

Preparation and Characterization of Ag/AgCl-Sensors with Higher Stability and Response

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Abstract

The preparation of Ag/AgCl-electrodes for use as electrocardiogram-sensors with high stability for a long time is difficult because Ostwald-ripening takes place on the surfaces of the AgCl-crystals especially in contact with the solid gel. The crystals smaller than the critical radius will dissolve, and all particles larger will grow. In these processes, the stability of Ag/AgCl-layers decreases and the sensor no longer works. Additives or impurities have great influence on nucleation, crystal growth, ageing, and recrystallization of silver halide crystals. In the present investigations, the great influence of additives on the partial steps of crystallization could be shown. The results were electrocardiogram-sensors with higher stability and better response. The habit and crystal size distribution of the AgCl-crystals were changed. We have investigated in detail, using radioactive isotopes, the influence of additives for the stability of

AgCl-layers on the surfaces on silver metal, which are used as electrocardiogram-sensors in medicine. The characterisation of stability of the AgCl-layer on silver metal surface was made by means of heterogeneous isotopic exchange with the isotopes Ag-110, Cl-36, Br-82 and I-131 on AgCl- and AgBr-crystals respectively, and by electron microscopy (REM), DEMBER-effect (photo-EMF), electrical methods, UV-VIS-spectrometry and medical advantage.

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Influence of complex ions with mixed ligand on course of photoprocess in grains AgHal.

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Abstract

The influence of complex compounds with mixed ligands $Cs_3[IrA_xB_{6-x}]$, where $A, B = Br, Cl$ on photochemical reactions in isometric AgBr grains has been investigated.

The methods for effective integrating and the determination of optimal concentrations of the doping ions were developed. The doped photoemulsions proved to be able of increasing their photographic speed and decreasing the low-intensity reciprocal failure (LIRF).

It was established that the integration of complex ions into AgBr grains resulted in changing the kinetics of the interaction of photoinduced charges. On the basis of the experimental data, the model for the photoprocess for doped silver bromide microcrystals (MC) is proposed.

Introduction

Doping allowed us to control the photoprocess in silver halide light-sensitive systems. Metals of the platinum group, Ir(III) ions in particular, are given most attention to. Despite it, the mechanisms for many phenomena are not clear, and the attempts to describe them are not convincing enough, e.g. the mechanism of the influence in AgCl grains (doped and pure) on sensitization when there are differences in the distribution of latent image centers (LIC) in size [1]. Different concentrations of the Ir (III) ions necessary for obtaining the photo films with highest photographic characteristics in sensitized and unsensitized AgBr grains {100} and {111} were shown in [2, 3]. Significant decrease in photosensitivity for such systems at the concentration 10^{-5} mole Ir/mole Ag was observed earlier in [4], where it was explained by the predomination of the reaction of electron capture on the Ir trap over the reaction of latent image formation.

The present paper is devoted to the investigation of the influence of complex compounds $Cs_3[IrA_xB_{6-x}]$, where $A, B = Br, Cl$, $x = 0; 1$ on the processes of the latent image formation centers in pure AgBr grains.

Experiment

The preparation of AgHal emulsions was carried out by the controllable two-jet crystallization technique. KHal and $AgNO_3$ solutions were introduced into the reactor containing a required amount of an aqua-gelatin solution at constant agitation. During synthesis the temperature, the pBr value and the rate of adding the reagent solutions were controlled. A solution containing the ions $[IrA_xB_{6-x}]^{3-}$ of the required concentration was added after 90 % of reagent solutions was introduced, providing for subsurface localization of doping centers in grains. The resulting emulsion grains had the average equivalent diameter 0,5 microns and variation in sizes' coefficient not more than 15 %. The minimum volume of the added solution of the $Cs_3[IrA_xB_{6-x}]$ ions was not less

than 0,5 % from the total volume of the emulsion. The water-soluble salts were removed from the resulting emulsion, and pBr and pH values were adjusted. To reveal the surface LIC the standard chemical-photographic technique was used. To reveal the inner LIC the Chibisov development technique [5] was most effective.

Results and Discussion

Earlier it was shown by us [2] that grains' doping influences the sensitization process. The concentration of doping ions for sensitized emulsions necessary for creating the photo films with highest photographic characteristics was in the $10^{-8} - 2 \cdot 10^{-8}$ mole Ir/mole Ag range and for unsensitized emulsions – in the $10^{-6} - 10^{-7}$ mole Ir/mole Ag range. It was also observed that the doping ions influenced both inner and total sensitivity (inner + surface). These observations seemed interesting and demanding more detailed research.

The influence of the Ir(III) ions on photoprocess in AgHal grains was studied in the works [2] and [3] and it was shown that increase in the concentration of the dopant did not result in photographic speed increase. The authors [4] attribute photographic speed decrease at a high concentration to the electron capture released from one Ir - center and its capture by another adjoining Ir - center. Also, photographic speed decrease can be explained by the formation of the inner not active during surface development center of sensitivity created by excess concentration in MC.

The resulting values of relative photographic speed received by various ways of developing the emulsion layers containing AgBr MC {100} doped with the $[IrA_xB_{6-x}]^{3-}$ ions ($C = 10^{-5}$ mole Ir/mole Ag) are submitted in Fig. 1.

It is seen that the undoped emulsion, actually, does not have inner photographic speed but simultaneous development of inner and surface LIC causes the additive effect of photographic speed increase. In the case of the presence of the doping ions in MC inner photographic speed increases, thereby, surface photographic speed either grows (doped with the $[IrBr_6]^{3-}$ ions) or remains unchanged (doped with the $[IrBr_5Cl]^{3-}$ and $[IrBrCl_5]^{3-}$ ions).

Doping centers in AgBr MC influence the photoprocess as follows:

1. they serve as temporary electron traps resulting in recombination probability decrease;
2. they act as the centers of the formation of the inner latent image (LI) subcenters which can migrate onto the surface in consecutive electron-ionic stages;
3. they act as the inner LI formation centers resulting in inner photographic speed increase.

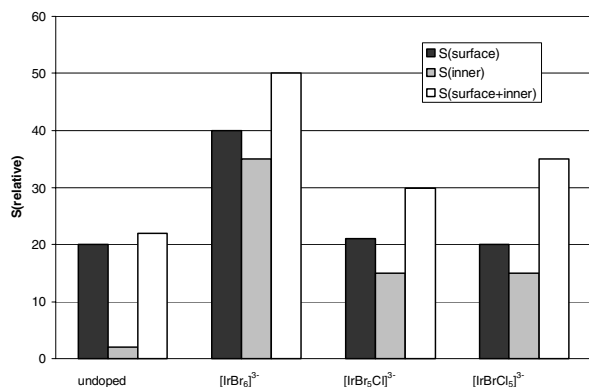


Figure 1. Relative photographic speed ($S_{rel} = 10 \cdot S_{0,2}$) values received by various ways of developing.

Based on the experimental data (Fig. 1), it can be stated that none of these proposed mechanisms can be neglected at the Ir(III) ions concentration $\approx 10^{-5}$ mole Ir/mole Ag.

The data on photographic speed corresponding to different exposure time support indirectly any of these mechanisms. The isopaques of doped and undoped emulsion layers are submitted in Fig. 2. It is seen that the undoped emulsion and the emulsion doped with the $[\text{IrBrCl}_5]^{3-}$ ions have the greatest deviation from the reciprocal failure. It can be asserted that the centers created by the $[\text{IrBrCl}_5]^{3-}$ ion form mainly the inner stable LIC which do not participate in surface LI formation (mechanism 3). $[\text{IrBr}_6]^{3-}$ and $[\text{IrBr}_5\text{Cl}]^{3-}$ doping weakens the reciprocal failure effect at low intensity light exposure that allows us to suppose that mechanism 2 could be involved. This can also account for the absence of additivity during total development of inner and surface LI (Fig. 1). Under low intensity light exposure surface LIC decompose [6] thus, the released electrons and Ag^+ ions can be trapped by the inner centers created by doping centers alongside with electrons generated in the MC bulk. Then, there occurs the migration of inner LIC onto the surface in the dark.

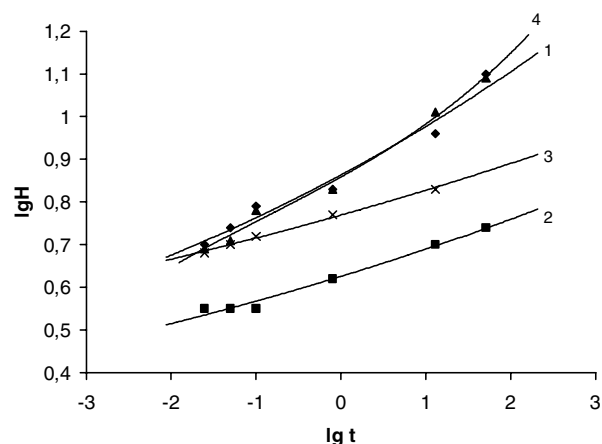


Figure 2. Isopaques ($D = 0,2$) and doped emulsion layers containing AgBr MC doped with the $[\text{IrBr}_x\text{Cl}_{6-x}]^{3-}$ ions ($C = 10^{-5}$ mole Ir/mole Ag) during surface development: 1 - undoped; 2 - $x=0$; 3 - $x=1$; 4 - $x=5$.

During simultaneous development of inner and surface centers (Fig. 3) reciprocal failure at low intensity light exposure is approximately the same for all the emulsions.

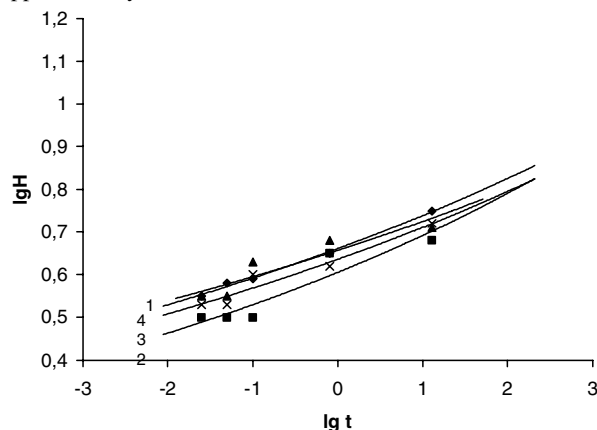


Figure 3. Isopaques ($D = 0,2$) and doped emulsion layers containing AgBr MC doped with the $[\text{IrBr}_x\text{Cl}_{6-x}]^{3-}$ ions ($C = 10^{-5}$ mole Ir/mole Ag) during simultaneous development of inner and surface centers: 1 - undoped; 2 - $x=0$; 3 - $x=1$; 4 - $x=5$.

Based on the experimental data, it can be concluded that the doping Ir(III) ions can act as the inner centers capable of effectively concentrating the photolytic silver at low intensity light exposure. The ability of inner centers to participate in the formation of surface LI depends on the neighborhood of the doping ions (ligands).

References

1. Masanobu Miyoshi, Shuji Murakami, Koichiro Kuroda. // IS*T/SPSTJ International Symposium on Silver Halide Imaging: "Silver Halide in a New Millennium", Canada, pg. 219-220 (2000).
2. B. A. Sechkarev, F. V. Titov, D. V. Djagilev, K. A. Bodak, A. A. Vladimirov Doping of AgHal heterophase microcrystals by $[\text{IrCl}_6]^{3-}$ ions // International Symposium on Silver Halide Technology "At the Forefront of Silver Halide Imaging", Ventura, California, USA, pg. 71-76 (2004).
3. Sechkarev B.A., Titov F.V., Djagilev D.V., Bodak K.A., Vladimirov A.A. Isometric emulsion AgBr microcrystals doped with the $[\text{IrCl}_6]^{3-}$ ions // The Proceedings of the International conference «Physical and chemical processes in inorganic materials», Kemerovo, v.1, pg. 223-225 (2004)
4. Slagt M., Iwasa Y., Owaki T., Hirago A. Effect of Iridium Doping in Cubic and Octahedral AgBr Grains on the Latent Image Formation Process // IS*T/SPSTJ International Symposium on Silver Halide Imaging: "Silver Halide in a New Millennium", Canada, pg. 221-226 (2000).
5. Chibisov K.V. Nature of photographic speed, M.: Science, (1980).
6. Meieclar P.V. Physical processes during the latent image center formation // M.: Science. (1972).

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Denis V. Djagilev graduated from the Physics Faculty, Kemerovo State University in 2000 (Russia), defended the Candidate's thesis (dissertation) on "Influence of Ir^{3+} and Pd^{2+} ions on photographic properties of isometric heterocontact silver halide grains" in 2003.

The scope of scientific interests: physical and chemical processes in AgHal; the author of more than 25 scientific publications.