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The influence of $K_4Fe(CN)_6$ on the photosensitivity of cubic AgCl microcrystal*

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The influence of $K_4Fe(CN)_6$ at various doping concentrations on the photosensitivity of cubic AgCl microcrystals has been investigated by using the microwave absorption and phase-sensitive measurement technique. The time behaviour of free photoelectrons in AgCl microcrystals is analysed by using computer simulation as a function of three parameters of shallow electron trap (SET) including doping concentration, trap depth and capture cross-section (CCS). It is found that the three parameters of SET play different roles on the free photoelectron decay time (FDT). After considering the threshold effects of the three parameters and their collective effects, the trap depth value, the CCS value, and the optimal doping concentration of the SET introduced by the dopant $K_4Fe(CN)_6$ in cubic AgCl microcrystals can also be determined, and the best photosensitivity of cubic AgCl can be obtained.

Keywords: shallow electron trap, photosensitivity, trap depth, doping concentration, capture cross section

PACC: 7220J, 8250, 4270G

1. Introduction

Silver halide microcrystals have been widely used as a kind of photographic material in some fields such as photography, optical information disposal, biology, medicine, military affairs, chemical industry, and navigation, etc. The photographic property of the crystals has been studied extensively.[1−5] It is well known that photosensitivity is dominated by the formation efficiency of latent images which are formed when free photoelectrons combine with the interstitial silver ions. The formation process of latent images consumes free photoelectrons, simultaneously accompanied by other ineffective processes of free photoelectrons, such as the recombination with trapped holes, the permanent trap by deep traps, and the participation of free photoelectrons in the formation of sub-latent images. These ineffective processes lead to a faster decay of photoelectrons and hence reduce the free photoelectron decay time (FDT) defined as the time during which the free photoelectrons decay from 90% of the maximum to 10%. Recently, it has been found that the shallow electron trap dopant, a kind of metal dopant, can increase photosensitivity effectively.[6,7] For a pure silver halide microcrystal, shallow electron traps (SETs) can store photoelectrons temporarily so that the recombination of free photoelectrons and trapped holes can be prevented effectively, and the diffusing velocity can be decreased. Furthermore, it can enhance the probability of the combination of photoelectrons and interstitial silver ions and thus increase the formation efficiency of latent images. Finally, the FDT will be lengthened. Thus, it is believed that a longer FDT is related to a better photosensitivity. In this paper $K_4Fe(CN)_6$ is chosen as a SET dopant and its influence on the FDT of AgCl microcrystals is studied both experimentally and theoretically using microwave absorption phase-sensitive technique and computer simulation. From such a study the effect of $K_4Fe(CN)_6$ on the photosensitivity of AgCl microcrystals can be obtained. Besides, for the given dopant, the trap depth and capture cross-section (CCS) of the introduced SET is fixed. According to the rules of the influence and the experimental result, the trap depth

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and CCS values of the SET introduced by $K_4Fe(CN)_6$ and the optimal doping concentration to obtain the best photosensitivity can be determined.

2. Experimental result and analysis

A microwave absorption and phase-sensitive measurement technique is utilized in our experiment; the experimental detail has been described in Ref.[9]. The pure cubic AgCl emulsion (used as the reference emulsion) was grown by a double-jet precipitation at room temperature. The average edge length of microcrystals was 0.70μm. The pure cubic AgCl emulsion was homogeneously doped with $K_4Fe(CN)_6$ at the same temperature. The doping concentrations were taken to be 0.05, 0.10, 0.50, 1.00, 5.00ppm.

Table 1. The variation of the experimental FDT with the doping concentration.

Doping concentration/ppm	0.00	0.05	0.10	0.50	1.00	5.00
FDT/ns	197	212	232	250	270	205

It can be seen from Table 1 that the FDT of the doped emulsion is always longer than that of the reference emulsion, indicating that the dopant $K_4Fe(CN)_6$ does introduce SET in AgCl and does increase the photosensitivity of the emulsion. In addition, FDT shows an increase from 197 to 270ns when the doping concentration increases to 1.00ppm, while it drops to 205ns when it reaches 5.00ppm, which shows that there exists a concentration threshold. The increase of FDT is due to the effect of SET. As doping concentration becomes higher, which means a higher density of SET, the detrapped photoelectrons from a trap will be immediately captured by another nearby trap. Thus the average time for photoelectrons staying in traps will become longer. It seems from the total effect that the trap is deepened, and the escaping of photoelectrons from the trap due to thermal excitation becomes more difficult, and needs a longer time. Here the concentration of shallow-trapped photoelectrons becomes relatively high, while that of free photoelectrons becomes low. The free photoelectrons wasted in ineffective processes reduce. The ultimate fate of the shallow-trapped photoelectrons is to combine with interstitial silver ions to form latent images. So the increase of SET concentration can lengthen the FDT and improve the formation efficiency of latent images. However, when the concentration is above the threshold, the trap will behave as a deep electron trap (DET) in effect, which will permanently trap the photoelectrons and lead the FDT to decrease. All these show that proper increase of the doping concentration can improve the photosensitivity, but it cannot be unlimitedly improved because of the threshold effect.

3. Theoretical analysis

3.1. Theory

Based on the kinetic theory, a model is proposed by analysing the movement behaviour of photoelectrons in silver halide crystal.[10] This model yields the following set of coupled differential equations:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = G - \frac{\mathrm{d}n_{\mathrm{e1}}}{\mathrm{d}t} - \frac{\mathrm{d}n_{\mathrm{e2}}}{\mathrm{d}t} - \kappa_{\mathrm{r}} p_{\mathrm{r}} n - \frac{\mathrm{d}n_{\mathrm{s}}}{\mathrm{d}t}, \tag{1}$$

$$\frac{\mathrm{d}n_{\mathrm{e1}}}{\mathrm{d}t} = \beta_{\mathrm{e1}}(N_{\mathrm{e1}} - n_{\mathrm{e1}})n - \beta_{\mathrm{e1}} N_{\mathrm{c}} n_{\mathrm{e1}} \exp\left(-\frac{\Delta E_{\mathrm{e1}}}{kT}\right), \tag{2}$$

$$\frac{\mathrm{d}n_{\mathrm{e2}}}{\mathrm{d}t} = \beta_{\mathrm{e2}}(N_{\mathrm{e2}} - n_{\mathrm{e2}})n - \beta_{\mathrm{e2}} N_{\mathrm{c}} n_{\mathrm{e2}} \exp\left(-\frac{\Delta E_{\mathrm{e2}}}{kT}\right), \tag{3}$$

$$\frac{\mathrm{d}n_{\mathrm{s}}}{\mathrm{d}t} = \beta_{\mathrm{s}}(N_{\mathrm{s}} - n_{\mathrm{s}})n - \beta_{\mathrm{s}} N_{\mathrm{c}} n_{\mathrm{s}} \exp\left(-\frac{\Delta E_{\mathrm{s}}}{kT}\right), \tag{4}$$

$$\frac{\mathrm{d}p_{\mathrm{r}}}{\mathrm{d}t} = \rho_{\mathrm{r}}(P_{\mathrm{r}} - p_{\mathrm{r}})p - \rho_{\mathrm{r}} N_{\mathrm{v}} p_{\mathrm{r}} \exp\left(-\frac{\Delta E_{\mathrm{r}}}{kT}\right) - \kappa_{\mathrm{r}} p_{\mathrm{r}} n, \tag{5}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = G - \left(\frac{\mathrm{d}p_{\mathrm{r}}}{\mathrm{d}t} + \kappa_{\mathrm{r}} p_{\mathrm{r}} n\right), \tag{6}$$

where n and p are the densities of free electrons and holes on the conduction and valence bands, respectively; n_{e1}, n_{e2}, n_{s} and p_{r} are the trapped electron densities in the two intrinsic electron traps, the SET and the trapped hole density in the trapped-hole free-electron (THFE) recombination centre, respectively. N_{e1}, N_{e2}, N_{s} and P_{r} are the densities of these centres, respectively. G is the formation rate of free-electron–hole pairs due to illumination; k is the Boltzmann's constant and T is the absolute temperature (300K). β_{e1}, β_{e2}, β_{s}, κ_{r}, ρ_{r} are the trapping rate constants of the two intrinsic electron traps and SET, the rate constants for hole trapping and the recombination with a free electron in the intrinsic THFE recombination centre. ΔE_{e1}, ΔE_{e2}, ΔE_{s}, and ΔE_{r} are their trap depths. N_{c} and N_{v} are the effective densities of states of conduction and valence band, respectively.

The trapping, detrapping, and recombination processes of photoelectrons are described by this set

of equations. By solving the above six equations with computer, the relationships of SET doping concentration, trap depth, CCS with FDT can be obtained, which reflect the influence of SET on photosensitivity. The intrinsic parameters of the pure AgCl used to solve the equations are listed in Tables 2 and 3.

Table 2. The trapping parameters of the three intrinsic centres.

Parameter	Electron trap 1	Parameter	Electron trap 2	Parameter	THFE recombination centre
N_{e1}/cm^{-3}	6.08×10^{16}	N_{e2}/cm^{-3}	4.22×10^{17}	P_r/cm^{-3}	3.89×10^{17}
S_{e1}/cm^2	9.92×10^{-18}	S_{e2}/cm^2	2.56×10^{-19}	S_{rh}/cm^2	4.32×10^{-19}
$\Delta E_{e1}/eV$	0.20	$\Delta E_{e2}/eV$	0.50	S_r/cm^2	2.88×10^{-20}
				$\Delta E_r/eV$	0.50

Table 3. The basic intrinsic parameters in cubic AgCl microcrystals.

Parameter	T/K	$G/(cm^{-3}s^{-1})$	N_c/cm^{-3}	N_v/cm^{-3}
Value	300	2.857×10^{22}	7.075×10^{18}	2.244×10^{21}

3.2. Simulation result and analysis

Given a CCS of SET, the variation of FDT curves with the trap depth at different concentrations are shown in Fig.1. While Fig.2 shows the variation of FDT curves with CCS and trap depth when the concentration is given.

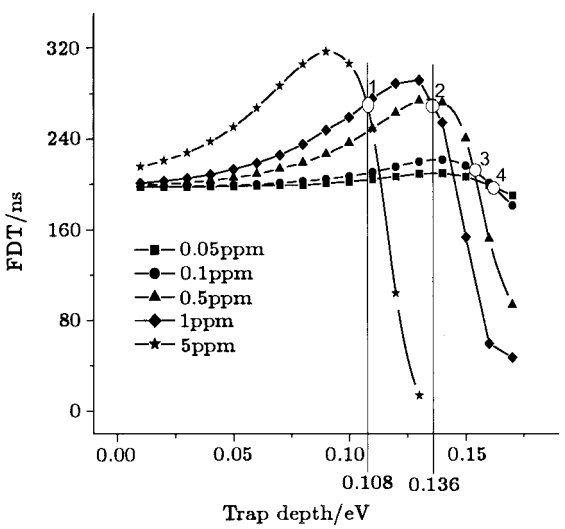


Fig.1. The variation of FDT curves with SET depth at different doping concentrations.

A. The influence of trap depth We can see from Fig.1 that FDT reaches the peak value at a shallower trap depth when the doping concentration is higher, while the peak value emerges at a deeper trap depth when CCS is larger, as shown in Fig.2, which indicates that the trap depth of SET has a threshold at which the FDT is the longest for a certain concentration or CCS, and that different concentration and CCS give different trap depth threshold. As the analysis in Section 2, a higher doping concentration is actually equivalent to a deeper effective trap depth, which leads the depth threshold to decrease with doping concentration, as shown in Fig.1. Because a larger CCS is equivalent to a shallower effective trap depth, the trapped photoelectrons escape from a SET more easily when CCS is larger. Then the free-photoelectron concentration will increase, which will enhance the probability of the occurrence of the ineffective processes. The free photoelectrons will reduce quickly, and the FDT will also decrease. Therefore, it needs a deeper trap depth for a larger CCS to gain the longest FDT, indicating that a larger CCS corresponds to a larger trap depth threshold. The FDT of a certain concentration or CCS keeps increasing with the trap depth before the depth threshold is reached, and decreasing after it. The depth threshold is the boundary of SET and DET for different doping concentrations or CCS. It is well known that SET lengthens FDT, and DET shortens FDT. Because FDT reflects photosensitivity, from the analysis of trap depth threshold effect on FDT we can conclude that a relatively shallower electron trap results in a better photosensitivity at higher doping concentrations, and a better photosensitivity can be obtained at a proper depth of the trap and a larger CCS.

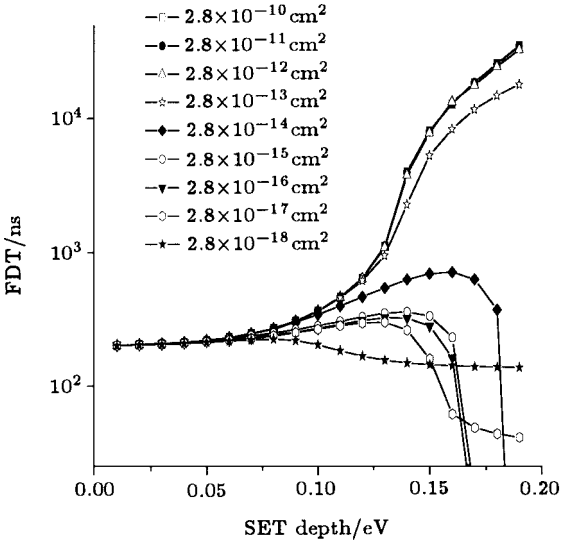


Fig.2. The variation of FDT curves with SET depth at different SET CCS.

B. The influence of concentration The influence of doping concentration can be analysed from the changes of FDT versus doping concentration in different trap depth ranges between the FDT intersection points of two contiguous concentration curves, i.e. in the ranges from 1 to 2, 2 to 3, and 3 to 4, as shown in Fig.1. We can see that the FDT has the tendency of rising up at first and then running down with the doping concentration at a certain trap depth, which indicates that there exists a doping concentration threshold for the SET at a certain depth. This result is in good agreement with the experimental data. Besides, by comparing the three ranges we can also draw the conclusion that the concentration threshold decreases with increasing depth, which in effect can be explained by the corresponding relation between the doping concentration and trap depth. Therefore, for a deeper SET, the longest FDT as well as the highest photosensitivity can be obtained under the condition of lower concentration; for a shallower SET, we need a higher doping concentration to obtain the longest FDT and the highest photosensitivity.

C. The influence of CCS The influence of CCS is obtained from analysing Fig.2. By considering the corresponding relation between the CCS and trap depth, a deeper depth corresponds to a smaller effective area of the CCS, which leads the CCS threshold to increase with increasing trap depth. When the concentration and trap depth remain unchanged, FDT lies within several hundred ns (the range of the experimental result), and the trap depth is smaller than the depth threshold (namely, the trap is still a SET in effect), the FDT almost does not change with CCS. So the influence of the CCS of SET on FDT as well as on the photosensitivity is not great; within 0.07–0.15eV (the defined depth range of SET), the FDT curves generally goes up with enlarged CCS. This indicates that given a doping concentration and trap depth, a larger CCS is corresponding to a higher photosensitivity.

4. Obtaining the best photosensitivity

The final aim of our study is to gain the best photosensitivity. The method to accurately realize this end is provided in the following two paragraphs. Meanwhile, the trap depth and the CCS values of the SET related to $K_4Fe(CN)_6$ concentration are obtained, and the optimal doping concentration value is determined.

From the above theoretical analysis, we can see that the longest FDT can be obtained under a certain doping concentration or CCS when the trap depth reaches the threshold. So the trap depth threshold is the optimal trap depth for obtaining the best photosensitivity. Likewise, the thresholds of doping concentration and CCS are the optimal concentration and CCS. But, considering the three factors together, we find that when the concentration and CCS reach their thresholds, the trap depth does not necessarily reach the threshold. So the thresholds of doping concentration, trap depth and CCS are not all necessarily the optimal. As the three factors affect one another, in order to gain the longest FDT and the best photosensitivity, the three factors must be adjusted according to the rules derived in the above so that the optimal values of the three parameters are determined. However, for a given dopant, the trap depth and CCS of the introduced SET are fixed. As long as the values of the two parameters are determined by fitting the simulated result to the experimental, the optimal concentration can be obtained by adjustment.

In Fig.1, the range between the two vertical lines corresponds to the experimental result within which the FDT goes up when the concentration ranges from 0.05 to 1.00ppm and runs down when it is 5.00ppm. Thus the approximate range of trap depth is 0.108–0.136eV. As shown in Fig.2, when the trap depth is out of the range between 0.07 and 0.15eV (the defined trap depth range of SET), the free photoelectron decay still increases when the CCS is larger than $10^{-13}cm^2$, while the decay decreases continu-

ously when the CCS is smaller than 10^{-18}cm^2. Because these two cases are impossible in fact, they cannot be used. Thus the range of CCS is chosen between 10^{-17} and 10^{-14}cm^2. Within 10^{-17}–10^{-14}cm^2, the CCS is adjusted as shown in Fig.3. We can see from Fig.3 that the experimental value is within the range from 10^{-17} to 10^{-16}cm^2. Then within this more accurate range of CCS and the trap depth range, the trap depth and the CCS are adjusted as shown in Fig.4 according to the rules obtained from the above theoretical analysis. As can be seen in Fig.4, the theoretical curve is fitted to the experimental values quite perfectly when the trap depth is 0.1115eV and the CCS is 1.41×10^{-17}cm^2. Therefore, the trap depth and the CCS values of the SET induced by $K_4Fe(CN)_6$ in cubic AgCl crystals are determined. Furthermore, the FDT is the longest when the doping concentration is 2ppm, so the optimal concentration is 2ppm. Now the best photosensitivity can be obtained.

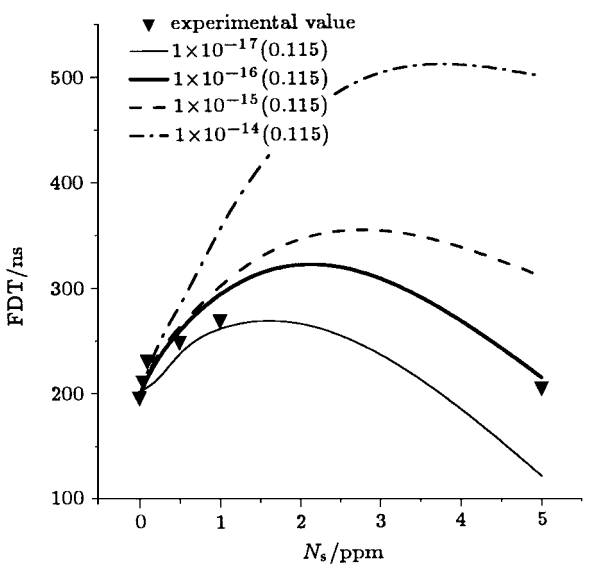


Fig.3. The variation of the FDT with the doping concentration at different CCSs, which are within the range from 10^{-17} to 10^{-14}cm^2.

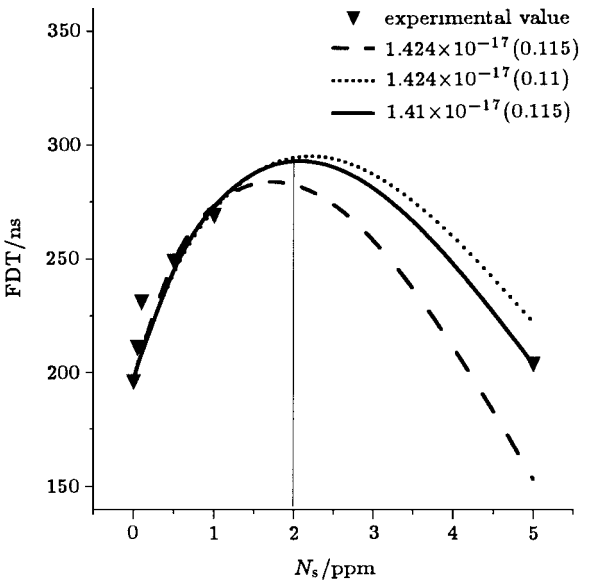


Fig.4. The variation of the FDT with the doping concentration. CCSs is adjusted within 10^{-17}–10^{-16}, and the trap depth is adjusted within 0.108–0.136eV.

5. Conclusion

In this paper, the mechanism for the improvement of the photosensitivity of cubic AgCl microcrystals by adding $K_4Fe(CN)_6$ is analysed, and the features of the influence of doping concentration, trap depth, and CCS of SET on FDT are discussed. On this basis, a method to obtain the best photosensitivity is introduced. The optimal doping concentration of $K_4Fe(CN)_6$ is 2ppm.This theoretically optimal doping concentration can be used to gain the best photosensitivity of AgCl emulsion in practice more quickly and more conveniently. The CCS and trap depth values of SET when introducing $K_4Fe(CN)_6$ in AgCl microcrystals are determined to be 1.41×10^{-17} cm^2 and 0.1115eV, respectively. These two values cannot be obtained merely by the experimental method. They can help us to understand the microscopic mechanism of the SET dopant working on the photographic emulsion and to probe into other properties of the photographic emulsion.

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