Journal of Imaging Science and Technology® 51(3): 197–201, 2007.

Comparison in Physical Properties among AgCl, AgBr, and AgI Grains

Tadaaki Tani
Frontier Core-Technology Laboratories, Fuji Photo Film Co., Ltd., 577 Ushijima, Kaisei-machi,
Ashigarakami-gun, Kanagawa-ken, 258-8577, Japan
E-mail: tadaaki_tani@fujifilm.co.jp

Abstract. *Physical properties have been compared among AgCl, AgBr, and AgI grains. The formation energy of interstitial silver ions through surface kink sites is in the order of AgCl, AgBr, and AgI, while the activation energy of the migration of interstitial silver ions is in the reverse order. This result is ascribed to the difference in ionic character among them, and leads to the fact that the concentration of interstitial silver ions acting as shallow electron traps is in the order of AgI, AgBr, and AgCl. This result is therefore responsible for the fact that the concentration of photoelectrons, as measured by means of a 35 GHz microwave photoconductivity apparatus, is in the order of AgCl, AgBr, and AgI. Since the solubility in water is in the order of AgCl, AgBr, and AgI, it is considered that the concentration of dissolving impurity ions acting as positive hole traps is in the order of AgCl, AgBr, and AgI, and that the silver ion concentration in the vicinity of latent image centers on the grain surface is in the same order. Although these facts make it more difficult to form latent image centers on AgI grains than on AgBr and AgCl grains in conventional photographic materials, in which the concentration of silver ions is kept low for their stability, it is indicated that AgI grains are suitable for photothermographic materials, in which AgI grains are placed in the environment with higher concentration of silver ions than in conventional ones, and are fixed during thermal development, contrary to AgBr and AgCl grains. © 2007 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2007)51:3(197)]

INTRODUCTION

Although the time-resolved photoconductivity measurement of silver halide grains by means of a microwave photoconductivity method[1–6] and a radio frequency photoconductivity one[1,6–8] have provided us with important knowledge for the clarification of the mechanism of photographic sensitivity and the design of silver halide grains for photographic products,[1] the exposure condition for the measurements (e.g., a nanosecond light pulse for the microwave photoconductivity one) is quite different from that for an ordinary sensitometry (e.g., 10 s).

Although AgI was used in "Daguerreotype" at the beginning of silver halide photography,[9] AgI is not used at the present in any photographic products owing to its low solubility in water,[10] which brings about difficulties in achieving high sensitivity and rapid processing in conventional photographic processes.[1] It is however noted that the absorbance of AgI in the blue region[11] is much larger than those of AgBr and AgCl,[12] and it should be useful for photographic sensitivity if the above stated difficulties could be overcome.

A series of papers was presented at ICIS'06[13–15] to disclose the discovery that AgI grains have several advantages over AgBrI and AgBr grains when they are used in photothermographic materials. In addition, the result of studies on physical properties of AgI grains was also presented in order to provide guiding principles to design them for photothermographic materials. Thus, AgI grains have become an interesting subject for photographic scientists and engineers, providing an opportunity to grasp comprehensively the physical properties of silver halide grains of photographic interest.

This study has been undertaken to analyze physical properties of all the silver halide grains of photographic interest (i.e., AgCl, AgBr, and AgI) grains under the same conditions for measurements of physical and photographic properties of these grains in emulsions.

MATERIALS AND EXPERIMENTS

The photographic emulsions used in this study were composed of aqueous gelatin suspensions of cubic AgCl grains with average size of 0.2 μm, cubic and octahedral AgBr grains with average size of 0.2 μm, and AgI grains with average size of 0.14 μm, as described in another paper presented at ICIS'06.[13] In order to study chemical sensitization, emulsions were reduction sensitized by digesting them for 60 min at 60°C in the presence of dimethylamine borane as sensitizer, and sulfur sensitized by digesting them for 60 min at 60°C in the presence of sodium thiosulfate as a sensitizer. These emulsions were coated and dried on TAC (cellulose triacetate) film base to give samples for the measurements of sensitometry and time-resolved photoconductivity. Conventional sensitometry was carried out by exposing the samples to light for 10 s. Photographic developments were made for the AgCl and AgBr samples by use of a surface developer MAA-1 at 20°C for 10 min,[16] and for the AgI samples by a developer with pyrogallol as a developing agent at 38°C for 60 min.[17]

A 35 GHz microwave photoconductivity apparatus with a 355 nm nanosecond light pulse[5,6] was used to get the time-resolved photoconductivity and sensitivity of the samples at room temperature.[18] Figure 1 shows the pieces of the film coated with an AgBr emulsion, which were exposed

---

Received Sep. 5, 2006; accepted for publication Jan. 3, 2007.
1062-3701/2007/51(3)/197/5/$20.00.

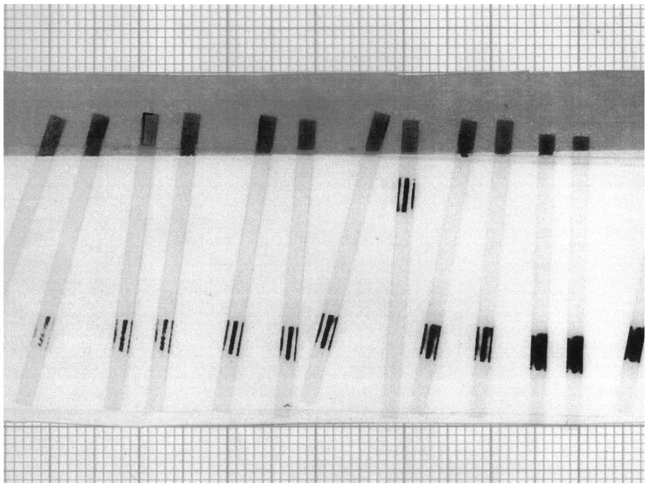

Figure 1. Pieces of film coated with an AgBr emulsion, which were exposed to light pulses for several nanoseconds through neutral density filters of variation of optical density, and developed by MAA-1.

to light pulses for several nanoseconds through neutral filters of varied density in the microwave photoconductivity apparatus and developed by use of MAA-1. The ionic conductivity of these grains in emulsions was measured by applying the dielectric loss method[19–21] at room temperature to dried emulsion layers which were about 100 μm thick.

RESULTS AND DISCUSSIONS

The results obtained in the series of this study are summarized in Table I. Some remarks and explanations are made below.

In a silver halide grain, a photoelectron is generally captured by a trap and combines with an interstitial silver ion to form a silver atom, when the concentration of interstitial silver ions is high under conditions yielding low activity of positive holes. Since the rate of this reaction (r_t) is in proportion to the product of the concentrations of interstitial silver ions and photoelectrons, the maximum concentration of photoelectrons as given by the peak height of the signal of a time-resolved photoconductivity measurement (V_e) is proportional to light intensity (I).[1,18] When the concentration of interstitial silver ions is low under conditions yielding high activity of positive holes, a captured electron is liable to recombine with a positive hole. Since the rate constant of this reaction (r_r) is proportional to I^2, V_e is proportional to $I^{1/2}$.

Figure 2 shows the ionic conductivity and ionic relaxation time in AgCl and AgBr grains. Since the ionic relaxation time in AgCl grains is very long as compared with that in AgBr grains, it is predicted that photoelectrons survive much longer in AgCl grains than in AgBr ones. This prediction could be confirmed by the microwave photoconductivity measurement of these samples, as shown in Figure 3. As seen in this figure, photoelectrons disappear within 20 nanoseconds in AgBr grains, while photoelectrons in AgCl grains survive for more than several microseconds. In accord with this result, a radio frequency photoconductivity apparatus could detect the photoelectrons in AgCl grains, while it could not detect the photoelectrons in AgBr and AgI grains.

Table I. Comparisons in physical properties and photographic performance among AgCl, AgBr, and AgI grains. (Ag_i^+: Interstitial silver ion; $pK_{sp} = pAg + pX$.)

	AgCl grains	AgBr grains	AgI grains
Ionic conductivity (ohm^{-1} cm^{-1})	$\sim 5 \times 10^{-8}$	Oct: $\sim 2 \times 10^{-5}$ Cub: $\sim 5 \times 10^{-6}$	$\sim 1 \times 10^{-5}$
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($c\parallel$)[27] 0.29 eV($c\perp$)[27] 0.40 eV[a]
Formation energy of Ag_i^+ from surface kink sites	0.51 eV	Oct: 0.31 eV Cub: 0.35 eV	~ 0.05 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)	$V \doteqdot 0$	$V \doteqdot 0$
Photoconductivity with positive holes	Not detectable	Small	Large
pK_{sp}[10]	9.75	12.31	16.09
Sensitiv. of primitive grains on ns exposure	High/weak pAg dependence	High/medium pAg dependence	Low/steep pAg dependence

[a] $(E_{\parallel} + 2E_{\perp})/3$.

The decay kinetics of photoelectrons in silver halide grains is not simple, since they depend on several factors, which differ among silver halide grains. Some of the aspects of photoelectron decay kinetics in silver halide grains could be observed by means of the 35 GHz microwave and 100 MHz radiofrequency photoconductivity measurements.[18] In accord with the prediction that r_r should increase with I more intensely than r_t, the proportionality of V_e to I in the region with low I was followed by the proportionality of V_e to $I^{1/2}$ in the region with high I in both the cases of the microwave photoconductivity of octahedral AgBr grains and the radio frequency photoconductivity of cubic AgCl grains. In accord with the prediction that r_t should increase with the ionic conductivity of silver halide grains with interstitial silver ions as carriers, the proportionality of V_e to I was observed in the microwave photoconductivity measurements only with octahedral AgBr grains, which have the highest ionic conductivity among the grains studied. It is inferred that the proportionality of V_e to I could not be observed in the microwave photoconductivity of AgI grains owing to the facts that the absorbance in the blue region and the activity of positive holes are much larger in AgI grains than in AgBr and AgCl grains.[13]

This short electron lifetime in AgBr grains leads to significant dependence of the photographic performance of reduction-sensitized AgBr emulsions on exposure time. It

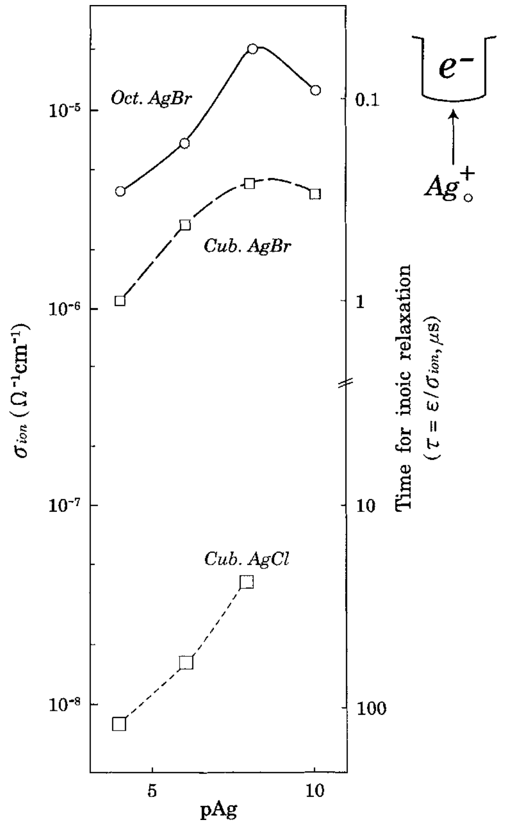

Figure 2. Ionic conductivity and ionic relaxation time as a function of pAg value for AgBr and AgCl grains in emulsions.

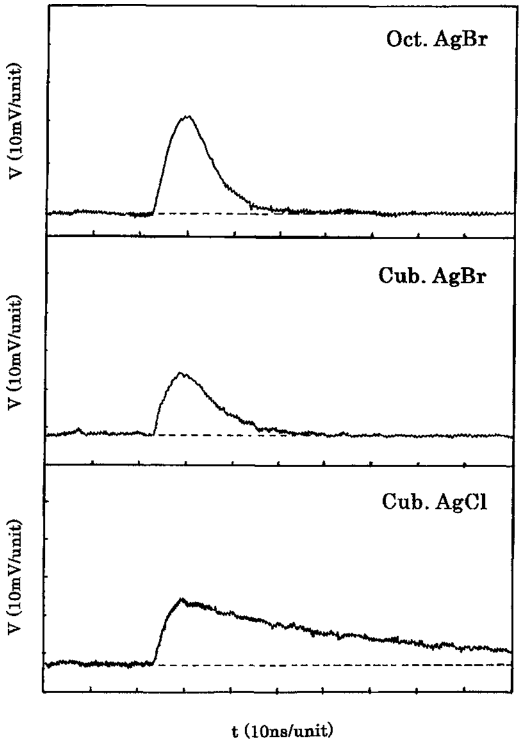

Figure 3. Time-resolved photoconductivity of AgBr and AgCl grains as measured by means of a 35 GHz microwave photoconductivity apparatus.

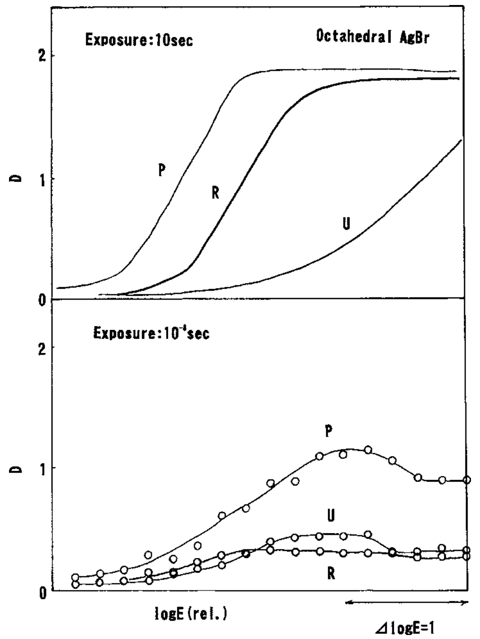

Figure 4. Characteristic curves of octahedral AgBr grains without (*U*) and with reduction sensitization *R* centers (*R*) and with *R* and *P* centers (*P*) in emulsions, which were exposed to light for 10 s (upper figure) and for several nanoseconds (lower figure).

has been made clear in a previous paper[22] that reduction sensitization centers are composed of dimers of silver atoms, and that they act as positive hole traps (i.e., *R* centers) or electron traps (i.e., *P* centers). As seen in the upper figure in Figure 4, reduction sensitization *R* centers together with *P* centers significantly enhance the latent image formation in AgBr emulsions on exposure for 10 s,[6,22] while they hardly enhance the latent image formation on exposure for several nanoseconds. Since photoelectrons disappear within 20 nanoseconds in AgBr grains as seen in Fig. 3, the result in Fig. 4 indicates that it takes more than 20 nanoseconds for reduction sensitization *R* centers to capture positive holes and to prevent them from recombining with photoelectrons.

Owing to long relaxation time of ionic processes associated with low ionic conductivity in AgCl grains, photoelectrons in AgCl grains survive for a long time and are liable to recombine with positive holes, r_r being in proportion to I^2. This prediction could be confirmed by observing the deterioration of the efficiency of latent image formation in AgCl grains with high intensity exposure.[23] As Brust and others reported at ICPS'98,[24] iodide ions with concentration as small as about 1 mol % increase the ionic conductivity of AgCl grains by about two orders of magnitude and significantly enhance the latent image formation, as seen in Figure 5. The present author has confirmed that there are three states of iodide ions on AgCl grains, i.e., adsorbed iodide ions, epitaxitially deposited AgI, and recrystallized AgClI,[25] and that the enhancement of the latent image formation by iodide ions in any state is more significant in a sulfur-sensitized emulsion than in an unsensitized one. The analysis of the ionic conductivity of AgCl grains with iodide ions has given the energy levels of silver ions in these samples, according to which iodide ions make silver ions at a surface

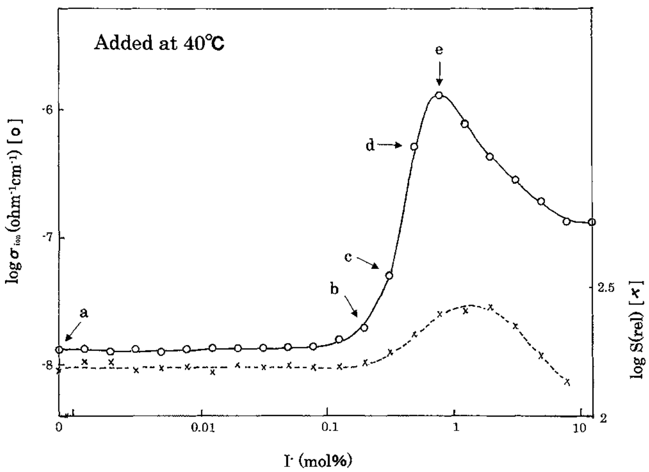

Figure 5. Ionic conductivity and photographic sensitivity of AgCl grains without and with iodide ions in recrystallized AgClI phase on the grain surface as a function of the amount of iodide.

kink site unstable and make it easy for them to jump into interstitial positions.[25]

It has already been reported that the electron trapping process in AgCl grains is diffusion limited owing to the presence of abundant silver ions at surface kink sites acting as traps for electrons, and hardly influenced by additional electron traps such as electron trapping sensitization centers on the grain surface.[5] On the other hand, the electron trapping process in AgBr grains, which also takes place on the grain surface, is reaction limited and influenced by such electron traps as sulfur sensitization centers on the grain surface.[5]

This prediction could be confirmed by measuring the dependence of electron lifetimes on the concentration of sulfur sensitization centers, as shown in Figure 6. Namely, the lifetime of photoelectrons was independent of the concentration of sulfur sensitization centers in pure AgCl grains. It is therefore considered that sulfur sensitization is not as effective in AgCl emulsions as in AgBr ones. As seen in this figure, the electron lifetime in AgCl grains becomes influenced by sulfur sensitization centers and effective for the enhancement of latent image formation when a small amount of iodide ions are introduced onto the grains.

As described in the papers presented at ICIS'06,[13–15] AgI grains play an unique role in making photothermographic materials sensitive and stable, since they are highly sensitive in photographic materials with a high concentration of silver ions such as photothermographic ones and are furthermore fixed during thermal development in the materials.[13–15] From the viewpoint of photographic science and engineering, these findings have made AgI grains more attractive than before.

As seen in Table I, the formation energy of interstitial silver ions through surface kink sites is in the order of AgCl, AgBr, and AgI, while the activation energy of the migration of interstitial silver ions is in the reverse order.[26,27] Since the ionic conductivity of AgI grains is comparable to that of octahedral AgBr grains, it is estimated that the concentration of interstitial silver ions acting as shallow electron traps is much larger in AgI grains than those in AgBr grains.

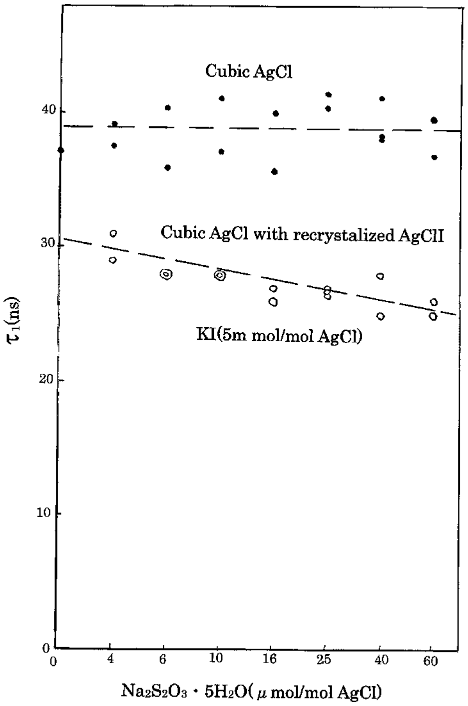

Figure 6. Photoelectron lifetimes in AgCl grains without and with recrystalized AgClI phases as a function of the amount of sodium thiosulfate used for formation of sulfur sensitization centers on the grains.

Figure 7 shows the comparison in photoconductivity among AgCl, AgBr, and AgI grains as a function of exposure to a 355 nm light pulse. In spite of the fact that the absorption coefficient of AgI at 355 nm is nearly one order of magnitude larger than those of AgBr and AgCl, the photoconductivity of AgI grains is much smaller than those of AgBr and AgCl grains. This result is in accord with the observation described in an other paper presented at ICIS'06.[13] Taking into account the fact that the absorption coefficient of AgCl grains at 355 nm is the smallest among the grains studied, it is inferred that the activity of photoelectrons is in the order of AgCl, AgBr, and AgI grains. It was also indicated on the basis of the photoconductivity with positive holes as carriers, measured by means of the radio frequency photoconductivity apparatus, that the activity of positive holes was higher in AgI grains than in AgBr grains.[13]

We consider that the ionic character of silver halide, which is in the order of AgCl, AgBr, and AgI, reflects the formation energy of interstitial silver ions through surface kink sites and the activation energy for the migration of interstitial silver ions. Since a silver ion at a surface kink site and an interstitial position in the crystal structure of silver halide bear one half and unit positive charge, respectively, the former is more stable than the latter, and the difference in energy level between them should increase with increasing ionic character from electrostatic viewpoint. It is known that interstitial silver ions migrate in AgBr and AgCl according to the interstitial mechanism,[26] whose effectiveness should increase with the increasing ionic character of silver halides. These results should lead to higher concentration of interstitial silver ions acting as electron traps and lower photo-

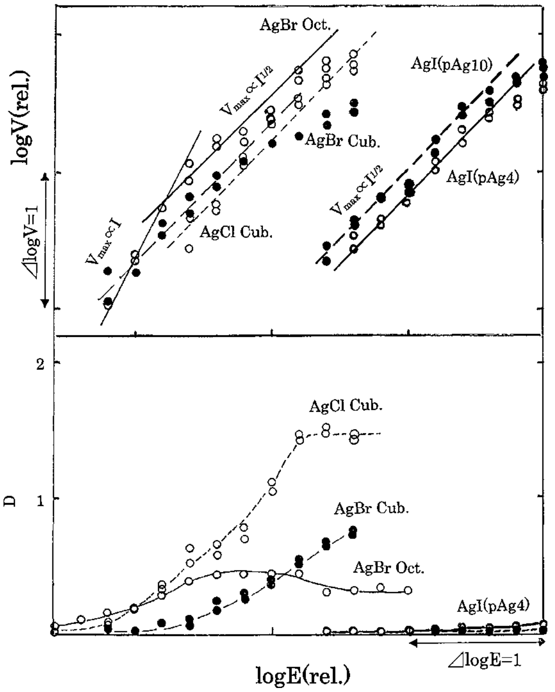

Figure 7. Photoconductivity (as signal intensity) with a 35 GHz microwave photoconductivity apparatus as a function of relative exposure, for AgCl, AgBr, and AgI grains in emulsions.

conductivity with electrons as carriers in AgI grains compared to AgBr and AgCl.

It has been often observed that electron traps are provided by crystal defects in silver halides, while positive holes are trapped by impurity ions.[1] The difference in the activity of positive holes is attributed to the difference in the solubility of impurity ions acting as positive hole traps in silver halides and in the height of the top of the valence band of silver halides. Since the solubility in water is in the order of AgCl, AgBr, and AgI, the solubility of impurity ions acting as positive hole traps in silver halides should be in the same order. According to the measurement of the electronic structures of silver halides by means of ultraviolet photoelectron spectroscopy, the height of the top of the valence band is in the order of AgI, AgBr, and AgCl.[28] Therefore the reactivity of positive holes in silver halide grains towards their surroundings is in the reverse order.

The low activity of photoelectrons and the high activity of positive holes in AgI grains, as stated above, make them less sensitive than AgBr and AgCl grains in conventional photographic materials, where the concentration of silver ions is kept low for the stability of photographic processes. In other papers presented at ICIS'06,[13–15] it has been indicated that the silver ion concentration in the vicinity of latent image centers on AgI grains is much lower than that in the vicinity of latent image centers on AgBr grains, and that the increase in the silver ion concentration in an emulsion enhances latent image formation, although it usually deteriorates the photographic stability of a conventional emulsion.

Owing to the presence of silver carboxylate, photothermographic materials contain silver ions in relatively high concentration as compared with conventional media,[13–15] they are nevertheless stable owing to antifogging actions of agents added to them. Silver iodide grains absorb blue light much more intensely than AgBr and AgBrI grains, and show their photographic ability under conditions of high concentration of silver ions. In addition, it has been recently discovered that AgI grains are fixed during thermal development of the photothermographic materials.[13–15] We therefore conclude that AgI grains are quite suitable and useful for photothermographic materials in order to achieve high sensitivity and stability.

REFERENCES

[1] T. Tani, *Photographic Sensitivity: Theory and Mechanisms* (Oxford University Press, New York, 1995).

[2] L. M. Kellogg, Photograph. Sci. Eng. **18**, 378 (1974).

[3] R. J. Deri and J. P. Spoonhower, Appl. Phys. Lett. **43**, 65 (1983).

[4] R. J. Deri, J. P. Spoonhower, and J. F. Hamilton, J. Appl. Phys. **57**, 1968 (1985).

[5] T. Oikawa, N. Saeki, T. Kaneda, A. Hirano, and T. Tani, J. Imaging Sci. Technol. **39**, 233 (1995).

[6] T. Tani, T. Tasaka, M. Murofushi, K. Hosoi, and A. Hirano, J. Imaging Sci. **47**, 1 (2003).

[7] L. M. Kellogg, J. Hodes, and J. Muenter, "Measurement of photocarrier decay times in silver halide emulsion grains using radiofrequency techniques", *Proc. IS&T and SPSTJ International East-West Symposium II* (IS&T, Springfield, VA, 1988) paper C11–15.

[8] K. Hosoi, A. Hirano, and T. Tani, J. Imaging Sci. Technol. **46**, 67 (2002).

[9] R. Jenkins, in *Pioneers of Photography: Their Achievements in Science and Technology*, edited by Eugene Ostroff (SPSE, Springfield, VA, 1987).

[10] J. F. Padday and A. H. Herz, in *The Theory of the Photographic Process*, 4th ed., edited by T. H. James (Macmillan, New York, 1977), pp. 25–36.

[11] M. Cardona, Phys. Rev. **129**, 69 (1963).

[12] Y. Okamoto, Nachr. Akad. Wiss. Goettingen, Math-Phys. Kl. IIa, Math-Phys-Chem. Abt. **275**, 14 (1956).

[13] H. Mifune, T. Tani, S. Yamashita, S. Aiba, T. Ohzeki, and K. Yamane, "Ionic and electronic properties silver iodide grains", *Proc. ICIS'06* (IS&T, Springfield, VA, 2006) pp. 224–226; T. Tani, H. Mifune, and S. Yamashita, J. Imaging Sci. Technol. **51**, 202 (2007).

[14] H. Mifune, K. Yamane, T. Ohzeki, F. Nariyuki, K. Watanabe, M. Yoshikane, M. Nakanishi, and T. Maekawa, "Photothermographic materials with nano-particles of silver iodide", *Proc. ICIS'06* (IS&T, Springfield, VA, 2006) pp. 227–229; T. Funakuba, H. Mifune, and T. Ohzeki, J. Imaging Sci. Technol. **51**, 207 (2007).

[15] H. Mifune, T. Funakubo, T. Ohzeki, K. Ohzeki, and K. Yamane, "Photothermographic materials with silver iodide tabular grains", *Proc. ICIS'06* (IS&T, Springfield, VA, 2006) pp. 230–232; T. Funakuba, H. Mifune, and T. Ohzeki, J. Imaging Sci. Technol. **51**, 212 (2007).

[16] T. H. James, W. Vanselow, and R. F. Quirk, J. Soc. Photogr. Sci. Technol. Jpn. **19B**, 170 (1953).

[17] T. H. James and W. Vanselow, Photograph. Sci. Eng. **5**, 21 (1961).

[18] T. Tani, "Photoconductivity and latent image formation in silver halide grains on nanoseconds exposure", *Proceedings of AgX 2004: International Symposium on Silver Halide Technology* (IS&T, Springfield, VA, 2004) pp. 83–86.

[19] J. van Biesen, J. Appl. Phys. **41**, 1910 (1970).

[20] S. Takada and T. Tani, J. Appl. Phys. **45**, 4767 (1974).

[21] K. Ohzeki, S. Urabe, and T. Tani, J. Imaging Sci. **34**, 136 (1990).

[22] T. Tani, M. Murofushi, J. Imaging Sci. Technol. **38**, 1 (1994).

[23] J. F. Hamilton, in *The Theory of the Photographic Process*, 4th ed., edited by T. H. James (Macmillan, New York, 1977), pp. 133–145.

[24] T. B. Brust, M. R. Mis, and K. J. Lushington, *ICPS'98, Proceedings of the International Congress of Imaging Science* (KVCV, Antwerp, Belgium, 1998) pp. 11–14.

[25] T. Tani, "Iodide ions on cubic AgCl grains as studied by their physical properties", *Proc. Autumn Meeting SPSTJ* (SPSTJ, Kyoto, Japan, 2006) pp. 73–74.

[26] R. J. Friauf, in *The Physics of Latent Image Formation in Silver Halides*, edited by A. Bradereshi, W. Czaja, E. Tosatti, and M. Tosi (World Scientific, Singapore, 1984), p. 74.

[27] R. J. Friauf, *op. cit.*, p. 79.

[28] R. S. Bauer and W. E. Spicer, Phys. Rev. B **14**, 4539 (1976).