On the Behavior of Photoholes in Silver Halide Emulsion Grains

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Experimental results on transient photoconductivity in AgBr emulsion grains as observed by a radiowave photoconductivity technique are reported. The decay component of the photoconductivity over several tens of microseconds observed using hole-injecting dyes is ascribed to photoholes in accord with the result reported by Kellogg, Hodes, and Muenter. We study dependence of the decay time of photoholes on grain size, excitation intensity, and pH and pAg of reaction solutions during AgBr precipitation. Hole traps in AgBr emulsion grains are ascribed to silver clusters in the grains. We discuss hole-trapping properties of some extrinsic centers detected by the technique.

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Introduction

Photoholes created by exposure in photographic silver halide emulsion grains introduce inefficiency of photographic sensitivity through recombination with photoelectrons and/or bleaching of silver clusters. Thus photoholes should be excluded efficiently from the system to attain high photographic sensitivity. On the other hand, photoholes increase photographic sensitivity via the reactions with reduction sensitization centers that introduce the so-called extra electrons.¹ Thus efficient reaction of photoholes with reduction sensitization centers are important to the improvement of photographic sensitivity. Although the role of photoholes in the photographic process is important, their behavior has not been revealed in great detail.

In the Second International East-West Symposium in 1988, Kellogg, Hodes, and Muenter² reported development of a radiowave photoconductivity apparatus and observed a photoconductivity decay component of about 26 μ s in AgBr grains. They observed that hole-trapping dyes adsorbed on the grains decreased both the decay time and the intensity of this signal, while electron-trapping dyes did not affect the decay time. They concluded that the component was due to photoholes.

In the same symposium, on the other hand, Nakayama, Ohtani, and Matsuzaka³ reported that they used a microwave photoconductivity apparatus to study AgBr(I) grains and observed decay of photoconductivity over several tens of microseconds. They assigned this component to photoelectrons.

In this report, we compare the results given by radiowave and microwave photoconductivity probes to confirm that the decay component in question was due to photoholes, and apply the radiowave photoconductivity

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technique to the study of intrinsic and extrinsic hole-trapping centers.

Experimental

Radiowave Photoconductivity Apparatus. Figure 1 shows the block diagram of the radiowave photoconductivity apparatus.⁴ Operating frequency was about 110 MHz. A sample film was sandwiched between an ITO electrode and a metal electrode, that comprised a capacitor in the LC resonator circuit of the sample holder. The resonator was tuned with a variable capacitor to 50 Ω in dark and the bridge was balanced. The sample was excited by a Xe flash pulse, photoconductivity in the sample brought about an unbalanced signal in the bridge, that was then amplified and detected by a mixer. The mixer was adjusted to detect the change of amplitude of the radiowave signal due to photoconductivity in the sample. The transient photoconductivity signal was monitored and recorded on a digital oscilloscope. The full width at half maximum of the Xe flash pulse was $1.2 \ \mu s$, that determined the time resolution of the apparatus. For blue excitation, that is, for intrinsic excitation of AgBr(I) grains, a bandpass filter (Fuji BPN 42) was used or white light was used, and for minus-blue excitation, that is, for excitation of adsorbed dyes, short-cut filters (Fuji SC46,48,50) were used. For comparison, we also made experiments on microwave photoconductivity by means of the conventional apparatus operated at 9 GHz.5

Samples. Samples used for the radiowave photoconductivity measurements were silver halide emulsion layers coated on a TAC base. The emulsions were composed of cubic, cubooctahedral and octahedral AgBr grains with various sizes. These emulsion grains were grown from seed crystals (0.15 μ m), that were precipitated at pAg = 8.4. Values of pAg during the growth were kept at 6.4 for cubes, 8.3 for octahedrons, and intermediate values for cubooctahedrons by the usual controlled double-jet method. AgBr_{1.x}I_x octahedral grains (0.5 μ m) and AgBrI core-shell grains (1.4 μ m AgBr_{0.75}I_{0.25} core/AgBr_{0.98}I_{0.02} core) were also used.

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Figure 1. Block diagram of a radiowave photoconductivity apparatus.



Figure 2. Structure of dyes used in the present experiments. The value of oxidation potential (E_{ox}) were measured by means of phase-sensitive second-harmonic voltanmetry (volts versus SCE).

Dyes with different oxidation potentials [versus standard calomel electrode (SCE)] shown in Fig. 2 were added to the emulsions before coating. Oxidation and reduction potentials of dyes were measured with the technique of phase-selective second-harmonic voltammetry.⁶ Dye 1 has the highest oxidation potential among these dyes and is a typical hole-injecting dye.^{7.8} We estimate the electronic energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Dye 1 relative to the AgBr conduction and valence band on the basis of its reduction and oxidation potentials, as shown in Fig. 3. Because the HOMO is lower than the top of the valence band, when Dye 1 is excited by exposure, a hole created in the HOMO is injected into AgBr

Figure 3. Energy level diagram of Dye 1 and AgBr.

valence band. As the top of valence band of AgBr(I) is higher than that of AgBr, Dye 1 is also a hole-injecting dye for AgBr(I).

As the LUMO of Dye 1 is also located lower than the bottom of the conduction band of AgBr, adsorbed Dye 1 molecules act as trapping centers for photoelectrons in AgBr. Other dyes such as Dyes 2 through 5 were used as dyes with varying ability to trap photoholes in silver halide grains according to their HOMO levels.

Reduction sensitization was carried out on octahedral $AgBr_{0.8}I_{0.2}$ grains $(0.5~\mu m)$ by ripening them at 60°C for 60 min with various concentration of dimethylamineborane (DMAB). For sulfur sensitization on octahedral AgBr emulsion grains (0.9 μm), we used sodium thiosurfate as a sensitizer with digestion at 60°C for 60 min. Hydrogen hypersensitization was carried out by keeping coated layers with 0.5 μm AgBr cubes in hydrogen gas at 40°C for 40 and 80 min.



Figure 4. A typical trace of radiowave photoconductivity signal of cubic AgBr grains $(0.5 \ \mu m)$, excited by blue exposure. The upper half shows measured photoconductivity signal and the lower half shows logarithm plot of the signal.

Results

Typical traces of radiowave photoconductivity signals in cubic AgBr grains $(0.5\text{-}\mu\text{m})$ are shown in Figs. 4 and 5. Figures 4, 5(a), and 5(b) show the results for blue excitation of AgBr grains without adsorbed dye, for minus-blue excitation of the grains with Dye 1 adsorbed, and for blue excitation of the grains with Dye 1 adsorbed.

We observed a high peak with faster decay and a small component with slower decay, as shown in Fig. 4. The faster component decayed within the time resolution of the apparatus. The slower component had a decay time of 24.3 µs and was quite similar to the one observed by Kellogg, Hodes, and Muenter.² Figure 5(a) shows the result with the same grains with adsorbed Dye 1; Dye 1 itself was excited in this case. Positive holes were accordingly injected into the grains and gave the signals. The observed time constant of the slower decay component was 22.4 µs, nearly the same as observed in Fig. 4. In the case that AgBr adsorbed by Dye 1 was excited by blue light [Fig. 5(b)], the relative intensity of the slower component increased and showed the almost the same decay time as in Figs. 4 and 5(a). In this case, Dye 1 provided traps for electrons in AgBr, thus decreased the electron contribution to the signal, but did not affect the hole signal.

Figure 6 shows the dependence of the amplitude of the hole signal in octahedral $AgBr_{0.8}I_{0.2}$ grains on oxidation potentials of adsorbed dyes. The amplitude of the hole signal was defined as the height of the slower component at



Figure 5. The same as Fig. 4 except that Dye 1 was adsorbed to AgBr grains: (a) minus-blue exposure and (b) blue exposure.



Figure 6. Dependence of the amplitude of hole signal defined as the signal height at $t = 5 \,\mu s$ on oxidation potential of dyes adsorbed to AgBr_{0.8}I_{0.2} octahedral grains.



Figure 7. Decay time of slower component in radiowave photoconductivity as a function of iodine content of $\operatorname{AgBr}_{1,x}I_x$ grains, with Dye 1 excited by minus blue exposure (\bullet) and without dye excited by white exposure (O).

 $t = 5 \ \mu s$ when the AgBr_{0.8}I_{0.2} were excited by blue light exposure. Dyes with less positive oxidation potential led to decreased signal amplitudes. Having higher HOMO levels, these dyes acted as positive hole traps and the decreased the hole signal. We accordingly could ascribe the slow component observed in radiowave photoconductivity to positive holes, confirming the conclusion of Kellogg, Hodes, and Muenter.

The slower decay components of radiowave photoconductivity signals in $AgBr_{1,x}I_x$ emulsion grains are plotted in Fig. 7 as a function of the content of iodide in the grains. With increasing iodide content, the decay time became longer in the case of $AgBr_{1,x}I_x$ grains without Dye 1, excited by white light, and as well as in the case of $AgBr_{1,x}I_x$ with Dye 1 adsorbed, excited by minus-blue light.



Figure 8. Semi-log plot of the radiowave photoconductivity signal of core-shell AgBrI grains on blue exposure without Dye 1 (_____) and on minus-blue exposure with Dye 1 (_____).

In Fig. 8, traces of photoconductivity signals of AgBrI core-shell emulsion grains are plotted. A slowly decaying component with decay time over 100 µs was observed, similar to the one observed by Nakayam, Ohtani, and Matsuzaka.³ The amplitude of this component was also enhanced by the excitation of Dye 1, as shown by a dotted line in Fig. 8, and depressed by hole-trapping dyes. A similar sample was measured using microwave photoconductivity. Figure 9(a) was obtained when excitation employed a laser pulse, and Fig. 9(b) was the result of excitation by a Xe flash light pulse. Both signals showed comparable slow decay components over several tens of microseconds; the sharp peaks reflected the different intensity profiles of the excitation pulses. The decay times were almost the same as those of the radiowave photoconductivity, as shown in Fig. 8.

The decay time did not depend on the size of the AgBr cubic grains, nor on the excitation intensity. The decay time of the slow component in AgBr grains varied with their precipitation condition. The reaction solution with low pAg and high pH during precipitation brought about the grains with shorter decay times. Figure 10 shows the dependence of the decay time on pH during precipitation.

Repeated exposures on the same specimen resulted in an increase of signal intensity and of decay time for the positive holes. For the excitation of AgBr without Dye 1, the amplitude of the slow decay component increased with increasing number of pulses for excitation. For the excitation into the absorption envelope of adsorbed Dye 1, both peak intensity and amplitude of the slow decay component increased with an increasing number of pulses. The higher the pAg and the lower the pH during precipitation, the more rapidly the hole signal increased with increasing numbers of pulses. Figure 11 shows the dependence of signal peak height on the number of repeated



Figure 9. Signals observed by using microwave photoconductivity apparatus in core-shell AgBrI grains on their excitation by (a) YAG laser pulse (355 nm) and (b) Xe flash pulse.



Figure 10. Decay time of slow components in radiowave photoconductivity signals in AgBr octahedrons as a function of pH values during the growth of the grains.



Figure 11. The change of peak height of photoconductivity signal with repetition of excitation pulses. Octahedral AgBr grains with Dye 1 adsorbed were used and the dye was excited.

excitation pulses, for octahedral AgBr grains with adsorbed Dye 1, for which the dye was excited. In grains precipitated at low pH, the signal intensity increased rapidly with repetition of excitation pulses. On the contrary, the signal intensity increased only slowly in grains precipitated at high pH.

Both reduction sensitization and hydrogen hypersensitization decreased the decay time of the signals as well as the amplitude. With increasing time of hydrogen hypersensitization, photographic sensitivity increased, and both the decay time and the positive hole signal intensity decreased in cubic AgBr grains (0.5 μ m). As shown in Fig. 12, with increasing concentration of DMAB for reduction sensitization of octahedral AgBr_{0.8}I_{0.2} (0.5 μ m), sensitivity increased and both decay time and amplitude of signal decreased. Although sulfur sensitization of AgBr octahedron (0.9 μ m) brought about a decrease in decay time and signal intensity, this decrease was obtained even with a small concentration of sulfur sensitizer, which hardly affected photographic sensitivity.

Discussion

We have assigned the slowly decaying component in the radiowave photoconductivity signal to hole conduction, insofar as the component was observed when only holes were injected by Dye 1. The radiowave photoconductivity apparatus was tuned to detect the change of conductivity within a sample and gave signals of conductivity regardless of the kind of charge carriers. Thus, a sharp peak was observed, for example, in Fig. 4, whose duration was almost the same as that of the light pulse and was within the time resolution of the apparatus. This peak was attributed mainly to electrons, and its relative amplitude decreased on adsorption of electron-trapping dyes to the grains. On the other hand, the slowly decaying component in Fig. 4 increased on adsorption of electron-trapping dyes [Fig. 5(b)], and decreased on adsorption of hole-trapping dyes to the grains. The decay time of the slow component in Fig. 4 was the same as



Figure 12. Photographic sensitivity and fog (a) and decay time of radiowave photoconductivity (b) in reduction-sensitized $AgBr_{0.8}I_{0.2}$ octahedrons.

that in Fig. 5(a), that is, the signal obtained when only holes were injected by Dye 1.

Figure 5(a) shows that even when only holes were created, there also appeared a fast decay component in the signal. This result means that there is also a fast decay process for positive holes. This process, however, has not yet been time-resolved in the present experiment, and more investigations are necessary to clarify its nature.

Iodide ions in $\operatorname{AgBr}_{1x}I_x$ grains increased the decay time of hole signals as shown in Fig. 7. These ions are wellknown hole-trapping centers at low temperatures.⁹ This implies that iodide ions are shallow traps for holes at room temperature. Shallow traps for *photoelectrons* are known to be temporary traps for electrons and to increase the decay time of photoelectrons. This phenomenon can be observed by microwave photoconductivity. Iodide ions should, by analogy, increase the decay time of photoholes.

Signals observed in AgBrI grains and in AgBrI/AgBr core-shell-structured grains were similar to those observed by Nakayama, Ohtani, and Matzsuzaka.³ As shown in Figs. 8 and 9, the slowly decaying components were observed by both microwave and radiowave techniques and were enhanced on excitation of Dye 1. They accordingly were hole signals whose decay time was increased by the iodide ions in these crystals. Therefore we conclude that the observation of Nakayama, Ohtani, and Matsuzaka in AgBrI core-shell grains using microwave photoconductivity was of the same phenomenon as observed by radiowave photoconductivity. These signals are not due to photoelectrons, but to photoholes.

The decay time of the component corresponding to hole conductivity was independent of grain size. Note that the decay time of *photoelectrons* observed with the microwave technique showed a size dependence in nano- and microsecond regimes,^{4,5} suggesting that the electron traps are located on the surface of the grains. The fact that the decay time of positive holes was independent of grain size correspondingly suggests that hole traps are present not on the grain surface, but in the bulk of the grains.

The decay time did not depend on the intensity of excitation. If the decay process involves recombination of holes with electrons, it should depend on the excitation intensity, since the recombination is a second-order reaction. Thus the decay of positive holes was not caused by recombination process.

It is implied that these hole traps in the bulk of the grains may be silver clusters, on the basis of the observation of the effects of pAg and pH during precipitation on the behavior of positive holes. Low pAg and high pH are likely to cause the formation of small silver clusters in a grain during precipitation, and to change the photographic properties of the grains.¹⁰⁻¹² The decay of holes became faster and the amplitude of the hole signal became lower with decreasing pAg and increasing pH during precipitation. Consistent with this interpretation, the signal amplitudes grew and the decay times became longer on repeated exposures. Silver clusters, especially dimers of silver atoms acting as hole traps, that is, R centers, disappear when they capture positive holes. Thus the number of hole traps decreases and the positive hole photoconductivity signal increases as the grains are repeatedly illuminated.

The effects of hydrogen hypersensitization and reduction sensitization on the radiowave photoconductivity gave direct evidence that these sensitization nodes produce hole traps on the grain surface. The effect of sulfur sensitization on radiowave photoconductivity showed that sulfur sensitization brought about not only electron-trapping sensitizing centers but also trapping centers for positive holes, even at low levels. These sensitization centers must introduce hole trapping centers on the surface of grains, because sensitization reactions occur at the surface. Thus the decrease of hole signal and decrease of decay time by these sensitization centers show not only that internal hole trapping centers but also surface hole trapping centers can affect our observations using the radiowave photoconductivity technique.

Conclusions

The slow decay component observed in both radiowave photoconductivity decay and microwave photoconductivity decay in microsecond regimes was verified to be due to photoholes based on observations using hole-injecting dyes. This conclusion confirmed the proposal of Kellogg, Hodes, and Muenter.² Iodide ions acted as shallow traps for photoholes and increased their decay time. Silver clusters inexorably produced within silver halide emulsion grains were assigned as hole-trapping centers that control the dynamics of holes in our observations. Direct evidence for the proposal that reduction sensitization and hydrogen hypersensitization bring about hole-trapping centers was obtained. Sulfur sensitization was also found to provide hole-trapping centers.

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