

# A Study on Electronic Structure of Interfaces between Substrate and Dyes for Electron Transfer Mechanism of Dye Sensitization

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**Abstract:** Dye sensitization is now understood as the electron transfer process from excited dye molecules to the conduction band of a substrate (AgX in photography and TiO<sub>2</sub> in dye-sensitized solar cell). The electronic structure that is compatible with the electron transfer is characterized by the vacuum level shift at the interface between AgX and dyes. It was found that the alignment of permanent dipoles in organic dye molecules to the surface of AgX dominantly contributed to the vacuum level shift, while the formation of coordinate bonds between sulfur atoms with lone-paired electrons in dye molecules and silver ions on the surface of AgX gave the minor and opposite contribution to the vacuum level shift.

**Key words:** Dye sensitization, Electron transfer mechanism, Vacuum level shift, Alignment of dipole moments, Chemical adsorption

## 1. Introduction

Dye sensitization was discovered by H. Vogel for AgX photographic materials in 1873<sup>1)</sup>, and is still attracting attentions of many scientists and engineers, being expected to play essential roles in new developing technologies<sup>2)</sup> such as dye-sensitized solar cells<sup>3)4)</sup> and organic thin film solar cells<sup>5)</sup>. It is now accepted that dye sensitization takes place through the electron transfer mechanism, according to which an optically excited electron in a sensitizing dye molecule is transferred to the conduction band of a semiconductor such as AgX in photography and TiO<sub>2</sub> in dye-sensitized solar cell, as illustrated in Figure 1(A)<sup>2)–4)6)7)</sup>. However, severe debates were made between the electron transfer mechanism and the energy transfer one in photographic science for many years in the past<sup>2)6)7)</sup>.

The electron transfer mechanism was proposed by Gurney and Mott in 1938 under the assumption that an optically excited electron in a sensitizing dye on an AgX grain is situated above the bottom of the conduction band of the grain<sup>8)</sup>. By means of molecular orbital theory, Coulson estimated that an electron in the highest occupied molecular orbital (HOMO) in a dye molecule was situated by ~7 eV below the vacuum level, and that an electron excited to the lowest unoccupied molecular orbital (LUMO) from the HOMO was therefore 4.5–5.0 eV below the vacuum level, being much lower than the bottom of the conduction band of an AgX grain, (i.e., ~3.5 eV below the vacuum level). Following Coulson's estimation, Mott<sup>9)</sup> dismissed the electron transfer mechanism, and instead proposed the energy transfer one, according to which an excited sensitizing dye molecule trans-

fers its excitation energy to the grain according to the Förster-type energy transfer<sup>10)–12)</sup>, as illustrated in Figure 1(B). It is assumed that the transferred energy excites an electron in the forbidden band to the conduction band of the grain.

Terenin and Akimov experimentally proved Coulson's estimate, confirming by UPS that the ionization energy of sensitizing dyes in isolated state in vacuum were ~7 eV<sup>13)</sup>, and supported the energy transfer mechanism, taking into account the fact that even sensitizing dye molecules in isolated state on the surface of AgX grains could bring about dye sensitization. On the other hand, it was observed by means of UPS that the difference in the ionization energy between an organic molecule in crystal and the corresponding molecule in vacuum was 1.5–2 eV and ascribed to the stabilizing effect of the polarization of molecules at lattice sites on the ionized molecule in the crystal<sup>14)</sup>. However, this result was not applied to the dye sensitization of AgX grains in photography. It seems that the electronic energy levels of a sensitizing dye in isolated state on an AgX grain was considered to correspond to that of the dye in isolated state in vacuum. Using Langmuir-Blodgett (LB) membrane method, Kuhn and others<sup>15)</sup> proved the occurrence of the energy transfer mechanism, observing the dye sensitization of the photographic process on a single crystal of AgBr by a monomolecular layer of a sensitizing dye, which was separated from the crystal with such a distance as to prevent the electron transfer and to allow the energy transfer from a dye layer in excited state to the crystal.

On the other hand, UPS measurements revealed that the ionization energies of most dye crystals were considerably smaller than those of the corresponding dyes in vacuum, and that the

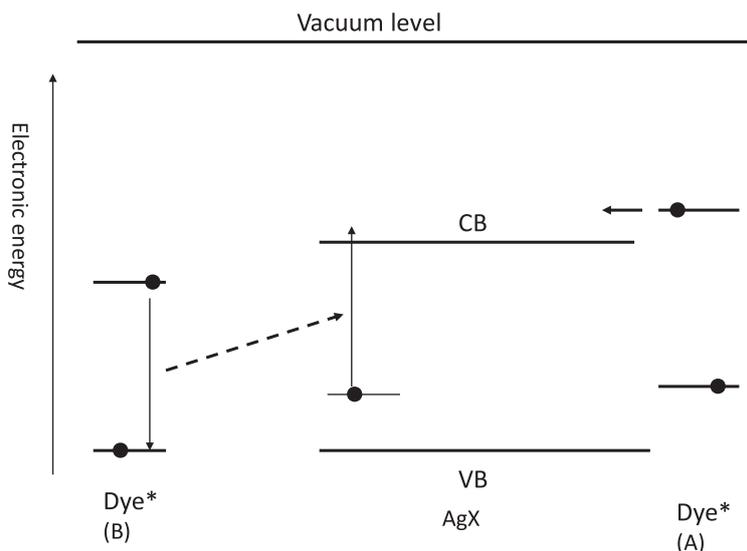


Fig. 1. Schematic illustration showing the electron transfer mechanism for spectral sensitization of AgX by dyes (A) and the energy transfer one (B).

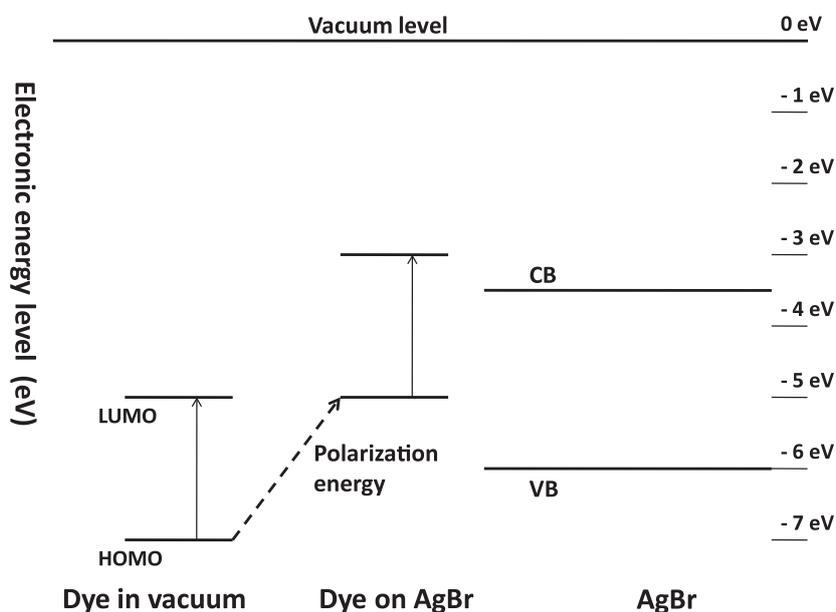


Fig. 2. Schematic illustration showing the electronic energy levels of a sensitizing dye in vacuum and on AgBr with respect to the conduction and valence bands (CB and VB, respectively) of AgBr.

electronic energy levels of excited electrons in the crystals were high enough (i.e., 3.0–3.5 eV below the vacuum level)<sup>16)–20)</sup> for them to be transferred to the conduction band of AgX. This result was not in accord with the fact that only limited fraction of dyes could sensitize photographic process with AgX<sup>2) 6) 7)</sup>.

The electron transfer mechanism has become to be accepted after it was confirmed that the electronic structure of the interface between AgX and dyes was consistent with the spectrally sensitizing ability of the corresponding dyes through the following two steps.

(a) It has been made clear by the present author and others that the ionization energy of a dye molecule in solid is smaller than that of the corresponding dye molecules in vacuum by 1.5–2 eV, not only for the dye molecule in crystal, but also for the corresponding dye molecules in isolated state on the sur-

face of an AgX grain in a photographic emulsion owing to the stabilizing effect on the ionized dye molecule by the polarization of its surroundings, and that the electron transfer from an excited sensitizing dye molecule to the conduction band of AgX is therefore energetically possible, as illustrated in Fig. 2<sup>2) 6) 21)</sup>.

(b) It was found as a result of the cooperative study by the laboratories of K. Seki and the present author that all of the vacuum levels of layers of Dyes A–E in Figure 3 were shifted and became to be lower than that of AgBr, and that the reasonable coincidence of the spectrally sensitizing ability of these dyes with the electronic structure at their interfaces with AgBr could be obtained by taking into account the vacuum level shift, as shown in the same figure<sup>22)</sup>.

The idea leading to Result (a) is the dependence of the ion-

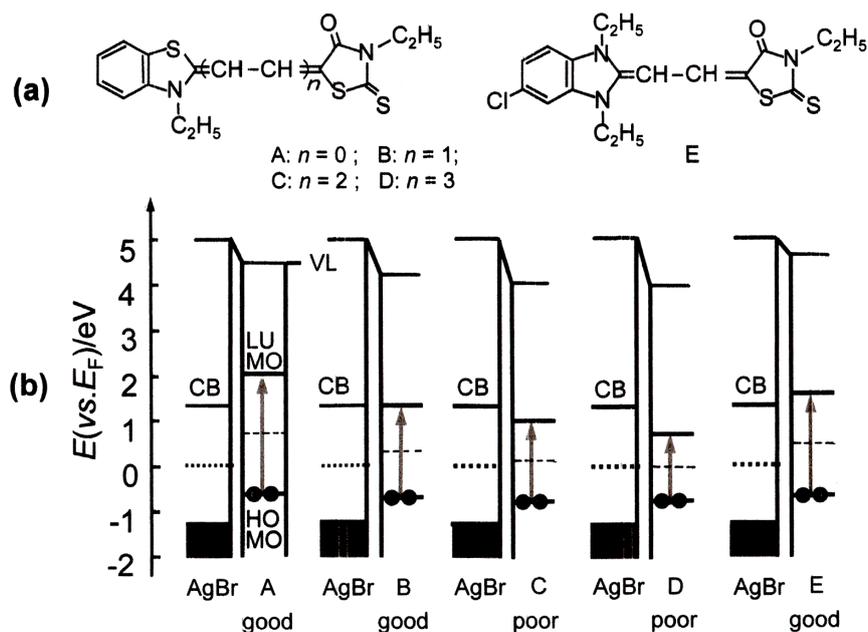


Fig. 3. The molecular structures of merocyanine dyes studied in this paper (a) and the electronic energy levels of Ag layer as indicated on the ordinate with respect to its Fermi level, AgBr layer on the Ag layer, and merocyanine dye on the AgBr layer as measured by means of UPS (b), where HOMO and LUMO are the highest occupied and lowest unoccupied molecular orbitals, respectively, and VL and CB are the vacuum level and conduction band<sup>22</sup>. Sensitizing dyes and non-sensitizing ones are designated as 'good' and 'poor'.

ization energy and electron affinity of organic molecules on the dielectric constants of their surroundings, and has been extended to the interpretation of electronic structures of organic layers under various conditions<sup>23</sup> such as the differences in the ionization energy and electron affinity of an organic molecule between the surface and bulk of an organic layer<sup>24)–26)</sup> and between the interface with a metal electrode and bulk of the layer.

As stated above, the vacuum level shift was observed first for the interface between AgBr and dyes<sup>22</sup>, and then extensively studied by Seki's group for the interfaces between metals and organic layers with a wide variety of ionization energy<sup>27)–29)</sup>, becoming to be inevitable knowledge for organic devices<sup>30)–32)</sup>. They have pointed out several mechanisms giving rise to the vacuum level shift, including charge transfer to equalize the Fermi levels between metals and organic layers, mirror effect, push-back effect, chemical interaction between metals and organic layers, effects of interfacial states, and orientation of polar molecules to the surface of a metal substrate<sup>33</sup>. However, the mechanism for the vacuum level shift at the interface between dyes and substrates other than metals such as AgBr has scarcely been analyzed.

This study was undertaken to make clear the mechanism of the vacuum level shift at the interfaces between AgBr and dyes on the basis of the result of the UPS measurement of the interfaces. It is expected that the result will provide, not only an additional evidence for the electron transfer mechanism of dye sensitization in photography by characterizing the electronic structure of the interface between AgBr and dyes, but also an insight into the vacuum level shift at the interface between organic layers and substrates other than metals.

## 2. Proposed Model for Electronic Structure of Interface between AgBr and Dyes

One of the most probable causes for the vacuum level shift at the interface between a substrate and an organic layer is the charge transfer between them to equalize their Fermi levels. As seen in Figure 3, the observed vacuum level shifts do not seem to result from the equalization of Fermi levels between AgBr and dyes when it is assumed that the Fermi level of a dye is situated at the midpoint between HOMO and LUMO levels of the dye. On the other hand, the degree of the observed vacuum level shift increased with increasing the methine chain length of the dyes studied. They are merocyanine dyes and have resonance structures, one of which has a permanent electric dipole, as exemplified by Dye B in Figure 4. It is therefore expected that the orientation of the dipoles of dye molecules to the surface of AgBr is responsible for the vacuum level shift.

The absence of the infrared absorption band of the  $>C=O$  stretching vibration of a merocyanine dye is the evidence for the idea that the dye molecule has the above-stated permanent dipole, and was confirmed for the dyes studied in this paper when they were adsorbed to AgBr<sup>34</sup>. It is known that merocyanine dyes with  $>C=S$  have stronger adsorptivity to AgX than those without  $>C=S$ <sup>35</sup>. The analysis by means of XANES has revealed that the double bond between C and S in a dye has been converted to the single bond on its adsorption to AgX<sup>36</sup>, indicating that a dye with  $>C=S$  is adsorbed to AgX by forming a coordinate bond between a sulfur atom with lone paired electrons in the dye molecule and a silver ion on the surface of AgX.

The above-stated results lead to a model, according to which a

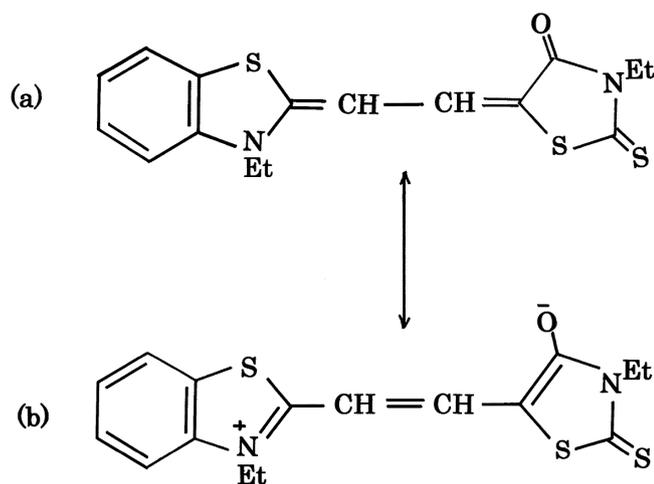


Fig. 4. Resonance between a neutral structure (a) and a polarized one of a Dye B molecule having a dipole that is indicated with + and - at its ends (b).

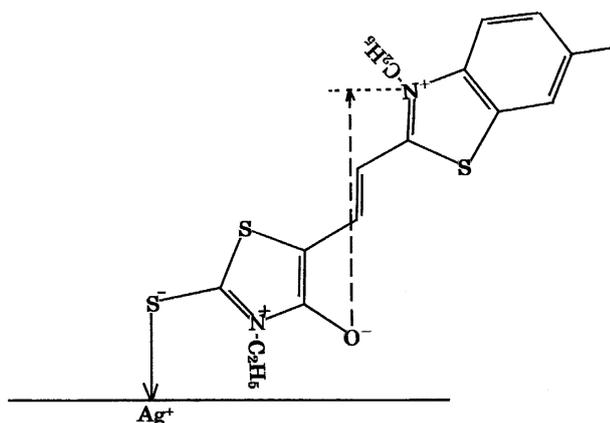


Fig. 5. The model proposed in this paper for a Dye B molecule adsorbed to AgBr surface. The length of a broken arrow is  $d$  in Table 1. A bar attached to the right end of the molecule is a C-H bond and is shown to indicate the length of the molecule.

merocyanine dye as shown in Figures 3 and 4 is adsorbed to the surface of AgX by forming the coordinate bond of an S atom having lone paired electrons in the dye molecule and a silver ion on the surface of AgX, and aligned the positive and negative charges of its dipole far and near the surface of AgX, respectively. This model is qualitatively in accord with the facts that the vacuum level of a dye layer was shifted and became to be lower than that of AgBr, and that the degree of the vacuum level shift increased with increasing the methine chain length of the dyes studied<sup>22</sup>.

Although it is desirable to make the model quantitative, it is difficult to exactly determine the degree of the contribution of Structure B in Figure 4 to the resonance in a dye and the molecular structure and orientation of the dye molecule with respect to the surface of AgBr owing to the presence of isomers, number of which increases with increasing the methine chain length of the dyes studied<sup>37) 38)</sup>. In this study, it has been undertaken to evalu-

Table 1. Evaluation of potential difference ( $V$ ) at the interface of AgBr and adsorbed dye molecules according to the model proposed in this paper and vacuum level shift ( $\Delta$ ) in the electronic structure of the interface as observed by means of UPS<sup>22)</sup>.

	Dye A	Dye B	Dye C	Dye D
$d$ (Å)	4.3	6.4	8.6	10.7
$l$ (Å)	13.8	15.9	16.6	17.8
$w$ (Å)	(3.9)	3.9	(3.9)	(3.9)
$\sigma$ (C/cm <sup>2</sup> )	( $2.8 \times 10^{-5}$ )	$2.6 \times 10^{-5}$	( $2.4 \times 10^{-5}$ )	( $2.2 \times 10^{-5}$ )
$\Delta$ (eV) <sup>22)</sup>	(0.98)	1.35	(1.67)	(1.81)
$V$ (eV)	1.70	2.35	2.92	3.32

$d$ ; distance normal to AgBr surface between a positive charge and a negative one of a dipole in a dye molecule according to the model in Figs. 5 for Dye B.

$l$ ; length of the projection of a dye molecule onto AgBr surface according to the model.

$w$ ; width of a Dye B molecule as evaluated from occupied area by the molecule and length of its projection onto AgBr surface.

$\sigma$ ; density of dipoles in the proposed model as estimated from the saturated amount of Dye B molecules adsorbed on AgBr surfaces.

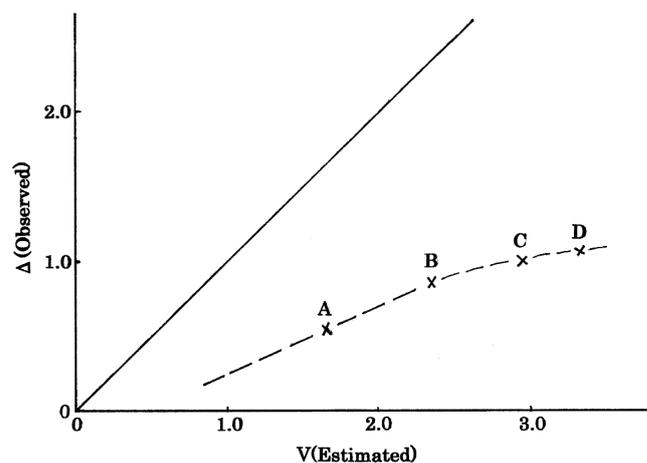


Fig. 6. Degree of the vacuum level shift ( $\Delta$ ) as observed by UPS<sup>22)</sup> and the maximum potential difference ( $V$ ) as given by the model proposed in this paper for Dyes A, B, C, and D adsorbed to AgBr.

ate the model, which should give the largest shift of the vacuum level at the interface between AgBr and the dyes studied. Namely, the proposed model is composed of the molecular structure with all-trans isomer and the resonance structure, to which the degree of the contribution of Structure B in Figure 4 is 100%. The model is exemplified and illustrated for Dye B in Figure 5.

### 3. Examination of Proposed Model

The adsorption isotherm of Dye B to AgBr grains gave the saturated amount of the dye to the grains as  $2.7 \times 10^{-6}$  mol/m<sup>2</sup> and the area occupied by a molecule of Dye B as 61.4 Å<sup>2</sup><sup>36)</sup>. The proposed model for the orientation of Dye B molecule to the grain as shown in Figure 5 indicates that the dye molecule occupies the length ( $l$ ) of 15.9 Å on the surface of AgBr to the direction of its long axis and should have the width ( $w$ ) of 3.9 Å. This value is compatible with the thicknesses of various organic semiconductor

molecules<sup>39) 40)</sup> together with the distances between adjacent lines of silver ions on the (100), (111), and (110) faces, which are stable on the surface of AgBr<sup>2)</sup>, and was used as the thickness of molecules of Dyes A, C, and D, since the molecular structures of Dyes A-D are the same except the length of methine chain. Thus, the proposed models for the orientation of Dyes A, C, and D give the value of  $l$ , the area occupied by a dye molecule, and the saturated amount of the dye molecules (i.e., the density of dipoles in the proposed model  $\sigma$ ). The obtained values are given in Table 1.

The potential difference  $V$  caused by the above-stated aligned dipoles is given by  $\sigma d/\epsilon_0\epsilon$  with the values in Table 1 for  $\sigma$  and  $d$  together with  $8.85 \times 10^{12}$  for  $\epsilon_0$ . The value of 8.0 was used for  $\epsilon$  as the average of the dielectric constants of AgBr and dyes (i.e., 12.5 and 3.5, respectively). The obtained values of  $V$  for Dyes A-D together with those of  $\Delta$  as the degrees of the vacuum level shifts given by the UPS measurement<sup>22)</sup> are also listed in Table 1. Figure 6 shows the relation between the values of  $\Delta$  and  $V$ , indicating the deviation of  $\Delta$  from  $V$ .

#### 4. Discussions

The obtained results as shown in Table 1 and Figure 6 are analyzed from the following viewpoints.

- (1) For all the dyes studied,  $\Delta$  was smaller than  $V$ .
- (2) Although the value of  $\Delta$  increased with increasing the methine chain length of the molecule of the dyes studied, the degree of the increase in the value of  $V$  decreased, resulting in the increase in the deviation.
- (3) Taking into account the viewpoint (2), Figure 6 suggests that electric dipoles with sign opposite to that of  $V$  were present at the interface between AgBr and dyes in the absence of  $V$ .

It is considered that Viewpoint (1) is consistent with the proposed model, since the model is based on the molecular and electronic structures with orientation of dye molecules, which should give the largest potential difference at the interface between AgBr and the dyes studied. It is considered that Viewpoint (2) arises from the increase in the number of isomers of a dye molecule with increasing its methine chain length. The increase in the number of isomers in cyanine and merocyanine dyes with increasing their methine chain length is reflected in the relation between their wavelengths of absorption peaks and methine chain lengths<sup>37) 38)</sup>.

Viewpoint (3) is then analyzed as an example of chemical interactions between substrates and organic layers (i.e., chemical adsorption of organic materials to substrates) for the formation of dipole moments at the interface between them. The chemical adsorption of organic molecules to metal silver by forming coordinate bond between a sulfur atom with lone-paired electrons in an organic molecule and a silver ion on the surface of a substrate is popular in self-assembled monolayers of organic molecules on silver substrates, and was reported to give the potential difference at their interface, which was nearly proportional to permanent dipole moments in the molecules<sup>41) 42)</sup>. Similar results were also observed for self-assembled monolayers of organic molecules on gold substrates<sup>43) 44)</sup>. Namely, it is considered from the above-

stated results that the coordinate bond formation does hardly produce the potential difference at the interfaces between metals and organic molecules with sulfur atoms having lone-paired electrons.

It is therefore considered that the coordinate-bonding between a sulfur atom with lone-paired electrons and a silver ion on a substrate surface brings about the potential difference at the interface, not for the case of metal silver, but for the case of ionic crystals of silver (i.e., AgX). The surface of an ionic crystal differs from that of a metal in that the rumpled effect brings about dipoles on its surface, as seen in AgX<sup>45)-47)</sup>, and that a silver ion or halide ion at a surface kink site is interchangeable with each other and responsible for the formation of dipoles at the surface of AgX<sup>2) 6) 7)</sup>.

The displacement of halide ions and silver ions on the surface as a result of the rumpled effect of AgX (i.e., the situation of halide ions and silver ions above and below the average surface, respectively) brings about the formation of dipoles at the surface and increase the ionization energy of AgX (i.e., the energy gap between the vacuum level and the top of the valence band). The ionization energy of AgBr was about 6.8 eV in the presence of the rumpled effect<sup>48) 49)</sup>. On the other hand, it was 5.6–5.7 eV when the rumpled effect was relaxed by coating a gelatin membrane on the surface of an AgBr layer<sup>49) 50)</sup>. Since the AgBr layers prepared and used in this study have the ionization energy of about 5.6 eV<sup>20)</sup>, it is considered that the rumpled effect was relaxed in the layer not responsible for the dipoles at the interface between AgBr and dyes as a result of Viewpoint (3).

On the contrary to silver metal, surface kink sites with a silver ion and halide ion on AgX bears positive or negative half-charge, respectively, as illustrated in Figure 7. As illustrated in the center of Figure 8, there is no dipole on the surface when the fraction of surface kink sites with silver ions is equal to that with halide ions. As illustrated in the left-hand and right-hand sides of Figure 8, the surfaces are positively and negatively charged as the results of the appearance of dipoles when the fraction of kink sites with silver ions is larger and smaller than that with halide ions, respectively. Figure 8 thus indicates that the ionization energy of AgBr decreases with decreasing the fraction of kink sites with silver

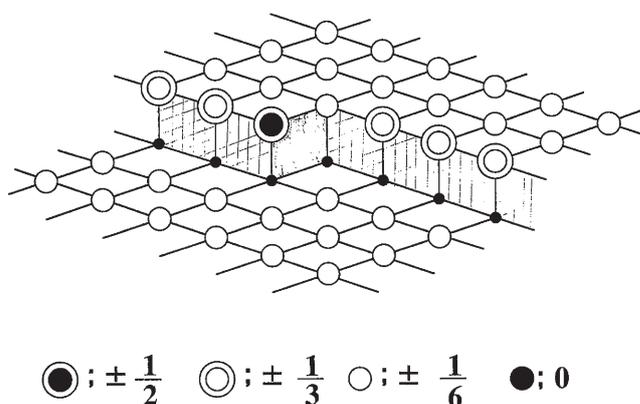


Fig. 7. An illustration of a (100) surface of AgBr with an ion at a kink site bearing electric charge of  $\pm 1/2$  and ions on steps bearing electric charge of  $\pm 1/3$ .

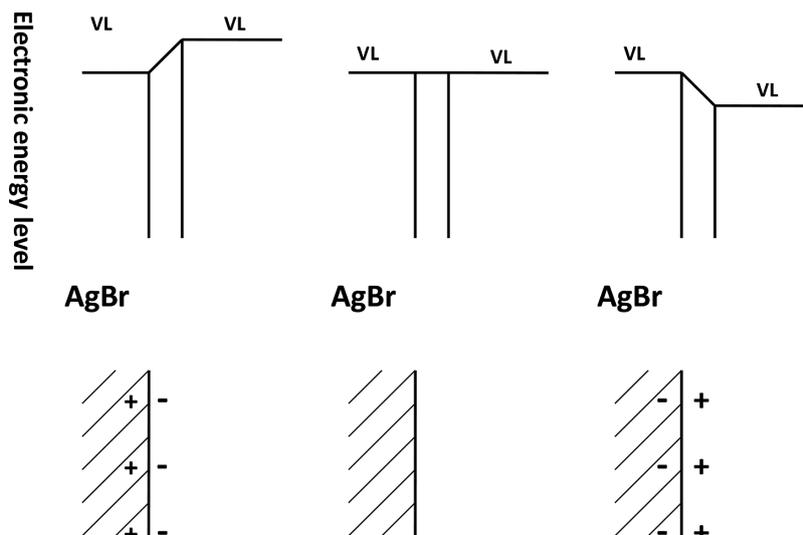


Fig. 8. Electronic energy levels showing the vacuum level shifts at the interfaces between AgBr and dyes (upper figures) arising from the formation of dipoles at the interfaces (lower figures).

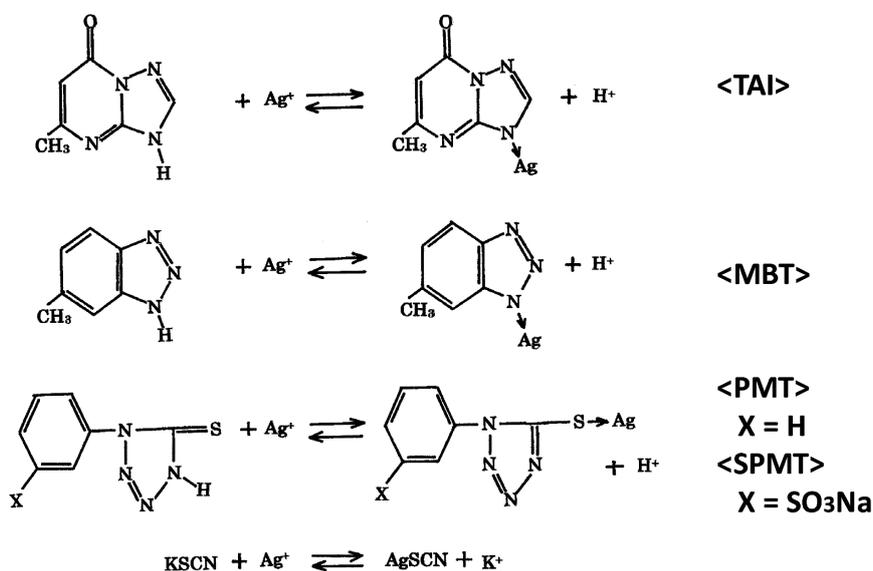


Fig. 9. Molecular structures and formation of silver salts of silver-complexing agents studied in this paper.

ions and thus with increasing the fraction of kink sites with halide ions. The fraction of silver ions at surface kink sites is in equilibrium with the concentration of silver ions in gelatin layer in contact with AgX. In accord with this idea, the increase in the concentration of silver ions in the membrane of gelatin on an AgBr layer increased the ionization energy of the AgX layer<sup>49)</sup>.

One of the most effective ways to increase the fraction of silver ions at kink sites on AgX surface is to stabilize them by the chemical adsorption to the surface of AgX of agents to form sparingly soluble silver salts. Some examples of such agents and the formation of their silver salts are shown in Figure 9. It is expected that the chemical adsorption of these agents to the surface of AgX should increase the fraction of silver ions at surface kink sites on it and increase the ionization energy of the layer, as illustrated in the left-hand side of Figure 8. As shown in Figure 10, the ionization energy of an AgBr layer increased and the top of its conduction band was lowered when it was in contact with gelatin layers con-

taining these agents<sup>49) 50)</sup>. It is noted that the chemical interaction of PMT and SPMT in Figure 9 with AgBr layers is similar to that of the dyes studied in this paper with AgBr layers.

The above-stated results support the model proposed in this paper in that the chemical interaction between sulfur atoms with lone-paired electrons in the dyes studied in this paper and AgX surface brings about the formation of the dipoles at the interface between them as illustrated in the left-hand side of Figure 8, giving an explanation for Viewpoint (3).

## 5. Conclusive Remarks

The model for the vacuum level shift at the interface between AgBr layer and merocyanine dyes was proposed and examined in this paper to support the validity of the electron transfer mechanism for dye sensitization in photography. It was found that the alignment of permanent dipoles in the dye molecules to the sur-

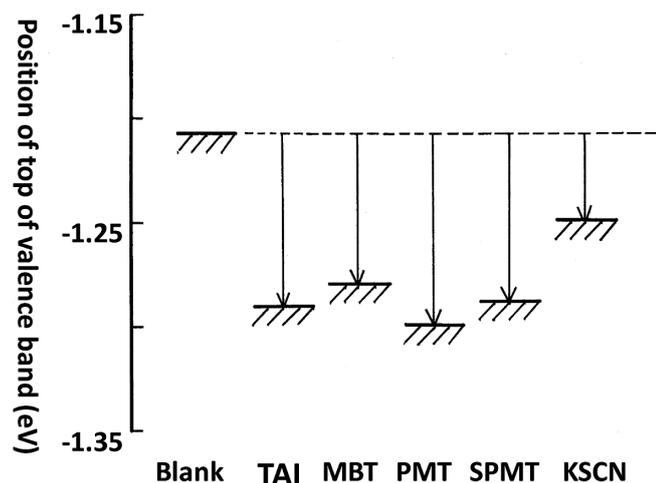


Fig. 10. Position of the top of valence band of AgBr layer with respect to the Fermi level of underlying Ag layer. The AgBr layer was covered with a thin gelatin membrane containing one of the silver-complexing agents that were indicated in Fig. 9.

face of AgBr layers gave the dominant contribution to the vacuum level shift, and that the chemical interaction between AgBr layers and the dye molecules gave the minor and opposite contribution to it. The chemical interaction was composed of the increase in the fraction of silver ions at surface kink sites owing to the coordinate bonding between them.

Although the vacuum level shift between organic layers and metals has been extensively studied with widely varied materials, the shift between organic layers and non-metal substrates has scarcely been examined, and can now include the result in this paper as an example of the model for it.

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