Investigations on the Dependence of Electron Lifetimes on Bulk Properties in AgCl and AgBr Emulsions by Microwave Absorption Measurements

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Abstract

The transient photoconductivity of silver halide emulsions was measured using microwave techniques. The decay curves reveal two components with first order kinetics.

The influence of the bulk properties on the electron lifetimes was studied by doping the crystals with transition metal complexes and with Zn ions.

Introduction

The measurement of microwave absorption (MWA) is a convenient method to study the transient concentration of photoelectrons in silver halide emulsion grains[1,2,3]. Phase sensitive MWA is therefore an important tool in the investigation of photoelectrons in silver halides as it allows to separate the decay kinetics of conduction band electrons and those trapped in shallow electron traps.

Photoelectron decay curves typically consist of two parts with first order kinetics. After a fast decay with the photoelectron lifetime τ_1 a slower decay occurs characterized by a lifetime denoted as τ_2. Recently, Oikawa et. al[4] investigated how both lifetimes depend on the grain size. With primitive AgCl emulsions they found that τ_1 was in proportion to the edge length, τ_2 in proportion to the square of the edge length, as expected for a diffusion limited process. Therefore, the authors proposed to correlate τ_2 with a trapping reaction at the surface of the grain with the diffusion of the electrons to surface traps being the rate determining step . Further measurements in AgCl emulsion grains stabilized with TAI changed the grain size dependence to a reaction controlled kinetic and indicated the silver ions at kink sites to be the electron traps. No explanation has yet been found for the process correlated with the electron lifetime τ_1.

The aim of this study is to check this interpretation and

to aquire more information regarding the nature of the decay processes. We investigated the influence of bulk properties by doping the emulsion grains with electron traps of different trap depths.

Experimental

Sample preparation

Pure silver chloride cubes that were prepared by a balanced double jet precipitation at a constant pAg of 7 were used. The grain size was determined by electrochemical grain size analysis. For these investigations we used a grain size of 0.5 μm (diameter of a sphere of equal volume).

The solutions of the dopant complexes were added by a third jet into the mixing zone of the silver nitrate and sodium chloride solutions.

Chemical ripening was performed by digestion with $HAuCl_4$ and $Na_2S_2O_3$ at 65°C.

The coated emulsions were cut to strips of 1 mm x 20 mm. Three of these strips were placed in the microwave cavity.

The Microwave Apparatus

The used microwave apparatus was a phase sensitive Q-band microwave instrument, described elsewhere[5]. 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, depending on the sample. The primary light source was a pulsed nitrogen laser emitting at 337 nm, this being used to pump a dye laser, emitting at 400 nm with a pulse width of 600 ps. The laser intensity was reduced by various filters with densities between 0.1 and 1.06 neutral density.

Results and Discussion

Fig. 1 shows a decay curve for cubic AgCl emulsion grains. Two regions with first order kinetics can be distinguished: a fast decay in the first nanoseconds after exposure, denoted by the lifetime τ_1 (about 50 ns), followed by a slower decay, denoted by τ_2 (93 ns).
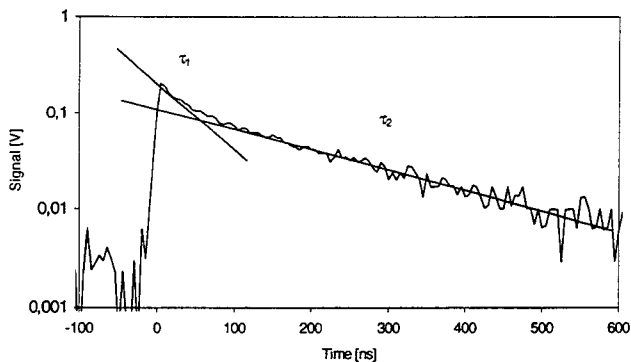

Fig. 1: Absorption signal of pure silver chloride emulsion grains.

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

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

where n_1 and n_2 being the number of electrons involved in the two decay processes. The influence of the light intensity on both photoelectron lifetimes for silver chloride emulsion grains is shown in Fig. 2.
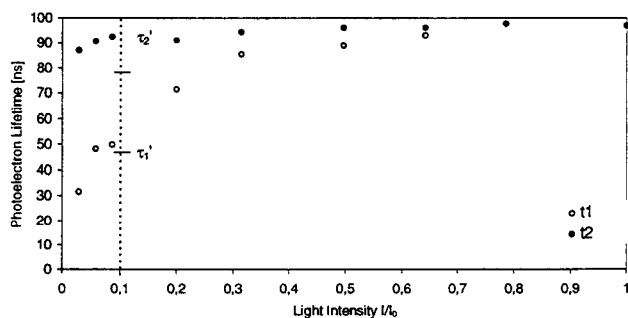

Fig. 2: The photoelectron lifetimes τ_1 and τ_2 as a function of the light intensity for pure silver chloride emulsion grains. In this paper the lifetimes are determined by interpolation for a light intensity of ten per cent of the maximum density, here denoted by τ_1 and τ_2.

Whereas the lifetime τ_2 is constant, the lifetime τ_1 is measurable only at small light intensities.

The dispersion signal reaches its maximum immediately after the decay process characterized by τ_1 has finished. As the dispersion signal is caused by shallowly trapped electrons we consider the lifetime τ_1 to be determined by shallow trapping of photoelectrons at the grain surface. Most likely, these shallow traps are formed by silver ions at kink sites.

At longer times both the dispersion and the absorption signal decrease indicating that the photoelectrons in shallow traps and those in the conduction band are removed by irreversible processes like deep trapping, recombination and latent image formation.

Doping with transition metal complexes

The influence of the incorporation of 10^{-6} mol $[IrCl_6]^{2-}$ per mol Ag into the crystals is shown in Fig. 3.

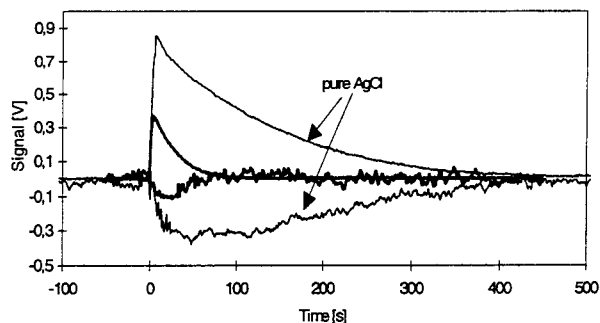*Fig. 3: Absorption and dispersion signal of $[IrCl_6]^{2-}$ doped emulsion grains compared with pure AgCl*

The height of both the absorption and the dispersion signal decreases, the latter can only be observed during the first nanoseconds after exposure. The kinetic analysis of the absorption signal reveals that τ_1 keeps unchanged compared with pure AgCl while τ_2 is significantly shortened. We explain this behavior by the action of the deep electron traps which are formed by the dopant complex forms and decrease the number of electrons in the conduction band and in shallow traps.

To confirm this interpretation, we changed the trapping properties of the transition metal complex by varying the ligand sphere around the iridium ion. The introduction of cyanide ligands should reduce the trap depth of the dopant as the splitting of the metals d-orbitals increases and the difference in energy between the LUMO of the complex and the conduction band of the silver halide decreases.

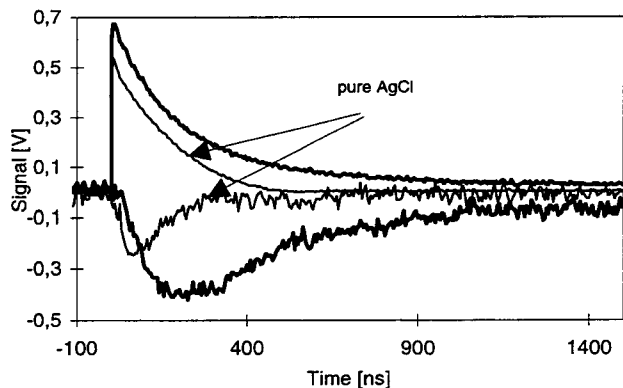The influence of doping with $[Ir(CN)_6]^{3-}$ on the decay curves is shown in Fig. 4.

Fig. 4: Absorption and dispersion signal of AgCl emulsions undoped and doped with 10^{-4} mol of $[Ir(CN)_6]^{3-}$/ mol Ag.

For a concentration of 10^{-6} mol / mol Ag, a small effect

can be detected. The absorption and the dispersion signal are still rather similar to those obtained with undoped AgCl. With 10^{-4} mol, however, both signals increase, the maximum of the dispersion signal being shifted to longer times indicating more shallow trapping. An analysis of the absorption shows again that the lifetime τ_2 is now as long as some microseconds, τ_1 being unchanged as in the case of iridium chloride doping.

.We repeated the concentration series but with $[Rh(CN)_6]^{3-}$ as dopant. This compound should also act as a shallow trap. The results are similar to those obtained for the analogous Ir-complex. A concentration of 10^{-6} mol Rh / mol Ag brings a slight increase of τ_2, however with 10^{-5} mol Rh we find a increased lifetime of about 900 ns. With an even higher concentration of 10^{-4} mol / mol τ_2 is surprisingly reduced to 90 ns for the first flash exposure, but after a second exposure we find 1 μs, after the third exposure 1.6 μs. A possible explanation for the short lifetime at the first flash could be that the dopant complex is aquated to some extent and that these aquated species form deep permanent electron traps. These are filled by the first flash and after that the electron lifetime increases due to the shallow trapping.

Doping with Zn^{2+}

In contrast to the transition metal complexes, photoelectrons can not be trapped in the valence shell of the metal in the case of Zn^{2+}. This ion can influence the bulk properties only by acting as a shallow coulombic trap or by shifting the Frenkel equilibrium.

Again, no influence of the dopant on τ_1 could be found. The values for τ_2 are given in the following table:

Zn^{2+} [mol / mol Ag]	τ_2 [ns]
0	93
10^{-8}	105
10^{-7}	120
10^{-6}	200
10^{-4}	80

The Zn ions increase τ_2 and behave similarly to the cyanide complexes of Ir and Rh. We suggest that these

dopants trap the photoelectrons temporarily and increase the time before they are consumed by irreversible processes. In contrast, the chloride complex of Ir is such a deep trap that the electrons are removed permanently from the system resulting in an short lifetime τ_2.

The analogous behavior can be found with AgBr cubes: τ_1 is independent on the Zn concentration, τ_2 increases and reaches a maximum with 10^{-5} mol / mol Ag. In this system it can be shown by dielectric loss measurements that the increase of τ_2 is parallel to a decrease of ionic conductivity, suggesting a dependence between these two properties.

Effect of chemical ripening

According to these results only τ_2 is affected by changing the electron trapping properties of the bulk. What happens if the surface properties are also changed? The effect of chemical ripening on the iridium doped emulsions is shown in the following table

dopant	τ_1		τ_2	
	primitive	Au/S	primitive	Au/S
none	50	30	95	95
$[IrCl_6]^{2-}$	30	20	80	80
$[Ir(CN_6)]^{3-}$	40	30	100	100

Within the experimental error τ_2 is left unchanged by the surface modification through chemical ripening. Now a decrease of τ_1 is found, indicating that this lifetime is correlated with the surface properties of the crystals.

References

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