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The influence of trapping centres on the photoelectron decay in silver halide*

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Photoelectron is the foundation of latent image formation, the decay process of photoelectrons is influenced by all kinds of trapping centres in silver halide. By analysing the mechanism of latent image formation it is found that electron trap, hole trap, and one kind of recombination centre where free electron and trapped hole recombine are the main trapping centres in silver halide. Different trapping centres have different influences on the photoelectron behaviour. The effects of all kinds of typical trapping centres on the decay of photoelectrons are systematically investigated by solving the photoelectron decay kinetic equations. The results are in agreement with those obtained in the microwave absorption dielectric spectrum experiment.

Keywords: silver halide, electron trap, recombination centre, hole trap
PACC: 7220J, 4270G, 4230, 5225M

1. Introduction

In modern society, photoelectric materials are being used in ever more diverse fields with the development of information technology. Silver halide microcrystals, as a typical photoelectric material, have been used in the photographic process for over 150 years, and much has been understood of their photochemical properties in gelatine emulsions.[1,2] New impetus to study silver halide comes from its kinetics. It is well known that its photographic property is dominated by the formation efficiency of latent images. The formation process of latent images consumes free photoelectrons, and there are also other processes which affect the density of free photoelectrons, including recombination with trapped holes, permanent trap by deep traps, and participation of free photoelectrons in the formation of sub-latent images. Therefore, the decay kinetics of photoelectrons in silver halide plays an important role in the photographic process. The study of the photoelectron kinetics can reveal the microscopic mechanism of the photographic process and provides a new way of studying the photographic property of silver halide. In the early studies of photoelectron kinetics microwave absorption technique was utilized.[3−10] Now, the investigations include the transient microwave photoconductivity (TMP) technique, microwave absorption dielectric spectrum (MADS) technique, and computer simulation. Using TMP and MADS techniques, the decay kinetics of photoelectrons in silver halide can be easily measured. For example, the decay kinetics and the influence of different dopants and sensitizers on the decay process of photoelectrons have been studied using TMP[3−5] and MADS[6−10] techniques. There are also works which utilize computer simulation and TMP, MADS techniques to study the doping effect at low temperatures as well as the shallow electron trap effect at room temperature.[11−17] So far, efforts were focused on investigations in various aspects of the photoelectron behaviours under different conditions and from different perspectives. But there lacks a systematic study of the influence of different trapping centres on the decay process of photoelectrons in silver halide. As a result, we cannot know clearly which kind of trapping centres obviously influences the photoelectron decay under a fixed condition

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and what the mechanism of their actions is. In this paper, with the aid of photoelectron decay microscopic kinetics equations and microwave absorption dielectric spectrum experiment, we investigate the influences of typical trapping centres on the decay kinetics of photoelectrons.

2. Mechanism of latent image formation

The mechanism of latent image formation has always been a central theme in photographic science. According to the Gerry–Mott theory, the process of latent image formation can be described as follows:[18]

Light Absorption $AgX + h\upsilon \rightarrow e^{-*} + h^{+*}$;
Trapping $e^{-*} + T \rightarrow e^{-}$, $h^{+*} + T_h \rightarrow h^{+}$;
Recombination $e^{-*} + h^{+} \rightarrow X$, $e^{-} + h^{+*} \rightarrow X$;
Nucleation $e^{-} + Ag_i^{+} \rightarrow Ag$, $Ag \rightarrow e^{-*} + Ag_i^{+}$,
$e^{-*} + Ag_i^{+} + Ag \rightarrow Ag_2$;
Growth $e^{-*} + Ag_i^{+} + Ag_2 \rightarrow Ag_3$,
$e^{-*} + Ag_i^{+} + Ag_3 \rightarrow Ag_4$,

where e^{-*} and h^{+*} are free photoelectron and free photohole, respectively; e^{-} and h^{+} are trapped photoelectron and trapped photohole, respectively; T and T_h are electron trap and hole trap, respectively; Ag_i^{+} is interstitial silver.

Light absorption of a photon by a silver halide grain creates a free photoelectron in the silver halide conduction band and a free photohole in its valance band. The indirect bandgap and momentum conservation rules prevent the direct recombination of the free photoelectron and free photohole, although they can recombine in other ways, as we will see below.[19] The photoelectron and photohole begin to execute a random walk through the microcrystals. Photoelectron and photohole can be trapped at lattice defect sites, such as kink sites at the surface. Therefore, the free photoelectron becomes a trapped photoelectron after it is trapped by electron trap (i.e. electronic process), and the free photohole becomes trapped photohole after it is trapped by the hole trap. Silver halides are characterized by a high concentration of mobile interstitial silver ions.[19] If a migrating interstitial silver ion encounters a trapped photoelectron (i.e. ionic process), a silver atom forms. However, silver atoms are unstable. If the electronic process and ionic process occur again at this site, a two-atom silver cluster forms. The two-atom silver cluster is considered to be permanently stable,[2] and the process of its formation is called "nucleation" stage. Although being stable, this two-atom silver cluster cannot initiate the development reaction. Thus, if this centre initiates development, additional silver atoms must be formed at this site by the repetition of the electronic and ionic processes. These additional events are called "growth" steps. The number of growth events required to produce a silver cluster that will initiate development depends on the developer and the development conditions,[20] but it is typically three or four.

There are many pathways by which photoelectrons may be lost and inefficiencies in silver cluster formation arise. But the principal one is recombination.[19] There are two types of recombination centres: one near the conduction band, where trapped electrons and free holes are recombined, is referred to as TEFH-recombination centre; the other lying above the valence band, where free electrons and trapped holes are recombined, is referred to as FETH-recombination centre. In silver halide photoholes have lower mobile velocity than photoelectrons, therefore, FETH-recombination centre is the main recombination centre.

From the above analysis, it can be seen that photoelectrons play an important role, that the decay process of photoelectrons can reflect the intrinsic photosensitive process and can influence the photosensitivity. The main trapping centres which affect the decay of free photoelectrons are electron traps (including shallow electron trap and deep electron trap), hole traps, and FETH-recombination centres. They have different effects on the photoelectron behaviour. With the assumption that there is only one kind or some kinds of trapping centres in the silver halide, the equations that describe the kinetics of barriers can be found. By solving the equations using computer simulation,[21] the photoelectron decay curves with different trapping centres can be obtained. In addition, the photoelectron decay curves of different silver halide emulsions can also be obtained by the microwave absorption dielectric spectrum experiment. The experimental setup and the principle have been described in Ref.[9]. Combining the simulated and experimental results, the influences of different trapping centres on the photoelectron decay can be investigated.

3. Influence of trapping centres on the photoelectron decay

3.1. Recombination centre

The influence of FETH-recombination centre on the decay of free photoelectrons can be described by the following equations:

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

$$\frac{\mathrm{d}p_\mathrm{r}}{\mathrm{d}t} = \rho_\mathrm{r}(P_\mathrm{r} - p_\mathrm{r})p - \rho_\mathrm{r} N_v p_\mathrm{r} \exp\left(-\frac{\Delta E_\mathrm{r}}{kT}\right) - \kappa_\mathrm{r} p_\mathrm{r} n, \tag{2}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = G - \left(\frac{\mathrm{d}p_\mathrm{r}}{\mathrm{d}t} + \kappa_\mathrm{r} p_\mathrm{r} n\right), \tag{3}$$

where n and p are the densities of free photoelectrons in the conduction band and free photoholes in the valence band, respectively; p_r is the density of the trapped photoholes in the FETH-recombination centre; G is the formation rate of free electron–hole pairs by illumination; ρ_r and κ_r are the rate constant for trapping hole of recombination centre and the rate constant for recombination between electrons and holes; ΔE_r is the difference of energy levels between recombination centre and valence band; P_r is the density of the recombination centre; k is Boltzmann's constant and T is the absolute temperature (300K); N_v is the effective density of state of the valence band.

Figure 1 shows the simulated result of free photoelectron decays for different densities of recombination centres at both low and high exposure intensities (y-axis is normalized). Here I denotes the exposure intensities. We assume that the hole capture cross section of the recombination centre is much larger than the electron capture cross section. As can be seen, at low intensity the density of recombination centres has little effect on the photoelectron decay, while at high intensity the effect is considerable. This indicates that the recombination centre has stronger trapping ability and affects the decay of free photoelectrons only at high exposure intensity. Van den Eeden *et al*[11] performed the transient microwave photoconductivity experiment of AgCl by adjusting the exposure intensity in a wide range, and their results are consistent with our conclusion.

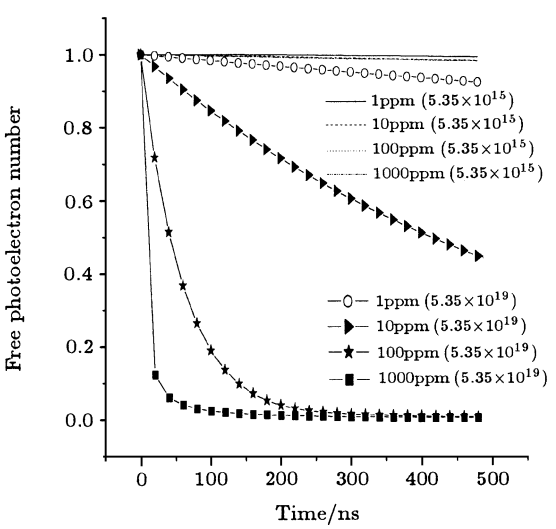


Fig.1. The simulated curves of free photoelectron decay with the variation of the density of the recombination centre at exposure intensity I=5.35×10^{15} photons/cm^3 and at I=5.35×10^{19} photons/cm^3.

3.2. Hole trap

The kinetic process of photoholes in hole trap can be described by the following equations:

$$\frac{\mathrm{d}p_\mathrm{h}}{\mathrm{d}t} = \rho_\mathrm{h}(P_\mathrm{h} - p_\mathrm{h})p - \rho_\mathrm{h} N_v p_\mathrm{h} \exp\left(-\frac{\Delta E_\mathrm{h}}{kT}\right), \tag{4}$$

$$\frac{\mathrm{d}p}{\mathrm{d}t} = G - \frac{\mathrm{d}p_\mathrm{h}}{\mathrm{d}t}, \tag{5}$$

where p_h is the density of the trapped holes in the hole trap;, ρ_h is the rate constant for hole trapping of hole trap; ΔE_h is the trap depth of hole trap; P_h is the density of hole traps. The other parameters are defined as previously.

Hole traps are situated above the valence band. They can capture free photoholes and prevent photoholes from recombining with photoelectrons, which is favourable to the efficient utilization of photoelectrons in forming latent images. As discussed in the previous section, the effect of recombination centres only appears at high exposure intensity. Therefore, it is expected that the effect of hole traps will become significant only at high intensity exposure, as the effect of recombination centres does. This is illustrated in the simulated results shown in Figs.2, 3 and 4. Figure 2 shows that the increase of the density of hole traps hardly causes any change of the free photoelectron decay behaviour at low exposure intensity. Figures 3 and 4 show that the decay behaviour begins to change with the density of hole traps at higher intensity, and the larger the density of recombination centres, the clearer the variation of the photoelectron decay behaviour with the change of density of hole traps. These results indicate that the influence of hole traps on the photoelectrons decay is an indirect process, and it acts on the decay behaviour through recombination centre. Thus no matter whether it is strong or not, the recombination centre can influence the behaviour of hole traps.

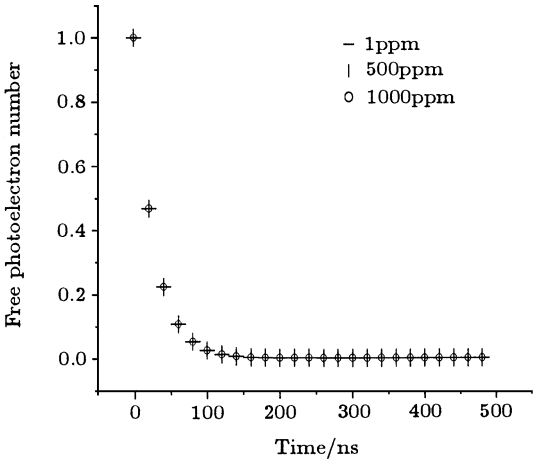


Fig.2. The free photoelectron decay curves with different densities of hole traps at I=5.35×10^{15} photons/cm^3.

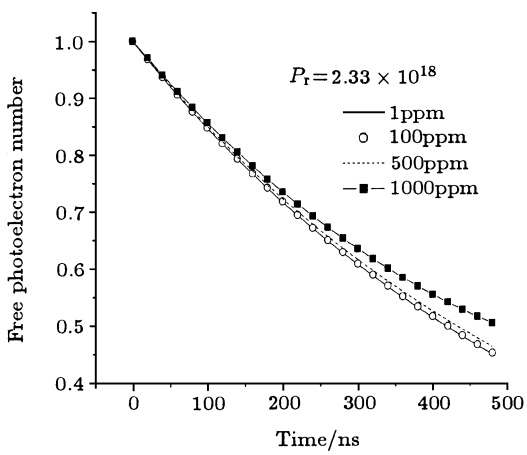


Fig.3. The free photoelectron decay curves with different densities of hole traps for I=5.35×10^{19} photons/cm^3.

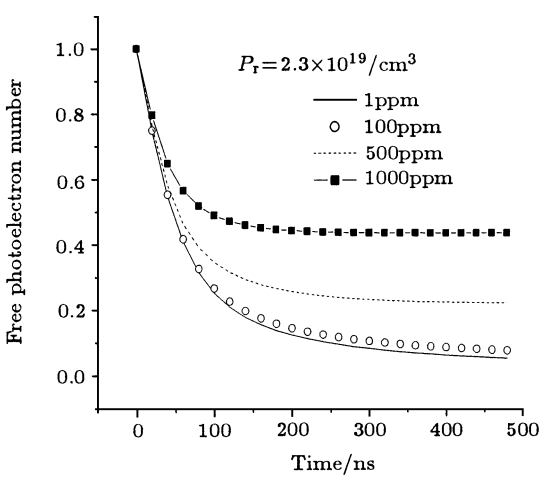


Fig.4. The free photoelectron decay curves with different densities of hole traps for I=5.35×10^{19} photons/cm^3.

3.3. Electron trap

The kinetic process of photoelectrons in electron trap can be described by the following equations:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = G - \frac{\mathrm{d}n_e}{\mathrm{d}t}, \tag{6}$$

$$\frac{\mathrm{d}n_e}{\mathrm{d}t} = \beta_\mathrm{e}(N_\mathrm{e} - n_\mathrm{e})n - \beta_\mathrm{e}N_\mathrm{c}n_\mathrm{e}\exp\left(-\frac{\Delta E_\mathrm{e}}{kT}\right), \tag{7}$$

where n_e is the density of the trapped electrons in the electron trap, β_e is the trapping rate constant for electron trapping of the electron trap. ΔE_e is the trap depth of the electron trap; N_e is the density of electron traps; N_c is the effective density of state of the conduction band. The other parameters are defined as previously.

3.3.1. Shallow electron trap

Figure 5 shows the experimental result obtained with increasing concentration of $K_4Fe(CN)_6$, which is well known as a kind of shallow electron trap dopant. We can see that there is a fast decay of photoelectrons initially, which is followed by a slower decay at the subsequent phase, named as the fast process and slow process, respectively (the increasing curve is the process of producing photoelectrons during exposure, while what we are especially interested in is the decay process of free photoelectrons after exposure). On the whole, the increase of the concentration of $K_4Fe(CN)_6$ will extend the decay time of free photoelectrons (the time during which the free photoelectrons decay from 100% of the maximum intensity to 10% of it).

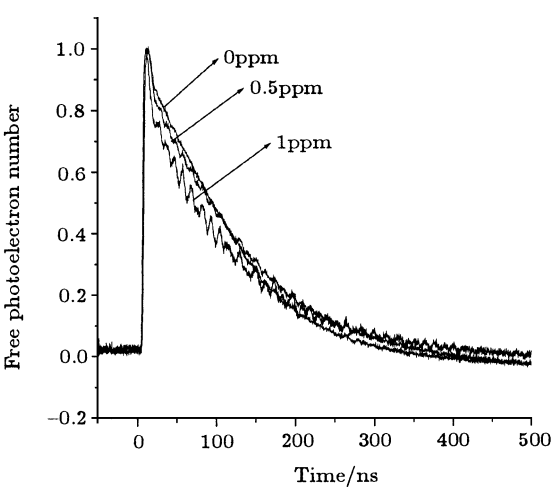


Fig.5. The experimental curves of the photoelectron decay when the doping concentration is 0ppm, 0.5ppm, or 1ppm.

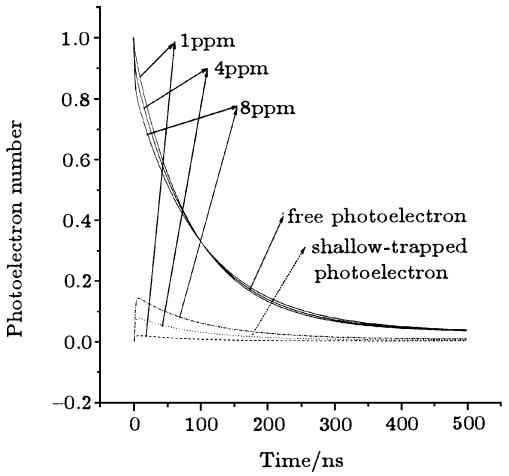


Fig.6. The simulated curves of the photoelectron decay when the doping concentration is 1ppm, 4ppm, or 8ppm.

The simulated result is shown in Fig.6. Not only the free photoelectron behaviour but also the behaviour of photoelectrons trapped in shallow electron traps is simulated simultaneously. The simulated result is in good agreement with the result for the experiment containing a fast process and a slow process. (Considering that all the photons are converted to photoelectrons in simulation, the number of photoelectrons is relatively larger in simulation than actually, so the concentration of electron traps is one order larger in simulation than in experiment to produce the similar effect.) The increase of the shallow electron trap's concentration will accelerate the fast process and slow down the slow process, and simultaneously increase the decay amount in the fast process. In Fig.6, the curve of the shallow-trapped photoelectrons is below that of the free photoelectrons. The curve of the shallow-trapped photoelectrons first rises up and then goes down. The rising-up section is the process in which photoelectrons are captured in the shallow electron traps, and the going-down section is the process in which photoelectrons are set free from the shallow electron traps. It is apparent that the rising-up section for the shallow-trapped photoelectrons corresponds to the fast process of free photoelectrons, and the releasing process of the shallow-trapped photoelectrons corresponds to the slow process of free photoelectrons. Figure 7 shows the simulated result when only shallow electron traps exist in silver halide. It can be seen that the free photoelectrons immediately reach an equilibrium after a fast decay process, and at the same time the shallow-trapped photoelectrons also reach an equilibrium after a fast ascending process. The decay of photoelectrons results from the competition between the trapped process by the electron traps and the de-trapping process from them. At the beginning, there are few trapped photoelectrons, so the amount of free photoelectrons is much larger than that of trapped photoelectrons. Thus the probability of photoelectrons being trapped by shallow electron traps is larger than that of de-trapping, leading to the acceleration of the free photoelectron decay. With the increase of trapped photoelectrons, the probability of de-trapping will increase gradually until the two competitive processes reach a balance. If there are other deeper trapping centres, they will capture free photoelectrons causing the decrease of the free photoelectron number and the destruction of the balance. At this moment the shallow-trapped photoelectrons will be released so as to provide photoelectrons for the deeper trapping centres. Then, the released photoelectrons will be trapped permanently by deep electron traps, or recombine with photoholes in recombination centres, or join in the formation of latent images.

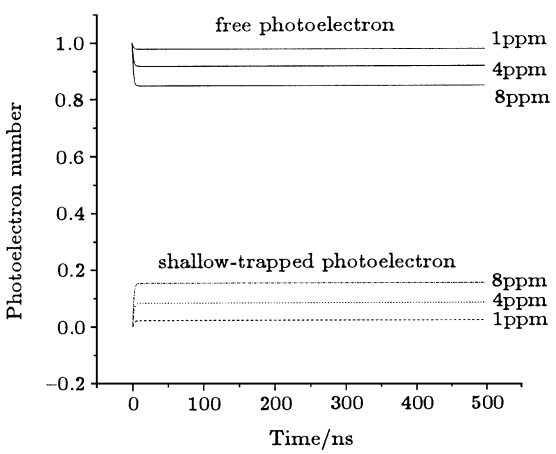


Fig.7. The simulated curves of the photoelectron decay when the doping concentration is: 1ppm, 4ppm, or 8ppm. The model used in this simulation includes just one shallow electron trap.

These results show that the shallow electron traps will temporarily capture photoelectrons, and the photoelectrons will escape from shallow traps because of thermal excitation and eventually get lost in the deep traps or recombination centres, or combine with interstitial Ag ions. Therefore, shallow traps are like a reservoir. Firstly, photoelectrons are stored up. During this stored-up period and the tardigrade process of releasing the shallow-trapped photoelectrons, there will be a certain amount of Ag clusters such as Ag, Ag_2, Ag_3,Ag_4 formed. Furthermore, the more tardily

the shallow-trapped photoelectrons are released, the more opportunity for the formation of Ag clusters there is. Now, Ag_3 or Ag_4 are commonly thought of as the effective latent image nucleus. The formation of latent image is a key tache in the photographic process. Thus, the lifetime or the decay time of the free photoelectrons plays an important role in the efficiency of latent images formation.

3.3.2. Deep electron trap

The effect of sulfur-plus-gold sensitization centre shifts from shallow electron traps to deep electron traps.[22] Figure 8 shows the case that sulfur-plus-gold sensitized centres appear as deep electron traps. The solid curve denotes the unsensitized T-shape AgBrI, and the dotted curve denotes the sensitized emulsion. From the figure we can see that the curve of sensitized emulsion is below that of unsensitized emulsion on the whole, which indicates that the deep electron trap accelerates the whole decay process resulting in the decrease of decay time. Figures 9 and 10 show the simulated curves of free photoelectrons and photoelectrons in deep electron traps in different concentrations after exposure, respectively. The simulated results agree with the experimental results, and also show that the higher the deep trap concentration, the more quickly the photoelectrons decay, and that almost all the photoelectrons are trapped by deep traps and the equilibrium between free photoelectrons and trapped photoelectrons have nearly disappeared. Certainly, the equilibrium will still exist of those deep electron traps with shallower depth. But the proportion between free photoelectrons and trapped photoelectrons in such an equilibrium is much smaller than that in the equilibrium produced by shallow electron trap. From the perspective of kinetic equations, for deep electron traps, ΔE_e is bigger. Inversely, the second term, namely the de-trapping term, is smaller. This indicates that the photoelectrons in deep electron traps have a low de-trapping ability, and that the deeper the trap, the lower the de-trapping ability. So deep electron traps have a distinct trapping ability on photoelectrons. Once the photoelectrons are trapped by deep electron traps, it is difficult to escape. Thus, under the action of deep electron traps, free photoelectrons will keep reducing. Simultaneously, the equilibrium produced by shallow electron traps are broken up continuously, leading to the continuous releasing of photoelectrons from shallow electron traps and eventually being trapped in deep electron traps. However, as mentioned above, the acceleration of the photoelectron decay process is not favourable to the enhancement of the latent image formation efficiency, for a short decay time is unfavorable to form the stable Ag_2, which is the key to the nucleation and growth of latent images.

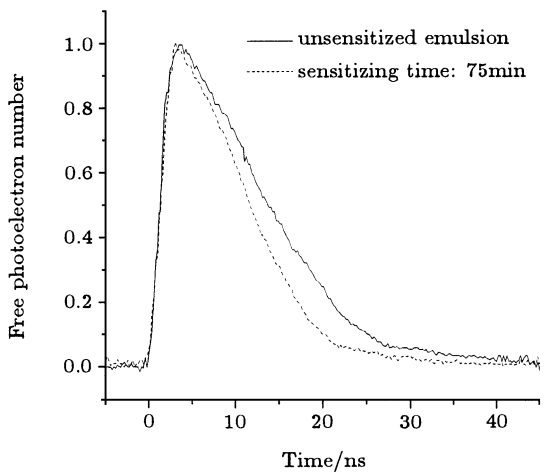


Fig.8. The comparison of the decay curves of unsensitized T-shape AgBrI emulsion and the sulfur-plus-gold sensitized emulsion with long sensitizing time.

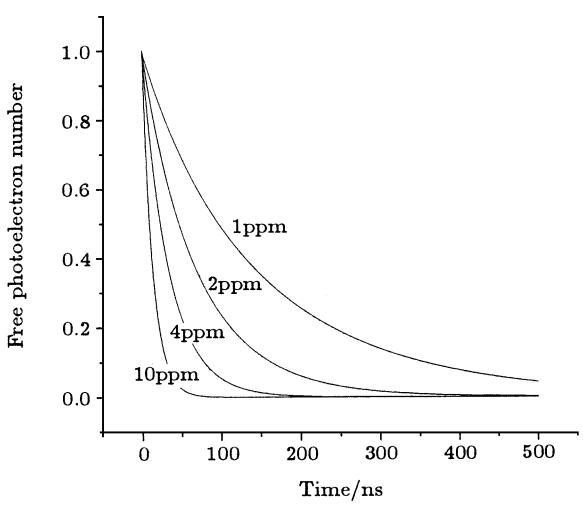


Fig.9. The simulated decay curves of free photoelectrons with changing density of the deep electron traps.

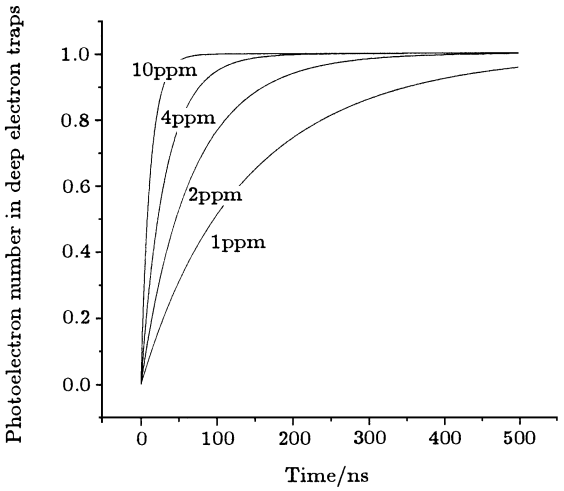


Fig.10. The curves of the trapped photoelectrons in deep traps corresponding to Fig.9.

4. Conclusion

Combining the photoelectron decay microscopic kinetics equations and the microwave absorption dielectric spectrum experiment, the influences of recombination centre, hole trap, shallow and deep electron traps on the decay of photoelectrons are investigated and the following conclusions can be arrived at: electron traps have effect at low exposure intensity, while recombination centres and hole traps have effect at high exposure intensity. Shallow electron traps accelerate the decay of photoelectrons at initial stage, and retard the subsequent process. On the whole, shallow electron traps can lengthen the decay time of free photoelectrons, and deep electron traps accelerate the whole process of the photoelectron decay.

Because the preparation of silver halide is influenced by many factors such as temperature, pressure, purity etc, the trapping centres are very different in different group, even with identical materials and under nearly the same conditions. According to these conclusions and the typical experimental curves, we can estimate how many kinds of trapping centres there are in a certain emulsion, and the photosensitivity can be improved by adjusting the parameters of trapping centres or doping with new trapping centres.

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