Review of the Photographic Mechanisms of Iridium Doping in Silver Halide Photographic Systems

Ingo H. Leubner
Crystallization Consulting
35 Hillcrest Drive, Penfield, New York 14526, USA

Abstract

Iridium doping of silver halides provides certain advantageous effects to silver halide photographic sys-tems. Industrial applications are for improved reciprocity failure and for direct reversal materials. Sakai, Baba, and Eachus have proposed hole-trapping mechanisms. The author proposed a temporary electron trapping mechan-ism. The models will be reviewed. Based on the temporary electron trapping mechanism, a model will be presented for the effect of the depth of incorporation on photographic effects. The concepts of these models are thought to also apply to other cationic dopants and to other photosensitive systems.

Introduction

It has been reported that iridium doping of silver halide pho-tographic emulsions can affect latent image for-mation, re-duce the reciprocity failure, sensitize the direct positive pro-cess, improve the developability of print-out emulsions, de-crease kinking and abrasion, and show anti-fogging and stabi-lizing effects.[1] Because of its technical importance, knowl-edge of its reaction mechanism can suggest new and improved applications. It can also be used as a model for other the mecha-nism of other dopants.

Hole Trapping Mechanism

Sakai and Baba observed that both reduction sensi-tization and iridium doping reduced the reciprocity failure of emul-sions. Since the effect of reduction sensi-tization was under-stood to depend on hole trapping, they concluded that iridium should also be a hole trap.[2] They did not assign a structure to the active iridium centers.

Eachus argued that the dopants were vacancy neu-tralized and that thus the Ir (vac)$_2$ centers were hole traps.[3]

Electron Trapping Mechanism

Leubner reviewed the photographic, physicochemical, and chemical experimental evidence and concluded that Iridium was a temporary electron trap or a recombination center.[4] It was suggested that the dopant was incorporated as centers that either were fully, partially, or not vacancy substituted. The fully vacancy substituted centers are neutral and attract neither elec-tron nor holes, but might be recombination centers. The par-tially vacancy neu-tralized centers temporarily trap electrons and release them for possible latent image formation. This reduces electron—hole recombination and reduces the reci-procity failure. The non-neutralized centers trap two electrons and catalyze the formation of Ag$_2$ centers. When iridium is doped as a shell within the silver halide, the internal latent image is associated with the iridium dopant shell. The equi-libria between the centers with different charge neutralization were discussed in a previous paper.[5]

The iridium centers considered are sketched in Figures 1a-d for the silver chloride lattice. For Ir 0, only the trans-position for the vacancies is shown. The cis-position (not shown) is expected to have a significant dipol moment.

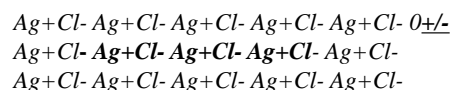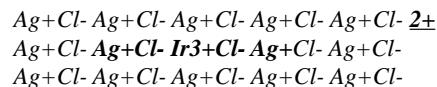**Figure 1a: Silver Chloride Lattice**

Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- 0+/-
*Ag+Cl- **Ag+Cl- Ag+Cl- Ag+Cl-** Ag+Cl-*
Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl-

Figure 1b: Ir2+ Center

*Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- **2+***
*Ag+Cl- **Ag+Cl- Ir3+Cl- Ag+Cl-** Ag+Cl-*
Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl-

Figure 1c: Ir + Center

*Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- **1+***
*Ag+Cl- **Ag+Cl- Ir3+Cl- vac**- Cl- Ag+Cl-*
Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl-

Figure 1d: Ir 0 Center

*Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- **0+/-***
*Ag+Cl- **vac**- Cl- **Ir3+Cl- vac**- Cl- Ag+Cl-*
Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl- Ag+Cl-

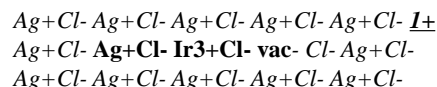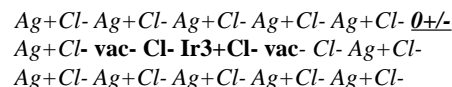## Effect of Iridium Shell Location on Photographic Properties

The association of positive charged centers with the photographic effects of iridium allows developing a model that relates the location of the iridium centers in the crystal with their photographic effects.

For convenience of modeling, we assume that the emulsion crystals are spherical with a radius R. The iridium is incorporated as a shell at a distance r from the center of the crystal (r < = R, Figure 1). The following assumptions are made:

- Iridium doping introduces positively charged centers in the crystal.
- These centers compete with surface centers for the photoelectrons.
- The relative charge and charge separation between surface and interior electron trapping centers drives the competition for photoelectrons.
- The driving force is given by a potential difference dE.

Shell-Doping

Using the model of a spherical condenser, the potential difference dE is given by Equation 2. It is assumed that the concentration and charge of the competing surface electron traps is kept constant.

$$dE = k\,C\,(1/r - 1/R)/4\,\pi\,\varepsilon\,\varepsilon_o \qquad (1)$$

C = dopant concentration
K = charge conversion factor
R = diameter of crystal
r = distance of dopant layer from center of the crystal
ε, ε_o = dielectric constants

The charge conversion factor converts the dopant concentration to an effective charge. This factor depends on the dopant, the composition of the crystal, and other factors that determine the vacancy neutralization of the dopant centers.
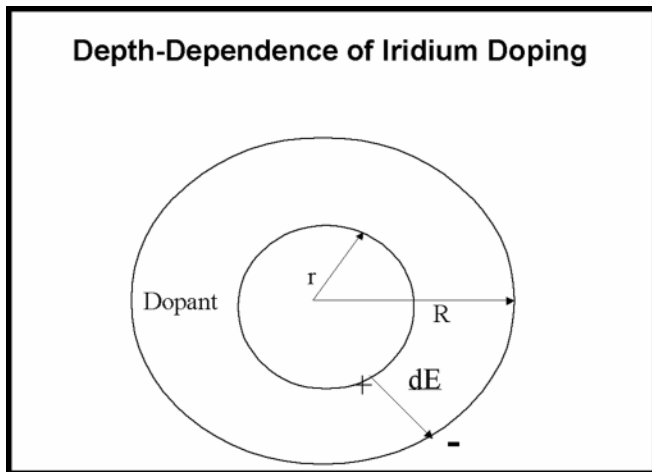

Figure 2.

For modeling convenience, a new factor Q is introduced which is proportional to the dopant concentration:

$$Q = k\,C\,/4\,p\,e\,e_o \qquad (2)$$

This simplifies equation 1 to:

$$dE = Q\,R\,(R/r - 1.0) \qquad (3)$$

dE is plotted as a function of R/r in Figure 3 for two relative values of Q.
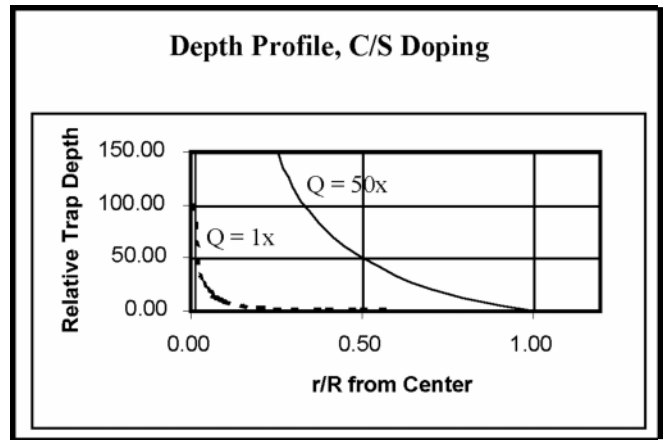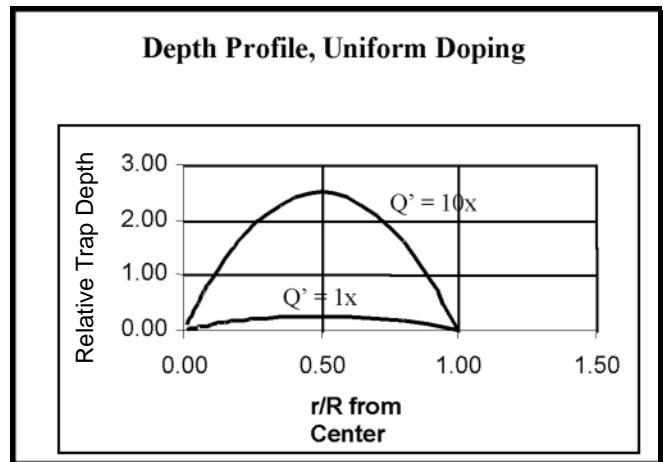

Figure 3.

Figure 4.

Since dE is proportional to the electron trapping capacity of the dopant, the following predictions can be made:

Electron trapping will increase with increasing Q (dopant concentration), R (diameter of the crystal), and increasing R/r. Since R is given for a given crystal, R/r will increase as r decreases. That is, the closer the dopant is added to the center of the crystal the more potent its electron trapping for a given dopant concentration. The model also predicts that the dopant will be inefficient at

the surface. An unrelated reason for its inefficiency at the surface is that the centers are fully vacancy neutralized at the surface. Dopant effects observed for surface addition are probably due to inadvertent coverage of some of the material during the sensitization process.

The model above must be modified if a significant level of positive surface charge exists, dE', for instance, by surface chemical sensitization. In this case, dE must be reduced by the surface positive potential. In practice, the dopant effect will only be observed at concentrations where the dopant potential, dE exceeds the surface potential dE'. This was observed in previous work where the iridium concentration dependence on desensitization and on the photomicrowave conductivity was studied on a uniformly doped silver chlorobromide emulsion.[5]

Uniform Doping

If a crystal is uniformly doped, Equation 3 can also be applied. However, Q must be replaced by

$$Q = Q_o \, 4 \, r^2 \, p \qquad (4)$$

dE is plotted vs. R/r in Figure 4 for two relative Q values. To obtain the overall effect of the dopant, it is necessary to calculate dE as a function of r, and integrate the results from r = zero to r = R.

References

1. B. H. Carroll, *Photogr. Sci. Eng.* **24:**265 (1980).
2. H. Sakai and S. Baba, *J. Soc. Photogr. Jpn.*, **31:** 34, 81, 134 (1968); **32:**13 (1969).
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4. I. H. Leubner, *J. Photogr. Sci.*, **31:** 93 (1983).
5. S. H. Ehrlich and I. H. Leubner, *J. Imaging Sci. Technol.* **36:** 105 (1992).