Journal of Imaging Science and Technology® 51(3): 202–206, 2007.

Ionic and Electronic Properties of Silver Iodide Grains

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Abstract. *It has been observed in the preceding paper that the ionic conductivity of AgI grains with interstitial silver ions as carriers is comparable to that of octahedral AgBr ones. Since the activation energy of the migration of interstitial silver ions in AgI is much smaller than that in AgBr, it is estimated that the concentration of interstitial silver ions acting as shallow electron traps is much larger in AgI grains than in AgBr ones, providing an explanation for the observation by a microwave photoconductivity method that the photoconductivity with photoelectrons as carriers is smaller in AgI grains than in AgBr grains. The observation that latent image centers on AgI grains is oxidized at more negative redox potential than that on AgBr grains has been ascribed to the fact that the concentration of silver ions in the vicinity of the former is smaller than that in the vicinity of the latter owing to the difference in the solubility in water between them. A radiofrequency photoconductivity method has revealed that the activity of positive holes in AgI grains in an emulsion is higher than that in AgBr grains in an emulsion, and is depressed by increasing the concentration of silver ions in the emulsion. Although these results make it more difficult to form latent image centers on AgI grains than on AgBr ones in conventional photographic materials, the latent image formation on AgI grains could be enhanced by increasing the concentration of silver ions in conventional materials, and by using them in photothermographic materials, in which the concentration of silver ions was usually much higher than in conventional ones owing to the presence of silver carboxylate. Recent discovery that AgI grains are fixed during thermal development in photothermographic materials has merged with the above-stated results to reveal that AgI grains are suitable and useful for photothermographic materials. © 2007 Society for Imaging Science and Technology.*
[DOI: 10.2352/J.ImagingSci.Technol.(2007)51:3(202)]

INTRODUCTION

Silver iodide grains were used in "Daguerreotype" at the beginning of silver halide photography.[1] However, AgI is not used at present in any photographic materials. One of the reasons for this is its low solubility in water,[2] which brings about difficulties in achieving high sensitivity and rapid processing in conventional photographic processes.[3] It is noted that the absorbance of AgI in blue region[4] is much larger than those of AgBr and AgCl,[5] and should be useful for photographic sensitivity if the above-stated difficulties could be overcome.

Although the physical properties of AgBr and AgCl grains have been extensively studied by means of experimental methods elaborated for them from the viewpoint of their application to photographic materials such as color films and color papers,[3] those methods have hardly applied to AgI grains to reveal their physical properties from photographic viewpoints.

Although photothermographic silver halide materials have a long history,[6,7] many photographic scientists and engineers have recently been driven to improve them[6,7] and to develop new systems for them,[8–10] since they are being successfully used for medical imaging owing to their dry processing. However, these investigators are faced with a problem to keep developed materials stable under illumination, since undeveloped silver halide grains are not fixed, remain after development, and are responsible for an increase in the fog density of the materials under illumination.

A series of papers has been presented at ICIS'06, the 30th International Congress of Imaging Science,[11–13] to disclose our discoveries indicating that AgI grains are suitable and useful for photothermographic materials. First of all, the above stated difficulties for AgI grains to form latent image centers are overcome in photothermographic materials, since they contain silver ions with high concentration owing to the presence of silver carboxylate. More importantly, AgI grains are unexpectedly fixed during thermal development in photothermographic materials.

As a result of this progress, the knowledge of the physical properties of AgI grains has become attractive and a worthwhile subject for study from the viewpoints of photographic science and technology. The present study has been undertaken to measure and analyze the physical properties of AgI grains in order to obtain guiding principles for their design for photothermographic materials.

MATERIALS AND EXPERIMENTS

In order to achieve the above stated purposes, we prepared AgI grains with average size of 0.14 μm and octahedral AgBr grains with average size of 0.2 μm by means of the controlled double jet method.[14,15] The electron micrograph of AgI grains used in this study and the illustration showing the structure of a typical one among them are shown in Figure 1. According to x-ray diffraction analysis,[16] the prepared grains were mostly in beta phase (i.e., hexagonal wurtzite), containing small amount ($\sim 1/4$) of gamma phase (i.e., cubic zincblende). Silver iodide emulsions with pAg of 7 and AgBr emulsions with pAg of 8 were coated and dried on TAC film bases. Coated AgI emulsion layers were exposed to light and developed by use of a developer with pyrogallol as a developing agent[17] at 38°C for 60 min.

In this paper, the ionic properties of AgI grains and

Received Sep. 5, 2006; accepted for publication Feb. 13, 2007.
1062-3701/2007/51(3)/202/5/$20.00.

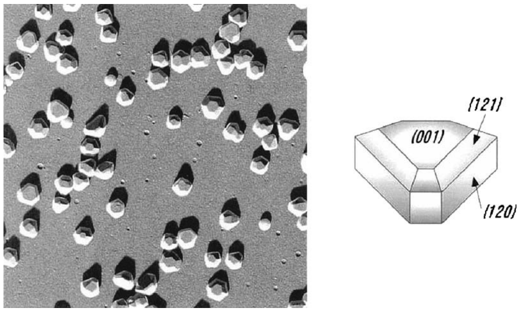

Figure 1. The electron micrograph of AgI grains with average diameter of 0.14 μm used in this study (left) and an illustration showing the structure of a typical AgI grain (right).

AgBr ones in emulsions were measured by means of the dielectric loss method.[3,18–20] The time-resolved photoconductivity of these grains was measured by means of a 35 GHz microwave photoconductivity apparatus[3,21–25] and a 100 MHz radiofrequency photoconductivity apparatus.[3,26,27]

To measure the oxidation potential of latent image centers on AgI grains and on AgBr ones in emulsion layers, exposed emulsion layers were immersed in Frei's redox buffer solutions[28–30] of pBr 3.0 at 25°C for 17 h, washed, developed, fixed, dried, and subjected to the measurement of their optical densities to obtain the residual concentration of latent image centers as a function of the redox potential of the buffer solution. The oxidation potential of latent image centers was given by the potential at which the optical density of an untreated emulsion layer was reduced by half.

RESULTS AND DISCUSSION

Figure 2 shows the dielectric loss curves of AgI and AgBr grains in emulsions in terms of the magnitude of dielectric loss as a function of frequency. It is known that the frequency, which gives a peak in a dielectric loss curve, is proportional to the ionic conductivity of the grains studied.[3,18–20] Silver iodide grains exhibited two peaks in the dielectric loss curve. Taking into account the similarity in crystal structure[31] and dielectric loss curve between AgI grains and octahedral AgBr ones, we ascribe the lower frequency peak of AgI grains in an emulsion layer to the conductivity of the grains with interstitial silver ions as carriers.[3,20] The ionic conductivity of AgI grains was comparable to that of octahedral AgBr grains. The Arrhenius plot of the ionic conductivity of AgI grains exhibited a straight line. The slope of the straight line gave the activation energy of 0.45 eV, which was much larger than that for the ionic conductivity of octahedral AgBr grains.[3,18–20]

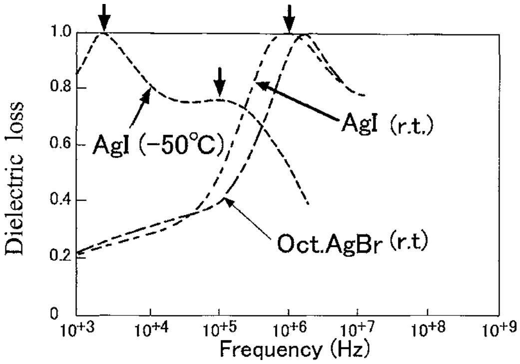

Figure 2. Dielectric loss as a function of frequency of AgI grains in emulsion layers at room temperature (r.t.) and −50°C, and of octahedral AgBr grains in an emulsion layer at room temperature.

Table I summarizes the ionic properties of AgI and AgBr. It is noted that the activation energy of the migration of interstitial silver ions in a large AgI crystal[32] is much larger than that in a large AgBr crystal,[33] and comparable to the measured activation energy of the ionic conductivity of AgI grains in an emulsion. Since the activation energy for the migration of interstitial silver ions in a large AgI crystal is the same as that in an AgI grain, the above result indicates that only small energy is necessary in order to form an interstitial silver ion from a surface kink site on AgI. Figure 3 shows the energy levels of silver ions in AgBr and AgI grains on the basis of the results in Table I as well as an illustration showing the displacement of a silver ion at a surface kink site to

Table I. Ionic properties of silver iodide and silver bromide.

	AgI (tetra-deca.)	AgBr (octahedral)	AgBr (cubic)
Activation energy of ionic conductivity[a]	0.45 eV	0.34 eV	0.39 eV
Activation energy for migration of interstitial silver ion (after Friauf)[b]	0.62 eV(∥) 0.29 eV(⊥) 0.40 eV[c]	0.042 eV	
Formation energy of Frenkel pair (after Friauf)[b]	0.60 eV	1.06 eV	
Formation energy of an interstitial silver ion through a surface kink site[a]	~0.05 eV	0.31 eV	0.35 eV
Formation energy of a silver ion vacancy through a surface kink site[a]	~0.55 eV	0.75 eV	0.71 eV
Potential difference between surface and interior[a]	~0.25 eV	0.22 eV	0.18 eV

[a] Measured and estimated values for AgI and AgBr grains in emulsions used in this study.

[b] Measured values for large AgI and AgBr crystals (Refs. 30 and 31).

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

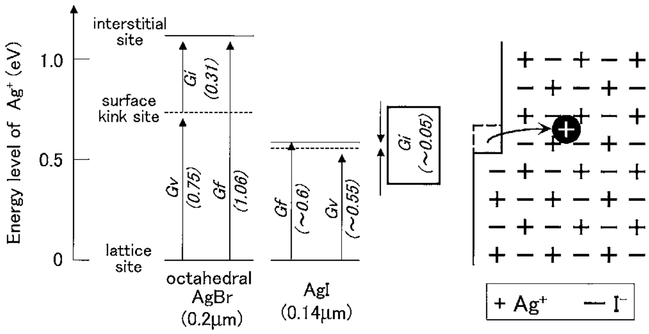

Figure 3. Estimated energy levels of silver ions in AgI and octahedral AgBr grains and an illustration showing the displacement of a silver ion at a surface kink site to an interstitial position to form a space charge layer.

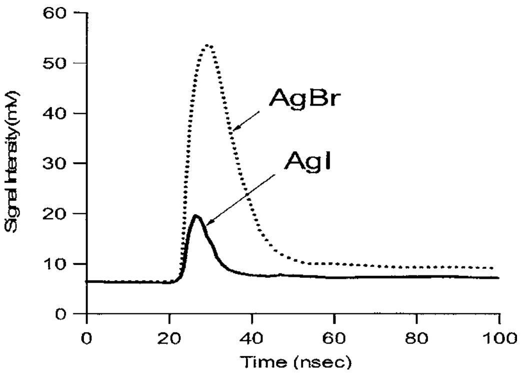

Figure 4. Time-resolved photoconductivity with photoelectrons as carriers in AgI and AgBr grains in emulsions as measured by means of a 35 GHz microwave photoconductivity apparatus on exposure to a light pulse with wavelength of 355 nm for several nanoseconds at room temperature.

an interstitial position to form a space charge layer. In an AgI grain, the energy level of a silver ion at a surface kink site is slightly lower than that of an interstitial silver ion. This situation enhances the formation of the space charge layer, and makes the potential difference between the surface and the interior of AgI as large as 0.25 eV, and much larger than those of octahedral AgBr grains (i.e., 0.22 eV), and cubic AgBr ones (i.e., 0.18 eV).

Although the ionic conductivity of AgI grains with interstitial silver ions as carriers is comparable to that of AgBr grains, the concentration of interstitial silver ions is much higher, so their mobility is much lower in AgI grains than in AgBr ones. Since interstitial silver ions act as shallow traps for photoelectrons, it is predicted that the drift mobility of photoelectrons in AgI grains is smaller than that of photoelectrons in AgBr grains.

Figure 4 shows the observed curves of the time-resolved photoconductivity with photoelectrons as carriers in AgI and AgBr grains, measured at room temperature by means of a 35 GHz microwave photoconductivity apparatus. We assume that the signal intensity is proportional to the concentration of photoelectrons and therefore to the photoconductivity. In spite of the fact that the absorption coefficient of AgI at 355 nm[4] is nearly one order of magnitude larger than that of AgBr,[5] the photoconductivity with photoelectrons as carriers in AgI grains was much smaller than in AgBr grains. One of the reasons for this result should be ascribed to the above stated fact that the concentration of interstitial silver ions acting as shallow electron traps is larger in AgI grains than in AgBr ones.

Figure 5 shows the observed curves of the radiofrequency photoconductivity with positive holes as carriers, which were injected from positive-hole-injecting dye molecules in the excited state. As seen in this figure, the photoconductivity with positive holes in AgI grains was much

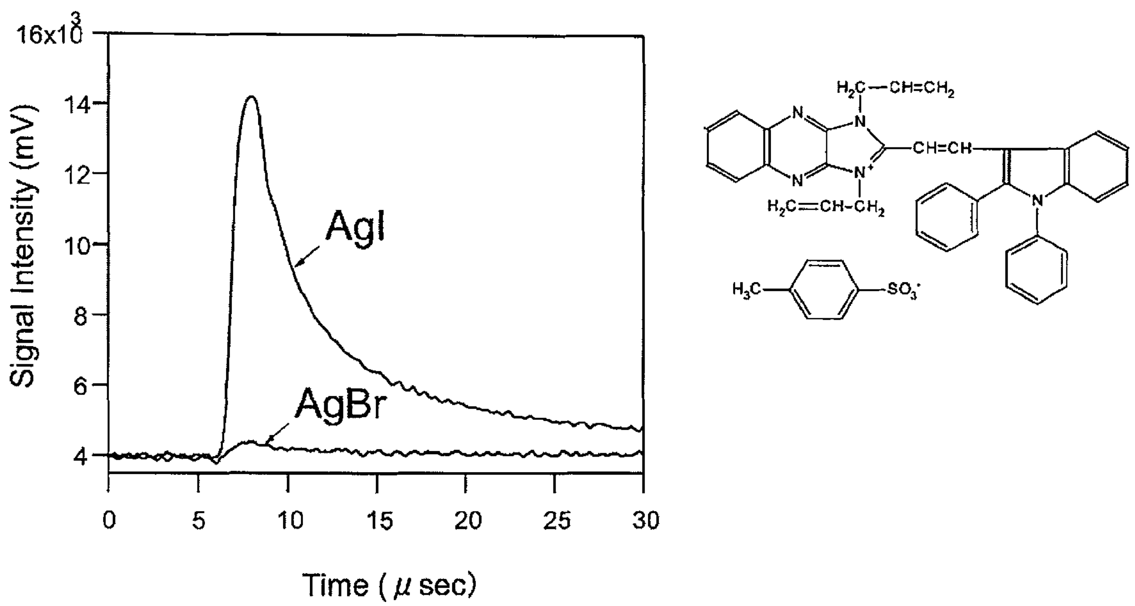

Figure 5. Time-resolved photoconductivity with positive holes as carriers in AgI and AgBr grains, as measured by means of a 100 MHz radiofrequency photoconductivity apparatus on exposure to a xenon flash lamp for several microseconds at room temperature. Positive holes were injected to the grains from excited dye molecules with chemical structure shown.

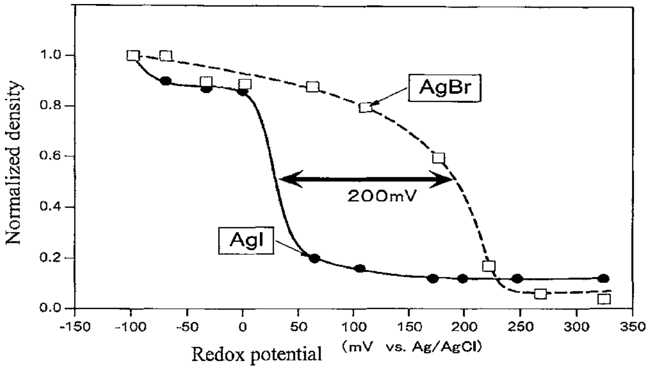

Figure 6. Fractions of AgI and AgBr grains having latent image centers in coated emulsion layers in terms of normalized optical densities of the emulsion layers when they were treated by Frei's buffer solutions with redox potentials indicated in the abscissa, washed, developed, fixed, and dried.

larger than in AgBr grains. These results indicate that the activity of positive holes is larger, and that of photoelectrons is smaller in AgI grains than in AgBr ones.

Figure 6 shows the oxidation of latent image centers on AgI and AgBr grains in emulsions by Frei's buffer solutions with redox potentials indicated on the abscissa. A coated emulsion layer was immersed in the buffer solution, washed, developed, fixed, dried, and subjected to the measurement of its optical density. We assume that the normalized optical density of a treated emulsion layer is nearly equal to the fraction of the grains with at least one latent image center. The oxidation potential of latent image centers was given by the redox potential, at which half of the grains could still have latent image centers after the redox treatment. As seen in this figure, the oxidation potential of the latent image centers on AgI grains was nearly 200 mV more negative than that of the centers on AgBr grains.

This result indicates that the silver potential of latent image centers on AgI grains in an emulsion is more negative than that on AgBr grains in an emulsion with the same concentration of silver ions in the bulk between these two emulsions, and that the concentration of silver ions in the vicinity of latent image centers is smaller in the former than in the latter. This situation makes it more difficult to form latent image centers on AgI grains than on AgBr grains, since the latent image formation is enhanced by increasing the silver potential and therefore the concentration of silver ions in the vicinity of latent image centers. It is therefore expected that the latent image formation on AgI grains in an emulsion is markedly enhanced by the increase in the concentration of silver ions (i.e., the decrease in pAg) in the emulsion. This prediction was confirmed by observing the remarkable pAg dependences of the sensitivity of AgI grains as shown in Figure 7, and the low-intensity reciprocity law failure of AgI emulsions as shown in Figure 8.

Figure 9 shows the pAg dependence of the observed curves of the radiofrequency photoconductivity with positive holes as carriers, which were injected from positive hole-injecting dye molecules in the excited state to AgI grains in an emulsion. A similar result was observed when AgI grains

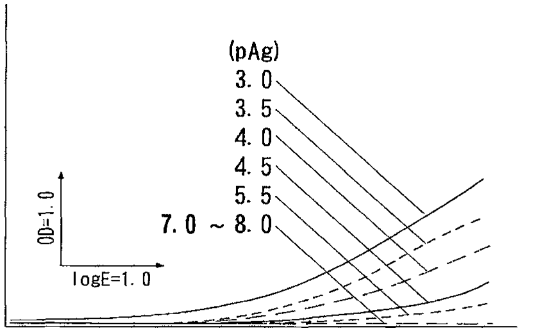

Figure 7. Characteristic curves of AgI grains in emulsions with variation of pAg.

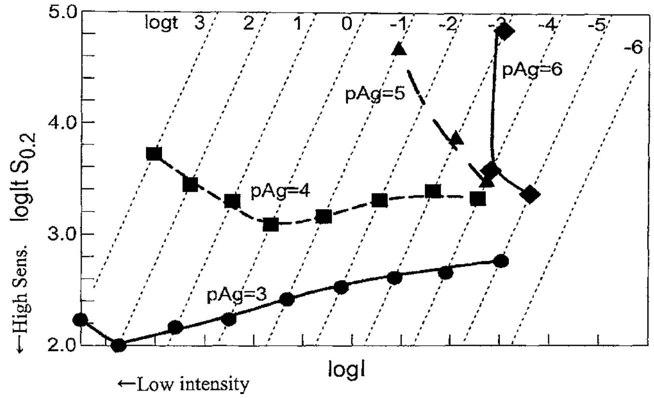

Figure 8. Reciprocity law behavior of AgI grains in emulsions with variation of pAg in terms of the relative exposure (*E*=*It*) required to give the optical density of 0.2 above fog after development as a function of *I*, where *I* and *t* are the intensity and time of exposure.

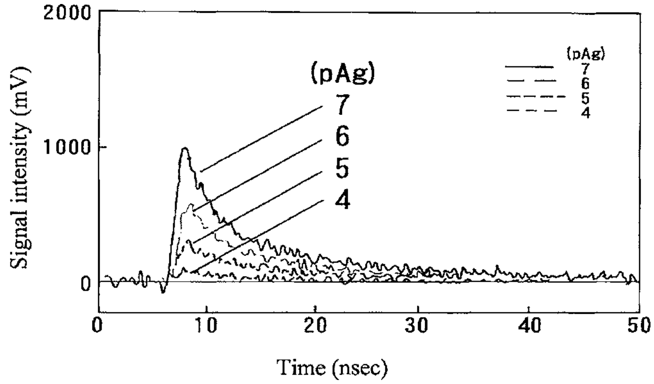

Figure 9. Effect of pAg on the time-resolved photoconductivity of AgI grains with positive holes as carriers, as measured by means of a 100 MHz radiofrequency photoconductivity apparatus at room temperature. Positive holes were injected to the grains from the excited dye molecules with chemical structure shown in Fig. 5.

instead of the dye molecules were excited in the same sample. The concentration of positive holes in AgI grains, as represented by the ordinate, significantly decreased with decreasing the pAg of the emulsion. It is therefore expected that a decrease in the pAg of an AgI emulsion brings about an enhancement of latent image formation in it, not only by increasing the silver potential in the vicinity of latent image centers, but also by depressing the activity of positive holes in AgI grains in the emulsion.

The inference that the silver ion concentration in the vicinity of latent image centers is much lower on AgI grains than on AgBr grains indicates that the surface of an AgI grain is not a favorable place for latent image formation in a conventional photographic emulsion, in which the concentration of silver ions is kept low for the stabilization of photographic processes, and also that the increase in the silver ion concentration in a conventional emulsion is expected to enhance the latent image formation, as seen in Figs. 7 and 8, although it usually deteriorates its stability.

Owing to the presence of silver carboxylate, photothermographic materials contain silver ions in considerably higher concentration compared to conventional media,[10–12] but 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 exhibit high sensitivity only under the condition with high concentration of silver ions. In addition, it has been recently discovered that AgI grains are fixed during thermal development in photothermographic materials on the contrary to AgBr and AgBrI grains.[11–13] We therefore propose that AgI grains should be quite useful and suitable for photothermographic materials to achieve high sensitivity and stability.

REFERENCES

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

[2] 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.

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

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

[5] Y. Okamoto, Nachr. Akad. Wiss. Goetti. Math-Phys. Kl. II a, Math-Phys-Chem. Abt., **275**, 14 (1956).

[6] D. R. Whitcomb, Photogr. Sci. Photochem. **21**, 1 (2003).

[7] M. R. V. Sahyun, J. Imaging Sci. Technol. **49**, 337 (2005).

[8] H. Tsuzuki, A. Hatakeyama, and K. Nakajima, "The aqueous-coated photothermographic material", *Proc. ICIS'02, The 29th International Congress of Imaging Science* (SPSTJ, Tokyo, 2002) p. 27.

[9] K. Yamane and S. Yamashita, "The role of silver halides in photothermographic materials with a water dispersible binder", *Proc. ICIS'02, The 29th International Congress of Imaging Science* (SPSTJ, Tokyo, 2002) p. 29.

[10] M. R. V. Sahyun, "Recent progress in understanding the development process in photothermographic material", *Proc. ICIS'06: The 30th International Congress of Imaging Science* (IS&T, Springfield, VA, 2006) pp. 203–204.

[11] H. Mifune, T. Tani, S. Yamashita, S. Aiba, T. Ohzeki, and K. Yamane, "Ionic and electronic properties silver iodide grains", *Proc. ICIS'06: The 30th International Congress of Imaging Science* (IS&T, Springfield, VA, 2006) pp. 224–226.

[12] 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: The 30th International Congress of Imaging Science* (IS&T, Springfield, VA, 2006) pp. 227–229.

[13] H. Mifune, T. Funakubo, T. Ohzeki, K. Ohzeki, and K. Yamane, "Photothermographic materials with tabular silver iodide grains", *Proc. ICIS'06: The 30th International Congress of Imaging Science* (IS&T, Springfield, VA, 2006) pp. 230–232.

[14] C. R. Berry and D. C. Skillman, Photograph. Sci. Eng. **6**, 159 (1962).

[15] K. Klein and E. Moisar, Photogr. Wiss. **11**, 3 (1962).

[16] C. R. Berry, Phys. Rev. **161**, 848 (1967).

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

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

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

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

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

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

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

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

[25] T. Tani, T. Tasaka, M. Murofushi, K. Hosoi, and A. Hirano, Imaging Sci. J. **47**, 1 (1999).

[26] 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.

[27] K. Hosoi, A. Hirano, and T. Tani, J. Imaging Sci. Technol. **46**, 67–74 (2002).

[28] E. A. Frei, Photogr. Korresp. **105**, 5 (1969).

[29] E. A. Frei, Photogr. Korresp. **105**, 21 (1969).

[30] E. A. Frei, Photogr. Korresp. **105**, 37 (1969).

[31] C. R. Berry, Photograph. Sci. Eng. **20**, 29 (1976).

[32] R. J. Friauf, in *The Physics of Latent Image Formation in Silver Halide*, edited by A. Bladereschi, W. Czaja, E. Tosatti, and M. Tosi (World Scientific, Singapore, 1984), p. 79.

[33] R. J. Friauf, Ref. 32, p. 74.