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Rolf Steiger*

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Introduction

The *surface* of silver-halide (AgHal) microcrystals, dispersed in gelatin ('photographic emulsions'), plays a dominant role in the formation of *developable latent images* consisting of silver clusters which contain only a few Ag-atoms. After development of latent images by a reducing agent (*e.g.* hydroquinone), *macroscopic* silver particles ('photographic images') are formed with an autocatalytic amplification factor of *ca.* 10^9. The quantum yield which determines the photolytic formation of these latent images is strongly influenced by recombination processes between photoelectrons and photoholes. *Surface states* play a dominant role in such reactions. If sensitizing dyes are present on AgHal surfaces, the recombination centre for electrons and holes is located near the dye chromophore. The quantitative description of sensitizer molecules which have been organized by the *Langmuir-Blodgett* technique at the surface of evaporated AgHal layers has helped to understand electron-hole recombination [1][2]. By extrapolation of these results to the case of spectral sensitizers *adsorbed* on AgHal *microcrystal surfaces*, the quantum yield for latent image formation was increased by modifying the AgHal surface in the nm range [3].

Results

The physical properties of AgHal surfaces on nm scales have been studied by *atomic force microscopy* (AFM). Structural features like steps and terraces, dislocations, epitaxial growth, and surface reconstruction (*Fig. 1*) have been revealed [4] on AgHal crystals with dimensions in the µm range (*Fig. 2*). For electrostatic reasons, the [1 1 1] surface of AgBr (NaCl-type lattice) should undergo substantial surface reconstruction, because it is composed of ions of the same sign. AFM has revealed this surface reconstruction (*Fig. 1*).

The *topographic* distribution of surface ions has been characterized by secondary-ion mass spectroscopy (SIMS) in the imaging mode (*Fig. 3*) using incident Ga^+ ions leading to very high lateral resolution [5][6]. Surface heterojunctions between I^- and Br^- ions in mixed AgHal microcrystals facilitate the charge separation between photoelectrons and photoholes (*Fig. 4*). Iodide ions in AgBr crystals

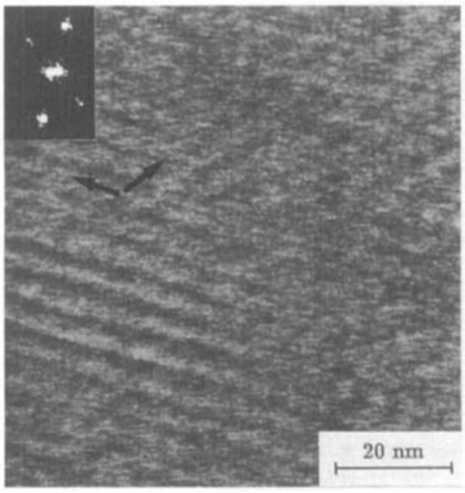

Fig. 1. *High-resolution AFM image of the reconstructed* [1 1 1] *surface of a tabular AgBr microcrystal. The lines are aligned parallel to two <110> directions of the surface lattice* (arrows). Period of the lines: 5.1 nm (bright spot) and 5.9 nm (weak spot). Intersection angle: 60° (insert: 2-dim. *Fourier*- spectrum, 57 ± 4° between both spots)

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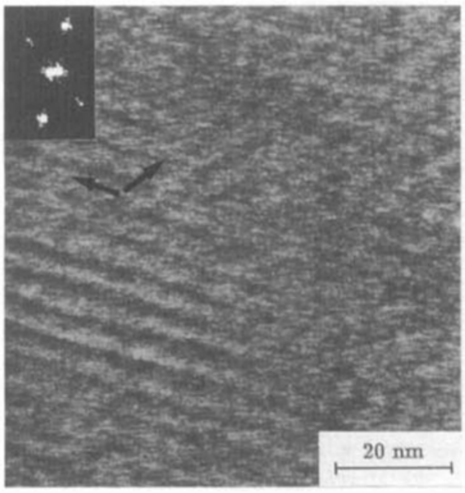

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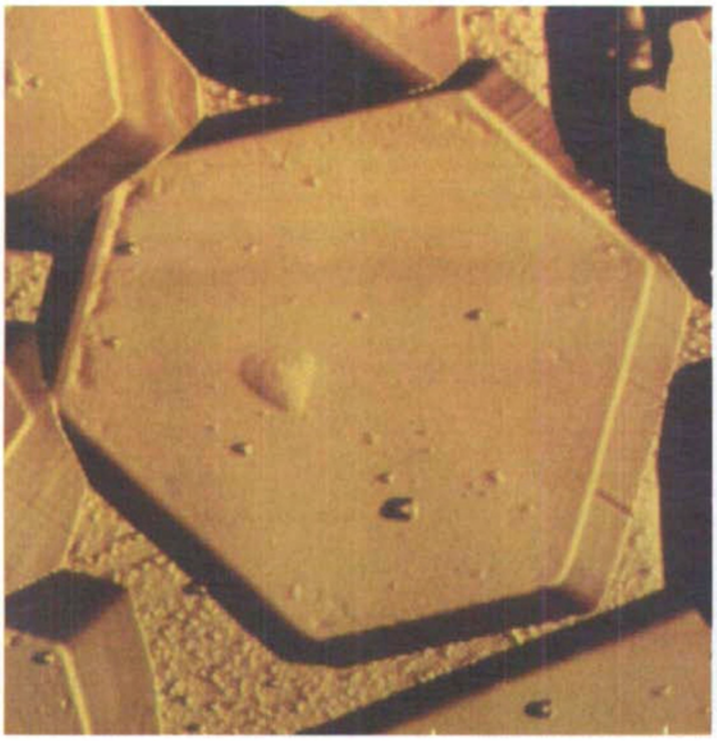

Fig. 2. *AFM Micrograph of a tabular AgBr microcrystal which also contains an epitaxial triangular growth hill on top of the* [111] *face*. The scanned area is 6.5 x 6.5 µm. Mean surface rougness of flat areas: *ca.* 0.5–2 nm.

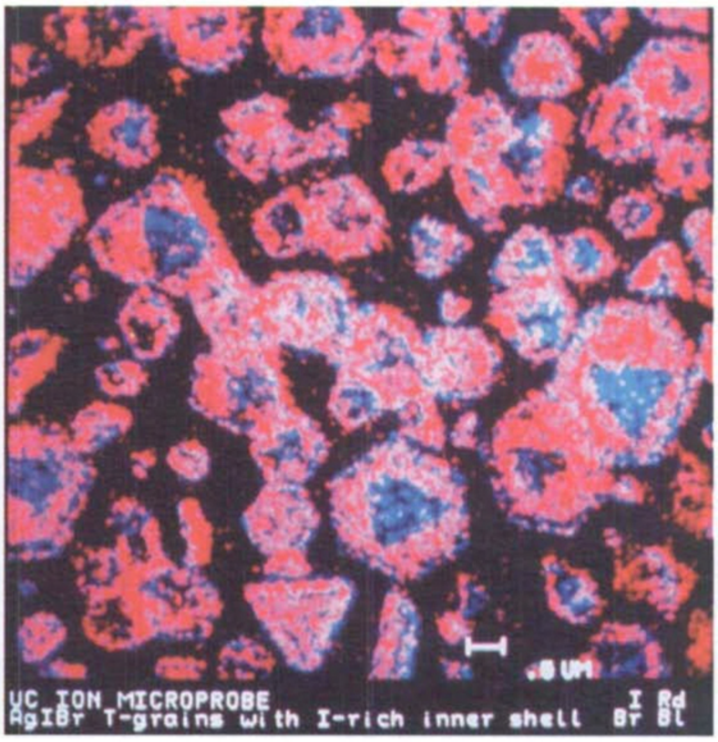

Fig. 3. *Imaging SIMS scan of the AgBrI crystal of* Fig. 4. Br^- ion distribution: blue; I^- ion distribution: red. Increased iodide concentration in the inner shell. The outer bromide-rich shell due to the deposition of pure AgBr at the crystal surface is clearly shown. Indicated scale: 0.5 µm.

act as hole traps. The partial replacement of Br^- surface ions by I^- has been studied [4] by photoelectron spectroscopy (ESCA) and AUGER electron spectroscopy using incident X-rays (X-AES). The ESCA-binding energy and the difference in the kinetic energy between photoelectrons (ESCA) and AUGER electrons (AUGER parameter, *Table*) show that the Ag–I binding energy depends on the concentration of surface iodide. At surface iodide concentrations ≤ 1.6 monolayers, a silver iodide species with a higher binding energy between the Ag and the I^- ion than in AgI is observed (*Table*). The electronegativity of the Ag^+ ion in this Ag–I species is increased as compared with Ag^+ in AgI. Imaging SIMS [7] has revealed that surface I^- is preferably formed along the edges and corners of the cubic AgHal microcrystals used in these experiments (*Fig. 5*). After Ga-ion depth erosion, this discrete I^- distribution disappears, which proves that the postulated geometry along the crystal periphery really occurs. Surface I^- is a strong nucleating agent for the formation of highly aggregated cyanine sensitizers [7]. This was shown by diffuse reflectance spectroscopy and by microcalorimetry (*Fig. 6*). While such cooperative dye aggregates (J-aggregates) are formed on *iodide-containing* AgBr surfaces at dye coverage ≤ 0.4 monolayers, only monomers and dimers were observed on pure AgBr surfaces by diffuse reflect-

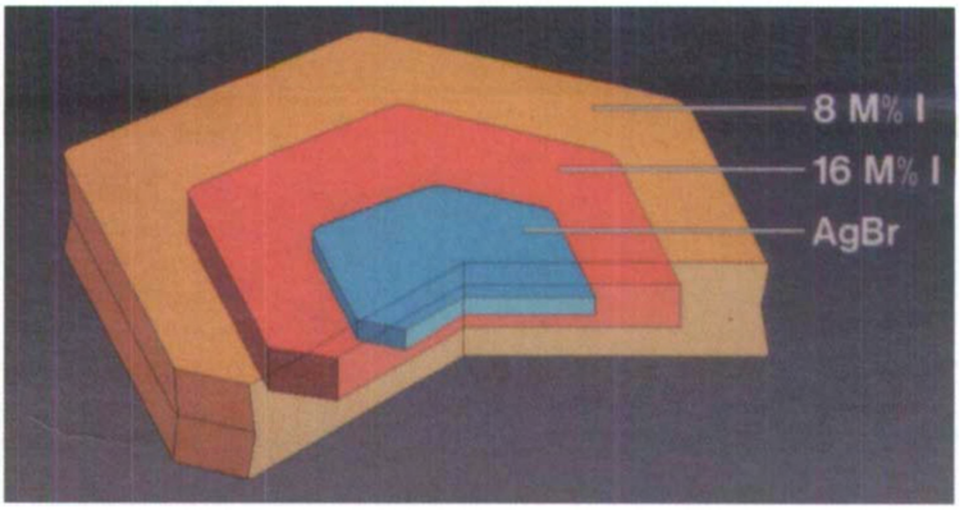

Fig. 4. *Computer design of a thin, tabular AgBrI crystal with iodide-rich inner shell and AgBr core, as suggested from crystallisation conditions*

Table. *Silver-Iodide Binding Energies for Two Different Kinds of Silver Iodide Surface Species Formed on Cubic AgBr Microcrystals of Edge-Length 0.47 µm* (ESCA, X-AES)

mol-% iodide added to AgBr	Surface iodide concentration (monolayers)	ESCA binding energy I $3d_{5/2}$ –Ag $3d_{5/2}$ [eV]	AUGER parameter [eV]	Surface iodide species formed
> 0.6	> 1.6	251.1 ± 0.1	1137.4 ± 0.1	AgI
≤ 0.6	≤ 1.6	251.6 ± 0.1	1138.6 ± 0.1	Ag-I with higher Ag electronegativity

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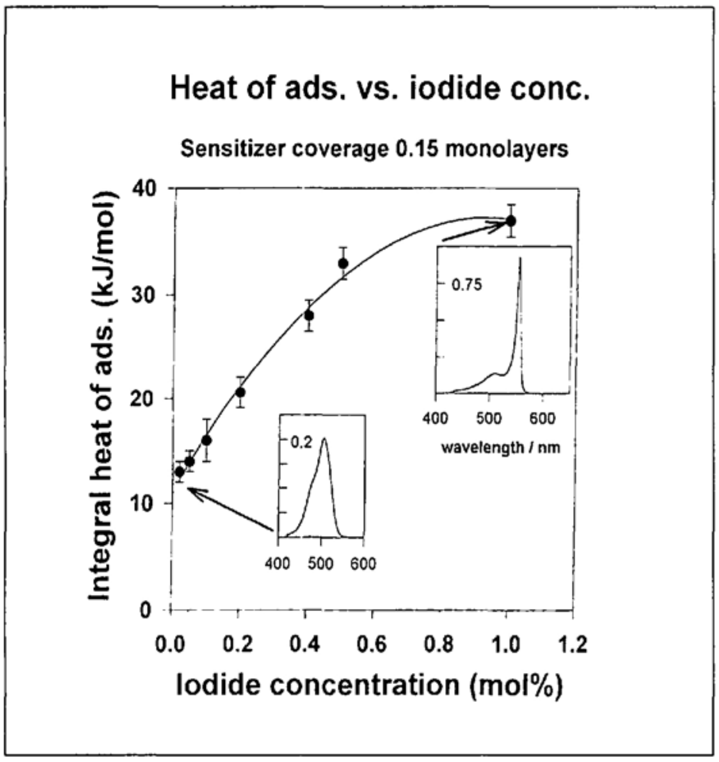

Fig. 6. *Integral heat of adsorption of an adsorbed oxacarbocyanine sensitizer (15% surface coverage)* vs. *iodide concentration in 0.47 µm cubic AgBr microcrystals.* Inserts: diffuse reflectance spectra (after *Kubelka-Munk* correction) of the adsorbed sensitizer on pure AgBr crystals (*left*) and on AgBr crystals containing 1 mol-% bulk iodide (*right*). Only monomers (508 nm) and a small amount of dimers (484 nm) are adsorbed on pure AgBr, while cooperative J-aggregates absorbing at 554 nm are predominantly formed with 1% iodide (corresponding to an overall surface coverage of 2.6 monolayers of AgI).

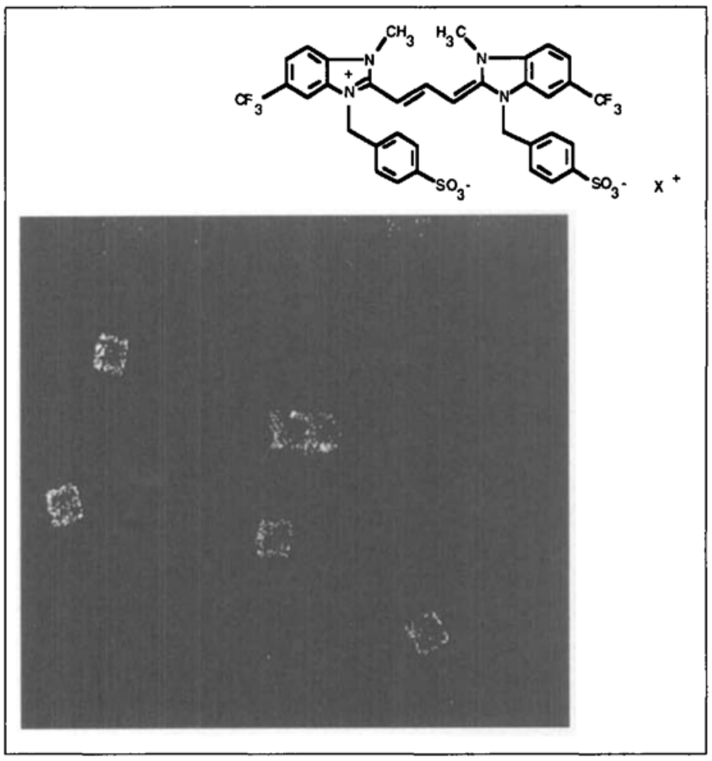

Fig. 7. *Imaging SIMS picture showing the distribution of F-atoms of a fluoro-cyanine dye* (insert in *Fig. 7*) *adsorbed at the surface of cubic crystals of pure AgBr* (edge length: 1.25 µm, 80% surface coverage). Only 6 F-atoms are present in the dye molecule containing 80 atoms, corresponding to *ca.* 7 x 10^6 F-atoms/μ^2 (assuming a homogenous distribution at the grain surface). SIMS, however, has shown that the J-aggregated cyanine is predominantly adsorbed along the AgBr-grain periphery (*Fig. 7*).

ance spectroscopy under the same conditions (*Fig. 6*, inserts). The difference in the integral adsorption enthalpy between J-aggregated and monomeric cyanine molecules is due to the dye-dye interaction energy in the aggregate. *Langmuir-Blodgett* (LB) experiments [2] allow to organize cyanine monomers into J-aggregates at the water surface and to calculate the work to overcome the repulsion forces between molecules from pressure-area isotherms. J-Aggregation during compression of dye monomers at the air-water interface was followed by reflectance spectroscopy [2]. From such experiments, complementary knowledge on the energetics of J-aggregate formation is obtained.

The question, whether edges and corners of cubic microcrystals of *pure AgBr* are also nucleating agents for sensitizer aggregates in the *absence of surface iodide* has been answered by adsorbing a cyanine dye (*Fig. 7*, formula inserted) forming J-aggregates *on pure AgBr*. To study the topographic distribution of this adsorbed cyanine by imaging SIMS, F-atoms had been introduced into the dye chromophore. *Fig. 7* shows that this dye is adsorbed along the edges and corners of the cubic AgBr crystals, showing that these are high-energy sites favorable for dye adsorption and aggregation (J-aggregation of this dye at 560 nm has been proved by diffuse reflectance spectroscopy). Complementary techniques like photoacoustic spectroscopy [8], dye-induced luminescence and ELLIPSOMETRY have been used [9] to characterize dye adsorption, photochemical interactions between excited dye molecules and silver halides as well as the optical properties and the thickness of adsorbed sensitizer layers.

Discussion

Experiments as those discussed above have also provided a more detailed understanding on the mechanisms of spectral sensitization. Electron-hole recombination occurring at the excited sensitizer chromophore could be decreased in practice by appropriate organisation of sensitizer molecules along surface structures like steps and terraces of atomic dimensions at AgHal microcrystal surfaces [10]. By incorporating such surface-modified, micro-engineered AgHal crystals into color photographic materials (*Ilfochrome Classic* films used for copying color slides), the exposure time of these products could be reduced [3] by a factor of 10 under certain conditions.

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