Investigation of Photoelectron Action in Cubic AgBr Emulsion Doped with Formate Ions

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Abstract

In recent years, the formate ion (HCO_2^-) as a kind of hole-to-electron converter has attracted much attention of photographic researchers. The formate ions can trap photo-generated holes, eliminating or reducing electron loss caused by electron¬hole recombination in latent image formation process. Through the hole-to-electron conversion, it can also release an extra electron or electron carrier, improving photosensitivity obviously. In this paper the microwave absorption and dielectric spectrum detection technique was used to detect the time-resolved spectrum of free photoelectrons generated by 35-ps laser pulses in cubic AgBr emulsions doped with formate ions. By analyzing the photoelectron decay action, the photoelectron decay time and lifetime were calculated. The influence of different doping conditions of formate ions on the photoelectron decay kinetics of AgBr was discussed. Finally the optimal doping condition of formate ions in AgBr emulsion was determined.

Introduction

Formerly, researchers paid more attention on studying the behavior of photoelectrons to search for the method for improving the efficiency of latent image formation in silver halide, but in recent years, they have been attracted by utilizing the photo-holes for the same purpose. By chemical method, holes can be converted into electrons or electron carriers to enhance the efficiency of latent image formation. Using absorbance measurement, Belloni et al detected the time evolution spectra and sensitivity of silver halide emulsion. They reported that the HCO_2^- as a kind of hole-trap dopant was able to improve photosensitivity significantly, and proposed the following mechanism for the sensitization by formate ions: [1-3]

$$HCO_2^- + h^+ \ \bullet CO_2^- + H^+ \tag{1}$$

$$\cdot CO_2^- + Ag_n^+ \ \ Ag_n + CO_2 \ , \tag{2}$$

where the formate ion in silver halide emulsion captures the photo-hole, and therefore enhances the escape of electrons from electron-hole recombination, and the resulting $\bullet CO_2^-$ radical in turn transfers an electron to another silver cation. In this way, the quantum yield increases to two silver atoms per photon absorbed. These authors also pointed that the formate ion was not a direct reduction sensitizer and was unable to reduce silver cation in the dark, so the risk of fogging was avoided. Using ESR technique, Guo Hong et al gave indirect evidence for the existence of Reaction（1）. [4] The former study has not reported the influence of the formate ions on the silver halide with the change of doping condition. In the present work with the microwave absorption and dielectric spectrum detection technique, and the formate sodium as hole-trap dopant, we detected the time evolution behavior of the photoelectrons in AgBr emulsions. The photoelectron decay action and trap-capture properties of formate ion were discussed. Finally the optimal doping amount and position of the formate ions in cubic AgBr emulsion were determined.

Experiment

Sample preparation

In this experiment a double-jet apparatus was used to prepare two series of cubic AgBr emulsions doped with formate sodium.

（1）The doping poison of formate ions in AgBr was fixed at 80%, the doping amounts were 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} mol/mol Ag, respectively.

（2）The doping amount of the formate ions was 10^{-4} mol/mol Ag. The positions in cubic AgBr grains were 20%, 40%, 60%, 80%, and 90%, respectively.

The undoped emulsion is marked with 0. All parameters of emulsifying process were controlled by computer. Electron microscopy was used for the measurement of the cubic grain sizes. The average edge length of cubic grains in the emulsions is 0.2µm. The doping amount is expressed as the doping molar amount of the formate ions per mole Ag. The doping position is defined as the ratio of the additional accumulative amount of Ag at the time of doping formate sodium to the total additional amount of Ag at the ending of precipitation. Therefore, the larger the value of the doping position, the closer the dopant is to the surface.

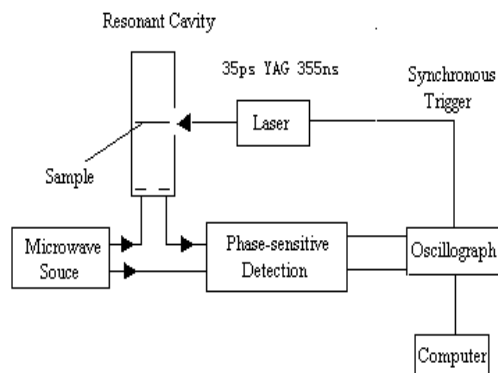### Measurement of the time-resolved spectrum of photoelectrons

Figure1. Block diagram of the experimental apparatus.

The microwave absorption and dielectric spectrum detection equipment [5] shown in Figure1 was used to measure the samples.

Photoelectrons are generated when the film sample of AgBr emulsion is exposed to laser pulse. The generation of photoelectrons leads to the change of the dielectric function ε ($\varepsilon = \varepsilon' + i\varepsilon''$), and to the change of the reflected microwave U. The reflected signal U can calculated by :

$$U = U_0 Q_0^2 \beta^2 - \frac{1}{2} U_0 f Q_0 \varepsilon'' + i U_0 Q_0 \beta - i \frac{1}{2} U_0 f Q_0 \varepsilon' , \qquad (3)$$

where Q_0 is the quality factor, f is the filling factor and U_0 is the input microwave. Reflected microwave U is the response signal of the microwave field for the change of the dielectric function. So U is called dielectric spectrum, which reflects the photoelectron action. The signal is recorded with a digital oscilloscope. By analyzing the photoelectron signal, we obtain the photoelectron action and its influence on the latent image formation.

Result and Discussion

Photoelectron decay process reflects the trend of the photoelectron amount with the time change, so the free photoelectron decay time and lifetime reflect the decay properties of photoelectron in the information process of the latent image. The photoelectron decay time （PDT） is defined as the time needed for the photoelectron amount decaying from 90% to 10%. The photoelectron lifetime （PLT） can be calculated from the half-logarithm curve of the photoelectron delay curve as follows:

$$\tau = -\frac{1}{k} = -\frac{dt}{d\left[\ln\left(U/U_0\right)\right]} \quad , \qquad (4)$$

where U_0 and U are input microwave and reflected microwave and k is the tangent slope of the half-logarithm curve.

Influence of different doping amounts of formate ions on the free photoelectron decay action of cubic AgBr emulsions
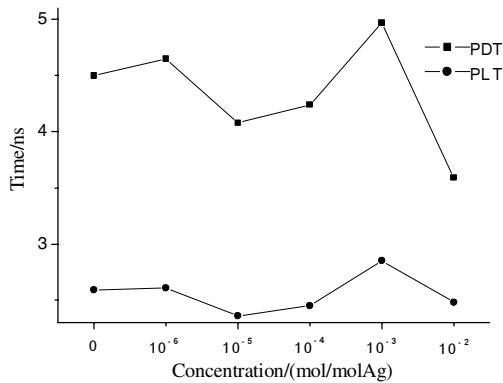

Figure2. Decay time and lifetime of free photoelectrons in AgBr doped with different amounts of formate ions at 80%.

When the doping position of the formate ions is 80%, the change of decay time and lifetime of the free photoelectrons of cubic AgBr emulsions doped with different amounts of formate ions are given in Figure2. It is seen that with increasing of the doping amount the decay time and lifetime reach the maxima at the doping amount of 10^{-3}mol/mol Ag.

Figure3 gives a comparison of the free photoelectron decay time and lifetime between the undoped sample and the one doped with 10^{-3}mol/mol Ag. From the half-logarithm curve and with formula （4）, we obtained $\tau(0) = 2.59ns$, $\tau(10^{-3}) = 2.85ns$, i.e. $\tau(10^{-3}) > \tau(0)$. These results indicate that the free photoelectron decay of the sample doped with 10^{-3}mol/mol Ag is slower than the undoped one in the entire process. Therefore, the doped formate ions act as hole traps effectively.
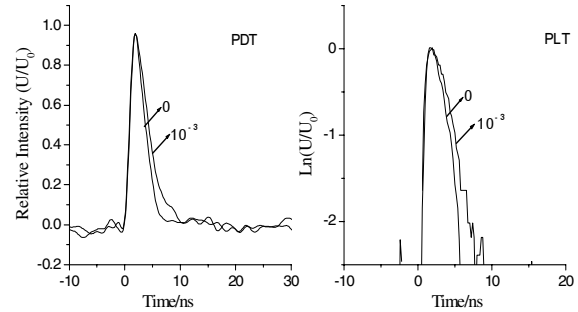

Figure3. Comparison of the photoelectron decay time and lifetime curves between the undoped sample and the one doped with 10^{-3}formate ions

Influence of different doping positions of formate ions on the free photoelectron decay action of cubic AgBr emulsions
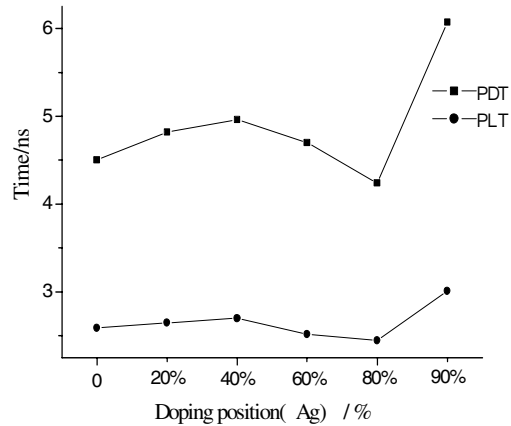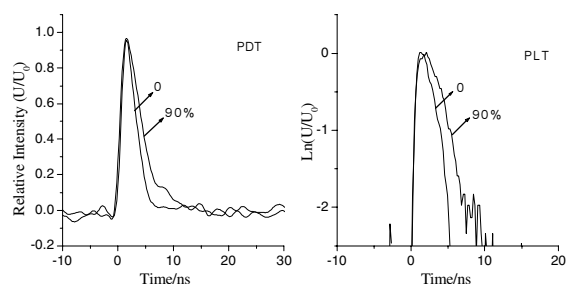

Figure4. Decay time and lifetime of free photoelectrons in AgBr with 10^{-4}mol/mol Ag formate ions at different doping positions.

Figure4 shows the change of free photoelectron decay time and lifetime of cubic AgBr emulsions doped with formate ions at different doping positions, when the doping amount of the formate ions is 10^{-4}mol/mol Ag. Clearly, when the doping position is 90%, the decay time and lifetime reach the maxima. Figure5 shows the comparison of the free photoelectron decay time and lifetime curves between undoped sample and the sample doped at 90%. From the half-logarithm curve, we obtained $\tau(0) = 2.59ns$, $\tau(90\%) = 3.01ns$, i.e. $\tau(90\%) > \tau(0)$. These results indicate that the free photoelectron decay of the sample doped at 90% is slower than the undoped sample in the entire process. This is due to the doped formate ions act as hole traps to capture photo-holes, thus

the escape of electrons from pair recombination is promoted and the photoelectron decay time and lifetime are prolonged.

Figure5. Comparison of the photoelectron decay time and lifetime curves between the undoped sample and the sample doped at 90%.

Conclusions

The time-resolved spectrum of the free photoelectrons in AgBr emulsion was detected with the microwave absorption and dielectric spectrum detection technique. The influence of the different doping conditions of formate ions on the photoelectron decay properties of cubic AgBr emulsions was discussed. We conclude that the optimal doping position is 90%, and the optimal doping amount is 10^{-3}mol/mol Ag. Further investigation of formate ion as hole-trap dopant is in progress.

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Author Biography

Professor Fu Guang-Sheng, a mentor of doctor students, was born in 1956, serves in College of Physics Science and Technology of Hebei University now, and engages in the research work of photoelectric communication materials and laser spectrum primarily.