 eV
Photoconductivity with electrons (V_e)	Large	Large	Very small
V_e vs light intensity (I) in ns	$V \propto I^{1/2}$	\<Oct\> $V \propto I$(low) $V \propto I^{1/2}$(high) \<Cub\> $V \propto I^{1/2}$	$V \propto I^{1/2}$
V_e vs I in µs	$V \propto I$(low) $V \propto I^{1/2}$(high)	$V \propto 0$	$V \propto 0$
Photoconductivity with positive holes	Not detectable	Small	Large
pK_{sp}	9.75	12.31	16.09
Sensitiv. of primitive grains on ns exposure	High/weak pAg dependence	High/medium pAg dependence	Small/steep pAg dependence

Ag_i^+: Interstitial silver ion, $pK_{sp} = pAg + pX$

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Author Biography

After Tadaaki Tani studied photographic science under the guidance of Prof. S. Kikuchi and Prof. K. Honda as a graduated student in the University of Tokyo, he was graduated there, and obtained the degree of Doctor of Engineering in 1968. In the same year, he became to be a member of Ashigara Research Laboratories, Fuji Photo Film Co., Ltd., and has been involved in fundamental research of AgX emulsions and systems until now. He is concurrently a guest professor of Tokyo Institute of Technology since 1999.