Influence of Grain Structures on the Photoelectron Lifetime

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Introduction

The extremely high speed of silver halide emulsions is achieved by the incorporation of phase boundaries into the emulsion grains. Today the application of this technology has reached a high level of perfection which results in silver halide microcrystals of complicated structures like core-shell, double-structured or multistructured grains.

Phase boundaries between regions of different halide composition in, for example, core shell systems have a strong influence on the electron-hole recombination rate and various other trapping and detrapping processes.

Microwave absorption is a powerful tool to under-stand the mechanism of phase structures of modern micro-crystals. With this method we will demonstrate the influence of various grain parameters like grain size, iodide content of $AgBr_{1-x}I_x$ phases, geometry of core shell boundaries and grain morphology on the time depen-dence of the number density of free and shallow trapped photoelectrons. A kinetic model will be given to explain the observed decay curves.

Experimental

Sample Preparation and Characterisation

In this work structured AgBr/I emulsions with tabluar shaped grains monodispersed distributed were used. The emulsion grains were precipitated in an aqueous solution of gelatine with a pBr of 1.75, using the balanced double-yet technique.[1] The structure of the emulsion grains which was produced by variation of the iodide concentration of the halide solution during the precipitation process was determined by X-ray powder diffraction.[2]. Figure 1 shows the changing of the characteristic (200) powder pattern peak with time during the crystal growth process. The first sample was taken directly after seeding, showing a pure AgBr-powder pattern peak. The growing of the iodide rich phase on the seed crystals for the samples taken after seeding is reflected by the shift of the powder pattern peaks to smaller angles . In the case of Figure 1 after half of the growing time the iodide concentration was reduced to x = 0.01 leading to a dominant powder peak for a sample at the end of the BDJ process.

The average grain size and grain distributions were measured by the Möller method.[3] The avarage grain thickness and diameter were evaluated from electron and atomic force micrographs.

For the microwave absorption measurements the emulsion samples were prepared as unsensitized AgBr/I emulsion coatings with $4g/m^2$ silver and were handled only under red safelight. The emulsion coatings were cut into 1.5 × 15 mm strips . All film strips were oriented parallel to the incident laser beam at the position of maximum electric field in the cavity.
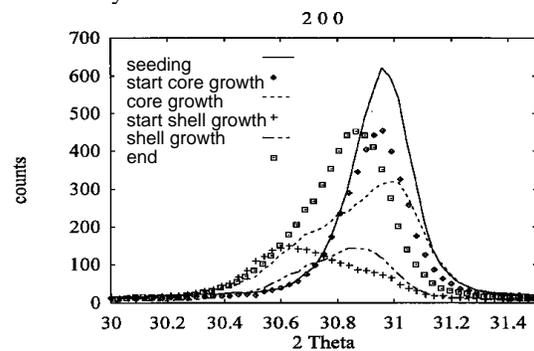
Figure 1: Emulsion-crystal-growing: Variation of the (200) powder pattern peak of the $AgBr_{1-x}I_x$ phases during the precipitation process and characterised with powder diffraction.
sample 1: after seeding
sample 2: starting the growing of I-rich core
sample 3: during core growing
sample 4: beginning shell growing
sample 5: during shell growing
sample 6: end of growing process
($AgBr_{0.97}I_{0.03}$, T-grain, V = 0.12 μm^3, core x = 0.2 , shell x = 0.01)

Equipment

The 35 GHz equipment has a phase sensitive detection system allowing the separation of the real and imaginary part of the reflected signal. Measurements are possible only at room temperature. The specifications of the equipment are:

— Oscillator: 35 GHz, 120 mW, 2GHz bandwidth
— Cavity: TE_{103}, loaded Q = 50 - 600, filling factor f = 10^{-3}

A nitrogen dye laser was used at a frequency of 440nm. The pulse width of the laser is 800ps. The samp-ling rate of the storage oscilloscope is 1ns. The overall time resolution of the 35 GHz equipment is between 1.7ns and 4ns.
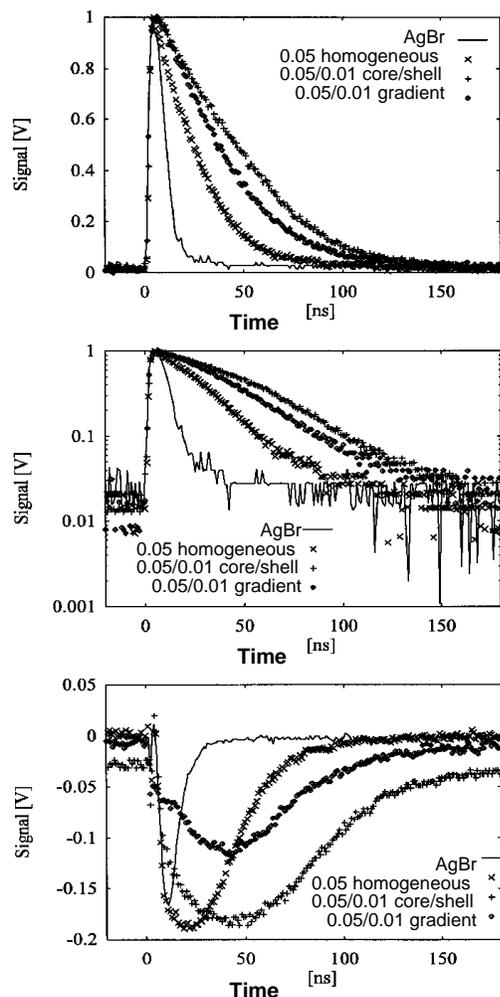
Figure 2. Absorption and dispersion signals of T-grain emulsions with different grain structures.
Volume of the grains V = 0.25 mm^3.
a.: Absorption (I/t)
b.: Absorption (ln(I)/t)
c.: Dispersion (I/t)

Results and Discussion

Figure 2 presents the influence of the grain structure of a T-grain emulsion (volume 0.25 mm^3) on the photoelec-tron lifetime. In this case the microwave absorption in-vestigations were done for samples with homogenous iodide content of x = 0.05, for core shell structured grains with an iodide content of x = 0.05 for the core and x = 0.01 for the shell and a core shell volume ratio of 1:1 and for so called gradient grains. These grains are generated with a continual reduction of the iodide content from the beginning of the crystal growth (x = 0.05) to the end of the growth process (x = 0.01). Both the core shell and the gradient grains are

showing a significant enhanced electron lifetime in comparison to the crystals with homogeneous iodide distribution or without iodide. This behaviour of structured grains was explained with the separation mechanism of electrons and holes at the AgBr/I phase boundaries.[4-7]
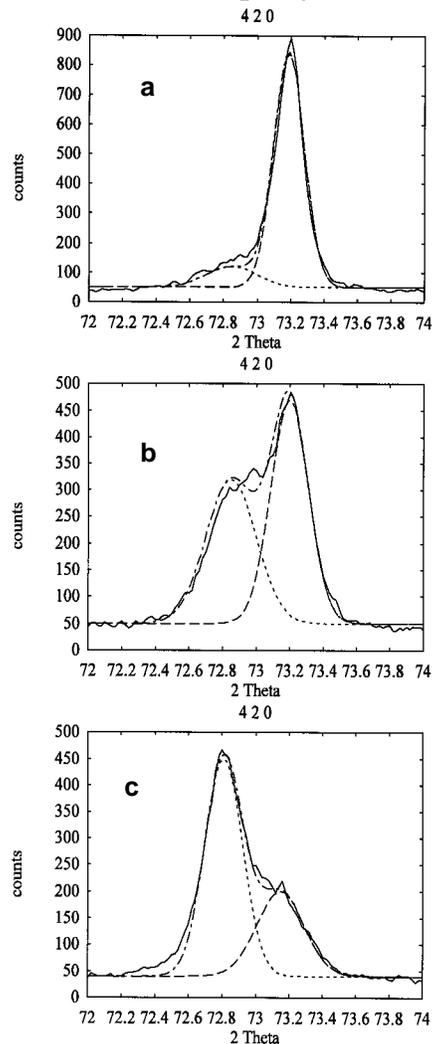
Figure 3. Typical (420) powder pattern peaks for three T-grain emulsions with nominal x = 0.01 (right peak) and x = 0.12 (left peak) for the core and the calculated powder pattern peaks. The core shell ratio was varied: a.: 1:2; b.: 1:1; c.: 2:1

For the microwave absorption measurements the typical decay curve with different time regions are found.[8,9] For the pure AgBr T-grains an initial quick decay of the free electrons is followed by a slow decay process.[8] The unstructured and structured T-grains with x = 0.05 show the decay regions, an initial process with long lifetimes followed by a quick and slow decay process.[9] The measurements show no change of the typical shape of the microwave absorption signal with the variation of the grain structures, indicating that a change of the photoelec-tron decay kinetic due to grain structures like core shell or gradient structures is not to be expected.

To get more information in detail for the influence of core-shell structured T-grains on the photoelectron lifetime, the grain size, iodide content and the core-shell ratio are varied. For all samples the aspect ratio is 1:8 and the iodide content for the shell is about x = 0.01.

The iodide content of the phase structure was analysed by X-ray powder diffraction. Figure 3 presents the characteristic (420) powder pattern peak for an nominal iodide content for the core of x = 0.012 (x = 0.085 value from analysed powder pattern peak) depending on the core shell ratio.

Figure 4 to Figure 6 are showing the photoelectron lifetime depending on the grain size, iodide content and core shell ratio.
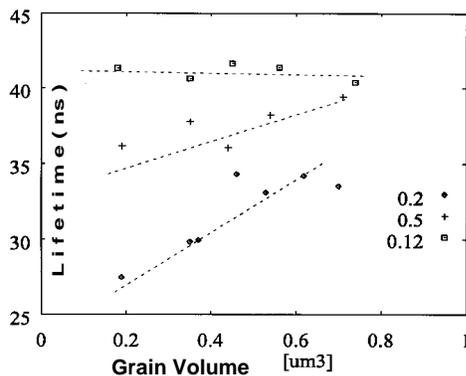
Figure 4: Average photoelectron lifetime vs. grain volume for core shell T-grains with x = 0.02, 0.05 (0.035) and 0.12 (0.085) for the core and x = 0.01 for the shell. The core shell ratio is 1:2.

Due to the fact, that the shape of the absorption curves is independent on the variation of the parameters described above, only mean values over the whole decay curves are used for the calculation of the lifetimes.

Figure 4 presents the photoelectron lifetime vs. the grain volume for a core shell ratio of 1:2 and iodide contents of x = 0.02 to x = 0.12. From the curves it can be con-cluded, that with increasing iodide content of the core in principle the photoelectron lifetime increases significantly. Further with a first approximation there is a linear dependence between the grain volume and the photoelectron lifetime.

Changing only the core shell ratio (see Figure 5) to 1:1 a surprising effect arises. The samples with the iodide content of x = 0.02 and 0.05 are showing the behavior described above. For x = 0.12 there is a dramatic change of this behavior. Whereas for small grain sizes the photoelectron lifetime increases with the grain volume, the lifetime decreases for grain volumes higher 0.4 $\mu m.^3$ This cannot be explained with change of the core shell structure in principle, due to the fact, that the shape of the powder pattern peaks does not change significantly. Moreover the micrographs of the samples are showing no change of the grain shapes and further on there is no change of the shape of the absorption and dispersion curves in principle.
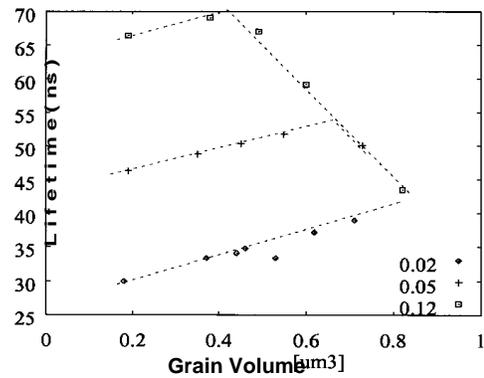
Figure 5. Average photoelectron lifetime vs. grain volume for core shell T-grains with x = 0.02, 0.05 (0.035) and 0.12 (0.085) for the core and x = 0.01 for the shell. The core shell ratio is 1:1.

In Figure 6 the absorption and dispersion curves of samples with a core shell ratio of 2:1 is shown. The samples with x = 0.02 and x = 0.05 have the same behavior which was found for the samples with a core shell ratio of 1:1. The samples with x = 0.12 shows no dependence on the grain size and gives for higher grain sizes the lowest value for the photoelectron lifetime.
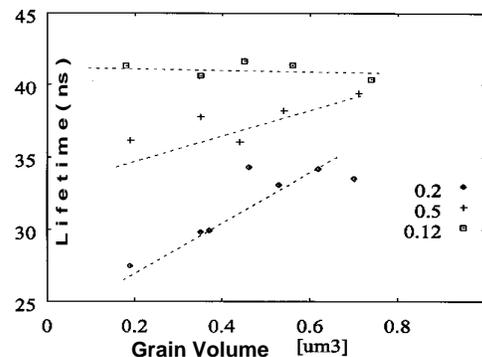
Figure 6. Average photoelectron lifetime vs. grain volume for core shell T-grains with x = 0.02, 0.05 (0.035) and 0.12 (0.085) for the core and x = 0.01 for the shell. The core shell ratio is 2:1.

The observations can be summarised in the following way:
- Core shell structures increasing the photoelectron lifetime
- With increasing iodide content the photoelectron lifetime increases
- With increasing core volume the photoelectron lifetime increases
- The photoelectron lifetime increases linear with increasing grain size in the range of $0.1 \mu m^3$ to $1 \mu m^3$
- There are limitations for the photoelectron lifetime with increasing grain size, iodide content of the core and size of the core. If one or several of these parameters exceeds the limitations, then the photoelectron lifetime decreases significantly.

The measurements can be explained with the quality of the iodide ions[9] and the mechanism of phaseboundaries.[6] A more detailed discussion of the results will be presented.

References

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