

The Meaning of Catalytic Contact or Close Proximity between Silver Halide and Organic Silver Salt in Photothermographic materials

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Abstract

According to the literature, catalytic proximity of photosensitive silver halide (AgX) with the silver organic salt (AgOS) is a necessary prerequisite for good performance of photothermographic materials. This catalytic proximity is often described in the literature as an "intimate physical association", which has been interpreted as an epitaxial growth of AgX on the silver organic salt. Experiments with spectral sensitization and observations made with electron microscopy, together with results from experiments reported in the literature by other authors, lead us to believe that there is no interface between AgX and AgOS of an epitaxial character. We propose a different kind of interface, which can explain why the expected recombination of an electron and a hole in the chemically unsensitized silver halide upon exposure to light can be prevented efficiently. Physical contact between AgX and AgOS in photothermographic materials as frequently observed with electron microscopy is to be expected in view of the high concentration of organic silver salt in the photosensitive layer, but also can be promoted by Van der Waals forces and entanglement of the fatty acid chains.

Introduction

Thermally developable, photosensitive imaging systems based on silver halide and silver carboxylates are known as photothermographic materials. In these materials, the silver halide is rarely chemically sensitized with the techniques well-known in conventional silver halide photographic films. This raises the question of which mechanism controls the latent image formation. It has been put forward that there is a silver halide-silver carboxylate interface of an epitaxial character and that this interface is photochemically reactive, leading to separation of a silver (0) phase¹. In this paper the epitaxial character was investigated and as a result a novel mechanism is proposed.

Epitaxial character of the interface

Silver halide can be introduced into a photothermographic composition in one of two ways²:

- (1) ex-situ silver halide, in which preformed silver halide is combined with the silver carboxylate;
- (2) in-situ silver halide, in which silver carboxylate is partially converted to silver halide by use of a halidizing agent.

In commercial photothermographic systems both forms of silver halide are usually present. However, the preformed AgX is the more relevant as regards the actual sensitivity of the material.

Bokhonov and co-workers² have studied the morphology of in-situ silver halide formed by halidization of silver stearate with CaBr₂, KBr and Br₂. The conversion to silver halide occurred mostly on the (010) (i.e. lateral) faces of the silver stearate crystals. In the case of ex-situ AgX, the silver halide grains were located on the (001) crystal plane. Evidence for the epitaxial nature of the silver halide-silver carboxylate interface was provided by TEM imaging^{2,3}.

In crystallography it is known that an epitaxial interface requires at least one common crystal plane between the two different crystal lattices.⁴ Therefore, we investigated samples in which several in-situ silver halide crystals were in contact with silver behenate crystals. The individual diffraction patterns of several silver halide crystals in contact with the same silver carboxylate crystal were determined by TEM. These diffraction patterns showed that all these silver halide crystals had different, randomlike crystallographic orientations with respect to the silver carboxylate crystal, which in respect of epitaxial crystals is hard to believe.

Latent Image formation

Further TEM experiments were conducted by combining pre-formed silver halide and silver carboxylate under controlled conditions of exposure to light. Two conclusions

could be made upon examining the results: (1) on a silver halide crystal in contact with silver carboxylate, the latent image can be formed on a crystal face other than that which makes the contact; (2) a latent image can be formed on the surface of silver halide crystals which show no visible contact or interface with the silver carboxylate.

It was suggested by Sahyun¹ that the interface effectively separates the electron-hole pairs photogenerated in the silver halide phase, due to accumulation of mobile silver ions caused by downward bending of the silver carboxylate bands at the interface. In this case one would expect the latent image to be in the direct neighborhood of this heterojunction. However, TEM results show that latent image formation can occur on the silver halide surface opposite to the interface. This indicates that band bending preferably occurs on the silver halide side instead of the silver carboxylate. The assumption of band bending on the silver carboxylate side of the interface was justified by Sahyun by postulating that the silver halide grains used in photothermographic materials are usually very small (0,01 – 0,1 μm) and hence are unlikely to support significant band bending. However, even accepting this assumption, it is hard to find an explanation for the fact that a latent image can be formed on the surface of silver halide crystals with no visible contact or interface with the silver carboxylate.

Given the large difference in solubility products between silver carboxylates and silver bromide, the preferred silver halide in photothermographic systems, an equilibrium is reached in which a very low concentration of bromide ions is present in the dispersion, i.e. a state of very low pAg. This causes the silver halide surface to be positively charged due to adsorbed Ag^+ -ions, which causes band bending. These charges can be compensated by components present in the dispersion such as gelatin, carboxylate ions, spectral sensitizer etc. In fact since measurements of pAg are difficult to perform accurately in polyvinylbutyral/methyl ethyl ketone, it is possible to use the spectral sensitizer to demonstrate the positively charged nature of the silver halide surface. In these experiments a merocyanine dye (fig.1) was used.

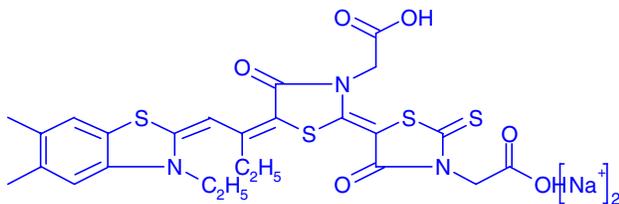


Figure 1. Spectral sensitizer

It was demonstrated that the λ_{max} of the spectral sensitizer (40% surface coverage) adsorbed on a cubic 0,4 μm AgBrI grain changed from 660nm to below 560nm upon reducing

the pAg. The same effect was obtained by mixing the AgBrI with a silver behenate-dispersion in water. As a control the absorption of the spectral sensitizer in the AgBeh-dispersion in the same concentration but now in the absence of the silver halide was determined. A low, flat absorption was found in the range 560 to 640nm. To eliminate a possible influence of the grain size, a preformed silver iodobromide (97 at.% Br) with a typical "photothermographic grain size" of about 70nm was included in the experiments. The same spectral shift of the dye was observed in the presence of silver behenate.

These spectral sensitization experiments show that the surface of the silver halide carries a positive charge, which causes band bending. Compensation of these positive charges by carboxylate ions and other negatively charged components leads to an alternative kind of interface concept, which offers an explanation why chemical sensitization has no positive effect on the sensitivity in photothermographic systems. When a silver halide is exposed to light, the silver/gold-sulfur centers, obtained by chemical sensitization of the silver halide, are positively charged, whereby they attract the photo-electrons to form a latent image. In the case of photothermography the silver halide surface carries a positive charge over much larger domains of the surface, thereby minimizing the effect of the chemical sensitization centers. Furthermore, one can imagine that by combining the AgBr with silver behenate and taking into account the low pAg-level and the solubility products of AgBr and silver behenate, the chemical sensitization centers are largely buried by precipitating AgBr on the silver halide surface and therefore they can not play a further role in catalyzing the development reaction.

Physical contact

As discussed above, we doubt the existence of an epitaxial interface between silver halide and silver carboxylate. However, we do not exclude the existence of physical contact between AgX and organic silver salt particles in photothermographic materials. In fact it can often be observed with electron microscopy. We propose that the physical contact is a logical consequence of the high concentration of the silver carboxylate (often up to 50% of the emulsion layer composition) and the methods used in the preparation of the coating dispersion. In the case of a preformed silver halide added during the synthesis of the silver carboxylate soap, one can expect that after synthesis physical contact can also be induced by the filtration and drying steps necessary to make the AgX/organic silver salt compatible with an organic solvent coating. In the case of in-situ AgX, it is also likely that adsorption of carboxylate ions, formed as a byproduct in the halidization of the silver carboxylate and in the immediate vicinity of the in-situ formed AgX, occurs. The physical contact of these hydrophobized AgX with organic silver salt can in this way be promoted by Van der Waals forces and entanglement of the fatty acid chains.

Conclusion

The experiments, results and discussion above lead us to believe that the possible contact between silver halide and silver carboxylate is not of an epitaxial nature, but the consequence of a physical interaction. Furthermore it is postulated that the latent image formation is not controlled by this assumed epitaxy, but by the band bending occurring in the silver halide.

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Biography

Ir. Hans Strijckers obtained his degree of chemical engineering from the University of Ghent in 1987. In 1989, he joined the Agfa-Gevaert research labs in Mortsel, Belgium. After being involved in product development and research of micrographic materials, he is presently conducting research on thermally developable materials based on organic silver salts.

Dr. Chris Van Roost obtained his Ph.D. in physics from the University of Limburg at Diepenbeek in 1991. At Agfa-Gevaert in Mortsel, Belgium, he was first involved in some IT-projects before joining the analytical department, where he is presently active in the area of microscopic characterization of imaging materials.