

Investigations on the Influence of Surface Properties on the Lifetime of Photoelectrons in Silver Chloride Emulsion Grains

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Introduction

Microwave absorption (MWA) is a well-known method to study the transient concentration of photoelectrons in silver halide emulsion grains.¹⁻³ Especially, phase sensitive MWA measurements allow to separate the decay kinetics of conduction band electrons and electrons in shallow traps.⁴

Typical photoelectron decay curves show two components with first order decay kinetics: A fast decay, characterized by the photoelectron lifetime τ_1 , and a slow decay, characterized by the photoelectron lifetime τ_2 . Recently, Oikawa et al.⁵ proposed that the photoelectron lifetimes τ_1 and τ_2 are correlated with different first order processes on the crystal surface and in the crystal bulk. Photoconductivity measurements of unsensitized silver chloride emulsion grains with different edge lengths showed that the electron lifetime τ_2 was in proportion to the square of the edge length. Therefore, Oikawa et al. considered that photoelectrons on the grains surface of AgCl emulsion grains were captured according to diffusion limited kinetics. Further measurements on AgCl emulsion grains stabilized with TAI indicated that silver ions at kink sites were the corresponding electron traps. Similar measurements on AgBr emulsion grains indicated that electrons were captured according to reaction limited kinetics on the AgBr grain surface. The different kinetics in AgCl and AgBr were explained with the different ionic conductivity of AgCl and AgBr. Dielectric loss measurements showed that the ionic conductivity of AgBr is three hundred times larger than that of AgCl. Thus, it can be considered that the density of silver ions in kink sites is much larger on the surface of AgCl emulsion grains than on the surface of AgBr grains.⁵

For the process correlated with the electron lifetime τ_1 no suggestion has been given yet.

In this study we investigated the influence of surface properties of cubic silver chloride emulsion grains on the photoelectron lifetimes τ_1 and τ_2 by means of phase sensitive microwave absorption measurements. Therefore, the surface properties of silver chloride emulsion grains were modified carefully by use of stabilizer, chemical

ripening, sensitizing dye and by changing the solution pAg of the emulsion grains.

Experimental

Sample Preparation

We used pure silver chloride emulsion grains with an edge length of 0,5 μm . They were precipitated at a pAg of 7, using balanced double jet technique. The grain size was controlled by electro-chemical grain size analysis (EGSA). After the precipitation the grain surface was modified by different treatments:

Stabilized grains were prepared by adding 5-Phenyle-1-Mercaptotetrazole (PMT). The concentration of the stabilizer was varied between 200×10^{-6} mol per mol AgCl and 1000×10^{-6} mol per mol AgCl.

The effect of ripening was studied by use of grains in different gold sulfur ripening states.

The solution pAg was varied between 3 and 9 using different concentrations of NaCl and AgNO₃. For comparison the solution pAg was also adjusted by using KBr and AgNO₃.

The grains were sensitized with different concentrations of a red sensitizer. The concentration of the sensitizing dye was varied between 25×10^{-6} mol per mol AgCl and 200×10^{-6} mol per mol AgCl.

For comparison cubic silver bromide emulsion grains with similar edge length were precipitated. To achieve a better resolution of the decay curves these grains were stabilized with 4×10^{-3} mol Tetraazaindene (TAI) per mol AgCl. The surface of these grains was modified by sensitizing the grains with different amounts a red sensitizer and by varying the solution pAg, respectively. The concentration of the sensitizing dye was varied between 25×10^{-6} mol per mol AgCl and 200×10^{-6} mol per mol AgCl. The solution pAg was adjusted between 7 and 9 by using both KBr and NaCl.

The coated emulsions were cut to stripes of 1 mm x 20 mm. Three of those stripes were put into the microwave

cavity. The emulsions were handled under red safelight only. Sensitized emulsions were handled under green safelight.

The Microwave Apparatus

The used microwave apparatus was a phase sensitive Q-band instrument, described elsewhere. As the absorption and the dispersion signal can be detected separately, this apparatus allows the investigation of both free electrons and electrons in shallow traps. The resonance frequency is 35 GHz. The loaded Q factor of the cavity is between 50 and 200, resulting in an overall time resolution between 1,4 and 4 ns, dependent on the sample. The primary light source is a pulsed nitrogen laser, emitting at 337 nm. It was used to pump a dye laser, emitting at 400 nm with a pulse width of 600 ps. The laser intensity was reduced with various filters with a density between 0.1 and 1.06 neutral density.

Results and Discussion

Fig. 1 shows a typical photoelectron decay curve of cubic silver chloride emulsion grains. Two regions with first order kinetics can be distinguished: a fast decay in the first nanoseconds after the exposure, denoted by the lifetime τ_1 , followed by a slower decay, denoted by the lifetime τ_2 .

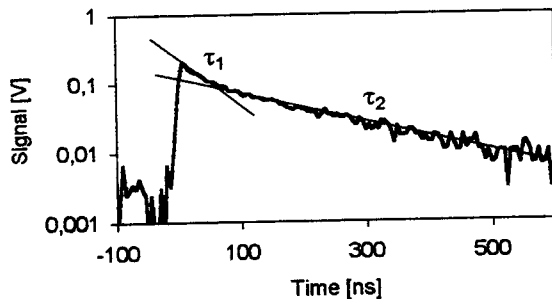


Fig. 1: Typical photoelectron decay curve of silver chloride emulsion grains showing different lifetimes τ_1 and τ_2 .

The transient concentration of photoelectrons $n(t)$ is given as

$$n(t) = n_1 \exp\left(-\frac{t}{\tau_1}\right) + n_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

where n_1 and n_2 describe the number of electrons which are involved in the corresponding process. The influence of the light intensity on both photoelectron lifetimes for silver chloride emulsion grains is shown in fig. 2. Whereas the lifetime τ_2 is constant, the lifetime τ_1 is measurable only at small light intensities and is increasing with increasing light intensity.

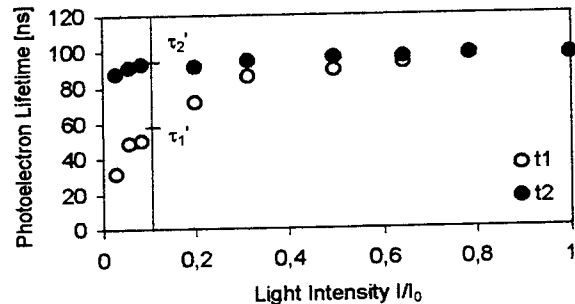


Fig. 2: The photoelectron lifetimes τ_1 and τ_2 as function of the light intensity for pure silver chloride emulsion grains. τ_1' and τ_2' are determined by interpolation for a light intensity of ten per cent of the maximal intensity.

For a light intensity of ten per cent of the maximum laser power both photoelectron lifetimes τ_1 and τ_2 could be measured with an error of $\pm 10\%$ or less. For larger intensities τ_1 is not measurable, for smaller intensities the experimental error of both lifetimes is increasing. Thus in the following for silver chloride emulsion grains the lifetimes τ_1 and τ_2 are characterized by their respective values for a light intensity of ten per cent of the maximum laser power. These values, in the following termed τ_1' and τ_2' , were determined by interpolation as shown in fig. 2.

Fig. 3 shows the photoelectron decay curve of cubic silver bromide emulsion grains, stabilized with TAI. This curve also shows two first order decays correlated with different lifetimes τ_1 and τ_2 .

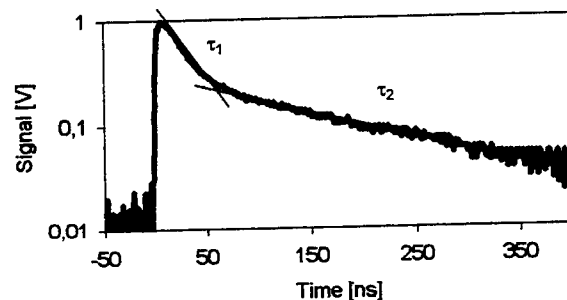


Fig. 3: Photoelectron decay curve of cubic silver bromide emulsion grains stabilized with TAI

For silver bromide emulsion grains no effect of the light intensity on the lifetimes could be seen. Therefore, these samples were measured using the full laser intensity.

Stabilizer, Chemical Ripening and Sensitization

The influence of the stabilizer on the lifetime of photoelectrons in silver chloride emulsion grains is shown in fig. 4. The lifetime τ_2' is constant, whereas the lifetime τ_1' is increasing with increasing concentration of stabilizer. As fig. 5 shows, the signal height of the decay curves is also increasing with increasing concentration of stabilizer.

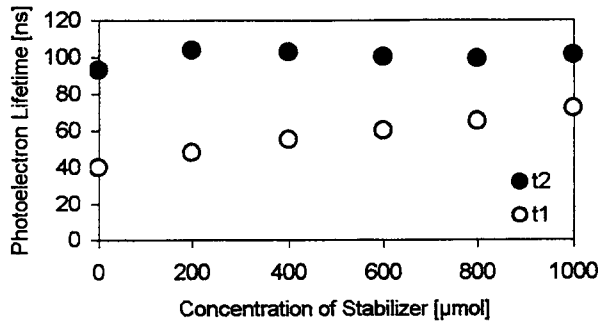


Fig. 4: Photoelectron lifetimes τ_1' and τ_2' in cubic AgCl grains as function of the concentration of stabilizer PMT

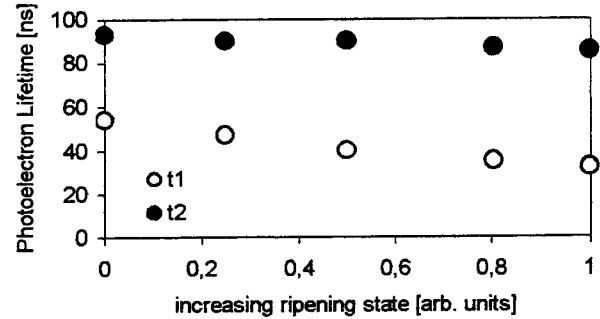


Fig. 7: Photoelectron lifetimes τ_1' and τ_2' of AgCl grains as function of the ripening state

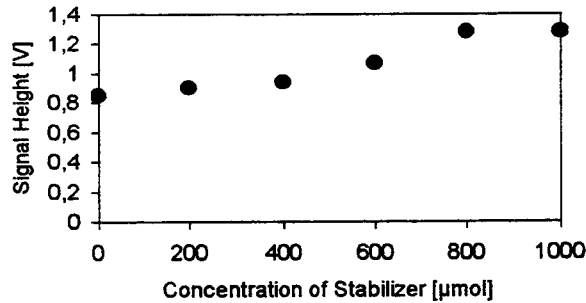


Fig. 5: The signal height of the decay curves of AgCl grains as function of the concentration of stabilizer PMT

Fig. 6 shows the influence of chemical ripening on the lifetimes τ_1 and τ_2 for silver chloride emulsion grains. Whereas the lifetime τ_2 is constant again, both the lifetime τ_1 and the signal height are decreasing with increasing ripening state.

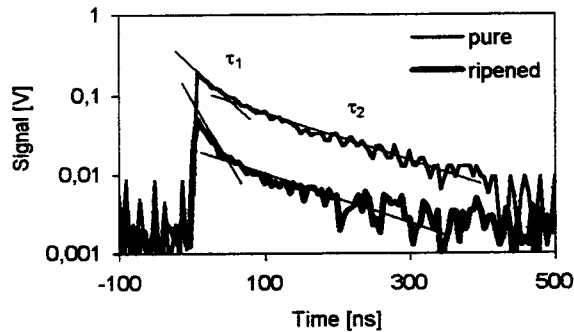


Fig. 6: Photoelectron decay curves of unripened and ripened AgCl emulsion grains

The photoelectron lifetimes τ_1' and τ_2' as function of the ripening state are shown in fig. 7. Whereas τ_1' is decreasing with increasing ripening state, τ_2' is nearly constant.

The spectral sensitization with sensitizing dye has the same effect on τ_1 and τ_2 . With increasing concentration of sensitizer the lifetime τ_1' is decreasing significantly, whereas the lifetime τ_2' is constant again.

It is commonly known that both stabilizer and sensitizing dye on the surface of AgBr emulsion grains do not only change surface properties but also affect the ionic conductivity. As the formation energy for Frenkel defects in AgCl emulsion grains is large compared to that of AgBr⁶, it can be expected that these modifications of the AgCl crystal surface have only a small effect on bulk properties, such as the ionic conductivity. For silver chloride emulsion grains the stabilizer, the ripening and the sensitizing dye change the lifetime τ_1' and the signal height of the decay curves, whereas the lifetime τ_2' is constant within the experimental error. This indicates that the lifetime τ_1 is correlated with a surface process. The dispersion signal of silver chloride emulsion grains, shown in fig. 8, reaches a maximum a short time after the trapping process correlated with the lifetime τ_1 is finished. As shallow trapped electrons cause the dispersion signal, we consider that the lifetime τ_1 is determined by the capture of photoelectrons by shallow traps on the crystal surface. Most likely, these shallow traps are formed by silver ions in kink sites.

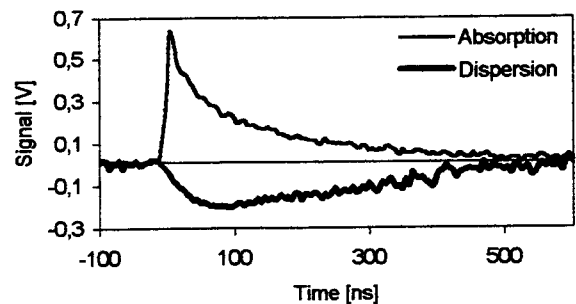


Fig. 8: Absorption and Dispersion signal of pure silver chloride emulsion grains

The photoelectron lifetime τ_2' is not influenced by surface treatments of AgCl emulsion grains. Thus, we

consider that the process correlated with τ_2 is governed by bulk properties, especially by the ionic conductivity. The dispersion signal is decreasing in this region. This indicates that τ_2 is determined by electrons captured by deep electrons traps. Two types of electron trapping processes are possible: Free electrons, e.g. electrons released by shallow traps, can be captured by deep electron traps such as silver clusters. On the other hand, shallow trapped electrons form an attractive potential for silver interstitial ions. The motion of an interstitial ion to a captured electron results in an electron trap with a depth of 0.75 eV ⁷.

The following results show the influence of modifications of the AgBr grain surface on the photoelectron decay. The lifetimes τ_1 and τ_2 as function of the concentration of a sensitizing dye are shown in fig. 9: Here both lifetimes τ_1 and τ_2 are decreasing with increasing concentration of sensitizer.

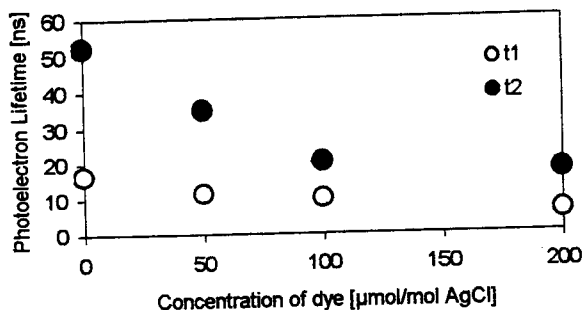


Fig. 9: τ_1 and τ_2 as function of the concentration of sensitizer in AgBr emulsion grains

The ionic conductivity of AgBr emulsion grains is reported to be three hundred times larger than that of AgCl emulsion grains.⁵ Therefore a modification of AgBr grain surface should have a more significant effect on the ionic conductivity than the same treatment on AgCl emulsion grains. Thus, it could be expected that a modification of the silver bromide grain surface has an influence on both τ_1 and τ_2 , assuming that τ_2 is determined by bulk properties, especially the ionic conductivity,

Solution pAg

The influence of the solution pAg on the ionic conductivity of silver bromide emulsion grains has been investigated in many studies⁸. Due to an increase of silver interstitial ions, the ionic conductivity is increasing with increasing pAg. Fig. 10 shows τ_1 and τ_2 as function of the solution pAg of AgBr grains. For samples where the pAg was adjusted using KBr τ_2 decreased rapidly with decreasing pAg. Compared to that τ_2 was decreasing only gradually for grains where the pAg was adjusted using NaCl. τ_1 is decreasing gradually in both cases. These results are in accordance with the earlier measurements of the ionic conductivity. These results also confirm our interpretation of τ_1 and τ_2 , though it has not been clarified yet why the use of NaCl for the adjustment of the pAg has a smaller effect on the photoelectron lifetimes than the use of KBr.

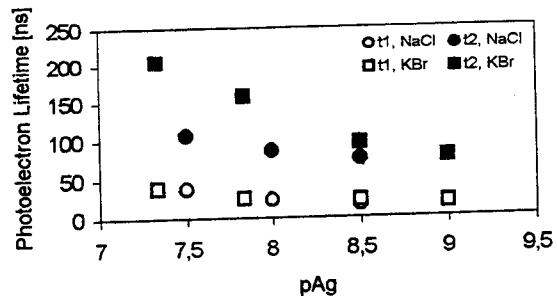


Fig 10: τ_1 and τ_2 as function of the solution pAg of AgBr emulsion grains.

For AgCl emulsion grains it can be expected that an increase of the solution pAg leads to a decrease of the lifetime τ_1 . Fig. 11 shows that this is the case only for samples where the pAg was adjusted using KBr. This result confirms our interpretation. For the other samples, adjusted with AgNO₃ and NaCl, τ_1 is increasing with increasing pAg. The reason for this behavior has not been clarified yet

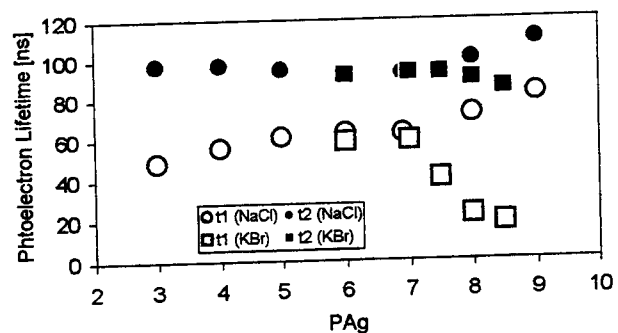


Fig. 11: τ_1 and τ_2 as function of the solution pAg of AgCl emulsion grains. For values larger than 7 the pAg was adjusted using both KBr and NaCl, values below 7 were adjusted using AgNO₃.

The results of an increasing pAg on the photoelectron lifetimes τ_1 and τ_2 for AgBr and AgCl are shown in the following table.

pAg adjusted with	AgBr		AgCl	
	τ_1	τ_2	τ_1	τ_2
KBr	-	--	--	(-)
NaCl	-	-	+	(+)

Increasing lifetimes are denoted by "+", decreasing lifetimes by "-". Further investigations have to show why the influence of the pAg on the photoelectron lifetimes is dependent on the use of NaCl or KBr.

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References

1. L.M. Kellogg, *Phot. Sci. Eng.* **18**, 378 (1974)
2. R.J. Deri, J.P. Spoonhower, *Phot. Sci. Eng.* **28**, 92 (1984)
3. J. Beutel, *J. Appl. Phys.* **46**, 4649 (1975)
4. Th. Müssig, G. Hegenbart, A. Russow, H. Fuess, *J. Imag. Sci. Tech.* **38**, 526 (1994)
5. T. Oikawa, N. Seaki, T. Kaneda, A. Hirano, T. Tani, *J. Imag. Sci. Tech.* **39**, 233 (1995)
6. S. Takada, *Phot. Sci. Eng.* **19**, 214 (1975)
7. C.R. Berry, *J. Phot. Sci.* **21**, 202 (1973)
8. F. Callens, L.W. Ketellapper, W. Maenhout-van der Vorst, *J. Phot. Sci.* **33**, 100 (1985) and references therein