Epitaxial Growth of Merocyanine Dye Molecules on AgBr Surfaces

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The configuration of photosensitive dye molecules with respect to AgBr lattice is investigated by transmission electron microscopy and electron diffraction, using merocyanine dye (3-ethyl-5-[2-(3-ethyl-2-(3H)-benzothiazolylidene)-ethylidene]-2-thioxo-4-thiazolidinone; BTET) films vacuum-deposited on (100) and (111) AgBr surfaces. Island and oriented growth of the dye films, in α -phase (triclinic), is found on these AgBr surfaces. The observed epitaxial relations are as follows: (155)[011]_{BTET}//(100)<011>_{AgBr} on the (100) AgBr surface and (011)[011]_{BTET}//(111)<101>_{AgBr} on the (111) AgBr surface, where the BTET molecules are adsorbed in edge-standing on the AgBr surfaces. The J-absorption peak is observed in optical spectra of these BTET films, which indicates that they form J-aggregates.

Journal of Imaging Science and Technology 42: 434-439 (1998)

Introduction

As is well known, photosensitive dye J-aggregates play an important role in the photographic process. We previously investigated the morphology and structure of the dye molecules adsorbed on practical AgBr microcrystals grown in gelatin.¹⁻⁹

First, we tried to observe cyanine dyes on AgBr microcrystals by analytical color fluorescence electron microscopy (ACFEM) and succeeded in visualizing J-aggregates as green and/or red cathodoluminescent (CL) spots.^{1,2} The aggregates were about 30×70 nm in size, aligned along the $<011>_{AgBr}$ or $<012>_{AgBr}$ directions on the AgBr (100) surfaces. A color change of the spots from yellowish green to orange red was observed in ACFEM images of oxacarbocyanine, ascribed to a change of energy state owing to release of secondary electrons by electron irradiation.³

Next, we observed the dyes using ultralow-energy scanning electron microscopy (SEM) and revealed that thiacarbocyanine dye nucleates epitaxially on the (100) AgBr surface and grows in stripes along the $[012]_{AgBr}$ and/or $[021]_{AgBr}$ direction.^{4,5} We also found that electron irradiation sprouts Ag filaments preferably on parts, covered with the dye J-aggregates, of the (100) AgBr surface.⁶ Hence, the ACFEM images proved that the dye does make the J-aggregate, while the SEM images gave us a real information about the morphology of the dye, such as shape, size, distribution, and orientation. The ACFEM and SEM, however, could not evaluate the thickness of the adsorbed dyes.

Then, we performed atomic force microscopy (AFM) of the adsorbed dyes on the AgBr microcrystals.^{7,8} AFM confirmed that the dyes grow in islands or stripes by Volmer– Weber growth mode and contradicted a general conception that the dyes might always adsorb in monolayer on the silver halide surfaces. Observed thicknesses of stripes varied from 0.5 (monolayer) to 30 nm or more. The thickness is multiples of a unit thickness that depends on a combination of dye species and counter ions; 2.1 nm for thiacarbocyanine with sodium ion, 1.04 nm for thiacarbocyanine with tosyl ion, and 0.5 nm for an oxacarbocyanine.^{8,9} It was also found that the dye stripe is constructed with a lot of rectangles [20 × (35 to 50) nm in size], each of which is regarded as a J-aggregated particle.^{7,8}

Our next subject was to depict the posture of the dye molecules on the silver halide surfaces. The electron diffraction (ED) was only a method to disclose the molecular configuration of the dye on the halide crystal or the crystal lattice relationship between the dye and halide. However, the cyanine dyes used in the previous experiments were too weak for the electron irradiation and the 1- μ m-sized AgBr microcrystals were too thick to perform ED experiments.

In the present article, using merocyanine and AgBr films both of which were prepared by vacuum deposition, we evaluate the lattice relationship between the silver halide and the adsorbed dye and confirm by optical spectroscopy that the merocyanine dye forms J-aggregates on AgBr surfaces.

Experimental

Merocyanine dye (3-ethyl-5-[2-(3-ethyl-2-(3H)benzothiazolylidene)-ethylidene]-2-thioxo-4thiazolidinone; BTET) powder (Nippon Kankoh-Shikiso Co., NK-1247) was purified by sublimation in a vacuum. BTET has a resonance structure¹⁰ as shown in Fig. 1 and

Original manuscript received October 14, 1997

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Figure 1. 3-Ethyl-5-[2-(3-ethyl-2-(3H)-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidinone (BTET) molecule with a resonace hybrid of the uncharged structure (a) and the dipolar structure (b).

was presumed to behave in the uncharged structure (a) in the crystalline state and in the dipolar structure (b) in the adsorbed state on AgBr. 11

Specimen Preparation for Electron Microscopy.

(100)- and (111)-oriented AgBr films, to be used as the substrate, were prepared by vacuum deposition on cleaved surfaces of NaCl at room temperature or mica at 100 to 150°C, respectively. The thickness of the AgBr films was controlled at 30 nm with a quartz oscillating thickness monitor. The film was wet-stripped from NaCl or mica and then mounted on a copper grid for electron microscopy.

BTET was vacuum-deposited on these AgBr films that were heated at 80°C on the grid. A BTET film, for use as a reference, was vacuum-deposited directly on a NaCl surface. This BTET film was reinforced by a thin carbon film before it was wet-stripped from the NaCl.

The thickness of the BTET films was nominally 30 nm. Transmission electron microscopy images and electron diffraction patterns were taken with a JEM-2000EX microscope operated at 200 kV.

Specimen Preparation for Optical Absorption Spec-

troscopy. The BTET films vacuum-deposited on the AgBr films were also used for optical absorption spectroscopy retaining the NaCl or mica substrate. BTET films vacuum-deposited directly on the substrates of NaCl and quartz glass, heated at 80°C, were also prepared.

Results and Discussion

BTET on NaCl. Figures 2(a) and 2(b) show a TEM image and the corresponding ED pattern of a BTET film deposited on a (100) NaCl surface, respectively. Chang, Lu and Qian¹² reported that merocyanine has two crystal structures; α form (triclinic; a = 0.7458, b = 1.0736, c= 1.1039 nm, α = 95.16°, β = 107.68°, γ = 103.09°) exhibiting pink color and β form (monoclinic; a = 1.1650, b = $0.9026, c = 1.5654 \text{ nm}, \beta = 92.24^{\circ}$) exhibiting green color. The deposited film looked pink in reflecting light, and the reflection spots in the ED pattern can be accounted to be from the α -form merocyanine. Photosensitive dyes such as carbocyanine are so easily damaged under the electron irradiation that they were not observed by conventional electron microscopy. BTET lasts long in electron irradiation and allowed to us to perform TEM and ED experiments.



Figure 2. A TEM image (a) and an ED pattern (b) of BTET vacuum-deposited on NaCl at 80°C.

The BTET grew in rod-like islands, which elongated along the [011] or $[0\overline{1}1]$ axes of the substrate NaCl [Fig. 2(a)]. The α -BTET crystals grew with the following epitaxial relation with respect to the NaCl crystal:

$$(155) [0\overline{1}1]_{BTET} //(100) [011]_{NaCl},$$

$$(155) [0\overline{1}1]_{BTET} //(100) [0\overline{1}1]_{NaCl},$$
(1)

or simply $(155)[0\overline{1}1]_{BTET}//(100)<011>_{NaCl}$. This relation is the same as that between BTET and AgBr lattices, as described below, and BTET molecules on NaCl take a similar configuration to that for molecules on AgBr, accordingly.

Absorption spectra of BTET deposited on the sheets of quartz and NaCl are shown in Fig. 3. The spectrum of BTET on quartz, indicated in Fig. 3(a), agrees quite well with that reported by Böttcher.¹³ He ascribed the peak at 560 nm to J-aggregates. A sharp peak at 580 nm appearing in the spectrum of BTET on NaCl [in Fig. 3(b)] can be regarded as a J-absorption band, although the peak position



Figure 3. Optical absorption spectra of BTET films vacuum-deposited on quart glass plate (a), NaCl (b), (100)oriented AgBr film deposited on NaCl (c), and (111)-oriented AgBr film deposited on mica (d).



Figure 4. (a) A TEM image and an ED pattern of (100)-oreinted AgBr film deposited on NaCl at room temperature; (b) a TEM image and an ED pattern (111)-oreinted AgBr film deposited on mica at 150° C.

shifts to high wavelength. Hence it can be concluded that BTET films grow epitaxially on the NaCl surface, taking the shape of rod-like islands composed of J-aggregates.

BTET on AgBr. With the knowledge of the analysis of the BTET on NaCl, the growth of BTET films on AgBr was examined. TEM images and ED patterns of AgBr films used as substrates are shown in Fig. 4, which reveals a continuous (100)-oriented film to be deposited on the NaCl (a) and a (111)-oriented film to be deposited on the mica (b).

TEM images of BTET taken along with the AgBr substrates are shown in Figs. 5(a) and 6(a), where the AgBr films were vacuum-deposited on NaCl and mica surfaces, respectively. The BTET, grown in ribbons, can be seen as additives to the images in Fig. 4. The ribbons elongated along the <110> axes of AgBr, that is, along two directions of [011] and [011] on the (100) AgBr surface and along three directions of [1011],[110], and [011] on the (111) AgBr surface. The corresponding ED patterns are show nin Figs. 5(b) and 6(b), with schemata in Figs 5(c) and 6(c), respectively. As seen from the ED patterns, the BTET ribbons grow in α -form of merocyanine, epitaxially with the following lattice relation on the (100) AgBr surface:

$$(155) [0\bar{1}1]_{\text{BTET}} //(100) [0\bar{1}1]_{\text{AgBr}}, (155) [0\bar{1}1]_{\text{RTET}} //(100) [0\bar{1}1]_{\text{ApBr}},$$
(2)

and on the (111) AgBr surface,

$$\begin{array}{l} (011) [0\overline{1}1]_{BTET} //(111) [10\overline{1}]_{AgBr}, \\ (011) [0\overline{1}1]_{BTET} //(111) [\overline{1}10]_{AgBr}, \\ (011) [0\overline{1}1]_{BTET} //(111) [0\overline{1}1]_{AgBr}. \end{array} \tag{3}$$

Haefke et al.¹⁴ observed a merocyanine dye film 3 nm thick vapor-deposited on an AgBr thin film by AFM and showed that the film grows in the form of three-dimensional islands rather than in layer growth by Frank-van der Merve mode. The height of rod-like islands varied







Figure 5. A TEM image (a) and an ED pattern (b) of vacuumdeposited BTET together with (100)-oriented AgBr film used as the substrate, and a schema of the ED pattern with reflection spots indexed (c).

Figure 6. A TEM image (a) and an ED pattern (b) of vacuum-deposited BTET together with (111)-oriented AgBr film used as the substrate, and a schema of the ED pattern with reflection spots indexed (c).

BTET on AgBr(100)



Figure 7. Molecular configuration of BTET crystal in the epitaxial relation of $(155)[0\overline{1}1]_{BTET}$ //(100)<011>_{AgBr} on the (100)-oriented AgBr surface. Projections on the $(100)_{AgBr}$ plane (a) and on the $(011)_{AgBr}$ plane (b).

between 40 and 80 nm and that of round islands were even 100 to 300 nm. The present results do not conflict with their observation and add two-dimensional information in a wide area as well as the crystallographic relation for the dye growth.

Spectra marked by Figs. 3(c) and 3(d) are from the BTET films on the (100) AgBr surface and on the (111) AgBr surface, respectively. The spectrum may be considered from the BTET although the measurement was performed through both the AgBr and NaCl (or mica), because their spectra were subtracted using the spectra from the referred sample without the BTET. The BTET exhibits sharp peaks at 575-nm on the (100) AgBr surface and at 625-nm on the $(111)\,AgBr$ surface, respectively. These peaks suggest that merocyanine J-aggregates are formed on AgBr surfaces, although the merocyanine dyes adsorbed on AgBr have been believed to form no J-aggregates through the adsorption isotherm studies.¹⁵ The difference in peak position among these samples shown in Fig. 3 may be caused by difference in size, orientation of adsorbed J-aggregates and so on, but we do not discuss the possibility any more here.

Molecular Arrangements of BTET on AgBr. The molecular configurations of BTET on (100) AgBr and (111) AgBr surfaces are illustrated in Figs. 7 and 8, respectively.



Figure 8. Molecular configuration of BTET crystal in the epitaxial relation of $(011)[0\overline{1}1]_{BTET}//(111) < 10\overline{1} >_{AgBr}$ on the (111)-oriented AgBr surface. Projections on the $(111)_{AgBr}$ plane (a) and on the $[\overline{1}\overline{1}2]_{AgBr}$ plane (b).

Figure 7(a) shows the molecular projection along the incident electron beam for TEM and ED in Fig. 5 and then on the (100)_{AgBr} plane. The BTET crystals take two orientations, which are correlated with the two orientations (Eq. 2) on the (100) AgBr surface. Figure 7(b) is a side view of the molecule configuration projected on the (011)_{AgBr} plane. The BTET molecule is placed lengthwise to the [011]_{AgBr} or [011]_{AgBr} axis with the molecule plane parallel to the $(01\overline{1})_{AgBr}$ or $(011)_{AgBr}$ plane. The configuration of the BTET molecules with respect to the AgBr lattice is equivalent between the two crystals with different orientations. The epitaxial relation of BTET with respect to the NaCl crystal (Eq. 1) is the same with the relation (Eq. 2). The BTET molecules on the (100) NaCl surface seem to have similar configurations to those on the AgBr surface.

Figure 8(a) shows the molecular projection along the incident beam or on the $(111)_{AgBr}$ surface, postulated from the ED pattern in Fig. 6, and Fig. 8(b) shows its side view

projected on the $[\overline{112}]_{AgBr}$ plane. The BTET crystals grow with three different orientations on the (111) AgBr surface with threefold symmetry. They have an equivalent molecule configuration for the AgBr lattice.

The adsorbed plane, or the plane parallel to the AgBr surface, is different between the BTET crystals grown on the $(100)_{AgBr}$ and $(111)_{AgBr}$ planes: $(155)_{BTET}$ plane on the $(100)_{AgBr}$ but $(011)_{BTET}$ on the $(111)_{AgBr}$ plane. However, the molecule configuration of BTET on the $(100)_{AgBr}$ and $(111)_{AgBr}$ surfaces is very similar; the BTET molecules are placed in the $(011)_{AgBr}$ -type planes lengthwise to the $[011]_{AgBr}$ -type axes, on both these AgBr surfaces. Then, the molecules seem to adsorb on the AgBr surface at the edges of the molecular planes, as shown in Figs. 7(b) and 8(b). The adsorption in the state of edge-on has been observed in different organic dye molecules vapor-deposited on the substrates.^{16,17} Araki et al.¹⁸ studied sulfur K-edge XANES (X-ray Absorption Near Edge Structure) of adsorbed merocyanine on AgCl powder and inferred that merocyanine dyes with C = S bond form a coordinate bond between the sulfur atom in the thiocarbonyl group and a silver ion on the AgCl surface. They added that the merocyanine molecules adsorb on AgCl powder in edge-on or end-on states. This supports our illustration of the molecule configuration, although the interaction of the charged ions in Fig. 1(b) with Ag and Br ions in the uppermost AgBr surface may have to be considered on the adsorption.

Conclusion

Vacuum-deposited BTET films 30 nm thick grow in αform ribbons with orientation relations with respect to the lattice of AgBr substrate crystal: (155)[011] BTET// $(100)<011>_{AgBr}$ on the (100) AgBr surface and (011)

 $[0\overline{1}1]_{BTET}/((111)<101>_{AgBr}$ on the (111) AgBr surface. Then, BTET molecules, being parallel to the $(011)_{AgBr}$ -type planes lengthwise to the [011]_{AgBr}-type axes, adsorb in the edgeon state on the (100) or (111) AgBr surface, probably by the S atom of C = S bond in contact with an Ag atom of the uppermost AgBr surface. The BTET deposited on these AgBr films forms J-aggregates, which has been confirmed by optical adsorption spectroscopy.

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