On the Behavior of Photoholes in Silver Halide Emulsion Grains

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Abstract

The present author reports experimental results on transient photoconductivity in AgBr emulsion grains as observed by radiowave photoconductivity technique. The component in several tens microsecond region as observed by use of hole-injecting dyes was ascribed to photoholes in accord with the result reported by Kellogg *et al.*.

We study dependence of the decay time of photoholes upon grain size, excitation intensity, and pH and pAg of reaction solutions during AgBr precipitation. Intrinsic hole traps in AgBr emulsion grains were ascribed to silver clusters in the grains. We discuss hole-trapping properties of some extrinsic centers by the technique.

Introduction

Photoholes created by exposure bring inefficiency of photographic sensitivity through recombination with photoelectrons and/or bleaching of silver clusters in a photographic system. Thus photoholes should be efficiently excluded from the system to attain high photographic sensitivity.

Kellogg *et al.*[1] developed radiowave photoconductivity apparatus and observed decay component of about 26μsec in AgBr grains. They observed that hole-trapping dyes adsorbed on the grains decreased the decay time, while electron-trapping dyes did not affect it. They concluded that the component was due to photoholes.

Nakayama *et al.*[2], on the other hand, used microwave photoconductivity apparatus for AgBrI grains and observed decay of photoconductivity in several tens microsecond region. They considered that the component was due to photoelectrons.

In this paper, the present author compared between the results as given by radiowave and microwave photoconductivity apparatuses to confirm that the component was due to photoholes, and applied the radiowave photoconductivity technique to the study of intrinsic and extrinsic hole-trapping centers.

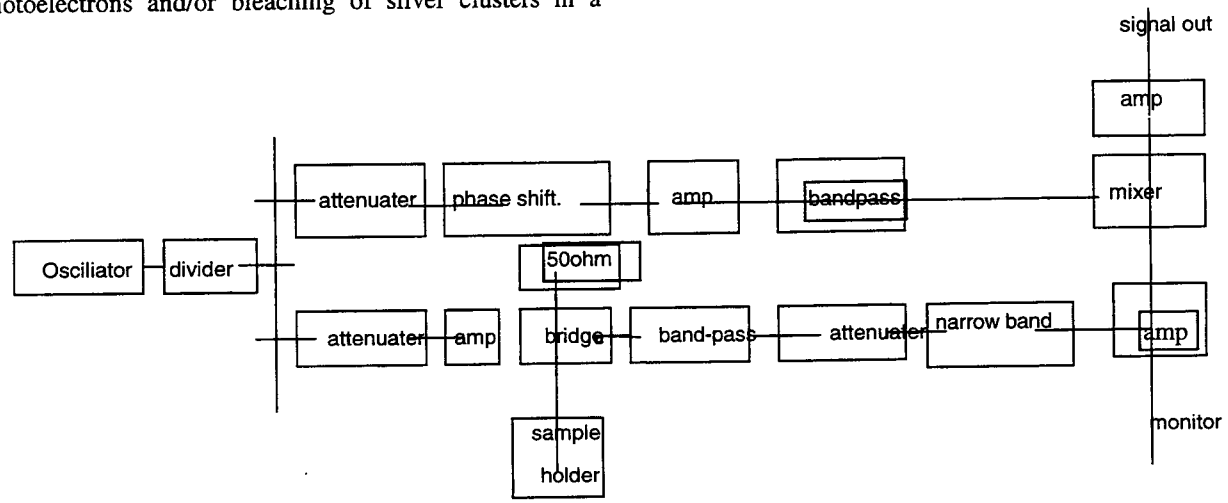

Fig.1 Block diagram of the radio wave photoconductivity apparatus

Experiments

Radiowave photoconductivity apparatus

Figure 1 shows the block diagram of radiowave photoconductivity apparatus[3]. Operating frequency was about 110MHz. A sample film was sandwiched between a TIO electrode and a metal electrode, which consisted a capacitor in LC resonator circuit of the sample holder. The resonator was tuned with a variable capacitor to 50ohm in dark and the bridge was balanced. The sample was excited by a Xe flash pulse and photoconduction in sample brought an unbalance signal in the bridge, which was amplified and detected by a mixer. The signal was monitored and recorded on a digital oscilloscope. The half width of the Xe flash pulse was 1.2μsec which determined the time resolution of the apparatus. For comparison, we made also experiments on microwave photoconductivity by means of the conventional apparatus operated at 9GHz.

Samples

Samples used for the radiowave photoconductivity measurements were AgBr emulsion layers coated on TAC bases. The emulsions were composed of AgBr grains of cube, cubooctahedron and octahedron with various sizes. AgBrI grains (0.9μm) and AgBrI core-shell octahedral grains were also used. These grains were grown from seed crystals by use of conventional controlled double jet method.

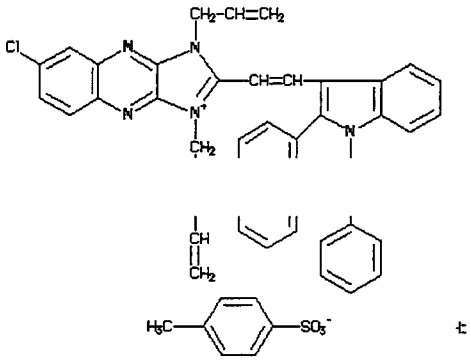

Fig. 2 Structure of Dye 1.

Dyes were added to the above stated emulsions before coating. Dye 1 depicted in Fig.2 is a typical hole-injecting dye[5]. We can estimate the electronic energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied one (LUMO) of Dye 1 relative to AgBr conduction and valence band on the basis of its reduction and oxidation potentials as shown in Fig.3. Since the HOMO is lower than the top of the valence band, thus, when dye 1 is excited by exposure, a hole created in HOMO is injected into AgBr valence band. On the other hand, LUMO of the dye 1 locates lower than bottom of conduction band of AgBr, the dye 1 acts as trapping centers for photoelectrons in AgBr.

Reduction sensitization was carried out on octahedral $AgBr_{0.8}I_{0.2}$ grains (0.5μm) by ripening them at 60°C for 60min with various concentration of dimethylamineboran (DMAB). For sulfur sensitization on octahedral AgBr emulsion grains (0.9μm), we used sodium thiosurfate as a sensitizer for the ripening at 60°C for 60min.

Hydrogen hypersensitization was carried out on coated layers with 0.5μm AgBr cube by exposure to hydrogen gas at 40°C for 40 and 80min.

Results

Typical traces of radiowave photoconductivity signal in cubic AgBr grains (0.5μm) are shown in Fig.4. We observed high peak with faster time and small component with slower decay. The faster component decayed within the time resolution of the apparatus. The slower component had decay time of 24.3μsec. Figure 5 shows the result with the same grains except that the grains adsorbed dye 1 and dye 1 was excited. In this case, positive holes were injected into the grains and gave signals. The observed decay time was 22.4μsec, being nearly the same as the one in Fig.4. We also observed that typical hole-trapping dyes decreased the intensity of the signal while electron-trapping dyes did not. Therefore we ascribed the slow component to photoholes, confirming Kellogg *et al*'s conclusion.

We measured microwave photoconductivity of $AgBr_{0.75}I_{0.25}$ grains and AgBrI core-shell emulsion ($AgBr_{0.74}I_{0.26}$ core/$AgBr_{0.97}I_{0.03}$ shell). Slowly decaying component with decay time of about 40μsec was observed, being similar to the one observed by Nakayama *et al.*. This component was also enhanced by the excitation of dye 1 and depressed by hole-trapping dyes.

Figure 6 shows the size dependence of the decay time of the slow component observed in AgBr cubes. The decay time did not depend on the grain size. We also observed that the decay time did not depend on excitation intensity.

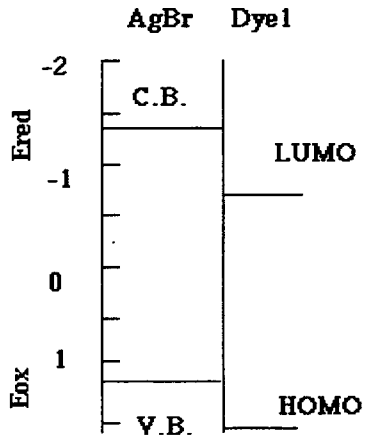

Fig.3 Energy level diagram of dye 1 and AgBr.

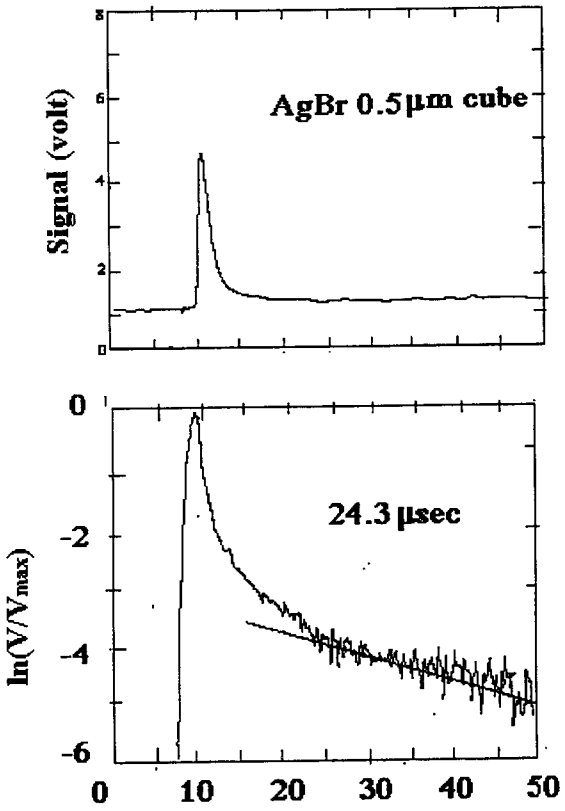

Fig. 4. Typical traces of radiowave photoconductivity signal in AgBr cube with blue light excitation.

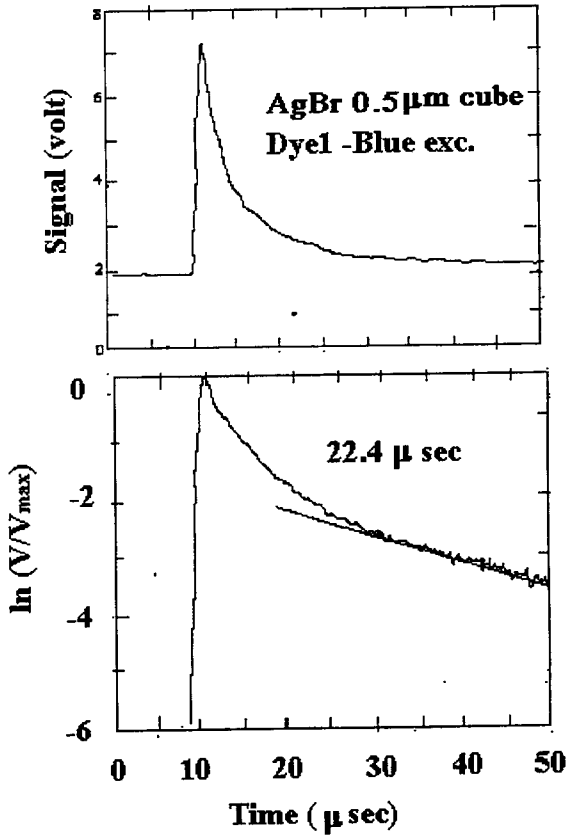

Fig.5 The same as Fig.4 except that dye 1 was adsorbed on the grains and excited.

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 time.

Repeated exposures on the same specimen resulted in increase of signal intensity and of decay time of positive holes. For the excitation of AgBr without dye 1, the height of slow decay component increased with increasing number of pulses for excitation. For the excitation of dye 1, both peak height and height of slow decay component increased with increasing the number of pulses. The higher was the pAg and the lower was the pH during precipitation, the more rapidly the hole signal increased with increasing the number of pulses.

Both reduction sensitization and hydrogen hypersensitization decreased the decay time of the signals. With increasing time for hydrogen hypersensitization, photographic sensitivity increased, and both the decay time and the height of signal decreased in cubic AgBr grains (0.5mm). With increasing concentration of DMAB for reduction sensitization of octahedral $AgBr_{0.8}I_{0.2}$ (0.5mm), sensitivity increased and both decay time and height of signal decreased.

Although sulfur sensitization of AgBr octahedron (0.9μm) brought about decrease in decay time and signal intensity, they decreased even with small concentration of sulfur sensitizer which hardly affected photographic sensitivity.

Discussions

We have already mentioned above that the signal with slow decay in radiowave photoconductivity was assigned to hole conduction. 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. Sharp peak was observed in Fig.4. Its 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 because its relative height was decreased by adsorption of electron-trapping dyes to the grains. On the other hand, the slowly decaying component in Fig.4 was increased by adsorption of electron-trapping dyes, and decreased by adsorption of hole-trapping dyes to the grains. The decay time of the slow component in Fig.4 was the same as that in Fig.5.

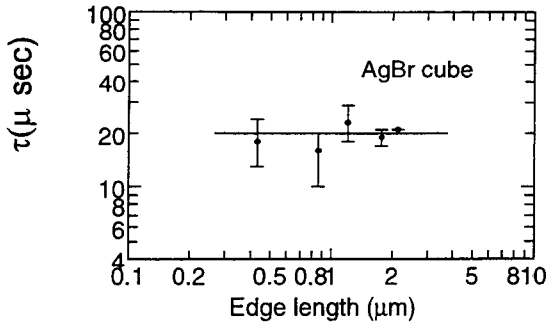

Fig.6 Decay time of radiowave photoconductivity as a function of edge length of cubic AgBr grains.

Figure 5 shows that even when only holes were excited, there appeared fast decay component in the signal. This result means that positive holes had a decay process faster than that discussing above. This process, however, has not yet been time-resolved in the present experiment. More investigations are necessary to clarify this process.

Signals observed in AgBrI grains and in AgBrI/AgBr core/shell-structured grains were similar to those observed by Nakayama *et al.*. The results in this study indicated that their observation in AgBrI and AgBrI core-shell grains in microwave photoconductivity was the same as that observed in radiowave photoconductivity due to photoholes.

The decay time of the component corresponding to hole conductivity was independent of grain size. On the contrary, the decay time of photoelectrons observed with microwave technique showed size dependence in nano and micro second regions[4], indicating that the electron traps locate at the surface of the grains. The fact that decay time of positive holes was independent of grain size indicated 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 would be recombination of holes with electrons, it should depend on the excitation intensity, since the recombination is a secondary reaction. Thus the decay of positive holes was not caused by recombination process.

It is implied that the above-stated hole traps in the bulk of the grains were silver clusters within silver halide grains, 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 liable to cause the formation of small silver clusters in a grain during precipitation and change photographic property of the grain[6,7]. The decay of holes became faster and height of hole-signal became lower with decreasing pAg and increasing pH during precipitation.

The above-stated idea also gave the reason why signals grew up and the decay time became longer by repeated exposures. Silver clusters, especially dimers of silver atoms acting as hole traps (i.e. R centers) disappear when they capture positive holes.

The effects of hydrogen hypersensitization and reduction sensitization on the radiowave photoconductivity gave direct evidences that these sensitization 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 sensitizer centers but also trapping centers for positive holes.

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