Activation Energies for the Trapping of Photoelectrons in Silver Chloride Emulsion Grains Obtained by Temperature Dependent Microwave Absorption Measurements

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Introduction

Microwave absorption (MWA) measurements are a well-known method for the investigation of the decay kinetics of photoelectrons in silver halide crystals. Especially, from the photoelectron lifetimes obtained by temperature dependent MWA measurements the activation energies for the trapping of electrons can be calculated.[1-3]

Recent MWA measurements have shown that at room temperature typical photoelectron decay curves consist of two different regions with first order decay kinetics. In the first nanoseconds after the illumination of the sample we observe a fast decay which is denoted by the photoelectron lifetime τ_1. The fast decay is followed by a slower decay, denoted by the photoelectron lifetime τ_2. A typical decay curve is shown in fig. 1.[4,5]
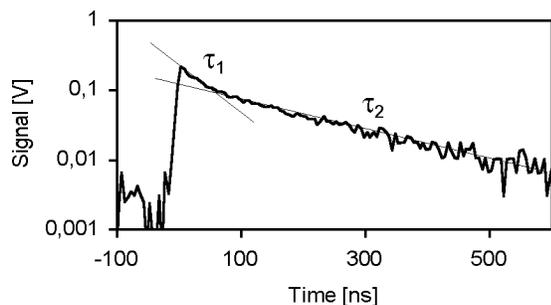
Figure 1. Typical photoelectron decay curve of silver chloride emulsion grains, showing two regions of first order decay kinetics

It has been shown that in the case of AgCl the lifetime τ_1 was influenced by modifications of the crystal surface, such as stabilizers or chemical ripening, whereas deep and shallow electron traps in the crystal bulk mainly influenced the photoelectron lifetime τ_2. Therefore, the lifetime τ_1 was attributed to the trapping of photoelectrons in traps on the crystal surface, whereas the photoelectron lifetime τ_2 was attributed to properties of the crystal bulk.[4,5] An interpretation of these trapping processes has been given by Hirano. He interpreted the process related to τ_1 as the capture of photoelectrons by silver ions in surface kink sites and the successive relaxation into a lattice relaxed state. The lifetime τ_2 was attributed to the reaction of these trapped electrons with interstitial silver ions.[6]

For a further investigation of this model, we calculated the activation energies of the different trapping processes from photoelectron lifetimes, obtained by temperature dependent MWA measurements. For this study, cubic silver chloride emulsion grains were used. The distribution of surface traps was varied by chemical ripening and by stabilization with 5-phenyle-1-mercaptotetrazole (PMT). Chemical ripening centers are additional electron traps, whereas by PMT the number of silver ions in surface kink sites and silver interstitial ions are decreased. The crystal bulk was doped with $[Rh(CN)_6]^{3-}$ ions. It has been shown by many authors that these ions are shallow electron traps.[4,6]

Experimental

Sample Preparation

Cubic silver chloride emulsion grains were precipitated using a balanced double jet technique. The edge length of the grains was 0.44 µm. The grain size was controlled by an electrochemical grain size analysis.

Chemical ripening was performed by digesting the grains with 9 ml $HAuCl_4$ and 18 ml $Na_2S_2O_3$ per mol AgCl at 65 K. Stabilized grains were prepared by adding 400 µmol 5-phenyle-1-mercaptotetrazole (PMT) per mol AgCl. Shallow electron traps were introduced by doping the crystal bulk with 0.4×10^{-5} mol $[Rh(CN)_6]^{3-}$ per mol AgCl.

The coated emulsions were cut to stripes of 3 mm × 30 mm. Three of those stripes were placed in the microwave cavity. The samples were handled under red safelight only.

Microwave Absorption Equipment

For temperature dependent MWA measurements, an X-band equipment with a resonance frequency of 8.5 GHz was used. A block diagram of this equipment is shown in fig. 2.
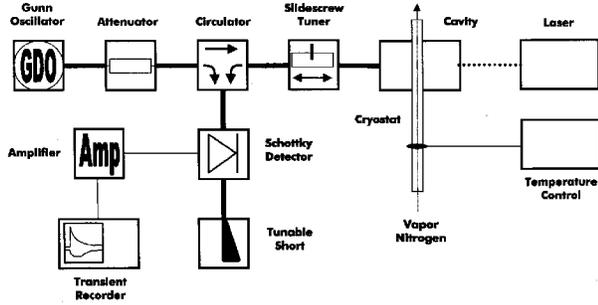
Figure 2. Block diagram of X-Band MWA equipment

The typical microwave incident on the cavity is 50 mW. The cavity quality factor is between 800 and 1000, resulting in a time resolution of 100 ns. Sample cooling was performed with vapor nitrogen in the range between 100 K and 300 K.

The samples were illuminated with a nitrogen/dye laser equipment. The nitrogen laser is emitting at 337 nm. It was used to pump a dye laser with a pulse width of 800 ps. The wavelength was 400 nm for AgCl samples and 440 nm for AgBr samples.

Data Analysis

The photoelectron decay curves were fitted with a sum of two exponentials:

$$n(t) = n_1 \exp(-t/\tau_1) + n_2 \exp(-t/\tau_2) \tag{1}$$

The lifetime τ is related to the activation energy E_A of the trapping process by Boltzmann's equation

$$\tau = \tau_0 \exp\left(\frac{-E_A}{kT}\right) \tag{2}$$

where k is Boltzmann's constant and T is the temperature. Therefore, the activation energy E_A can be calculated as

$$\frac{E_A}{k} = -\frac{d(\ln \tau)}{d(1/T)} \tag{3}$$

by plotting the photoelectron lifetimes in Arrhenius diagrams. The typical error margin of E_A is $\pm 10\%$.

Results and Discussion

Pure Silver Chloride Emulsion Grains

For the surveyed temperature region the decay curves usually consisted of two regions with different first order decay kinetics. Fig. 3 shows the corresponding photoelectron lifetimes τ_1 and τ_2 for pure silver chloride emulsion grains, plotted in an Arrhenius diagram. The values for 300 K were measured using a phase sensitive Q-band equipment.
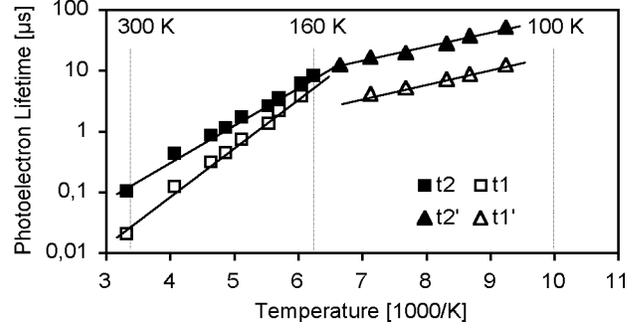
Figure 3. Arrhenius plot of photoelectron lifetimes τ_1, τ_2, τ_1' and τ_2'; measured at pure silver chloride emulsion grains

At temperatures between 300 K and 160 K both lifetimes are increasing significantly with decreasing temperature. In this temperature range the following activation energies E_1 and E_2 can be calculated from the slopes of τ_1 and τ_2, respectively:

$$E_1 = 150 \ meV$$
$$E_2 = 120 \ meV$$

According to our model, E_1 is the activation energy for the shallow trapping of photoelectrons by silver ions in surface kink sites, whereas E_2 is the activation energy for the subsequent reaction of the trapped electron with interstitial silver ions.

At temperatures between 300 K and 160 K the slope of τ_1 is larger than that of τ_2. Therefore, the relative distance between τ_1 and τ_2 is decreasing with decreasing temperature. At 160 K τ_1 and τ_2 can not be distinguished. This indicates that the photoelectron decay is determined by only one trapping process at 160 K. It is unlikely that silver interstitial ions are involved in this trapping process, because the concentration of silver interstitials is decreasing with decreasing temperature. Thus, in accordance with our model this trap could be interpreted as a silver ion in a surface kink site. It is considered, that this trap is a shallow electron trap at room temperature but a deep electron trap at temperatures below 160 K.

In fig. 4 the decay curve signal intensity is plotted versus the temperature. At temperatures between 200 K and 150 K the signal intensity is decreasing with decreasing temperature. For lower temperatures the signal intensity is constant. It has been shown that the signal intensity is decreased by the introduction of deep electron traps.[4] Therefore, it could be considered that the observed decrease of the signal intensity with decreasing temperature is due to deep electron trapping.

For temperatures below 160 K the decay characteristic is changing significantly. As fig. 3 shows, in this temperature range the photoelectron lifetime τ_2' and for temperatures below 140 K also the lifetime τ_1' were found. The photoelectron lifetime τ_1' is about ten times faster than τ_2'. Both lifetimes are increasing only slightly with decreasing temperature. From the slopes of τ_1' and τ_2' the following activation energies for the corresponding trapping processes were calculated.

$$E_1' = 45\ meV$$
$$E_2' = 45\ meV$$

At the moment, it is not clear why these activation energies are smaller than those calculated for higher temperatures. The small signal intensity, shown in fig. 4, indicates a deep electron trapping process. However, the nature of this process has not been clarified, yet.
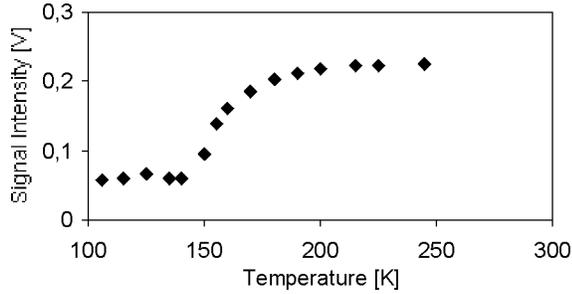
Figure 4. Signal intensity versus temperature; measured at pure silver chloride emulsion grains

Chemically Ripened Silver Chloride Emulsion Grains

For chemically ripened AgCl grains the same decay characteristics as for pure AgCl grains were found. In fig. 5 the photoelectron lifetimes τ_1, τ_2, τ_1' and τ_2' are plotted in an Arrhenius plot.
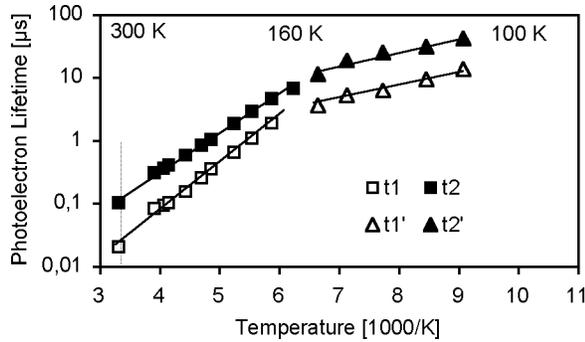
Figure 5. Arrhenius plot of photoelectron lifetimes τ_1, τ_2, τ_1' and τ_2'; measured at chemically ripened AgCl grains

For temperatures between 300 K and 160 K the following activation energies were calculated:

$$E_1 = 140\ meV$$
$$E_2 = 120\ meV$$

Both activation energies are slightly smaller than those obtained for pure silver chloride emulsion grains. This could be explained with the ripening centers, which are additional electron traps.

For temperatures below 160 K the same activation energies as for pure AgCl emulsion grains were calculated:

$$E_1' = 45\ meV$$
$$E_2' = 45\ meV$$

Silver Chloride Emulsion Grains with Stabilizer

The photoelectron lifetimes obtained for AgCl grains with stabilizer PMT are shown in fig. 6.
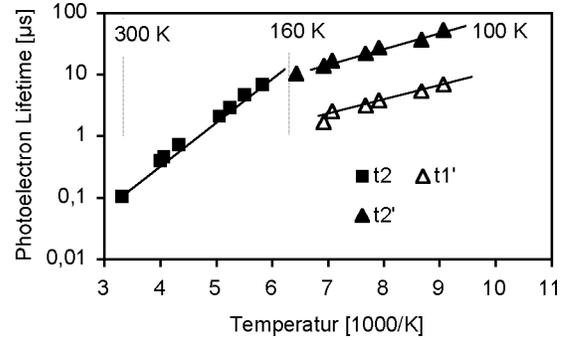
Figure 6. Arrhenius plot of photoelectron lifetimes τ_2, τ_1' and τ_2', measured at silver chloride grains with stabilizer PMT

At temperatures between 300 K and 160 K only the lifetime τ_2 could be evaluated. As the preexponential factor n_1 (see eq. 1) of the fast process was too small, the lifetime τ_1 could not be analyzed. From the slope of τ_2 the following activation energy was calculated:

$$E_2 = 140\ meV$$

This value is slightly higher than that calculated for pure AgCl grains. Most probably this is due to the fact that PMT is stabilizing silver ions in surface kink sites. Thereby, the concentration of interstitial silver ions is decreased and the activation energy for the trapping process is increased.

At temperatures below 160 K both lifetimes τ_1' and τ_2' were found, as shown in fig. 7. From these values the following activation energies were calculated:

$$E_1' = 45\ meV$$
$$E_2' = 45\ meV$$

These values are the same as those calculated for pure and chemically ripened AgCl grains. This indicates that at temperatures below 160 K the photoelectron decay is determined by intrinsic electron traps.

Silver Chloride Emulsion Grains Doped with [Rh(CN)$_6$]$^{3-}$

The photoelectron lifetimes measured at AgCl grains doped with [Rh(CN)$_6$]$^{3-}$ ions are shown as Arrhenius plots in fig. 7.

The lifetimes τ_1 and τ_2 are about ten times higher than those measured at pure silver chloride grains. It has been reported by many authors that Rh(CN)$_6$ ions are shallow electron traps, which are increasing the photoelectron lifetime. From the slopes of τ_1 and τ_2 we calculated the following activation energies:

$$E_1 = 160\ meV$$
$$E_2 = 160\ meV$$
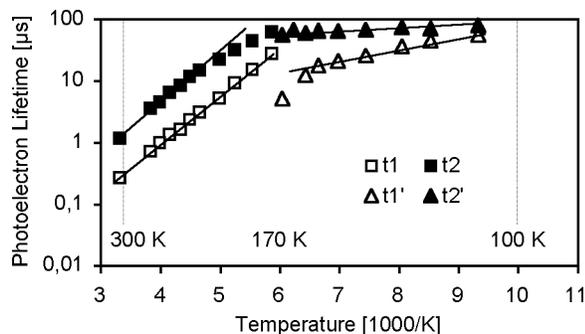
Figure 7. Arrhenius plot of photoelectron lifetimes τ_1, τ_2, τ_1' and τ_2', measured at silver chloride grains doped with $Rh(CN)_6$ ions

Compared with the values calculated for pure AgCl grains, E_1 is slightly higher, whereas E_2 is significantly higher. The increase of both activation energies is considered to be due to the fact that the mobility of photoelectrons is decreased by shallow electron traps.[4]
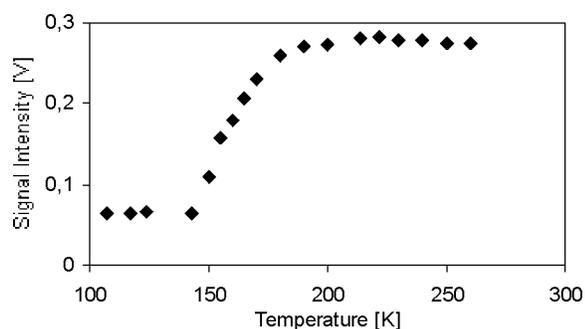
Figure 8. Signal intensity versus temperature, measured at silver chloride grains doped with $Rh(CN)_6$ ions

At temperatures below 170 K the photoelectron lifetime τ_2' is nearly constant, whereas τ_1' is increasing slightly with decreasing temperature. From the slopes of τ_1' and τ_2' we calculated the following activation energies:

$$E_1' = 40\ meV$$
$$E_2' = 6\ meV$$

Fig. 8 shows the signal intensities of the decay curves, plotted against the temperature.

At temperatures between 200 K and 160 K the signal intensity is decreasing with decreasing temperature. At lower temperatures the signal intensity is constant. This indicates that at temperatures below 160 K the photoelectron decay is determined by a deep electron trapping process. However, the nature of this trapping process has not been clarified, yet.

A model for the decay kinetics at deep temperature will be presented.

Acknowledgements

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