Phase Sensitive Microwave Absorption Studies on Ag1-xBrx Emulsion Crystals

Th. Müssig

Du Pont de Nemours (Deutschland) GmbH, Neu Isenburg, Germany

A. Russow

Technische Hochschule Darmstadt, Germany

Introduction

The photoconductivity transients that follow pulsed laser exposure of silver halide crystals give useful information about their electronic properties and detailes in their photo chemistry. In particular this method is a powerful tool to analyze the influence of phase boundaries incorporated in modern AgBr emulsion crystals.

Phase boundaries between regions of different halide compositions in, for example, core shell systems have a strong influence on the electron-hole recombination rate and various other trapping and detrapping processes. Therefore it is of high interest to get information in detail about the mechanism of phase boundaries.

With the microwave absorption method we have analyzed the influence of phase boundaries in emulsion crystals varying the iodide content of AgBrI phases, the geometry of the core shell system, the grain size and the grain habitus on the time dependence of the number density of free and shallow trapped photoelectrons which correlates directly with the speed of the emulsion. Furthermore an investigation is done for a special "gradient system."

Experimental

Sample Preparation and Characterisation

In this work structured AgBr/I emulsions with tabular 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 fig. 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 average 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 X 15 mm strips . All film strips were oriented parallel to the incident laser beam at the position of maximum electric field in the cavity.
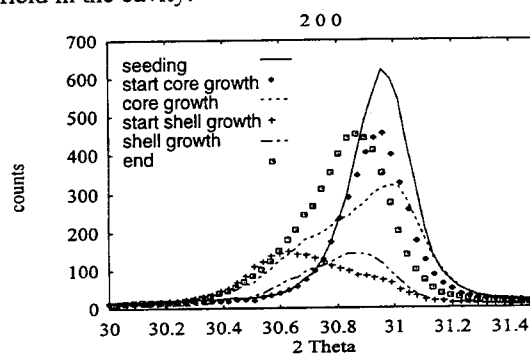

Fig. 1 : Emulsion-crystal-growing : Variation of the (200) powder pattern peak of the $AgBr_{1-x}I_x$ phases during the precipitation process and characterised with powder diffraction.

    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, $V = 0.12 \mu m^3$, 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
- Detector: one balanced, 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 sampling rate of the storage oscilloscope is 1ns. The overall time resolution of the 35 GHz equipment is between 1.7ns and 4ns.
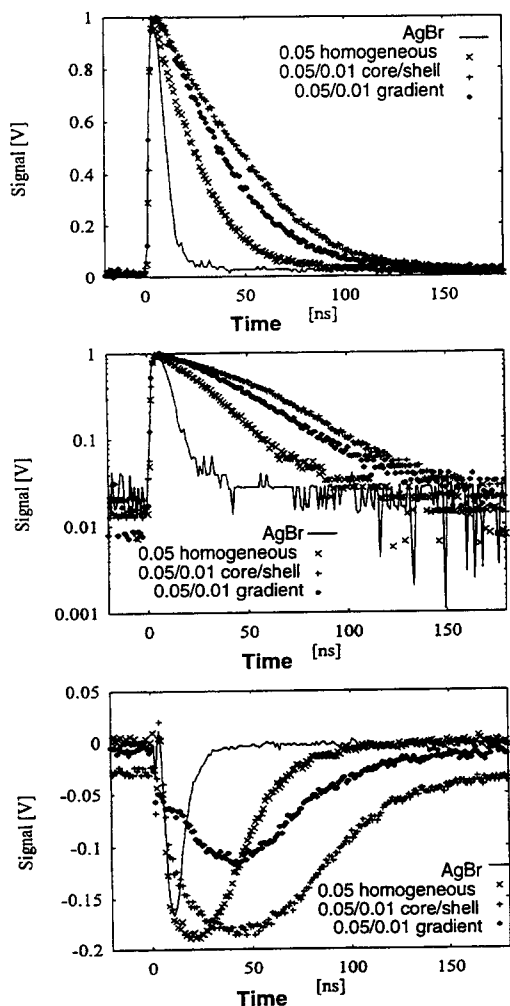

Fig. 2 : Absorption and dispersion signals of T-grain emulsions with different grain structures.

Volume of the grains V = 0.25 μm^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 mm³) on the photoelectron lifetime. In this case the microwave absorption investigations were done for samples with homogeneous 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].

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 three 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 photoelectron decay kinetic due to grain structures like core shell or gradient structures is not to be expected.
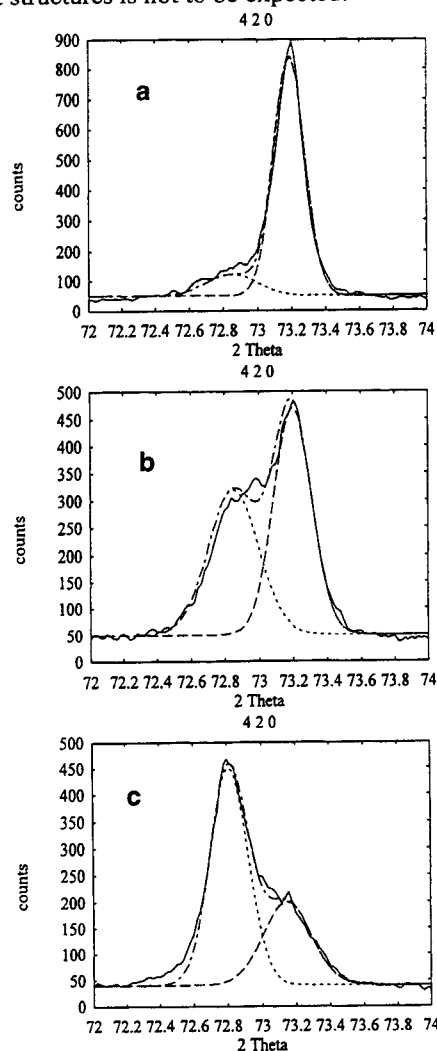

Fig. 3: Typical (420) powder pattern peaks for three T-grain emulsions with nominal x= 0.01 (right→ peak) and x = 0.12 (left peak) for the core and the calculated powder pattern peaks. The core shell ratio was varied:

→ *a. : 1:2*
→ *b. : 1:1*
→ *c : 2:1*

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 core-shell grains with 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.

The so-called ´gradient´- systems are emulsion grains with a continuous decrease of the iodide concentration from the core to the surface of the crystals. Fig. 4 presents the (420) powder pattern peak of a $AgBr_{1-x}I_x$ T-crystal with a typical iodide distribution for ´gradient´ - systems.

Figure 5 to Figure 7 are showing the photoelectron lifetime depending on the grain size, iodide content and core shell ratio.

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 5 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 concluded, 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. Only the samples with a iodide content of x = 0.12 have another behaviour. Here with increasing grain volume there is no change of the photoelectron lifetime.
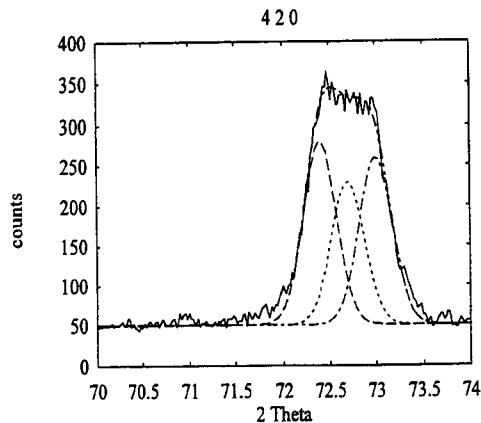

Fig. 5 : Average photoelectron lifetime vs. grain volume for core shell T-grains with x = 0.02, 0.05 → (0.035) and 0.12 (0.085) for the core and x = 0.01 for the shell. The core shell ratio is 1:2.

Changing only the core shell ratio (see Fig. 6) 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 smoothly with the grain volume, the lifetime decreases for grain volumes higher 0.4 μm^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.

Fig. 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 1:1.

In Figure 7 the photoelectron lifetime 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 show no dependence on the grain size and give for higher grain sizes the lowest value for the photoelectron lifetime.

Fig. 4: Typical (420) powder pattern peak of a T-crystal emulsion with a ´gradient´iodide distribution. The reflex profile is fitted with three gaussian profiles os same half width.
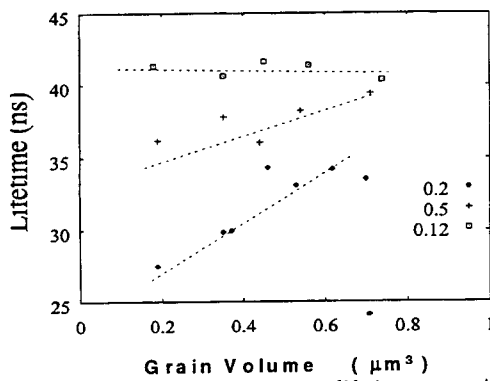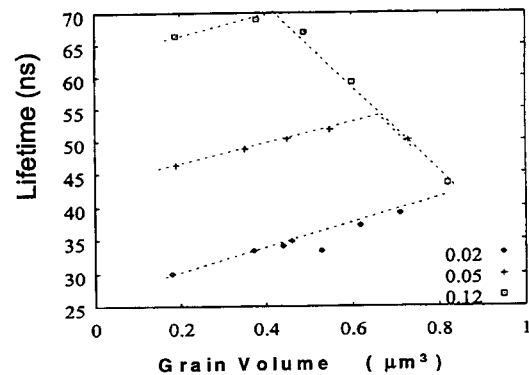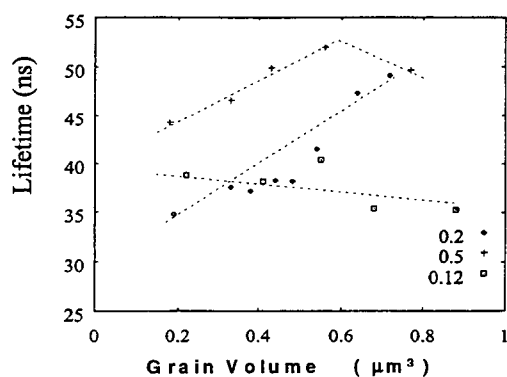
Fig. 7 : Average photoelectron lifetime vs. grain volume for core shell T-grains with x = 0.02, 0.05 (0.035) and 0.12 (0.085) for the core and x = 0.01 for the shell. The core shell ratio is 2:1.

For the 'gradient'-systems the microwave measurements were done for T-grain emulsions with small iodide rich core (≈ 15% of the overall crystal volume) and a thin shell with low iodide content. The iodide content was varied from x = 0.05 to x = 0.12 of the core and of the shell from x = 0.0 to x = 0.02. The core-shell volume ratio was 1:5, the mean value of the grain volume was 0.3 μm^3 and the aspect ratio was 1:8.

Figure 8 shows the average photoelectron lifetime versus the maximal iodide content of the core. In principle the same dependence between photoelectron lifetime and iodide content is found for 'gradient'emulsion grains in comparison to the core-shell systems. With increasing iodide content of the core, the photoelectron lifetime increases. Only for iodide concentrations > 8% the photoelectron lifetime decreases. Further with increasing iodide content of the shell the photoelectron lifetime decreases.
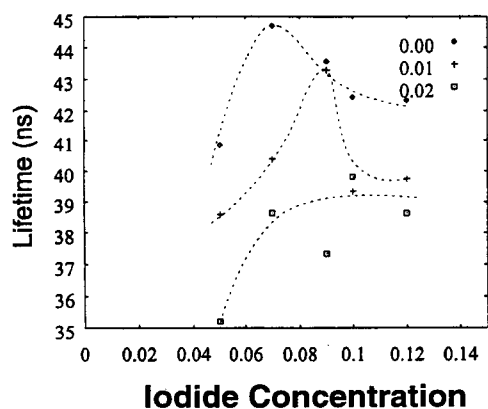

Iodide Concentration

Fig. 8 : Average photoelectron lifetime vs. the maximal value of the iodide content for three iodide concentrations of the shell (x= 0.0, 0.01, 0.02). A $AgBr_{1-x}I_x$ T-grain emulsion was used with NV = 0.3 μm^3

Contrary to emulsion crystals with homogeneous iodide distribution the 'gradient'grains are showing a significant higher photoelectron lifetime. Looking only on the averaged iodide of the grains for low iodide concentrations the 'gradient'grains have longer lifetimes in comparison to core-shell grains. Only for high iodide contents x » 0.05 and a core-shell ratio of 1:1 the photoelectron lifetime is for core-shell systems higher than for 'gradient' grains.

The observations can be summarized in the following way:

- Core shell structures increase the photoelectron lifetime
- With increasing iodide content the photoelectron lifetime increases
- With increasing core volume the photoelectron lifetime increases
- The photoelectron lifetime increases linearly 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 exceed the limitations, then the photoelectron lifetime decreases significantly.
- 'Gradient' systems are showing for low averaged iodide concentrations higher photoelectron lifetimes, as it can be seen for core-shell systems.

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

References

1. W.R. Nottorf, European Patent EP 263507 (13 [th] April 1988)
2. A. Russow, W. Schmahl, H. Fuess, Th. Müssig, J. of Imaging Sci. and Tech. **38**: 532 (1994)
3. G. Möller, Proceedings of the International Congress of Photographic Science. Section **AB**: A14 (July 1970) Moscow, USSR
4. Th. Müssig, F. Granzer, R. Hudson, Proceedings of IS&T St. Paul, 1991: 95
5. Th, Müssig, F. Granzer, Phys. Stat. Sol. (a) **87**: K85 (1985)
6. F. Granzer, R.Kricsanowits, Th. Müssig, Proceedings of the International Congress of Photographic Science Köln, 1986: 273
7. F. Granzer, J. Imag. Sci., **33**:207 (1989)
8. Th. Müssig, G. Hegenbart, A.Russow, H. Fuess, J. of Imaging Sci. and Tech. **38**: 526 (1994)
9. A. Russow, Ch. Jenisch, Th. Müssig, Proceedings of the IS&T's 47th Annual Conference Rochester, 1994:171