

UV photoemission study of dye/AgBr interfaces in relation to spectral sensitization

Kazuhiko Seki

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

Hiroshi Yanagi, Yasushi Kobayashi, and Toshiaki Ohta*

Department of Materials Science, Faculty of Science, Hiroshima University, Hiroshima 730, Japan

Tadaaki Tani

Ashigara Research Laboratories, Fuji Photo Film Company, Ltd., Minamiashigara, Kanagawa 250-01, Japan

(Received 12 March 1993; revised manuscript received 2 September 1993)

The electronic structure of dye/AgBr interfaces has been studied by UV photoelectron spectroscopy for several merocyanine dye films vacuum deposited on AgBr films. With these results energy diagrams of interfaces were obtained, which include the vacuum level, Fermi level, top of the valence band, and bottom of the conduction band of AgBr, and the energy levels of the highest occupied molecular orbital and the lowest unoccupied molecular orbital of the dyes. These energy diagrams were consistent with the trend in the measured abilities of these dyes for spectral sensitization in the framework of the electron-transfer mechanism. The vacuum level of AgBr was found to be significantly lowered by dye deposition. We discuss the factors determining the electronic structure, including the origin of the electric double layer at the interface, which gives rise to the shift of the vacuum level.

I. INTRODUCTION

Spectral sensitization is one of the key phenomena in silver halide photography.¹ In spectrally unsensitized silver halide (AgX) emulsion, a photoelectron created by light absorption by a AgX grain is captured by an electron trap, and then attracts and reduces an interstitial Ag^+ ion to form a Ag^0 atom. The repetition of this process at the same site leads to the formation of a latent image center composed of Ag_4 or a larger cluster. This center acts as a catalyst for the reduction of a AgX grain to silver by a developer, by receiving an electron from a reductive developing agent. The initial photoexcitation process for the intrinsic sensitivity of AgX is shown in Fig. 1(a) by the arrow labeled I . An important difficulty is that this process can be caused only by a photon with energy larger than the band gap of AgX [2.6 eV (477 nm) for AgBr and 3.0 eV (413 nm) for AgCl], which is only a small fraction of the visible region.

This difficulty is overcome by adding an appropriate dye to an emulsion in which AgX grains adsorb dye molecules and become sensitive to the light with longer wavelength, which the dye absorbs. Use of various dyes enables spectral coverage over a wide range extending to infrared light, and sharp absorption bands of J aggregates of dyes on AgX enables the reduction of their sensitive range into three principal colors.¹

The mechanism of this phenomenon, called spectral sensitization, has been a subject of long debate, in particular between electron-transfer^{2,3} and energy-transfer⁴ mechanisms. Now it seems to be accepted that the former, depicted in Fig. 1(a), is dominant under usual conditions.^{1,3} An electron photoexcited in the dye from the highest occupied molecular orbital (HOMO) to the lowest

unoccupied molecular orbital (LUMO) [arrow $S1$ in Fig. 1(a)] is transferred to the conduction band of AgX (arrow $S2$), and takes part in the latent image formation. In this mechanism, the energy of the LUMO (ϵ_{LU}) must be higher than that of the bottom of the conduction band (CB) of AgX (ϵ_{CB}) for efficient sensitization. Thus we ex-

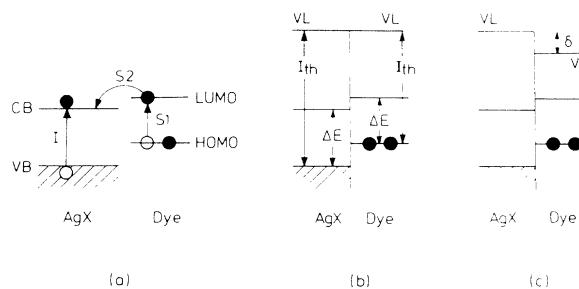


FIG. 1. (a) Sensitization of a silver halide (AgX). In the intrinsic sensitivity region, an electron is excited from the valence band of AgX to the conduction band (the arrow labeled I). In the electron transfer mechanism of spectral sensitization, the electron in the highest occupied molecular orbital (HOMO) of the dye is excited to the lowest unoccupied molecular orbital (LUMO) (arrow $S1$), and injected into the conduction band of AgX (arrow $S2$). (b) Traditional way of estimating the interfacial energy diagram. Assuming a common vacuum level (VL) between AgX and the dye, the ionization threshold energies (I_{th}) and the gap between the highest occupied and lowest vacant states (ΔE) are used for estimating the relative location of the LUMO of the dye and the bottom of the conduction band of AgX (CB). (c) Realistic energy diagram at dye/substrate interface suggested by Nielsen (Ref. 10). There is a shift of vacuum level δ across the interface due to an electric double layer.

pect a sharp dependence of sensitizing efficiency of dyes on the location of their LUMO with respect to that of the CB, under the condition that other factors affecting this efficiency, such as the competition between the electron-transfer and deactivating processes in the dye phase do not differ too much among the dyes.¹ Indeed, the electrochemically estimated height of the LUMO for each dye as given by its reduction potential E_{red} in a solution under common condition has enabled the confirmation of the above-stated expectation.⁵

Still there remain fundamental questions about the electronic structure of dye/AgBr interfaces. The above-stated electrochemical estimation gives only the relative heights of HOMO and LUMO of a dye in monomeric state in a solution. For further understanding of spectral sensitization, it is required to obtain absolute heights of HOMO and LUMO for a dye in an aggregated state on the surface of AgX. There have been attempts at determining energy-level diagrams of dye/AgBr interfaces with absolute energy scales through the procedure shown in Fig. 1(b).⁶⁻⁹ The ionization threshold energies I_{th} of AgX and a dye were determined by separate photoemission experiments, and ϵ_{LU} and ϵ_{CB} deduced by using the optical transition energies of AgX (ΔE_{AgX}) and the dye (ΔE_{D}) by assuming a common vacuum level. The obtained results, however, did not correlate well with the observed sensitizing behavior of the dyes studied. Some dyes with ϵ_{LU} situated above the CB were poor sensitizers.

Nielsen¹⁰ criticized this way of constructing the energy-level diagram, proposing that the interface energy diagram shown in Fig. 1(c) is more realistic. There is a gap δ between the vacuum levels of both sides, and there is little band bending, since the carrier densities in those wide-gap insulators are small. He obtained some experimental evidence for this idea by studying several interfaces.^{10,11} However, no experimental study has ever been performed for dye/AgX interfaces. Thus a direct examination of the dye/AgX interface has been highly desirable.

In this paper we report such a study by UV photoemission spectroscopy (UPS) for interfaces formed by vacuum depositing several kinds of merocyanine dyes on evaporated films of AgBr.

We note that UPS has already been used for studying AgBr^{9,12-18} and several interfaces composed of organics.^{10,11} We also have examined the correlation of I_{th} with the oxidation potential (E_{ox}) and the energy of the HOMO (ϵ_{HO}) as given by MO calculations for merocyanine¹⁹ and cyanine²⁰ dyes. This work is an extension of our efforts toward understanding spectral sensitization from the viewpoint of electronic structure.

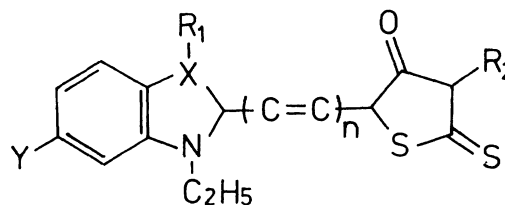
II. EXPERIMENT

A. Sample materials

Five merocyanine dyes shown in Table I were used. They were synthesized according to the method of Brooker *et al.*²¹ Their purities all exceeded 99% as assessed with elemental analysis and thin-layer chromatog-

TABLE I. Dyes used in this work.

Dye	n	X	R_1	R_2	Y
A	0	S	—	C ₂ H ₅	H
B	1	S	—	C ₂ H ₅	H
C	2	S	—	C ₂ H ₅	H
D	3	S	—	C ₂ H ₅	H
E	1	N	C ₂ H ₅	C ₆ H ₁₃	Cl



raphy. Silver bromide powder was provided by Aldrich (99.999%). The photographic emulsions used were the suspensions of octahedral and cubic AgBr grains (average edge lengths 0.83 and 0.73 μm , respectively) in aqueous gelatin solutions, and prepared by a controlled double jet method.²² A methanolic solution of dye was added to the above-described emulsion, which was agitated, coated on a triacetate cellulose film base, dried, and subjected to the measurements of reflectance spectrum and photographic sensitivity. The added amount of each dye was 1.67×10^{-4} mol/mol AgBr. It was confirmed by a conventional separation method that dye B was adsorbed to the emulsion grains according to Lagmuir's adsorption isotherm, occupying a 62 \AA^2 /molecule on the grain surface. The surface coverage of the grains by the molecules of dye B was therefore 28% in the cases of the above-described experiments.

B. UPS spectra

The UPS spectrometer was a combination of a rare-gas resonance lamp and a retarding-field-type electron energy analyzer. Most of the data reported here was obtained by the Ar I (11.62- and 11.83-eV doublet) resonance line supplemented with data by He I (21.22 eV) and Xe I (8.42 eV) emission.

The samples were prepared by successively evaporating AgBr and dyes onto a Ag substrate heat cleaned at 500 $^{\circ}\text{C}$ for 10 h. The use of Ag excluded the possibility of cation exchange between AgBr and the substrate.¹⁸ The film thickness was monitored by quartz thickness monitors, and calibrated for dye films by a photometric analysis after dissolving in *N,N'* dimethylformamide.

At first the UPS spectrum of a Ag substrate was measured. Then AgBr was evaporated from a Pt-wire evaporator to a thickness of 7–10 nm, and UPS measurements were made at intermediate stages of evaporation. X-ray diffraction revealed that a deposited AgBr film was polycrystalline composed of randomly oriented crystallites. A merocyanine dye was deposited on this AgBr film step by step, using an evaporator designed for organic compounds,²³ and UPS measurements were made at

each step.

For energy analysis of photoelectrons, the sample was surrounded by a collector electrode inside coated with Au. The electrons were detected as photocurrent I_{ph} by the collector as a function of retarding voltage V_r applied between the sample and collector. The UPS spectrum was obtained as dI_{ph}/dV_r by electrically differentiating I_{ph} by an ac modulation method²⁴ with a modulation of $0.2V_{pp}$. The energy resolution was estimated to be about 0.2 eV from the Fermi edge of Au. The precision was estimated to be 0.05 eV. This method of energy analysis has the advantage of an accurate energy axis as compared with electrostatic deflection, where even small electromagnetic fields tend to affect the energy distribution of slow electrons.

The base pressure of the UPS apparatus was 10^{-8} Torr. As shown below, the results for AgBr agree well with those obtained under ultrahigh vacuum,¹³ indicating the low sensitivity of the AgBr surface to contamination. This insensitivity was confirmed by invariance of the spectra through exposure of a sample to air of atmospheric pressure. Ordinary organics such as the dyes studied here can be safely measured under present vacuum conditions.^{25,26}

Evaporation and measurements were carried out by paying attention to preventing exposure to light or electrons. UPS spectra did not change due to the exciting light used for the measurements.

C. Diffuse reflectance and spectral sensitivity

The diffuse reflectance spectra of coated emulsion layers were measured by use of a Hitachi Color Analyzer Model 307. The spectral sensitivity of the same emulsions with adsorbed dyes were measured using a homemade apparatus.

III. RESULTS AND DISCUSSION

A. AgBr

Figure 2 show the Ar I UPS spectra of AgBr films of increasing thickness d on a Ag substrate. These spectra and He I spectra (not shown) agree well with those measured by Bauer and Spicer¹³ under ultrahigh vacuum. The onset voltage V_0 and the saturation voltage V_s , corresponding to the right- and left-hand cutoffs, respectively, are indicated for the top curve in Fig. 2.

The energy parameters of the sample can be derived as²⁷

$$\phi_s = \phi_c + eV_s, \quad (1)$$

$$\Delta = h\nu - \phi_c - eV_0, \quad (2)$$

$$I_{th} = \phi_s + \Delta = h\nu - e(V_0 - V_s), \quad (3)$$

where ϕ_s and ϕ_c are work functions of the sample and collector, and Δ is the energy difference between the Fermi level E_F and the top of the occupied states, respectively (cf. inset of Fig. 2). Thus the energy before photoexcitation relative to the Fermi level $E(E_F)$ is given for an electron stopped at V_r by

$$E(E_F) = h\nu - \phi_c - eV_r. \quad (4)$$

The bottom curve in Fig. 2 is the spectrum of a Ag substrate. From the value of $V_0 = 7.35$ eV and the condition of $\Delta = 0$ for a metal, we obtain $\phi_c = 4.35$ eV using Eq. (2). The abscissa at the top of Fig. 2 corresponds to $E(E_F)$ as derived from Eq. (4). The topmost part of the valence band at $V_r = 3.5 - 7$ V is formed by Ag 5s orbitals, and Ag 4d orbitals form the peak at about 2 V.²⁸ From the left-hand cutoff and Eq. (1), we obtain $\phi_{Ag} = 4.26 \pm 0.23$ eV. This is in fair agreement with the reported values of 4.26,²⁹ 4.0,³⁰ and 4.3 eV.³¹

Increasing the thickness d of deposited AgBr, both V_0 and V_s shift significantly, and stop changing beyond $d = 4$ nm. The upper valence band is formed by Br 4p and Ag 4d electrons.¹³⁻¹⁶ From the data for many AgBr films and Eqs. (1)-(3), the energy parameters of the UPS sample are derived as $\phi_s(\text{AgBr}) = 5.3 \pm 0.3$ eV, $\Delta(\text{AgBr}) = 1.3 \pm 0.2$ eV,

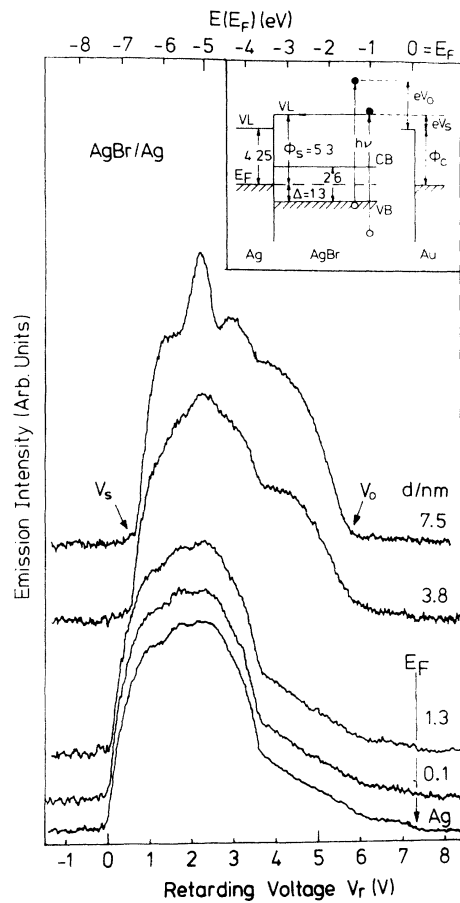


FIG. 2. Change of the Ar I spectrum of a Ag substrate by AgBr deposition. The abscissa at the bottom is the retarding voltage V_r , and that at the top is $E(E_F)$ derived from Eq. (4). The total average thickness d of the deposited film is indicated for each spectrum. The right-hand onset of the Ag spectrum at the bottom corresponds to the Fermi level E_F . The onset voltage V_0 and saturation voltage V_s are also shown for the top curve. The inset depicts the energy level diagram of AgBr/Ag interface deduced from the spectra and the relation among energy parameters of the UPS sample and Au collector [cf. Eqs. (1)-(3)].

TABLE II. Experimentally observed energy parameters of AgBr (in eV).

Method		Sample	I_{th}	Δ	ϕ_s	Ref.
Yield	$(10^{-3})^a$	Ag+Br ₂	≤ 6			32
Yield	$(10^{-4})^a$	sheet	5.8–6.3			33
		evap. film	$+(>1 \text{ eV})^b$			
Yield	$(10^{-4})^a$	bulk	ca. 6.0			12
(+UPS)		sheet				
Yield	$(10^{-9}$ $-10^{-10})^a$	Ag+Br ⁻	5.9–6.0			9
UPS		evap. film	7.15			13
UPS		evap. film		1.2		14
UPS		evap. film	6.3 ± 0.3	1.3 ± 0.2	5.0	15
UPS		evap. film		ca. 1.8		17
UPS		evap. film	6.6 ± 0.4	1.3	5.3 ± 0.3	this work

^aPhotoemission yield at which the threshold was determined.

^bThreshold energy of evaporated film was larger than that of a sheet by more than 1 eV.

and $I_{th}(\text{AgBr}) = 6.6 \pm 0.4 \text{ eV}$.

Thus we obtain an energy diagram for a AgBr/Ag system in the inset of Fig. 2, assuming a flat band throughout the solids. The work function of AgBr is much larger than that of Ag, resulting in a rise of the vacuum level. The energy at the bottom of the conduction band ϵ_{CB} of AgBr in the $E(E_F)$ scale is given by

$$\epsilon_{CB} = -\Delta_{\text{AgBr}} + \Delta E_{\text{AgBr}}, \quad (5)$$

where ΔE_{AgBr} is the band gap of AgBr. Since $\Delta E_{\text{AgBr}} = 2.6 \text{ eV}$,¹ ϵ_{CB} is situated at 1.3 eV in $E(E_F)$ scale, and 3.7 eV below the vacuum level. The Fermi level is at the middle of the band gap.

The values of I_{th} and ϕ_s of AgBr were scattered from sample to sample, while the value of Δ , on which subsequent discussion mainly relies, was fairly well reproducible. This trend is also seen in Table II, where we compare present results with ones reported by other workers.^{12–17,32,33} The reproducibility of I_{th} and ϕ_s among workers is not good, while Δ is well reproducible except for an epitaxially grown AgBr(111) film.¹⁷

B. Merocyanine dyes on AgBr

Figure 3 shows a series of Ar I (UPS) spectra for dye C on AgBr with increasing average dye thickness d . A peak due to the HOMO of the dye appeared at $V_r = 5.9 \text{ eV}$. The significant shift of V_s indicates a lowering of the vacuum level from that of AgBr [Eq. (1)]. The same trends were also observed for other dyes. The dye spectra in the $E(E_F)$ scale were well reproducible within 0.2 eV. In this energy scale, the HOMO energy of the dye is given by

$$\epsilon_{HO} = -\Delta. \quad (6)$$

An example of the dependence of ϵ_{HO} and the vacuum level on d is shown in Fig. 4 for dye B. This indicates that ϵ_{HO} was almost independent of d , even for submonomolecular layers. This finding is important, since a submonomolecular layer of dyes adsorbed on AgBr

grains is used in the photography. The vacuum level is lowered by about 1 eV, and becomes constant beyond $d = 1 \text{ nm}$. Similar results were also obtained for other dyes studied. Similar trends were reported by Nielsen^{10,11} for furan quinone pigments on metal substrates.

Figure 5 depicts the Ar I spectra of thick dye layers on

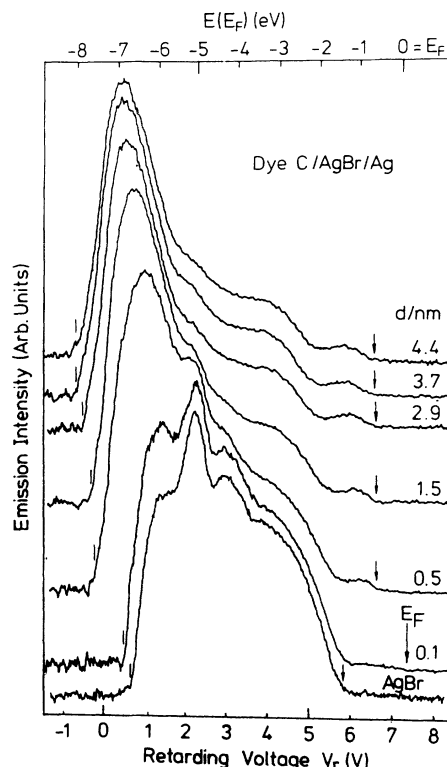


FIG. 3. The change of the Ar I spectra brought about by depositing an increasing amount of dye C on a AgBr film of a 10-nm-thick Ag substrate. The abscissa at the bottom is the retarding voltage, and that at the top is the $E(E_F)$ derived from Eq. (4). The total average thickness of dye D is indicated for each spectrum. The locations of V_0 are indicated by the arrows, except for the case of $d = 0.1 \text{ nm}$, where the determination of V_0 was difficult owing to the weak signal from the dye.

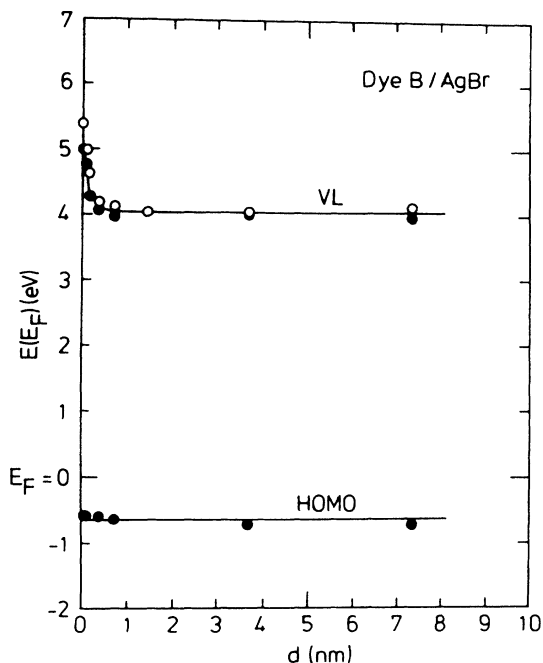


FIG. 4. Thickness dependence of ϕ_s and $\Delta (= -\epsilon_{HO})$ of dye B deposited on AgBr. The open and filled circles correspond to independent measurements. The ϕ_s of AgBr without dye is also shown.

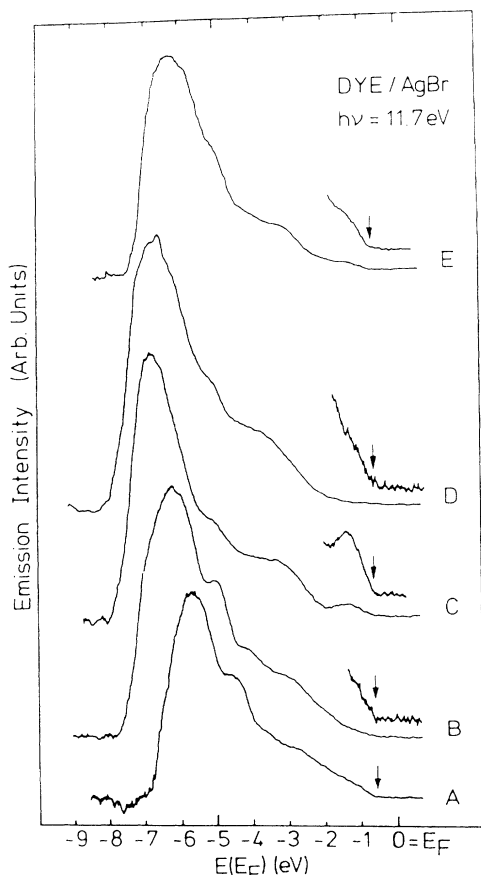


FIG. 5. Ar 1 UPS spectra of thick films of dyes A-E on AgBr. The thicknesses are 1.4 (A), 7 (B), 3.5 (C), 5.6 (D), and 2.1 nm (E). The abscissae are the same as for Fig. 2. The positions of V_0 are indicated by arrows.

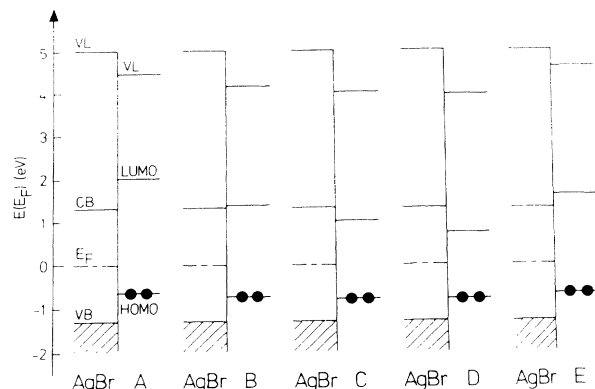


FIG. 6. The energy-level diagrams of dye/AgBr interfaces. Each column corresponds to the combination of AgBr with a dye in the $E(E_F)$ scale. VL: vacuum level; CB and VB: the bottom of the conduction band and top of the valence band of AgBr; LUMO and HOMO: lowest unoccupied and highest occupied molecular orbitals of the dye. The locations of CB and LUMO are deduced from Eqs. (5) and (7).

AgBr, and in Fig. 6 energy-level diagrams of the dye/AgBr interfaces in the $E(E_F)$ scale derived from the spectra are shown. The numerical data ϕ_s , δ , I_{th} , and $\Delta (= -\epsilon_{HO})$ of dyes are summarized in Table III, with reported values¹⁹ for dyes on the Cu substrate. The agreement in I_{th} between present and reported ones is good, and those in ϕ_s and Δ are reasonable.

The energy of the LUMO ϵ_{LU} of each dye can be deduced as

$$\epsilon_{LU} = \epsilon_{HO} + \Delta E_D = -\Delta + \Delta E_D, \quad (7)$$

where ΔE_D is the HOMO-LUMO gap corresponding to the longest-wavelength absorption of dye. The value of ΔE_D was deduced from diffuse reflectance spectra of emulsion layers containing cubic AgBr grains with the dye adsorbed shown in Fig. 7. The absorption band from UV to about 500 nm in the reflectance spectrum of an emulsion layer without dye was assigned to the indirect exciton of AgBr.¹ The value of ΔE_D of each dye was obtained as the absorption maximum indicated by an arrow. The results with octahedral and cubic AgBr grains agreed with each other. The numerical values for ΔE_D and ϵ_{LU} are summarized in Table III.

TABLE III. Energy parameters of dyes deposited or adsorbed on AgBr (in eV).

Dye	Present work						Ref. 19		
	ϕ_s	Δ ($-\epsilon_{HO}$)	δ	I_{th}	ΔE_D	ϵ_{LU}	ϕ_s	Δ	I_{th}
A	4.4 ₅	0.6 ₅	0.5 ₅	5.1 ₅	2.64	2.0	4.5	1.05	5.55
B	4.1 ₅	0.7 ₅	0.8 ₅	4.9 ₅	2.11	1.3 ₅	4.5	0.7	5.10
C	4.0	0.8	1.0	4.8	1.82	1.0	4.5	0.35	4.85
D	3.9 ₅	0.8	1.0 ₅	4.7 ₅	1.52 ^a	0.7	4.2	0.55	4.80
E	4.6	0.7	0.4	5.3	2.30	1.6	4.6	0.55	5.15

^aWe note that the value in a preliminary report (Ref. 36) (1.70 eV) was slightly in error, but this does not affect the discussion in the present paper.

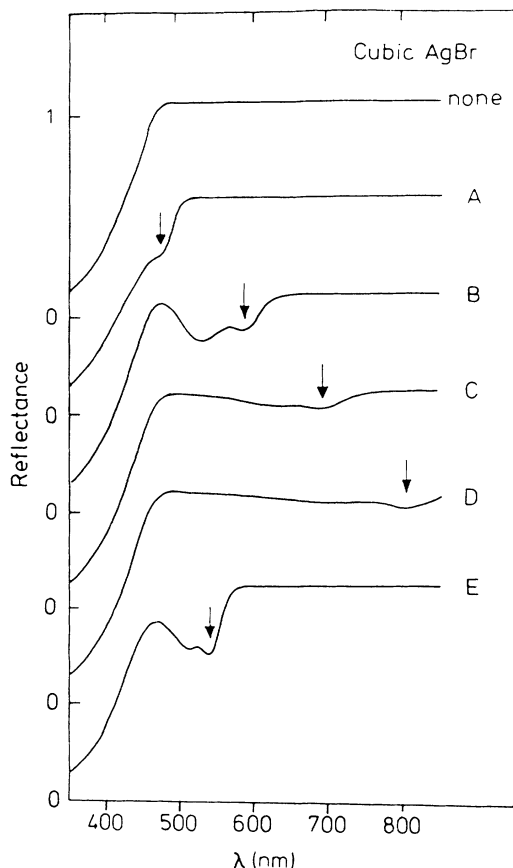


FIG. 7. Diffuse reflectance spectra of AgBr emulsions with and without adsorbed dyes for cubic AgBr grains. The adsorbed dye is indicated at the right-hand side of each spectrum. The amount of each dye was 1.67×10^{-4} mol/mol AgBr. The absorption maximum of the longest-wavelength absorption peak of each spectrum is indicated by an arrow.

According to the electron-transfer mechanism [Fig. 1(a)], we expect that (1) the sensitizing ability of a dye should change significantly by the relative location of ϵ_{LU} of the dye and ϵ_{CB} of AgBr;³⁴ and (2) if sensitization occurs, sensitivity will be enhanced at the energy of the photoabsorption ΔE_D for each dye. The variation of ΔE_D is the origin of the spectral selectivity of different dyes.

As seen in Fig. 6, the LUMO's of dyes *A*, *B*, and *E* are above the bottom of the conduction band of AgBr, while those of *C* and *D* are below it. Thus we expect that *A*, *B*, and *E* are reasonably good sensitizers, and *C* and *D* should be poor sensitizers. We note that the traditional method of aligning the vacuum level places the LUMO's of dyes *C* and *D* above the CB, leading to the opposite prediction that these dyes are also good sensitizers.

C. Comparison with photographic sensitization

Figure 8 shows the wedge spectra of the cubic AgBr emulsions with dyes added. Octahedral AgBr emulsions showed similar results. The wavelength of the light incident to a film was indicated in the abscissa, the light in-

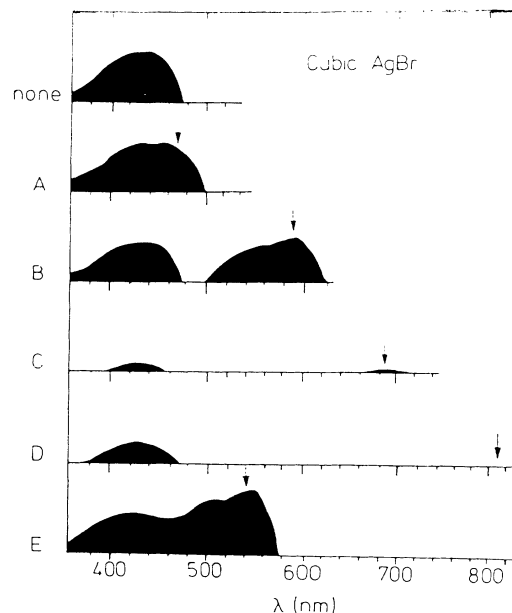


FIG. 8. Wedge spectra of undyed and dyed photographic emulsions containing cubic AgBr grains. The wavelength of the absorption maximum of the reflectance spectrum in Fig. 7 is indicated by an arrow.

tensity being exponentially decreased from the bottom to the top, and the exposed film was developed.

We see that the sensitivity of the grains with adsorbed dyes *A*, *B*, and *E* is large at the maxima of longest-wavelength absorption indicated by arrows, showing that these dyes are good sensitizers. On the other hand, grains with adsorbed dyes *C* and *D* show little sensitivity at the maxima, showing their poor sensitizing ability. These results are in excellent agreement with the expectations in Sec. III B from the interfacial energy diagram. On the other hand, the traditional method of estimation failed to predict the poor sensitizing ability of dyes *C* and *D*, due to the neglect of the shift of vacuum level [Fig. 1(c)].

We note two other details about Fig. 8. First, the decrease in the intrinsic sensitivity of AgBr (blue sensitivity) caused by dyes *C* and *D* can be ascribed to the capture of photoelectrons by the dyes.¹ Dye *D* was not so effectively adsorbed to AgBr, and this may explain the small decrease in blue sensitivity of dye *D*. Second, the relative intensity of the doublet peaks of dye *B* (525 and 585 nm) is reversed between Figs. 7 and 8. We consider that the peak at the shorter wavelength, assigned to *H* bands of the dye, has a smaller quantum yield for spectral sensitization than the peak of the longer wavelength.

Thus the energy diagram of interfaces experimentally determined by direct measurements could remove the difficulty of the previous scheme shown in Fig. 1(b), and this strongly supports the electron-transfer mechanism for spectral sensitization. We recognize the difference in experimental setups between UPS and spectral sensitivity measurements: the former was carried out for the dye overlayer on a AgBr film, while in the latter we used

AgBr grains with highly diluted adsorbed dyes. Nevertheless, the good correspondence between electronic structure and sensitizing behavior suggests that the mechanism of spectral sensitization can be accessed by experiments such as the UPS study reported here.

D. Factors determining the interfacial electronic structure

Finally, we discuss how the interfacial electronic structures develop such as those in Fig. 6, although experimental information for fully discussing this point is not yet available.

The significant lowering of the vacuum level indicates the formation of an interfacial electric double layer. Further, the average thickness of ~ 1 nm, where the energy of the vacuum level stops changing, corresponds roughly to the monolayer thickness. Thus we may suppose a double layer just within the first monolayer, with the HOMO energy being determined in each molecule and little affected by dipole layer formation from surrounding molecules.

The simplest explanation for this is the coincidence of the Fermi levels due to electron transfer from the dye to AgBr. Such Fermi-level alignment at the interfaces was reported for C_{60} deposited on metals and n -doped GaAs.³⁵ In the present case, however, the expected number of intrinsic carriers in AgBr and dye is small, and the thickness of the space-charge layer may be very large. Thus electron transfer alone is not satisfactory for explaining the band offset within the thin interfacial layer.

Another possible candidate for the origin of such a double layer is the alignment of molecular dipoles on the

interface, with a negative charge on the AgBr side and a positive one on the vacuum side. There are several experimental results to suggest that the merocyanine dyes used here are adsorbed on Ag halides at the thiocarbonyl (C=S) sulfur,³⁷⁻³⁹ with polarized structure $N^+(C_2H_5)=C-S^-\cdots Ag^+$ in the rhodanine ring. Further, the extended π -electron system along the methine chain is known to polarize easily due to the resonance between $N-\cdots=O$ and $N^+=\cdots-O^-$ forms. The above-mentioned polarized structure in the rhodanine ring, and the positive charge of the Ag^+ ion will favor the latter form. These factors indicate that the first adsorbed layer of dye may have a large dipole moment with the negative part at the AgBr side. The small effect of further dye deposition may be explained in terms of the small dipole of the nonadsorbed dye and/or the random orientation of dye molecules. Reconstruction of the topmost layer of AgBr by dye deposition, if it occurs, may also contribute to the dipole layer, but at present we do not have detailed information about this.

Note added in proof. Recently more detailed information about the adsorption geometry of dyes has been obtained from adsorption isotherm measurements.^{40,41}

ACKNOWLEDGMENTS

The authors thank Professor H. Inokuchi and Professor H. Kanzaki for continuous interest and encouragement. This work was partly supported by a Grant-in-Aid for Scientific Research (Nos. 03640410, 03NP0301, and 04NP0301) from the Ministry of Education, Science, and Culture of Japan.

*Present address: Department of Chemistry, Faculty of Science, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan.

¹The *Theory of Photographic Process*, 4th ed., edited by T. H. James (Macmillan, New York, 1977).

²R. W. Gurney and N. F. Mott, *Proc. R. Soc. London, Ser. A* **164**, 1512 (1938).

³T. Tani, *J. Im. Sci.* **34**, 143 (1990).

⁴H. Buecher, J. Kuhn, B. Mann, D. Moebius, L. von Szentpaly, and P. Tillman, *Photog. Sci. Eng.* **11**, 122 (1967).

⁵T. Tani, T. Suzumoto, and K. Ohzeki, *J. Phys. Chem.* **94**, 1298 (1990).

⁶F. I. Vilesov, *Dok. Akad. Nauk SSSR* **132**, 632 (1960) [*Proc. Acad. Sci. USSR, Phys. Chem. Sec.* **132**, 437 (1960)].

⁷F. I. Vilesov and A. N. Terenin, *Dok. Akad. Nauk SSSR* **133**, 1060 (1960) [*Sov. Phys. Dokl.* **5**, 840 (1961)].

⁸R. C. Nelson, *J. Opt. Soc. Am.* **51**, 1186 (1961).

⁹I. A. Akimov, V. M. Bentsa, F. I. Vilesov, and A. N. Terenin, *Phys. Status Solidi* **20**, 771 (1967).

¹⁰P. Nielsen, *Photog. Sci. Eng.* **18**, 186 (1974).

¹¹G. Pfister and P. Nielsen, *J. Appl. Phys.* **43**, 3104 (1972).

¹²C. W. Peterson, *Phys. Rev.* **148**, 335 (1966).

¹³R. S. Bauer and W. E. Spicer, *Phys. Rev. Lett.* **25**, 1283 (1970); *Phys. Rev. B* **14**, 4529 (1976).

¹⁴D. R. Williams, J. G. Jenkin, R. C. G. Leckey, and J. Liesegang, *Phys. Lett.* **49A**, 141 (1974).

¹⁵J. Tjeda, N. M. Shevchik, W. Braun, A. Goldman, and M. Cardona, *Phys. Rev. B* **12**, 1557 (1975).

¹⁶G. N. Kwawer, T. J. Miller, M. G. Mason, Y. Tan, F. C. Brown, and Y. Ma, *Phys. Rev. B* **39**, 1471 (1989).

¹⁷M. K. Wagner, J. C. Hansen, R. deSouza-Machodo, S. Liang, J. G. Tobin, M. G. Mason, S. Brandt, Y. T. Tan, A.-B. Yang, and F. C. Brown, *Phys. Rev. B* **43**, 6405 (1991).

¹⁸P. S. von Bacho, G. P. Ceasar, H. M. Saltsburg, and R. C. Baetzold, *J. Vac. Sci. Technol.* **13**, 107 (1976).

¹⁹T. B. Tang, K. Seki, H. Inokuchi, and T. Tani, *J. Appl. Phys.* **59**, 5 (1986).

²⁰T. B. Tang, H. Yamamoto, K. Imaeda, H. Inokuchi, K. Seki, M. Okazaki, and T. Tani, *J. Phys. Chem.* **93**, 3970 (1989).

²¹L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman, and S. G. Dent, Jr., *J. Am. Chem. Soc.* **73**, 5332 (1951).

²²C. R. Berry and D. C. Skillman, *Photog. Sci. Eng.* **6**, 159 (1962).

²³N. Sato, K. Seki, and H. Inokuchi, *Rev. Sci. Instrum.* **58**, 1112 (1987).

²⁴R. C. Eden, *Rev. Sci. Instrum.* **41**, 252 (1970).

²⁵H. Inokuchi, K. Seki, and N. Sato, *Phys. Scr.* **T17**, 93 (1986).

²⁶K. Seki, in *Optical Techniques to Characterize Polymer Systems*, edited by H. Baessler (Elsevier, Amsterdam, 1989), p. 115.

- ²⁷L. Apker, E. Taft, and J. Dickey, *Phys. Rev.* **74**, 1462 (1948).
- ²⁸See, for example, S. Huefner, in *Photoemission in Solids*, edited by L. Ley and M. Cardona (Springer-Verlag, Berlin, 1979), Vol. 2, p. 173.
- ²⁹H. B. Michaelson, *J. Appl. Phys.* **48**, 4729 (1977).
- ³⁰D. E. Eastman, *Phys. Rev. B* **1**, 1 (1970).
- ³¹G. V. Fomenko, in *Handbook of Thermoionic Properties*, edited by G. V. Samsonov (Plenum, New York, 1966).
- ³²R. Fleischman, *Ann. Phys.* **5**, 73 (1930).
- ³³E. A. Taft, H. R. Phillip, and L. Apker, *Phys. Rev.* **110**, 876 (1958).
- ³⁴Strictly speaking, the quantity given by Eq. (7) is not equal to the LUMO energy, since electron-hole interaction (excitonic effect) is neglected. Nevertheless, the prediction for sensitizing ability is still valid. Sensitizing ability is determined by the energy required for electron transfer from the dye HOMO to the conduction-band bottom of AgBr ($\epsilon_{CB} - \epsilon_{HO}$) which is supplied by the optical excitation of the dye; that is, $\Delta E_D \geq \epsilon_{CB} - \epsilon_{HO}$, or $\epsilon_{CB} \geq \epsilon_{HO} + \Delta E_D$. The right-hand side of the latter equation is the definition of ϵ_{LU} in Eq. (7).
- ³⁵T. R. Ohno, Y. Chen, S. E. Harvey, G. H. Kroll, J. H. Weaver, R. E. Haufler, and R. E. Smalley, *Phys. Rev. B* **44**, 13747 (1991).
- ³⁶K. Seki and T. Tani, in *Polymer-Solid Interfaces*, edited by J. J. Pireaux, P. Bertrand, and J. L. Bredas (Institute of Physics, Bristol, 1992), p. 62.
- ³⁷W. West and B. H. Carrol, *J. Phys. Chem.* **56**, 1054 (1952).
- ³⁸S. Takada and T. Tani, *J. Appl. Phys.* **45**, 4767 (1974).
- ³⁹T. Araki, K. Seki, S. Narioka, Y. Takata, T. Yokoyama, T. Ohata, S. Watanabe, and T. Tani, *Jpn. J. Appl. Phys., Suppl.* **32 - 2**, 434 (1993).
- ⁴⁰K. Seki, T. Araki, E. Ito, K. Oichi, S. Narioka, T. Yokoyama, T. Ohta, S. Watanabe, A. Matsunaga, and T. Tani, *J. Im. Sci. Tech.* (to be published).
- ⁴¹K. Seki, T. Araki, K. Sugiyama, T. Ohta, S. Watanabe, and T. Tani, *Proceedings of the Third International Conference on Advanced Materials* (Elsevier, Amsterdam, in press).