

Crystallization of AgCl Shell on Bromoiodide Emulsion Microcrystals

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Abstract

Creation of "double structure" photographic systems with pure AgCl shell have certain technological difficulties because of serious difference in solubility of these halides. We have studied a process of a crystallization of AgCl shell on AgBr(I) nuclei with AgI content from 0 up to 6 moll. %. An influence of the shell precipitation conditions (pAg, temperature, rate of solution introduction) on the uniformity of the final grains and thickness of the shell is investigated. Conditions of uniform shell precipitation up to the thickness of 50 nm on cubic microcrystals AgBr(I) are determined. Preliminary experiments on AgCl shell formation by a method of a physical ripening of fine emulsions in the presence of various concentrations silver halide solvents are carried out.

Introduction

Thickness uniformity and halide consistence strongly affect a photoprocess in systems of the "core/shell" type[1]. AgBr grain with AgCl shell are advantageous among the "core/shell" systems with inner sensitivity. A competition for photoelectrons occurs in the "core/shell" systems between surface and inner sensitivity centers. Silver choride has an extremely low sensitivity to the visible light. That causes prevailing of the inner sensitivity over surface one in AgBr core/AgCl shell grain.

Experimental and discussion

A precipitation of the AgCl shell on the AgBr(I) core is accomplished with serious technologic difficulties due to the high solubility of AgCl. We have carried out the precipitation of the AgCl shell on the AgBr(I) core by two procedures: double jet precipitation (DJP) and fine AgCl recrystallization[2,3]. In DJP experiment an influence of the pAg, temperature and precipitation rate on the precipitated shell uniformity are studied. In fine AgCl recrystallization experiments an influence of the temperature, fine grain size and the pAg of the ripening are studied.

$AgBr_{0,94}I_{0,06}$ emulsion grains of average size 0,4+/-0,02 mcm and Cv=15% have been used as a "seed" emulsion. The shell thickness uniformity has been studied by means of electron microscopy.

We have shown recently[4] that DJP procedure is mostly preferable for shell precipitation of the thickness up to 0,03 mcm. In case of the AgCl shell the upper scale of the obtained by DJP uniform shell is much thinner—0,013 mcm.

Shell precipitation by means of DJP

We have estimated that a threshold of the shell precipitation rate (W) lays in range 5×10^{-4} and 5×10^{-3} mol/cm^2. The higher precipitation rate causes new AgCl phase formation. (MeCl solution concentration was 0,3 - 0,8 M). The precipitation temperature also influences the precipitation rate threshold position. At the temperature 60°C it is 2×10^{3} mol/cm^2. In the temperature range under investigation 40 - 70°C it varies from 7×10^{-4} up to 3×10^{-3} mol/cm^2. A vast scale of the threshold position is caused by the wide varia-tion of the AgCl solubility with the temperature increase. Since AgCl forms only cubic grains, it is possible to carry the shell precipitation out in a wide range of the pAg value. A correlation between the pAg level and AgCl solubility gives additional condition to govern the shell uniformity.

The following set of DJP conditions allows to precipitate the most uniform "AgBr core/AgCl shell" grains: $W = 0,8 \times 10^{-3}$ mol/min, pAg = 5,8+/-0,05; T = 60+/-0,5°C, precipitation time—28 min.

Shell Precipitation by Means of Fine AgCl Recrystallization

Fine grain size has been varied on scale 0,05-0,12 mcm, having been measured both by the electron microscopy and nephelometry. The recrystallization procedure is arranged as follows: pBr = 3,00, T = 60°C, fixed amount of the "seed" emulsion is mixed with different amount of the fine AgCl. The recrystallization has been carried out in absence of AgHal solvater. The end of the process is checked by the fine grain disappearance. The uniform shells have thickness from 0,005 to 0,03 mcm.

Experimental data prove possibility to precipitate uniform AgCl shells both by DJP and recrystallization procedures.

References

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