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Investigation of photoelectron temporal characteristics in silver halide microcrystals using the microwave absorption technique*

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The free photoelectron lifetime reflects to a large extent the latent image formation efficiency and sensitivity of silver halide material. The microwave absorption dielectric-spectrum technique enables measurement of the photoelectron decay process of silver halide emulsion exposed to 35ps laser pulse. For T-grain AgBr emulsion, the relationship between exciting energy and photoelectron action has been obtained, and the influence of iodide dopants on photoelectron lifetime was measured and analysed. The photoelectron lifetime of dye-sensitized AgBr emulsion with tabular grains is shorter than that with cubic grains, and the latent image formation efficiency of the former is higher than the latter.

Keywords: silver halide emulsion, photoelectron lifetime, microwave absorption, dye-sensitization
PACC: 7120, 5225M

1. Introduction

Measurement of the free photoelectron and the shallow-trapped electron lifetime of silver halide microcrystals can provide important information about the photoelectron action in the latent image formation process. Among the various methods, the microwave absorption technique has often been applied to AgX microcrystals.[1−8] Microwave instruments described in previous papers[2−6] were used to measure a mixture of both free photoelectron signal and shallow-trapped electron signal. Müssig and Hegenbart measured the free electron lifetime (FELT) and shallow-trapped electron lifetime of silver halide crystal using 800ps N_2 pulsed laser.[7,8] Because the photoelectron signal rise time of some silver halide crystals is less than 1ns, considering the light reflection in cavity, the 800ps laser pulse cannot provide the required measuring precision. In this paper, by using a 35ps YAG laser pulse (355nm), we measured the decay process of free photoelectrons and shallow-trapped electrons simultaneously. The influences of grain structure, dye sensitization and shallow electron trap dopants on the formation of latent image specks are investigated and the relationship between exciting energy and photoelectron action of AgBr crystal is obtained.

2. Experimental

The scheme of the microwave absorption dielectric spectrum measurement (MADM) equipment has been shown in Refs.[9–11]. A film sample is inserted into a microwave cavity at the position where the electric field is a maximum and is exposed by a 35ps YAG pulsed laser. The valence band electrons are excited under the irradiation of short-pulsed laser, and a large amount of free electrons and shallow-trapped electrons are produced, resulting in the change of the susceptibility tensor. Both free and shallow-trapped electrons are generated in the sample synchronously. The reflection signal in microwave cavity is calculated by

$$U' = UQ_0^2\delta^2 - 0.5UfQ_0\varepsilon'' + \mathrm{i}UQ_0\delta - 0.5\mathrm{i}UfQ_0\varepsilon', \quad (1)$$

where U is the incident microwave, U' is reflected microwave, $\delta = (\omega_{\mathrm{res}} - \omega)/\omega$ is the change of reso-

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nant vibration frequency, ω_{res} is the resonant vibration frequency (35GHz), ω is the resonant vibration frequency after adding the sample, $\varepsilon = \varepsilon' + i\varepsilon''$ is the complex dielectric constant, Q_0 is the quality factor of the resonant vibration cavity and f is the fill factor. The first and third items in the above equation are direct-current parts and the static state signals without illumination, the second item ($0.5UfQ_0\varepsilon''$) is in direct proportion to the density of free electrons, and the fourth item ($0.5iUfQ_0\varepsilon'$) is in direct proportion to the density of electrons in shallow electron trap. The two signals were measured separately using a phase sensitive detection system. The observed absorption signals are approximately in direct proportion to the density of free electrons while the dispersion signals are in direct proportion to the density of shallow trapped electrons. By analysing the free electron signal and the shallow-trapped electron signal, we obtain the photoelectron behaviour and its influence on latent image formation. The signals are amplified by a SR440 amplifier (SRS) and displayed by a TDS3052 digital storage oscilloscope (Tek).

Photoelectron lifetime is estimated from semilogarithmic plots of the photoelectron decay curves corresponding to[4]

$$\tau = -\mathrm{d}t/\mathrm{d}\{\ln(V/V_{\max}\}, \qquad (2)$$

where V is the photoelectron signal intensity, and $V_{\max}$ is its peak value. In general, for intrinsic or unsensitized grains, long free photoelectron lifetime leads to high photographic efficiency, and for sensitized crystals, to low photographic efficiency.

3. Results and discussion

By adjusting laser energy from 1mJ to 14mJ, we obtain the relationship between exciting energy and photoelectron action of tabular grain (T-grain) AgBr emulsion. The variation of electron signal intensity (V_0) and free photoelectron lifetime (FELT) with laser energy are shown in Fig.1. It shows that the maximum of photoelectron number linearly increases when laser energy is between 4mJ and 10mJ. The signal has reached saturation when laser energy is higher than 10mJ and all the AgBr crystals entirely participate in the photo-absorption process. Photoelectron number reaches the maximum and holds the curve flat at further increase of laser energy.

The electron number slowly increases when laser energy is lower than 3mJ. The change of electron number with laser energy accords with the characteristic curve of exposure process of silver halide crystal. In Fig. 1, the free photoelectron lifetime in AgBr crystals is constant and does not increase with laser energy. This shows that photoelectron lifetime is an inherent characteristic of AgBr crystals.

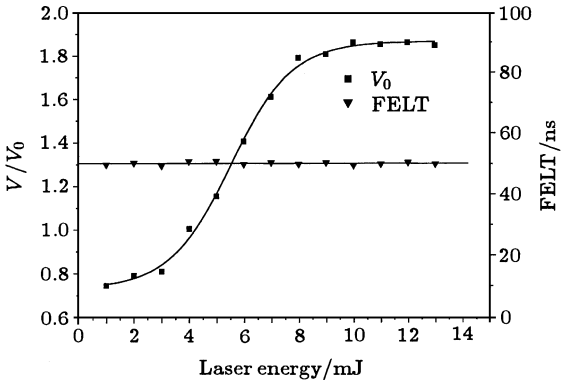


Fig.1. Photoelectron signal intensity and the FELT with laser energy.

Figure 2 shows the influence of iodide doping content on the free photoelectron lifetime of T-grain AgBr emulsion. The FELT increases gradually when the iodide content is from 1.2% to 3% and decreases when the iodide content is greater than 3%. Iodide ions can act as traps for defect electrons. This leads to reduced reaction at the silver clusters and the FELT reaches maximum when iodide content is 3%.

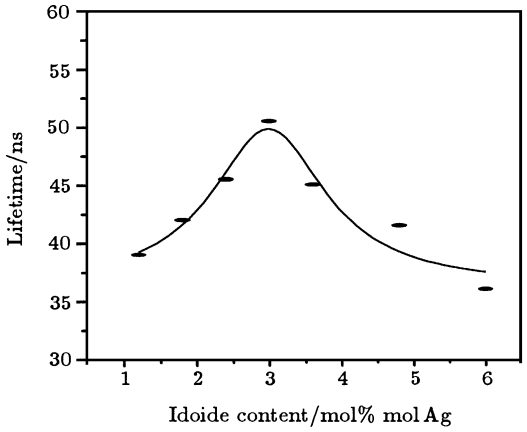


Fig.2. The FELT of T-grain AgBr emulsion with iodide content.

Figure 3 (a) shows two typical time regions B and C in the free electron signal curve when iodide content is higher or lower than 3%. The initial quick decay region B is related to the filling of deep and shallow electron traps, whereas the increasing lifetime in region C is a result of the thermal detrapping from occupied shallow electron traps. Figure 3(b) shows the regions B, C and an additional region A when iodide content

is 3%. This new region with long lifetimes observed is related to a kind of very-shallow trap, comprising unstable silver clusters and iodide-bonded excitons. The increasing effect of iodide (max. by 3%) on the photoelectron lifetime for T-grain AgBr emulsion is that iodide ions can act as a trap for defect electrons. For iodide concentrations higher than 3%, this behaviour is lost due to the formation of iodide agglomerations.

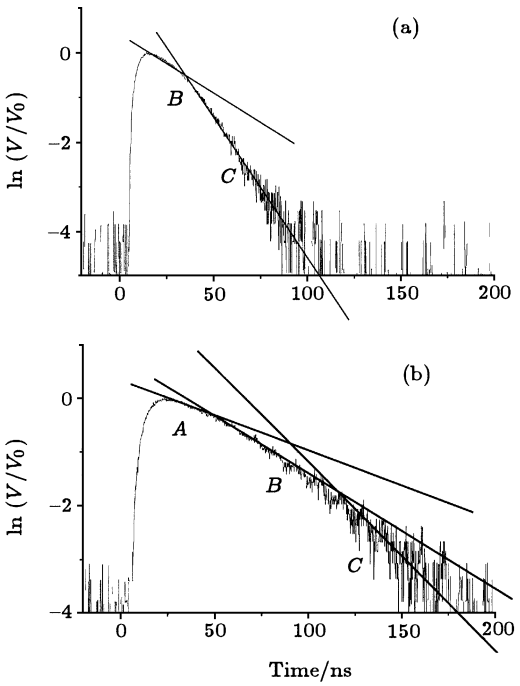


Fig.3. The semilogarithmic curve of free electron decay signal of T-grain AgBr emulsion doped iodide: (a) iodide content higher or lower than 3%, (b) iodide content 3%.

Subsequently, AgBr T-grain and cubic-grain emulsion is dye-sensitized by adsorbing the dye. The dye in crystal surface is oxacarbocyaine. The adsorbing temperature and adsorbing time of the dye are 45°C and 30 minute, respectively. Figure 4 shows a comparison of photoelectron lifetimes of dye-sensitized AgBr tabular grain and cubic grain emulsion. For first-matured T-grain and cubic-grain emulsions, free electron lifetimes are 50ns and 40ns, respectively. In contrast, free electron lifetimes of dye-sensitized emulsions sharply decrease, being lower than 2ns and 4ns, respectively. Dielectric loss measurements show that the adsorbed dye increases the ionic conductivity.[12] This indicates that the spectral sensitizers increase the concentration of Ag_i^+. An increased Ag_i^+ concentration results in sharp decrease of free electron lifetimes of dye-sensitized emulsions and facilitates the formation of latent image silver specks. Therefore, the sensitizing dyes increase the photoelectron utility and the latent image formation efficiency. By comparing photoelectron lifetime of T-grain emulsions with that of cubic-grain emulsions, we find that for the former the photoelectron lifetime is in principle significantly smaller than that for the latter. This may indicate that the dye adsorption on the (111) surface of the tabular grain is more effective than on the (100) surface of cubes. The smaller electron lifetime measured for tabular grains is the result of the difference in structure of the (111) in comparison with the (100) surfaces.[8]

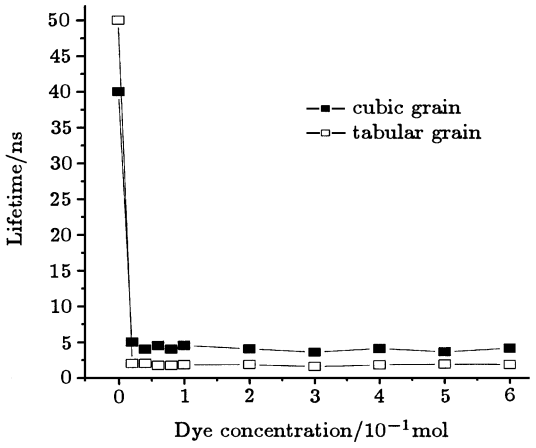


Fig.4. Comparison of the FELT of dye-sensitized AgBr tabular grain and cubic grain crystals.

4. Conclusions

The curve of photoelectron lifetime versus the laser energy shows that the lifetime is an inherent characteristic of silver halide crystal. For T-grain AgBr emulsion, the FELT reaches a maximum when the iodide content is 3%. For dye-sensitized T-grain AgBr emulsion, the free photoelectron lifetime is in principle smaller than that with cubic grains, and the latent image formation efficiency of the former is higher than the latter. With the MADM technique, it is possible to investigate the photoelectron decay processes of AgX grains in relation with different crystal structures, spectral and chemical sensitization, shallow electron-trap dopants and hole-trap dopants.[13] As the next step, we will investigate respectively the influence of various sensitization processes and dopant parameters on the photoelectron decay process.

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