Investigations of Reaction and Diffusion Limited Decay Kinetics of Photoelectrons in AgCl- and AgBr-Emulsion Grains by Microwave Absorption

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Introduction

Microwave absorption is a powerful IN-SITU method to measure the transient photoconductivity, which provides directly the lifetime of photoelectrons in silver halide systems. By measuring the transient photoconductivity of emulsion grains with different grain size, this method provides further information like diffusion constant, drift mobility and reaction velocity on the surface. These informations characterize the electronic properties of silver halide emulsion grains, which play an important role in the primary photographic process.

In the following we will report the theoretical background of the relation of transient photoconductivity and diffusion constant, drift mobility and reaction velocity on the surface. Further we will report on measurements of the transient photoconductivity, performed on primitive, cubic AgBr- and AgCl emulsion grains of different size, and therefore on the possibilities to evaluate the diffusion constant, drift mobility and reaction velocity on the surface. First experimental results referring on the theory of reaction and diffusion limited decay kinetics were presented at the IS&T Annual Conference 1996 in Minneapolis [1]. In the following we will present our latest results.

Theory

The continuity equation in its most general form, is given by:

$$\frac{\partial n(t)}{\partial t} = g(t) - \frac{n(t)}{\tau} + \mu * \nabla n * \vec{E} + D * \Delta n \qquad (1)$$

n(t) is the momentaneous concentration of photoelectrons, g(t) the generation rate, τ is a characteristic electron lifetime, μ the drift mobility, E the electric field and D the diffusion coefficient. The diffusion coefficient is related to the drift mobility by the Nernst-Einstein relation,

$$\frac{D}{kT} = \frac{\mu}{e} \qquad (2)$$

where k is the Boltzmann constant, e the elementary charge and T the temperature. With the simplifying assumptions of a negligible electric field (small microwave field) and a very short laser pulse g(t)->δ(t) the continuity equation (Equ 1) will reduce to:

$$\frac{\partial n}{\partial t} = -\frac{n(t)}{\tau} + D * \Delta n \qquad (3)$$

Equ (3) is a linear partial differential equation. It's rather complicated rigorous solution, given in [2], [3], can be fairly approximated by:

$$n(x,y,z,t) = n_0 \frac{64}{\pi^3}\left(\cos\frac{\pi}{2a}x \ \cos\frac{\pi}{2b}y \ \cos\frac{\pi}{2c}z\right)e^{-\nu * t} \qquad (4)$$

where n_0 is the electron concentration at t=0 and ν is a DECAY RATE, given by

$$\nu = \frac{1}{\tau} + D_n \frac{\pi^2}{4}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right) \qquad (5)$$

The characteristic lifetime τ can be interpreted as the lifetime for infinite grains (a, b, c-> ∞) and will be named "bulk lifetime" τ_B. If an orthorhombic AgX-grain with edgelength 2a, 2b, 2c is located within the confinement volume, then electrons generated in the grain volume will diffuse to the grain surface. The particle current density of the electrons diffusing toward the grain surface is given by:

$$(D * \vec{\nabla} n) * \vec{n} = \pm k * n \qquad \textit{at the surface} \qquad (6)$$

where $k\left[\frac{cm}{s}\right]$ is a "trapping velocity" at the surface and $\vec{n}$ denotes an unit vector normal to the corresponding surface.

Combining Equs (5) and (6) and using the procedure outlined in [3], the general expression for the decay rate, Equ (5) can be specialized for two limiting cases and cubic AgX-grains (edgelength a) as follows:

a) High Trapping Efficiency: $k \rightarrow \infty$

$$\nu_{k\rightarrow\infty} = \frac{1}{\tau_B} + \frac{3 * D * \pi^2}{a^2} \qquad (7)$$

b) Low Trapping Efficiency: $k \rightarrow 0$

$$\nu_{k\rightarrow 0} = \frac{1}{\tau_B} + 6k \qquad (8)$$

An high trapping efficiency means, that an electron, which diffused to the grain surface will be immediately trapped at the surface. Therefore the decay rate depends only on the time an electron needs to reach the surface and the decay kinetic is called diffusion limited. An low trapping efficiency means, that a lot of electrons are at the surface, but only few of these electrons are trapped. The decay rate depends only on the reaction velocity of this process and is called reaction limited.

To distinguish between diffusion- and trapping limited decay kinetics using Equ (7) and (8), the decay rate ν, which is the reciprocal lifetime of the measurement, has to be plotted versus the reciprocal edgelength or the square of the reciprocal edgelength as shown in Fig. 1 (left).

Another method to distinguish between diffusion- and trapping limited decay kinetics of the transient photoconductivity using the equations (7) and (8) was presented by R.J. Deri and J.P. Spoonhower [4], A. Hirano [5] and T. Oikawa et al. [6]. Here the lifetime is plotted versus edgelength in a double logarithmic scale (Fig. 1 right) The disadvantage of this method is the assumption of a very large bulk lifetime τ_B, in comparison with the measured lifetimes.

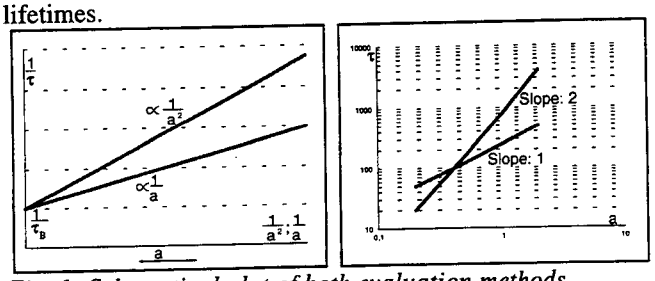

Fig. 1: Schematical plot of both evaluation methods

Experimental

All measurements were performed in a 35GHz microwave equipment at room temperature, shown in Figure 2. It allows to separate the absorption signal caused by "free" electrons in the conduction band from the dispersion signal caused by shallow trapped electrons. [7]

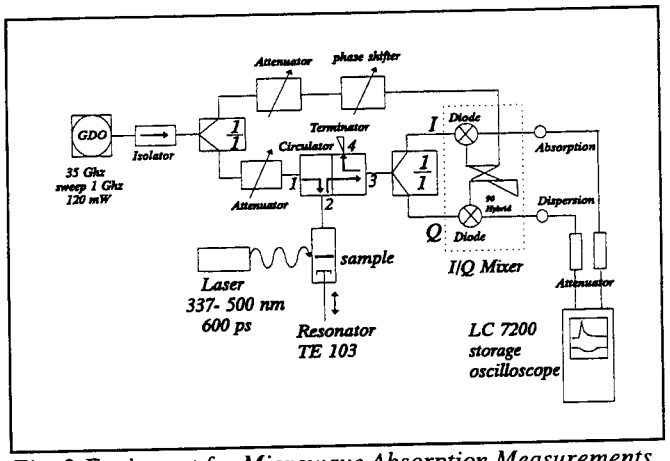

Fig. 2 Equipment for Microwave Absorption Measurements of the photoelectron lifetime.

The investigated samples were primitive cubic AgBr emulsion-grains with edgelengths ranging from 0,3μm to 2μm.

Results

In the following we will report the results for pure cubic AgBr emulsion grains. In Fig. 3 a typical MWA decay curve obtained for cubic AgBr emulsion grains of 0,85μm edgelength is shown. There are two different decay regions, which lead to two different lifetimes (τ_1 and τ_2).

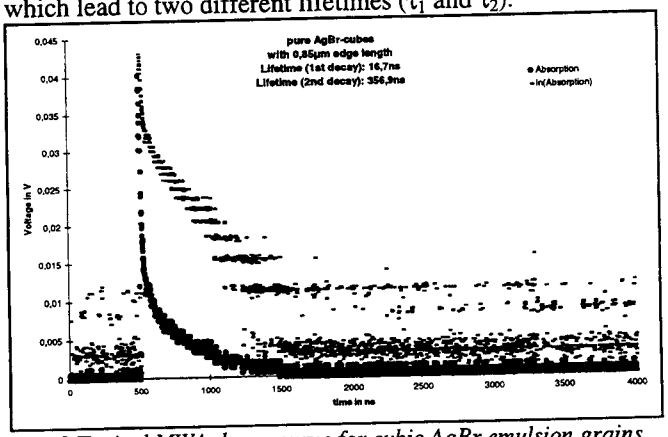

Fig. 3 Typical MWA decay curve for cubic AgBr emulsion grains.

These measurements were repeated several times to eliminate statistical deviation. The measured lifetimes τ_1 and τ_2 for pure AgBr emulsion cubes are plotted versus the edgelength in Fig.4 (τ_1) and Fig.5 (τ_2).

The lifetime τ_1 calculated by the fast decay of the first region fluctuates in the different measurements much more than the lifetime τ_2.

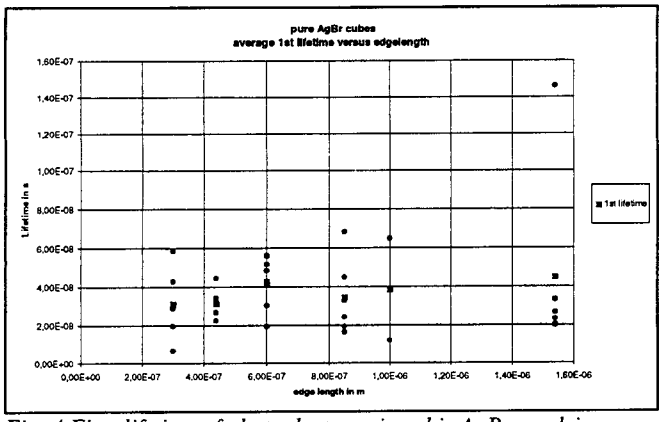

Fig. 4 First lifetime of photoelectrons in cubic AgBr emulsion grains.

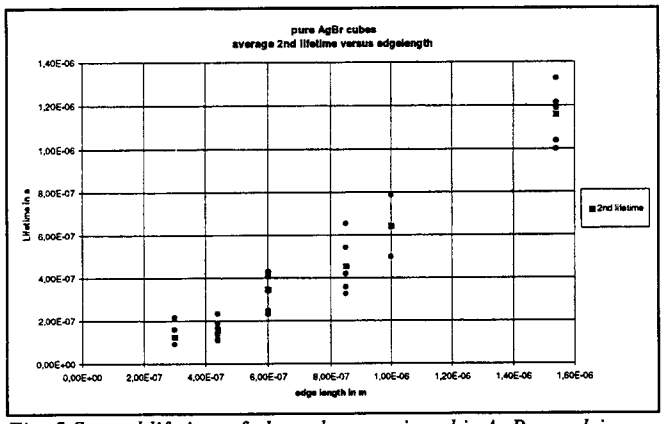

Fig. 5 Second lifetime of photoelectrons in cubic AgBr emulsion grains.

The fluctuation of the lifetime τ_1 makes it very difficult to decide, which kind of kinetic (reaction or diffusion limited) leads to the first very fast decay. For the second lifetime τ_2 according to Equ. 13 we plot the reciprocal lifetime τ_2 versus the reciprocal edgelength in Fig. 5 and versus the square of the reciprocal edgelength in Fig. 6. Another method is to plot lifetime versus edgelength in a double logarithmic scale and to look on the slope in this diagram. For our case the slope is between 1 and 2.

In case of a reaction limited decay kinetic the straight line of Fig.5 provides the reaction velocity on the surface and the bulk lifetime τ_B (see Equ. 13), in case of a diffusion limited decay kinetic the straight line of Fig. 6 provides diffusion constant and bulk lifetime. A reaction limited decay kinetic is impossible, because it provides a negative bulk lifetime. Therefore the second decay lifetime τ_2 seems to be limited by the diffusion. The slope provides a diffusion constant D of $2{,}4 \times 10^{-4} \frac{cm^2}{s}$, a drift mobility μ of $10^{-2} \frac{cm^2}{Vs}$ and a bulk lifetime τ_B of 1000 nanoseconds. Similar investigations on TAI-stabilized emulsion grains and on AgCl-emulsion grains will be presented.

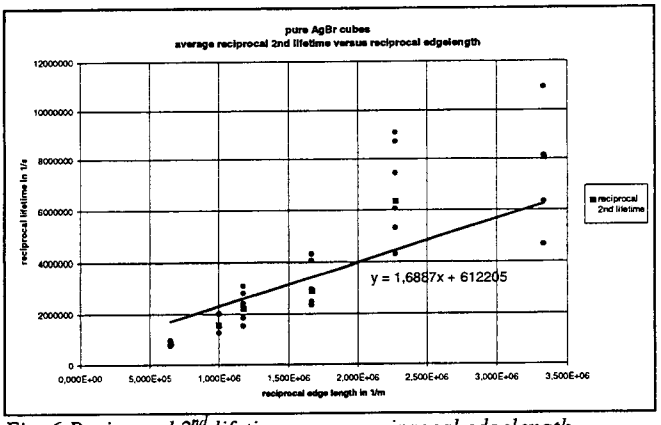

Fig. 6 Reciprocal 2nd lifetime versus reciprocal edgelength.

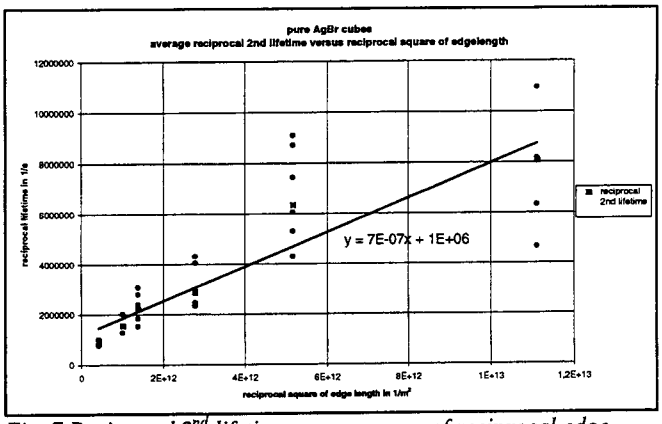

Fig. 7 Reciprocal 2nd lifetime versus square of reciprocal edge-length.

References

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