

Space Charge Layer Model: Verification by UPS, Ionic Conductivity, and Photographic Effect of AgBr

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Abstract

Ultraviolet photoelectron spectroscopy (UPS) has been successfully applied to the measurement of the height of the top of the valence band (VB) of the surface of AgBr layers on Ag substrates for the verification of the space charge layer (SCL) model, according to which the positive SCL of AgX grains influences their photographic effects by causing the difference in the electronic energy levels between their surface and interior. The depression of the positive SCL of AgBr caused by such adsorbates as stabilizers and antifoggants was characterized by the decrease in the height of the top of the VB of the surface of AgBr layers, the increase in the surface potential of AgBr grains and the increase in the fraction of the grains forming latent image centers at sulfur sensitization centers on the surface.

Introduction

The sensors of photographic materials are AgX grains in photographic emulsions. The absorption of incident photons by the grains creates photoelectrons and positive holes, which then play essential roles in latent image formation.¹ There are various traps for photoelectrons and positive holes, which influence the efficiency of latent image formation. On the other hand, it is known that there is a positive SCL, which causes the band-bending in the subsurface of AgX grains,² and is influenced by various adsorbates, as shown in Figures 1 and 2. In order to understand the roles of the above-stated traps on the grains, it is important to understand the SCL in terms of the height of the top of VB and the bottom of CB of the surface of AgX with respect to that in the interior.

In this paper, the SCL of AgBr was characterized by the determination of the height of the top of VB of the surface of AgBr layers with respect to that in the interior through UPS measurement as well as the analyses of ionic conductivity and photographic effect of AgBr emulsion grains.

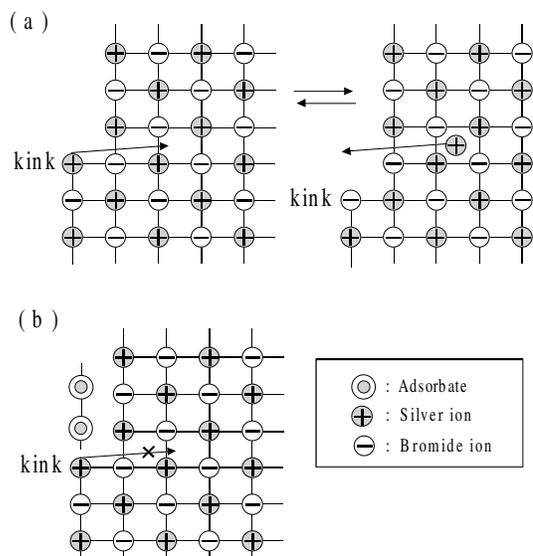


Figure 1. Illustrations of the SCL in AgBr resulting from distribution of silver ions between surface kink sites and interstitial positions without (a) and with (b) organic adsorbates.

Experiments

Compounds studied were 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene (TAI), 5-methyl-benzotriazole (MBT), 1-phenyl-2-mercapto-tetrazole (PMT), 1-(3'-sulfo)-phenyl-2-mercaptotetrazole (SPMT), and potassium thiocyanate.

Emulsions composed of cubic and octahedral AgBr grains with average circular diameter of 0.7 μm were prepared by the controlled double-jet method. For the study of their photographic effect, sulfur sensitization was carried out by digesting them in the presence of sodium thiosulfate as a sensitizer at 60°C for 60 min. Dried emulsion layers were prepared for the measurements of photographic effect by sensitometry and ionic conductivity of the grains by dielectric loss method.

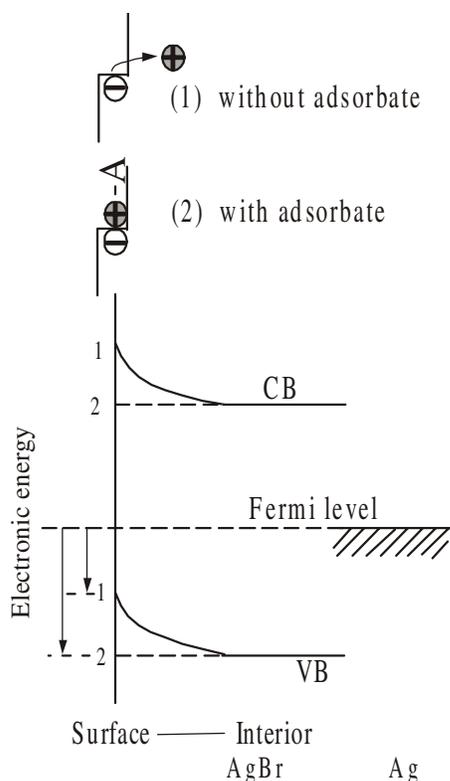


Figure 2. Illustrations showing the SCL and band-bending in AgBr without (1) and with (2) organic adsorbates.

Silver bromide layers with 1000Å thick were evaporated on well-cleaned Ag substrates, and used without and with thin gelatin layers on the surface as samples for UPS measurement. The UPS measurement was made by use of a spectrometer with a combination of a retarding-field-type electron energy analyzer and a rare-gas resonance lamp.³

Results and Discussions

The height of the top of VB of the surface of AgBr layers, on which aqueous solutions with varied pAg had been deposited and dried, was independent of the pAg value, while that of AgBr layers with thin gelatin layers on the surface increased with increasing the pAg value. On the other hand, the ionic conductivity of AgBr emulsion grains increased with increase the pAg value of the molten emulsions. It was considered under the light of the explanation for SCL in Figures 1 and 2 that the change in the ionic conductivity of AgBr emulsion grains with increasing pAg was in accord with the change in the height of the top of VB of AgBr layers with thin gelatin layers on the surface.

All the compounds studied decreased the height of the top of VB of AgBr layers with thin gelatin layers on the surface, on which their aqueous solutions had been

deposited and dried. In the absence of thin gelatin layers on the surface, MBT and PMT (Group 1) decreased the height of the top of the VB, while TAI, SPMT, and KSCN (Group 2) did not. On the other hand, all these compounds decreased the ionic conductivity of AgBr emulsion grains. It is noted that the solubility of AgBr is larger than those of silver salts of Group 1, and smaller than those of silver salts of Group 2.

It was thus found from the above-stated results that the surface state of AgBr layers with thin gelatin layers on the surface could simulate that of AgBr emulsion grains.

According to the explanation for SCL in Figures 1 and 2, surface potential U_s is given by the following equation,⁴

$$2eU_s = \Delta G_i - \Delta G_v - kT \ln 2$$

where ΔG_i and ΔG_v are the formation energies of an interstitial silver ion and a silver ion vacancy through surface kink sites, respectively. The value of U_s was given by the measurement of the activation energy of the ionic conductivity ΔH_i^\ddagger and the following relationships,

$$\Delta H_i^\ddagger = \Delta G_i + \Delta H_m^\ddagger$$

$$\Delta G_i + \Delta G_v = \Delta G_f$$

where ΔH_m^\ddagger is the activation energy of the mobility of interstitial silver ions, and ΔG_f is the formation energy of a Frenkel pair. It was observed that U_s of AgBr emulsion grains, which was negative, became to be less negative owing to the adsorption of the compounds studied, and that the degree of the change in U_s was comparable to that of the change in the height of the top of VB of AgBr layers caused by the adsorbates. This result also supported the SCL model.

All the compounds studied increased the fraction of the grains which formed surface latent image centers, and decreased the fraction of the grains which formed internal latent image centers when the emulsions were sulfur-sensitized. Namely, the above-stated compounds enhanced the capture of photoelectrons at sulfur sensitization centers on the grain surface in competition with that at traps in the interior. This result also supported the SCL model under the light of the fact that these compounds decreased the height of the top of VB and electronic energy levels including electron-accepting levels of sulfur sensitization centers on the grain surface with respect to the electron-accepting levels of traps in the interior according to the result of the UPS measurement in this study.

References

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