Reversible photoswitching behavior in bulk resistance and in color of polycrystalline AgI at room temperature

Reversible photoswitching behavior in bulk resistance and in color of polycrystalline AgI at room temperature

Rahima Khaton, Shin-ichiro Kashiwagi, Toshifumi Iimori, and Nobuhiro Ohta[a)]
Research Institute for Electronic Science, Hokkaido University, 001-0020 Sapporo, Japan
and Graduate School of Environmental Science, Hokkaido University, 060-0810 Sapporo, Japan

(Received 21 July 2008; accepted 19 November 2008; published online 10 December 2008)

A photoinduced reversible change in bulk resistance of polycrystalline AgI is observed at room temperature. The original yellow color of the sample changes to dark brown with UV (308 nm) photoirradiation, associated with the small decrease in the bulk resistance. A reversible switching of color between dark brown and yellow is observed by alternative UV-visible photoirradiation, associated with a switching between high and low resistance states. The observed reversible photoswitching is interpreted in terms of the photoinduced reversible change in the β-γ-polytype stacking structure of the polycrystalline AgI. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.3044385]

Phase transition in materials is promising and technologically important, and it is currently used for electrically induced resistive switching and rewritable optical data storage applications.[1] A rapid and reversible transition between the resistive state and the conductive state in various types of disordered materials, induced by the electric field, has been reported.[2]

Silver iodide (AgI) is well known by the variety of structures, i.e., at least six polymorphic modifications exist in AgI.[3] Among the various modifications, the stable hexagonal wurtzite-type β-AgI and the metastable zinc blende-type γ-AgI coexist at room temperature and both transform to the α phase having the superionic conductivity at 147 °C.[4–10] Both β-AgI and γ-AgI phases exhibit anomalous optical properties but the conductivity of γ-AgI is higher than the other because of the presence of the large number of tetrahedral cation vacancies in the anion sublattice of γ-AgI.[4–6,11]

Various types of photoswitching and photomemory effects in organic and inorganic materials as well as in different polymers have been proposed[12–15] but reversible photoswitching in polycrystalline AgI has not been reported so far although the resistive switching phenomena in AgI films were reported recently.[16] In the present study, photoinduced change in bulk resistance and in color has been examined in the polycrystalline AgI pellet at room temperature with impedance spectroscopy.

Commercially available AgI was grinded in the agate mortar by hand, and the pellet having 13 mm diameter and 0.7–0.8 mm thickness was prepared by using the pellet die under pressure of 200 kg f/cm^2 at room temperature. The color of the pellet just after the preparation was greenish yellow indicating γ modification of AgI, and this color was converted to pale yellow by aging the sample, indicating β modification in the β-γ polytype of the polycrystalline AgI. The microscopic images of the β-AgI and γ-AgI are totally different from each other. In γ-AgI, there was no photoirradiation effect at room temperature. In the experiments, more than eight samples of the pale yellow pellets, the so-called β-AgI, were used to investigate the photoswitching phenomenon regarding the change in the color as well as the bulk resistance under alternate UV and visible light irradiations. With excitation light from a fluorescence spectrometer (JASCO, FP777), the UV light (308 nm) of intensity 7×10^{-2} W/cm^2 or the visible light (450 nm) of intensity 1×10^{-1} W/cm^2 was used to irradiate the sample between the parallel carbon electrodes on the same surface of the β-AgI pellet with a distance of 1–2 mm, and the Cole–Cole plots were measured in the frequency range from 42 Hz to 5 MHz with an impedance analyzer (Agilent technologies, 4294A) following the four probe method. The bulk resistance was determined from the minimum value of the reactance of the Cole–Cole plots in the lower frequency region. The absorption spectra of the polycrystalline AgI pellets were measured by using the Hitachi U-3500 spectrophotometer.

Figure 1 shows plots of the photoinduced change in the bulk resistance, i.e., ΔR $[\equiv(R_{\mathrm{dark}}-R_{\mathrm{ex}})/R_{\mathrm{dark}}]$, as a function of wavelength. Here, R_{dark} and R_{ex} represent the resistance under dark condition and under photoirradaition, respectively. Absorption spectra of polycrystalline AgI before and after 308 nm excitation (photoirradiation) are also shown in Fig. 1. The ΔR spectrum shows a large decrease in the bulk resistance at ~450 nm, while the absorption intensity is

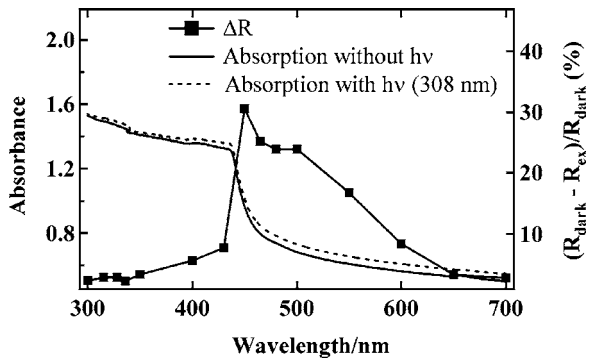

FIG. 1. Excitation wavelength dependence of the photoinduced change in the bulk resistance of polycrystalline AgI pellet at room temperature (■) and absorption spectra obtained before photoirradiation (solid line) and after 308 nm excitation (dotted line). The sudden change in absorbance at around 340 nm is the experimental artifact resulting from the apparatus.

a)Author to whom correspondence should be addressed. Electronic mail: nohta@es.hokudai.ac.jp.

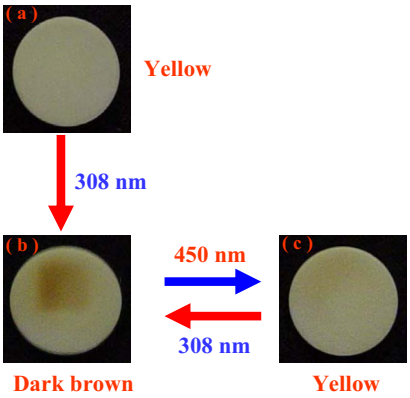

FIG. 2. (Color online) The color change in polycrystalline AgI induced by photoirradiation. (a) Before photoirradiation. (b) 308 nm excitation in the spot, which induces the change from yellow to dark brown. (c) 450 nm excitation following the 308 nm excitation.

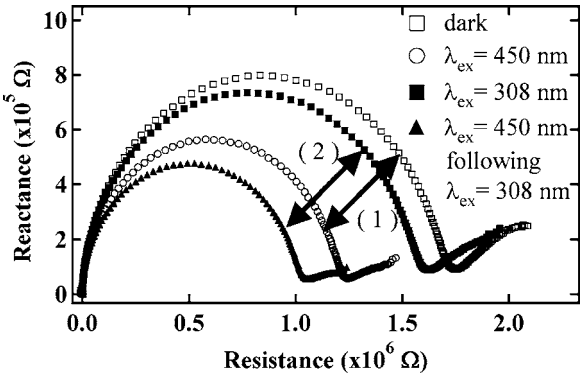

FIG. 3. Impedance spectra of polycrystalline AgI under the dark condition (□), with 450 nm excitation from the dark condition (○), with 308 nm excitation from the dark (■), and with 450 nm excitation following the 308 nm excitation (▲).

weak in the visible region and very strong in the UV region. By 308 nm excitation, the AgI pellet immediately becomes dark brown in color, whereas the color of AgI remains yellow under the 450 nm excitation. Figure 2 shows pictures of the color change in the polycrystalline AgI induced by photoirradiation. Figure 2(a) shows the original yellow color of the polycrystalline AgI pellet before photoirradiation. Figure 2(b) shows the dark brown color of the pellet after 5 min photoirradiation at 308 nm. Figure 2(c) shows the yellow color pellet after 5 min photoirradiation at 450 nm following the 308 nm excitation. With the 450 nm excitation, the color of the dark brown spot was reverted to the original yellow, and this color switching behavior was well repeatable and reproducible for all the samples. The absorption spectra shown in Fig. 1 indicate that the dark brown color induced by the 308 nm excitation comes from the increase in the absorption intensity in the visible region.

The dark brown color induced by 308 nm excitation is somehow similar to that of α-AgI but the change in bulk resistance induced by the 308 nm excitation was much smaller than that expected for α-AgI. The structural change of the stacking component to the α phase in the β-γ polytype may be partly induced by 308 nm excitation and stabilization of the stacking fault may hinder the increase in conductivity of the α phase due to the presence of the Ag clusters.[4] The strongly absorbed light of 308 nm generates high concentration of the electron and hole pair, and after taking part in the direct transition, the electron is trapped by the interstitial Ag^+ ion. As a consequence, Ag clusters may be generated at the 308 nm excitation.[17] By 450 nm excitation, the dark brown colored AgI pellet changed rapidly to the yellow colored one, suggesting that Ag clusters are dissociated by 450 nm excitation.

Impedance spectra of the yellow colored polycrystalline AgI, i.e., β-AgI, observed without photoirradiation and with photoirradiation at 308 or 450 nm are shown in Fig. 3. By 450 nm excitation from the dark condition, the bulk resistance decreases, as marked by the arrow (1) in Fig. 3. The decrease in the bulk resistance by 450 nm excitation seems to be attributed to a partial transformation from β-AgI to γ-AgI in the β-γ polytype stacking, which may induce the stacking fault and the change in local surroundings of the cation layer within the polytype stacking.[4–6] This means that at 450 nm excitation, the photogenerated electron can transmit the photon energy to the interstitial Ag^+ ions of β-AgI by self-trapping of the electron with the hole. After getting the photon energy, interstitial Ag^+ ion moves to the γ-AgI because of the presence of cation vacancy in the γ-AgI, and this movement of Ag^+ ion initiates the lattice distortion and the stacking fault occurs in the β-γ polytype of the polycrystalline AgI. Because of this faulted stacking, a lot of interstitial Ag^+ ions are generated, indicating the increase in the amount of γ-AgI in the mixed β-γ-AgI polytype.[18] As a result, a lot of Frenkel defects are generated by 450 nm excitation, which switches the resistance to the lower state. After stopping the 450 nm excitation, the original high bulk resistance was obtained probably due to the conversion of the γ-AgI phase to the β-AgI phase in the β-γ polytype stacking.

When the dark brown colored AgI pellet induced by the 308 nm excitation was photoirradiated by 450 nm light, the bulk resistance decreases further, as indicated by the arrow (2) in Fig. 3, and the dark brown color reverts to the yellow [see Fig. 2(c)]. The switching between the high and low resistance states was obtained both by alternation between the dark condition and the 450 nm excitation and by alternation between the 308 and 450 nm excitations. The resistance with 450 nm excitation following the 308 nm excitation is smaller than the one with 450 nm excitation following the dark (see Fig. 3). The further reduced bulk resistance with 450 nm excitation following the 308 nm excitation may be attributed to a partial transformation from β-AgI to γ-AgI as well as a photoionization of the Ag clusters resulting in the higher concentration of the Ag^+ ions.[19]

Figure 4 represents the reversible switching behavior of the bulk resistance of polycrystalline AgI. The resistance decreases with 450 nm excitation but reverts to the original dark condition without photoirradiation. When the samples were photoirradiated at 308 nm, the bulk resistance decreased a little, and the color of the pellet changed to dark brown, as mentioned above. The 450 nm excitation on the dark brown colored pellet further decreases the bulk resistance, and the color changes to yellow. The recovery to a high resistance state by 308 nm excitation was very rapid. After stopping the photoirradiation, the bulk resistance returns to the original one of the dark state. With the consecutive photoirradiation at 308 and 450 nm, the color as well as the bulk resistance in AgI pellet changes reversibly. The switching behavior between the dark condition and the 450

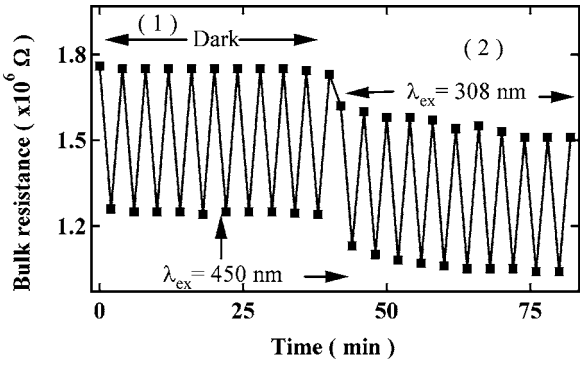

FIG. 4. The reversible change in the bulk resistance of polycrystalline AgI between the dark and the 450 nm excitation for the first ten cycles and between 308 nm and 450 nm excitations (for the last ten cycles).

nm excitation is very similar to the one between 308 and 450 nm excitations. It should be stressed, however, that 308 nm excitation is memorized before the 450 nm excitation in the sense that the resistance obtained by 450 nm excitation following the 308 nm excitation is a little smaller than that obtained by 450 nm excitation from the dark state. The switching behavior of the bulk resistance between high and low resistance states was well reproducible. However, the magnitude of the bulk resistance depends on the sample, probably because it depends on the mixing ratio between β-AgI and γ-AgI in the β-γ polytype of the polycrystalline AgI.

In summary, the bulk resistance as well as the color of the polycrystalline AgI can be switched back and forth by photoirradiation. The 450 nm excitation induces a low resistance state, probably due to a partial transformation to the γ phase from the β phase. The change in color as well as in resistance is induced by 308 nm excitation. The reversible photoswitching of the bulk resistance between high and low states can be attributed to the reversible structural change in the β-γ polytype stacking, and the switching of color simultaneously occurs with the change in bulk resistance of the polycrystalline AgI.

We thank Dr. Masaki Takesada at Hokkaido University for lending us the impedance analyzer. This work was supported by the Grant-in-Aid for Scientific Research (Grant Nos. 15205001 and 20245001) from the Ministry of Education, Culture, Sports, Science and Technology in Japan.

[1]M. Wuttig and N. Yamada, Nature Mater. **6**, 824 (2007).
[2]S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).
[3]B. L. Davis and L. H. Adams, Science **146**, 519 (1964).
[4]N. F. Uvarov and E. F. Hairetdinov, Solid State Ionics **96**, 219 (1997).
[5]N. F. Uvarov, E. F. Hairetdinov, A. I. Rykov, and Yu. T. Pavlyyukhin, Solid State Ionics **96**, 233 (1997).
[6]J. N. Mrgudich, J. Electrochem. Soc. **107**, 475 (1960).
[7]T. Takahashi, K. Kuwabara, and O. Yamamoto, J. Electrochem. Soc. **116**, 357 (1969).
[8]S. V. Baryshnikov, C. Tien, E. V. Charnaya, M. K. Lee, D. Michel, W. Bohlmann, and N. P. Andriyanova, J. Phys.: Condens. Matter **20**, 025214 (2008).
[9]M. R. Vukic, D. S. Veselinovic, and V. G. Markovic, J. Serb Chem. Soc. **72**, 857 (2007).
[10]G. Burley, Acta Crystallogr. **23**, 1 (1967).
[11]A. Hao, C. Gao, M. Li, C. He, X. Huang, G. Zou, Y. Tian, and Y. Ma, J. Appl. Phys. **101**, 053701 (2007).
[12]M. J. Comstock, N. Levy, J. Cho, L. Berbil-Bautista, M. F. Crommie, D. A. Poulsen, and J. M. J. Frechet, Appl. Phys. Lett. **92**, 123107 (2008).
[13]T. Iimori, T. Naito, and N. Ohta, J. Am. Chem. Soc. **129**, 3486 (2007).
[14]T. Iimori, T. Naito, and N. Ohta, Appl. Phys. Lett. **90**, 262103 (2007).
[15]E. Kim and H. W. Lee, J. Mater. Chem. **16**, 1384 (2006).
[16]X. F. Liang, Y. Chen, L. Shi, J. Yin, and Z. G. Liu, J. Phys. D **40**, 4767 (2007).
[17]A. Rakitin, M. Kobayashi, and V. N. Strekalov, Phys. Rev. B **53**, 11356 (1996).
[18]F. Seitz, Rev. Mod. Phys. **23**, 328 (1951).
[19]C. B. Childs and L. Slifkin, Phys. Rev. Lett. **5**, 502 (1960).