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Investigation of the photoelectron decay of silver halide microcrystal*

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The microwave absorption dielectric spectrum can be used to study the decay process of free photoelectrons and shallow-trapped electrons in semiconductor crystals. The decay curve of free photoelectrons and shallow-trapped electrons of silver halide grains is measured using this technique. The influence of iodide and $K_4Fe(CN)_6$ shallow electron trap dopants on the photoelectron lifetime of silver halide grains is studied. For the unsensitized cubic AgCl crystals, when the free photoelectron lifetime (FLT) reaches a maximum, the photographic efficiency is optimal. From our analysis, we conclude that FLT is the longest for the cubic AgCl crystals doped with 0.5% iodide at 80% doping position and 1×10^{-6} mol $K_4Fe(CN)_6$/molAg, whereas, for the highly photosensitized cubic AgBrCl crystals doped with $K_4Fe(CN)_6$, the photographic efficiency is optimal when the FLT reaches its minimum. The free photoelectron lifetime reaches minimum and the sensitivity of AgBrCl emulsion reaches maximum when the doping position is 30%Ag at $K_4Fe(CN)_6$ content of 10^{-6}mol/molAg.

Keywords: silver halide microcrystal, microwave absorption dielectric spectrum, photoelectron lifetime

PACC: 7120, 5225M

1. Introduction

The photoelectron decay characteristic in the latent image formation process directly reflects the photographic efficiency of silver halide crystals. The generation of photoelectrons is the basis of latent image formation, so photoelectron action is an important factor in the photographic efficiency and has attracted the attention of many researchers.[1−4,6−9] The measurement of photoelectron decay in the image process using the microwave absorption technique (MWA) can provide important information about the electronic properties of latent image formation. [1,3,7] Beutel first developed the microwave absorption technique,[2] with which information of the electronic properties and detailed steps in the photochemistry can be observed. Müssig improved this method by introducing the microwave phase separation technique, and measured the influence of grain shape, iodide adulteration, heterostructures and dye sensitization of trimethinthiocyanin (red) on the lifetimes of electrons in cubic grains.[1,3] Kellogg studied the influence of gold sensitization, sulfur-plus-gold sensitization and spectral sensitization on the lifetime of the free photoelectron in cubic silver halide grains.[1] Kaneda studied the effect of the electron trap on photoelectrons in cubic silver halide grains.[2] Belloni *et al* found that dopants such as formate (HCO_2^-) can trap free holes effectively and thus prevent recombination between trapped electrons and silver halide grains, so the photosensitivity can be improved tenfold.[5] However, may be limited by experiment instruments, these researchers only studied the photoelectron transportation in the process of the latent image formation, but the kinetic mechanism of the photoelectron decay properties has never been discussed. Because the photoelectron generating time of sensitized crystals is of the order of ns, the ultrashort pulse laser is necessary for the latter purpose. In this work, a YAG laser system with pulse width of 35ps is used as the exposure light.[10−12]

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In this paper, using microwave absorption dielectric spectrum equipment with a high time-resolution less than 1ns, the decay curves of the free photoelectrons and the shallow-trapped electrons are obtained accurately, and the influence of iodide and $K_4Fe(CN)_6$ dopants on the photoelectron action of silver halide grain is analysed.

2. Experimental principle and equipment

The principle of microwave absorption dielectric spectrum equipment has been shown in Ref.[10]. A film sample is inserted into a microwave cavity at the position where the electric field is a maximum and is exposed to a 35 ps YAG pulse laser. Because free and shallow-trapped electrons are generated in the sample, imaginary parts and real parts of the susceptibility tensor are changed. The change of the complex susceptibility is detected as the power absorption of the sample. Normally the variation of imaginary parts and real parts of the complex susceptibility tensor of the sample change the response signal of the cavity. Real parts of reflected signal are correlated to free photoelectrons, whereas imaginary parts are correlated to shallow-trapped electrons. A phase-sensitive detection system including two frequency mixers would separate both parts. To examine the influence of free electrons and shallow-trapped electrons on the recombination processes of the photoelectrons due to sensitization specks on the crystal surface, an extremely high time resolution of about 1 ns is necessary. The time resolution in the phase- sensitive detection system of our equipment is less than 1 ns. Because the light absorption process and the photoelectron decay process of some AgX crystals are about several ns, the 35 ps YAG pulsed laser is applicable. By analysing the free electron signal and the shallow- trapped electron signal, we obtain the photoelectron action and its influence on the latent image formation. The signals are amplified by an SR440 amplifier and displayed by a TDS3052 digital storage oscilloscope.

3. Results and discussion

A long free photoelectron lifetime (FLT) can improve the photographic efficiency of intrinsic or unsensitized grains but reduces the photographic efficiency of highly photosensitized grains.[3,4] In general, the AgBr and AgCl are intrinsic or unsensitized emulsions, but the AgBrCl is a highly photosensitized emulsion.

In this work, we measure the photoelectron behaviour of intrinsic cubic AgCl grains and the highly photosensitized AgBrCl grains. We calculate the free photoelectron lifetime (FLT) and the shallow- trapped electron lifetime (SLT). Photoelectron lifetime τ is estimated from semilogarithmic plots of the photoelectron decay curves corresponding to

$$\tau = -\mathrm{d}t/\mathrm{d}\{\ln(V/V_0)\}, \qquad (1)$$

where V is the photoelectron signal intensity, and V_0 is the maximum photoelectron signal intensity.

The shallow electron traps (SETs) can hold the free photoelectrons temporarily and release them at the proper moment in the positions of latent subimages to form developable latent images, so the SETs can reduce the recombination and improve the efficiency of the latent image formation. Therefore, some dopants such as iodide and $K_4Fe(CN)_6$ can be used as shallow electron-trap dopants to improve photographic efficiency.[3,4,13–17]

3.1. Influence of iodide doping position on photoelectron properties of cubic AgCl crystals

The influence of the content and distribution of iodide in AgX crystals on sensitivity has attracted the attention of researchers.[3,4] The change of the interior structure in AgX grains introduced by doping iodide will result in the change of the chemical and physical characteristics of the grain surface and the change of the position and distribution of sensitive specks, so the latent image speck formation, the fog formation and the photographic efficiency of the crystals will be ultimately affected. In Fig.1 typical electron decay curves are shown for a cubic AgCl crystals doped with 0.5% iodide at 60% doping position. The free photoelectron decay curve is given in Fig.1(a). A maximum of the free photoelectron density appears at 2–3 ns after exposure, and is followed by an exponential decay. The shallow-trapped electron decay curve is given in Fig.1(c). A maximum of the shallow-trapped electron density appears at 4–5 ns after the exposure, and also followed by an exponential decay. From the semilogarithmic plot, like that shown in Fig.1(b) for the free photoelectron, lifetimes can be estimated (Table 1). The temporal behaviour of the photoelectron includes the photoelectrons being trapped by electron trap, recombination with holes, and the electron capture involved in the silver cluster formation, so the free photoelectron lifetime reflects the information of

the latent image formation process.

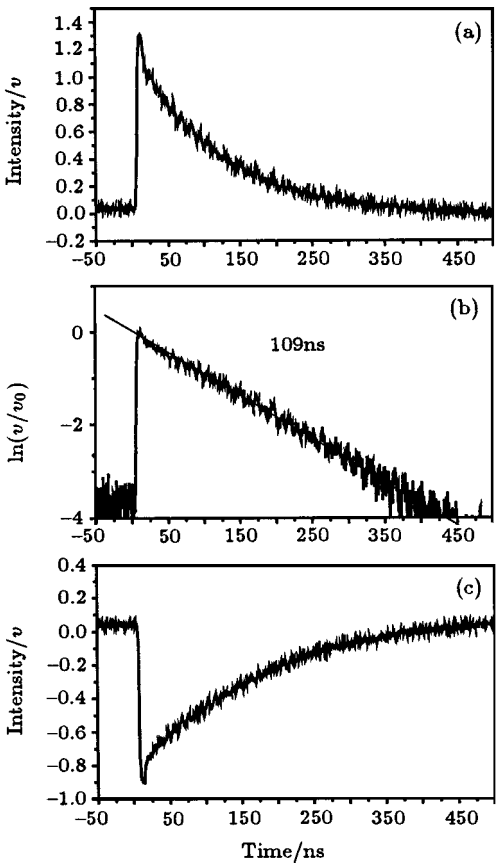


Fig.1. Photoelectron decay curves of cubic AgCl crystals doped with 0.5% [I^-] at 60% doping position: (a) free electron signal (b) semilogarithmic plot of free electron signal (c) shallow-trapped electron signal.

Figure 2 shows a comparison of photoelectron decay curves for three crystals doped with 5% iodide at different doping positions. We use the term "doping position" to label the doping time. It is defined by the percentage of the silver content at the beginning of the doping related to its final content in the matured crystal. So the larger the value of the doping position, the nearer the dopant is to the surface. It can be seen that the photoelectron generation time is the same but the decay time is different for the AgCl crystals at different doping position. The initial decay for the crystals at 70% doping position is slower than that of the other two. This indicates that a large amount of shallow electron traps are generated at this doping position just after exposure. But the subsequent decay at the 70% doping position is as slow as that at the 60% doping position, although faster than that at the 80% doping position. This may be due to increased trapping by deep electron traps during the transportation of free photoelectrons to the crystals surface.

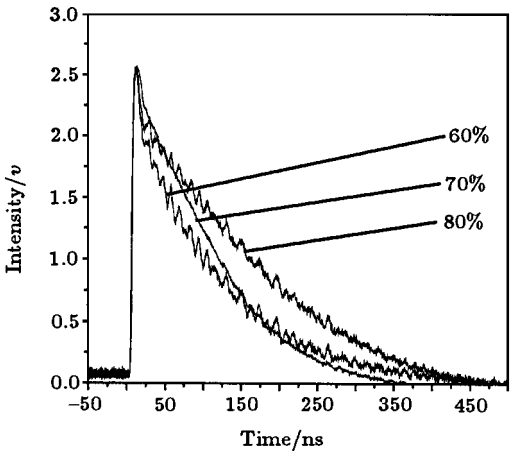


Fig.2. Comparison of free photoelectron decay curves in AgCl cubic grains doped with 0.5%AgI at 60%, 70% and 80% doping position.

In Table 1 the FLT and the SLT are shown. The FLT and SLT of the sample with 80% doping position are longer than the others. The reason may be that the nearer is the [I^-] to the surface, the higher the density of hole traps and the lower the recombination rate of electron and hole. With regard to the 70%Ag doping position, the short FLT indicates that iodide restricts the effect of SETs and so spoils the efficiency of latent image formation. The reasons may be the following: firstly, the trapping rate for the holes by iodide and the trapping rate for the photoelectrons by SETs are very high at the 70%Ag doping position, so the recombination rate between the holes and the photoelectrons is very high too; in addition, [I^-] occupies the positions of [Cl^-] and prevents the formation of SETs at these positions. This is in good agreement with the conclusions obtained by other authors.[16]

Table 1. Decay properties for cubic AgCl crystals with 0.5% iodide at different doping positions.

Iodide/(%Ag)	60	70	80	60 and with 10^{-7} $K_4Fe(CN)_6$
FLT/ns	109	84	142	123
SLT/ns	151	135	178	168

3.2. Influence of $K_4Fe(CN)_6$ on photoelectron properties of cubic AgCl crystals

As a kind of transition metal complex dopant, $K_4Fe(CN)_6$ can form shallow electron traps in AgX crystals. The shallow electron traps can temporarily store electrons. The electron in a shallow trap is not recombined by a hole immediately. The shallow traps are so shallow that they cannot capture the electrons forever. At the appropriate time, the electron can transfer to the latent image conglomeration centre,

and bring about the growth of some sub-latent image centre. In this way, utilization efficiency of photoelectron has been improved.[13–15] Table 1 shows that $K_4Fe(CN)_6$ can lengthen the FLT, so it can be used as a SET dopant to improve the photographic properties of silver halide emulsions.[15,16] By varying the doping amount as shown in Table 2, we can find the optimal doping amount. $K_4Fe(CN)_6$ can lengthen the FLT only when the amount is less than 1×10^{-6}mg/molAg. If the doping amount is beyond 1×10^{-6}mg/molAg the FLT decreases, but is still larger than that of the pure AgCl emulsion. This implies that $K_4Fe(CN)_6$ can preferably improve the photographic properties only when the doping amount is less than 1×10^{-6} mg/molAg. This indicates that $K_4Fe(CN)_6$ of proper concentration is a sort of effective SET dopant. This is in good agreement with the result reported in Ref.[18].

Table 2. Decay properties of cubic AgCl crystals with different $K_4Fe(CN)_6$ doping amount (mol/molAg).

$K_4Fe(CN)_6$	0	5×10^{-8}	1×10^{-7}	5×10^{-7}	1×10^{-6}	5×10^{-6}
FLT/ns	84	115	123	145	158	100
SLT/ns	135	160	170	172	230	200

3.3. Influence of $K_4Fe(CN)_6$ on photoelectron properties of cubic AgBrCl crystals

Figure 3 shows the photoelectron decay curves of highly photosensitized cubic AgBrCl crystals doped with 10^{-6}mol $K_4Fe(CN)_6$/molAg at 30% doping position. The free electron number reaches maximum after 2–3 ns of the laser pulse, and the decay process lasts 6–7 ns. The shallow-trapped electron signal reaches its maximum after 4–5 ns of light absorption and the decay process lasts 11–12 ns. Table 3 shows the relative sensitivity (RS) of AgBrCl emulsion with different $K_4Fe(CN)_6$ doping positions at doping content of 10^{-6}mol/molAg. The RS of AgBrCl emulsion reaches the maximum when the doping position is 30%Ag.

Table 3. The RS of AgBrCl emulsion with different $K_4Fe(CN)_6$ doping position.

Doping position/%	30	75	85	93
RS	114	86	106	100

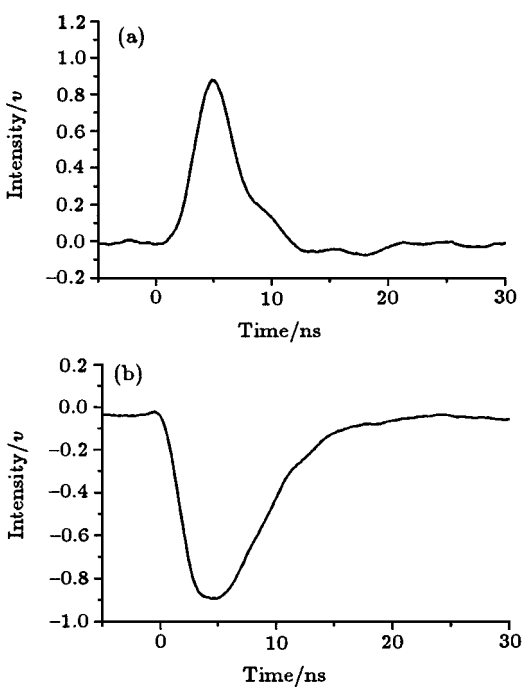


Fig.3. Photoelectron decay curves of cubic AgBrCl crystals doped with 10^{-6}mol $K_4Fe(CN)_6$/molAg at 30% doping position: (a) free electron signal (b) shallow-trapped electron signal.

Figure 4 shows four free photoelectron signal curves of AgBrCl emulsion with different $K_4Fe(CN)_6$ doping positions at doping content of 10^{-6}mol/molAg. The free photoelectron lifetime reaches the minimum when the doping position is 30%Ag. For highly photosensitized AgBrCl emulsion doped with $K_4Fe(CN)_6$, the lower the free photoelectron lifetime, the higher the sensitive efficiency is.

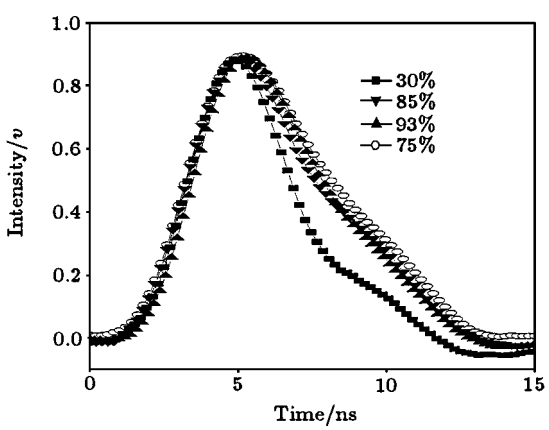


Fig.4. Free photoelectron signal curves of AgBrCl emulsion with different $K_4Fe(CN)_6$ doping position at doping content of 10^{-6}mol/molAg.

4. Conclusions

For the first-maturation cubic AgCl crystals, when the FLT reaches the maximum, the photographic efficiency is optimal. From our experiment and analysis, we conclude that FLT is the longest for the cubic AgCl crystals doped with 0.5% iodide at 80% doping position and 1×10^{-6} mol $K_4Fe(CN)_6$/molAg, whereas, for the cubic AgBrCl crystals doped with $K_4Fe(CN)_6$, when the FLT reaches the minimum, the photographic efficiency is optimal. The free photoelectron lifetime reaches the minimum and the RS of AgBrCl emulsion reaches the maximum when the doping position is 30%Ag at $K_4Fe(CN)_6$ content of 10–6mol/molAg.

References

[1] Kellogg L M 1974 *J. Photogr. Sci. Eng.* **18** 378
[2] Kaneda T 1989 *J. Imag. Sci.* **33** 115
[3] Müssig T 1997 *J. Imag. Sci. Tech.* **41** 118
[4] Müssig T and Hegenbart G 1994 *J. Imag. Sci. Tech.* **38** 526
[5] Belloni J, Treguer M and Hynd R 1999 *Nature* **402** 865
[6] Harada T, Lijima T and Koitabashi T 1982 *J. Photogr. Sci. Eng.* **26** 137
[7] Hasegawa A and Sakaguchi T 1986 *J. Imaging. Sci.* **30** 13
[8] Ehrllch S H 1994 *J. Imag. Sci. Tech.* **38** 201
[9] Beutel J 1975 *J. Appl. Phys.* **46** 4649
[10] Yang S P, Li X W, Han L and Fu G S 2002 *Chin. Phys. Lett.* **19** 429
[11] Fu G S, Yang S P, Li X W, Han L, Hu X Y, Sun Y C and Ma L Q 2002 *J. Photogr. Sci. Photochem.* **20** 60 (in Chinese)
[12] Dong G Y, Li X W, Wei Z R and Yang S P 2003 *Acta. Phys. Sin.* **52** 745 (in Chinese)
[13] Research Disclosure 1994 *November* **367** Item 36736R
[14] Bryant R A, Olm M T and Fenton D E 1998 *US patent* **5** 728 517
[15] Mydlarz Z G, Budz J A and Bell E L 1998 *US patent* **5** 783 373
[16] Dai H, Liang B, Zhuang S Y and Zhang D D 2002 *Inform. Record. Mater.* **1** 20 (in Chinese)
[17] Hua J P, Callens F, Cardon F and Vandenbroucke D 2000 *J. Phys. D: Appl. Phys.* **33** 574
[18] Dai H and Liang B 2001 *J. Photogr. Sci. Photochem.* **19** 262 (in Chinese)