

Ionic and Electronic Properties of Silver Iodide Grains

Hiroyuki Mifune, Tadaaki Tani, Seiji Yamashita, Satoshi Aiba, Tomoyuki Ohzeki, Katsutoshi Yamane
Materials Research Division, Fuji Photo Film Co.,Ltd., Japan

Abstract

Extensive studies have been made on the ionic and electronic properties of silver iodide emulsion grains to characterize the latent image formation on the grains in photothermographic materials.

Introduction

Silver iodide was practically used in such photographic materials as Daguerreotype at the very early stage of silver halide photography. Even at room temperature, silver iodide has a strong exciton band in the blue region of its absorption spectrum, which results from the direct transition in it, and is much stronger in absorbance than the absorption bands of silver bromide and silver chloride in the blue region, which result from their indirect transitions. However, silver iodide could not continue to contribute to practical photographic materials for a long time owing to the difficulties in achieving efficient latent image formation, rapid development and fixation on the grains, and is not used at the present in any photographic material at all.

Recently, we have discovered that silver iodide grains have many advantages over silver iodobromide and silver bromide grains for use in photothermographic materials^{1,2}. However, we have not any adequate guiding principle to design silver iodide grains for better use, since our poor knowledge on the solid state physics of silver iodide, especially the ionic and electronic properties of silver iodide grains, are too poor to characterize the latent image formation on the grains.

Various useful experimental methods for studying physical properties of silver halide emulsion grains have been already developed in the past³. In this paper, we have tried to apply the above-stated methods to study the ionic and electronic properties of silver iodide grains from the viewpoint of their photographic behavior.

Experimental

A photographic emulsion with silver iodide grains was prepared by a conventional controlled double-jet method, according to which aqueous solutions of silver nitrate and potassium iodide were simultaneously poured into an aqueous gelatin solution, in which pAg was kept to be 7.1 at 70°C during the precipitation of the grains. The average equivalent circular diameter of the grains was 0.14 μm . The grains were tetradecahedrons in shape, and composed of hexagonal and cubic phases of silver iodide. Octahedral silver bromide emulsion grains with equivalent diameter of 0.2 μm were also prepared for reference by a controlled double jet method. These emulsions were coated on TAC film bases, dried, stripped, and subjected to various experiments. A film strip was exposed to light through a continuous wedge, and developed by a developer⁴ containing pyrogallol as a developing agent at 38°C for 60min.

The dark conductivity (i.e., ionic conductivity) of silver iodide grains was measured by means of the dielectric loss method³. The time-resolved photoconductivity of the grains was measured by means of the 35GHz microwave photoconductivity and radiowave photoconductivity methods³. The oxidation potential of latent image centers was determined by use of redox buffer solutions with a Fe^{2+}/Fe^{+3} redox system⁵.

Results and Discussion

1. Ionic Properties of Silver Iodide Grains

Figure 1 shows the dielectric loss of silver iodide grains as a function of frequency, giving a curve with two peaks. As the ionic conductivity derived from the lower frequency peak was proportional to the surface/volume ratio of the grains, it was ascribed to the movement of carriers, which were formed from the surface and moved in the grains. Since the ionic conductivity of silver iodide grains was lowered by the adsorption to the grains of such compounds as 1-phenyl-5-mercaptotetrazole, which have strong affinity to silver ion, we therefore attributed the lower frequency peak to the ionic conductivity with interstitial silver ions as carriers, and the higher frequency peak to the one with the movement of silver ions on the surface by analogue with the ionic conductivity of octahedral silver bromide grains³. The above-stated results indicate that a positive space charge layer is formed in a silver iodide grain as is formed in a silver bromide one.

It is already known that the activation energy of the ionic conductivity of silver halide grains is the sum of the energies for the formation and migration of interstitial silver ions. The activation energy of the ionic conductivity of silver iodide grains was determined as 0.45eV, and was the same as that for the migration of interstitial silver ions in silver iodide crystal⁶ (see Table1).

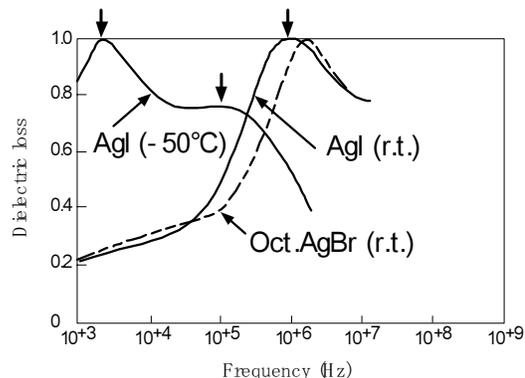


Figure 1. The dielectric loss as a function of frequency for silver iodide grains at room temperature and -50°C (solid lines), and silver bromide grains at room temperature (dashed line)

Table1. The Activation Energies for Ionic Processes and Surface Potentials due to the Space Charge Layers in Silver Iodide, Silver Bromide and Silver Chloride Grains

| (eV) | AgI | AgBr (Octahedral) | AgBr (Cubic) | AgCl (Cubic) |
|---|---|-------------------|--------------|--------------|
| Activation Energy for Ionic Conductivity (ΔE) | 0.45 | 0.34 | 0.39 | 0.53 |
| Activation Energy for Migration of Ag_i^+ (U) ⁶ | 0.62 (c) 0.29 (c \perp) 0.45 (ave) | 0.042 | | 0.018 |
| Formation Energy of Frenkel Defect (W) ⁶ | 0.60 | 1.06 | | 1.25 |
| Formation Energy of Ag_i^+ from Surface Kink (ΔGi) | ~ 0 | 0.31 | 0.35 | 0.51 |
| Formation Energy of Ag_{\square}^+ from Lattice (ΔGv) | ~ 0.6 | 0.75 | 0.71 | 0.74 |
| Surface Potential due to Space Charge Layer (Us) | - 0.30 | - 0.22 | - 0.18 | - 0.12 |

$\Delta E = \Delta Gi + U$, $W = \Delta Gi + \Delta Gv$, $2eUs = \Delta Gi - \Delta Gv + kT \ln 2$
 Ag_i^+ : Interstitial Silver Ion, Ag_{\square}^+ : Silver Ion Vacancy

Accordingly, the formation energy of interstitial silver ions from kink sites on the surfaces of silver iodide grains is nearly zero. This result means that the energy level of silver ions at surface kink sites on the surfaces of silver iodide grains is nearly equivalent to that of interstitial silver ions. The potential energy difference between the surface and interior of silver iodide due to the space charge layer in it is therefore nearly one half of the formation energy of a Frenkel pair in silver iodide (i.e., about 0.30eV).

It might be interesting to compare in ionic conduction between silver iodide grains and octahedral silver bromide ones. The formation energy of interstitial silver ions from surface kink sites is larger in octahedral silver bromide grains (i.e., 0.31eV) than in silver iodide ones (i.e., ~ 0 eV). On the other hand, the activation energy for the migration of interstitial silver ions in silver bromide grains (i.e., 0.042eV) is smaller than that in silver iodide ones (i.e., 0.45eV). In other words, the concentration of interstitial silver ions in silver iodide grains is higher than that in octahedral silver bromide ones. The potential energy difference within the space charge layer in silver iodide grains (i.e., 0.30eV) is larger than that in octahedral silver bromide ones (i.e., 0.22eV).

2. Electronic Properties of Silver Iodide Grains

A 35GHz microwave photoconductivity method with a 355 nm laser light pulse with half width of several ns was applied to silver iodide grains at room temperature. Although the absorption coefficient of silver iodide at 355nm is by ca.10 times larger than that of silver bromide, the signal intensity, which is proportional to the concentration of charge carriers, was smaller in silver iodide grains than that in silver bromide ones (see Fig.2).

The radiowave photoconductivity of silver iodide grains was ascribed to the movement of positive holes, since it was observed when positive holes were injected into the grains by hole-injecting dyes when they were excited by light pulses with half width of several μs . The signal intensity in silver iodide grains was much larger than that in silver bromide ones (see Fig.3). Similar result was also obtained as a result of the absorption of the light pulse by the grains in the absence of hole-injection dye. It is inferred from the above-stated results that the concentration of positive holes traps in silver iodide grains is much smaller than that in silver bromide ones.

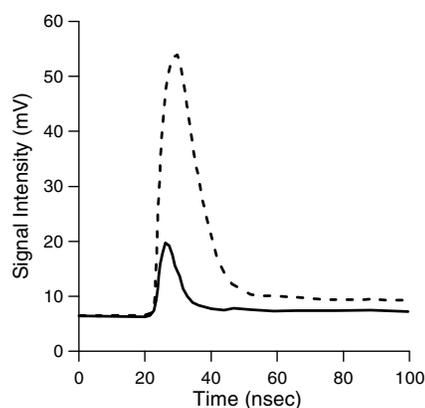


Figure2. The signal intensity of the 35GHz microwave photoconductivity as a function of time for silver iodide grains (solid line) and silver bromide ones (dashed line). Each sample was exposed to a laser light pulse with wavelength of 355nm.

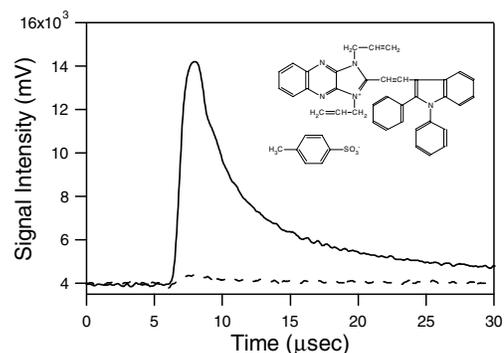


Figure 3. The signal intensity of the radiowave photoconductivity for silver iodide grains (solid line) and silver bromide ones (dashed line) with a hole-injection dye adsorbed. Each signal was observed when the dye was excited by a light pulse

It is considered from the above-stated results that the concentration of photoelectrons was much smaller in silver iodide

grains than in silver bromide ones at the very early stage of latent image formation owing to the rapid capture of photoelectrons by interstitial silver ions, and subsequent recombination with positive holes. This consideration is supported by the facts that the concentration of interstitial silver ions was larger in silver iodide grains than in silver bromide ones, and that the concentration of positive holes was larger in silver iodide grains than in silver bromide ones. At the same time, we do not have any evidence to exclude the possibility that the efficiency of the dissociation of an exciton to give a free electron and a positive hole is smaller in silver iodide grains than in silver bromide ones.

3. Latent Image Formation on Silver Iodide Grains

The silver potential of an aqueous solution is more negative in the vicinity to a silver iodide grain than in the vicinity to a silver bromide grain, since the solubility of silver iodide in water is lower than that of silver bromide. Accordingly, it is considered that the rates of the formation and development of latent image centers composed of silver clusters on silver iodide grains are much smaller than those on silver bromide grains. In addition, the rate of the oxidation of the latent image centers on silver iodide grains should be much larger than that of the centers on silver bromide grains. These ideas were supported by the result that the oxidation potential of latent image centers on silver iodide grains was by ca.200mV more negative than that on silver bromide ones (see Fig.4).

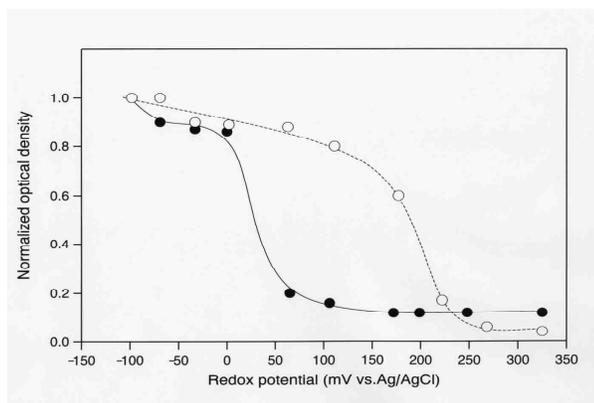


Figure 4. The amount of the residual latent image centers, which is given by the optical density of a developed film strips as a function of the redox potential of a buffer solution for latent image centers formed on silver iodide grains (filled circle) and silver bromide ones (open circle)

One of the most distinctive photographic features of silver iodide grains is in that no latent image center is formed in an emulsion layer with such pAg value as 8, which is normal in a silver bromide emulsion, and that the latent image formation is steeply enhanced by decreasing the pAg value of the emulsion^{7,8}.

The signal intensity of the 35GHz microwave photoconductivity of silver iodide grains was nearly the same between the emulsions with pAg values of 4 and 7. On the other hand, the signal intensity of the radiowave photoconductivity of

silver iodide grains in an emulsion with pAg of 4 was nearly one tenth of that in an emulsion with pAg of 7. The ultraviolet photoelectron spectroscopy has been applied to a silver iodide layer covered with a thin gelatin membrane, and revealed that the height of the top of the valence band decreases, and therefore the rate of the capture of positive holes by the surroundings of the grains (i.e., gelatin and water) should be enhanced with decreasing the pAg value of the gelatin layer.

Conclusion

This study has made clear the following significant features for the physical properties and latent image formation in silver iodide grains as compared with those in silver bromide ones.

1. Although the ionic conductivity is comparable between silver iodide and silver bromide grains, the concentration of interstitial silver ions is higher in the former than in the latter, while their mobility is lower in the former than in the latter.
2. The concentration of photoelectrons as detected by the microwave photoconductivity method with time-resolution of several ns was much lower in silver iodide grains than in silver bromide ones, while the concentration of positive holes as detected by the radiowave photoconductivity method with time resolution of several μ s was much higher in the former than in the latter. It is considered that photoelectrons are rapidly captured by many interstitial silver ions, and recombined with positive holes in silver iodide grains.
3. Silver iodide grains are photographically active only under conditions with low pAg, and are suitable for photothermographic materials, in which pAg is low owing to the presence of silver carboxylate as the source of silver ions.

References

- [1] H.Mifune, K.Yamane, T.Ohzeki, F.Nariyuki, K.Watanabe, M.Yoshikane, M.Nakanishi, T.Maekawa, "Photothermographic materials with nano-particles of silver iodide" to be presented at this Congress (ICIS'06)
- [2] T.Funakubo, H.Mifune, T.Ohzeki, K.Ohzeki, K.Yamane, "Photothermographic materials with tabular silver iodide grains" to be presented at this Congress (ICIS'06)
- [3] T.Tani, "Photographic Sensitivity: Theory and Mechanisms", Oxford Univ. Press, New York, 1995
- [4] T.H.James, W.Vanselow, *Photogr.Sci.Eng.*, **5**, 21(1961)
- [5] E.A.Frei, *Photogr.Korresp.*, **105**, 5,21,37 (1969)
- [6] R.J.Friauf, in *The Physics of Latent Image Formation in Silver Halide*, A.Bladereschi, W.Czaja, E.Tosatti, M.Tosi, eds., World Scientific, Singapore, 1984, p.79.
- [7] T.H.James, W.Vanselow, R.F.Quirk, *Photogr.Sci.Eng.*, **5**, 216(1961)
- [8] R.L.Jenkins, G.C.Farnell, *J.Photogr.Sci.*, **28**, 163(1980)

Author Biography

Hiroyuki Mifune received his M.S.degree in Chemistry from Kyoto University in 1974. Since 1974 he has been a member of Ashigara Research Laboratories and Materials Research Division, Fuji Photo Film Co.,Ltd.