

The Influence of Surface Adsorption on the Decay Kinetics of Photo-e.m.f. Signals from AgBr-Emulsion Crystals

J. Harenburg¹, F. W. Müller¹, J. Siegel², G. Israel¹

¹FB Chemie, MartinLuther-Universität, Halle-Wittenberg, Germany

²Agfa-Gevaert AG, Leverkusen, Germany

Abstract

In the present study photo-e.m.f. (DEMBER) measurements were performed using surface manipulated AgBr micro crystals to get information about the effect of concentration and spatial distribution in interstitial silver ions Ag_i^+ on the transient photo charge.

Treating experimental photo-e.m.f. decay curves by a bi-exponential rate law, the overall signal can be divided into two parts, a fast decay process that may be attributed to reactions in the subsurface and a nearly ten times slower process attributed to the reactions of charge carriers in the bulk. Both, preexponential factors U_1 , U_2 and rate constants k_1 , k_2 of the whole process depend — in a different degree — on changes of surface situations, for instance pAg, amount of stabilizers or dyes adsorbed on the crystals.

Observed effects are much larger in the case of octahedral crystals than in the case of cubic ones.

Introduction

From dielectric loss measurements (dl) one can deduce, that Ag_i^+ ions are distributed inhomogeneously within an individual real AgX emulsion crystal.¹ The concentration $[\text{Ag}_i^+]$ of interstitials in the bulk region is determined by the FRENKEL-equilibrium and depends mainly on the nature of the halide anion X- and on dotations or lattice disorders. Hence the value of $[\text{Ag}_i^+]$ should be constant within the interior of a large crystal.

Near the surface the degree of disorders and also $[\text{Ag}_i^+]$ will increase noticeable. Dramatic effects in $[\text{Ag}_i^+]$ were observable by modifications near or direct on the surface of the crystals: Changing from [100] to [111] surfaces, increasing pAg, adsorbing dyes, stabilizers, antifogging compounds, iodide ions, or decreasing the grain size to edge lengths $< 0,5 \mu\text{m}$. For instance, the dl-spectrum of cubic AgBr microcrystals changes from single peak with a maximum frequency $f_{\text{max}} = 55 \text{ kHz}$ to a double peak with $f_{\text{max}} = 830 \text{ kHz}$ (LF-peak) and $f_{\text{max}} = 9,2 \text{ MHz}$ (HF-peak) in the presence of 0,8 mmole/mole AgBr of a red sensitizing thia-

carbocyanine dye.² The difference between LF- and HF-peak will be much larger using AgBr octahedra with or without addition of dye. Adsorption of tetraazaindene or 2-mercaptobenzoxazole MBO on AgBr will shift both peaks down to frequencies in the range of cubic emulsions, in the case of MBO even to the unification of LF- and HF-peaks.

The behavior of photochemical produced charge carriers should be influenced by such large differences in the spacial distribution of $[\text{Ag}_i^+]$. Especially the lifetime and diffusion of electrons should differ in the subsurface and in the bulk region of the crystals as a result of the concentration of interstitials and the energetic situation, see Figure 1.

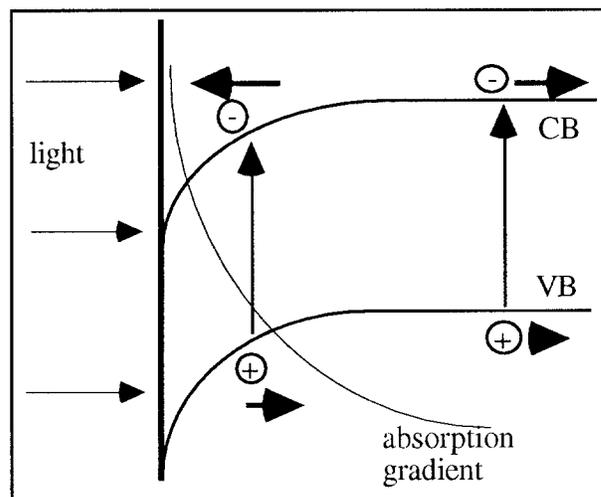


Figure 1. Movement of charge carriers generated near the surface and in the bulk region of an AgBr emulsion crystal after light irradiation

The aim of the paper is to check out this model using photo-e.m.f. measurements from AgBr emulsion crystals as a function of adsorbed stabilizer MBO, of pAg and grain size. Photo-e.m.f. is known as a method very sensitive against diffusion and concentration effects.^{3,4}

Experimental

The sample emulsions consist of monodisperse cubic and octahedral AgBr grains, 0,5 μm edge length, chemically nonripened. Stabilizer 2-mercaptobenzoxazole was added to and pAg was adjusted in molten emulsions. Edge lengths of cubic emulsions were varied within 0,4 - 2,0 μm .

Dielectric loss measurements were performed using an impedance analyzer HEWLETT PACKARD 4192. The whole apparatus and procedure are described in [5]. Photo-e.m.f. signals were measured with the following arrangement: nitrogen laser pumped dye laser, $t_{1/2} = 0,5$ ns, storage oscilloscope, 200 Ms, and a sample holder with preamplifier and a NESA-glass front electrode. The potential is measured on the front electrode. The sign of the signal is related to the same electrode: positive voltage for n-type photo-conductors and vice versa.

A biexponential rate law is used for calculation of maximum voltages U_1^0 , U_2^0 at $t = 0$ and rate constants k_1 , k_2 of the two partial photo-e.m.f. 1, 2 resp., see equation 1:

$$U(t) = U_1^0 \exp(-k_1 t) + U_2^0 \exp(-k_2 t) \quad (1)$$

U_1^0 , k_1 and U_2^0 , k_2 refer to the fast and slow decay process.

Results

Dielectric loss measurements were shown in Figure 2 from an octahedral AgBr emulsion, pAg = 8, as a function of the added amount of stabilizer MBO. f_{max} from high and low frequency peak is shifted down in a different degree until unification at 450 $\mu\text{mole MBO/mole AgBr}$. The value $f_{\text{max}} = 8,5$ kHz at 900 $\mu\text{mole MBO/mole AgBr}$ is quite similar to the same of a cubic AgBr emulsion under comparable conditions. The results are consistent with an inhomogeneous distribution of $[\text{Ag}_i^+]$. The large concentration of interstitials near the [111] surface drops down to the value similar to the bulk indicating a strong influence of MBO on the subsurface region.

Photo-e.m.f. measurement, $\lambda_{\text{exc}} = 425$ nm, from the same octahedral AgBr emulsion yields a negative signal over the whole decay process. Addition of MBO to the emulsion leads in all cases to a change of the sign from - to + within the decay process. The fast negative part of the signal decreases and a long living positive part increases with increasing [MBO]. All signals can be fitted easily using equation 1 over the full decay process. The maximum voltages $U_{1,2}^0$

and rate constants $k_{1,2}$ calculated of the two partial photo-e.m.f. 1 (fast reaction) and 2 (slow reaction) were shown in Figures 3 and 4.

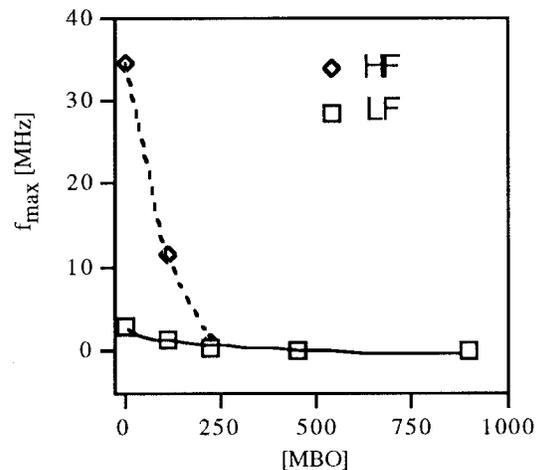


Figure 2. Dielectric loss frequencies f_{max} from octahedral AgBr emulsion crystals, $d = 0,5$ μm , pAg = 8, chemically non-sensitized, as a function of added stabilizer 2-mercaptobenzoxazole [MBO] $\mu\text{mole/mole AgBr}$. HF, LF: High, low frequency peak, 20°C.

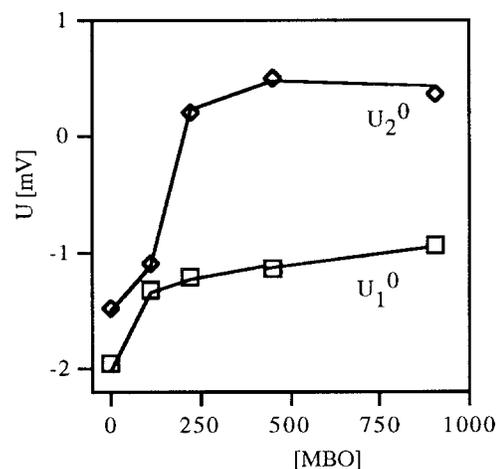


Figure 3. Maximum photo-e.m.f. voltages U_1^0 , U_2^0 of the fast and slow decay reaction from octahedral AgBr emulsion crystals according to figure 2 as a function of [MBO] ($\mu\text{mole/mole AgBr}$), $\lambda_{\text{exc}} = 425$ nm.

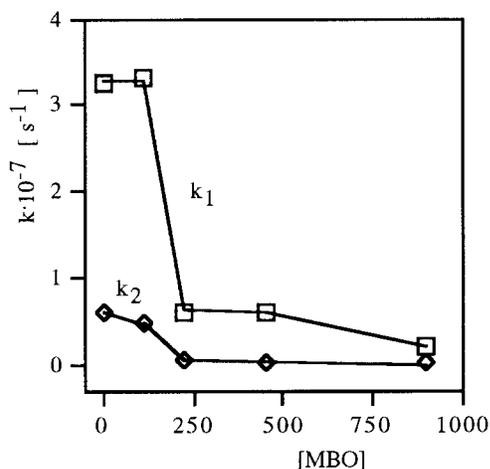


Figure 4. Photo-e.m.f. rate constants k_1 and k_2 of the fast and slow decay reaction from octahedral AgBr emulsion crystals according to Figure 2 as a function of [MBO] ($\mu\text{mole/mole AgBr}$); $\lambda_{\text{exc}} = 425 \text{ nm}$.

The maximum photo-e.m.f. of the fast reaction U_1° decreases at low [MBO], and remains negatively at a low level after addition of 900 $\mu\text{mole MBO/mole AgBr}$. Too, the rate constant k_1 of the fast decay reaction decreases at low [MBO] by more than the factor 5. Both experimental facts can be explained by a strong decrease in $[\text{Ag}_i^+]$ within the subsurface region of AgBr microcrystals. A low concentration of interstitials will reduce the reaction rate of electrons⁶ and band bending according to Figure 1. The strong effect of MBO on f_{max} (HF peak) supports this interpretation, see Figure 2.

Calculated U_2° assigned to the slow partial decay reaction change their sign to positive values at [MBO] > 112 $\mu\text{mole/mole AgBr}$. Again, this is in agreement with experimental photo-e.m.f. signals measured in the presence of MBO.

The unexpected negative U_2° in the absence of MBO may be attributed to the small size of octahedral grains, $d = 0,5 \mu\text{m}$ and the large $[\text{Ag}_i^+]$ in the subsurface region. Consequently, f_{max} (LF) changes from 2,9 MHz to 500; 48; and 8,5 kHz at [MBO] = 0; 225; 450; and 900 $\mu\text{mole/mole AgBr}$.

The rate constant k_2 decreases in the presence of largest amounts MBO to $k_2 \leq 1 \cdot 10^5 \text{ s}^{-1}$, comparable to those signals with a positive sign arising from large cubic AgBr crystals.

Variation of $p\text{Ag} = 4$ to 8 from octahedral AgBr crystals will produce similar effects on dielectric loss and photo-e.m.f., showing a strong differentiation between subsurface and bulk properties. Cubic emulsion grains show much smaller effects on variation of $p\text{Ag}$ or adsorption of MBO. This indicates a weak discrimination within these crystals. Larger discrimination will be detected in cubic AgBr crystals with edge lengths $d = 0,4 - 2,0 \mu\text{m}$.

Acknowledgment

Financial support from Agfa-Gevaert AG, Leverkusen and Deutsche Akademie der Naturforscher Leopoldina, Halle is greatly appreciated.

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