Achieving Synergy Between Theory and Experiment by Computer Simulation

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Introduction

Clean, decisive experiments with conventional silver halide materials are difficult to achieve. As a result interpretation is often ambiguous. A theoretical basis for much of silver halide photochemistry is found within the nucleation-and-growth (N&G) model of latent image formation. However, direct comparison between theory and experiment is generally not possible. Computer simulation is required for bridging the gap and bringing us to a quantitative understanding of the photographic properties of silver halide materials.

Theory

The N&G model of latent-image formation[1] assumes that the initial trapping of an electron and the formation of a silver atom by capture of an interstitial silver ion at the site of the trapped electron are totally reversible processes. Nucleation occurs when an electron is captured at a transient silver atom, followed by the capture of a second interstitial silver ion at the site to give a thermally stable silver dimer. Growth occurs by the alternate capture of photoelectrons and interstitial silver ions at the nucleation site. Growth continues as long as photoelectrons are available, since the number of interstitial silver ions is considered to be large, at least in AgBr.

The dominant loss process in the N&G model is recombination of the photogenerated electrons and holes. The indirect-gap nature of silver halides prevents the geminate recombination process and generally forbids the recombination of free electrons and holes.[2] Thus, recombination occurs between a trapped and a free carrier. The usual recombination pathway is between free electrons and trapped holes, because holes are less mobile than electrons due to multiple trapping and because of their higher effective mass holes are more deeply trapped. In some circumstances the recombination between free holes and trapped electrons becomes important.[3] This is true for chemically sensitized emulsions that have been sensitized beyond the optimum speed point. In these situations there are too many electron traps, leading to the alternative recombination pathway. This situation is called the oversensitization region of chemical sensitization.

This rather simple model of latent image formation has enjoyed a wide degree of success.[1,4] It can quantitatively explain the effects chemical sensitization with sulfur, sulfur-plus-gold, and reduction sensitization. These sensitometric effects include a variety of photographic experiments such as reciprocity failure, latensification, and development center behavior. All can be accounted for self-consistently with the N&G model. More recently, highly sophisticated classical and quantum mechanical calculations have produced results consistent with the assumptions upon which the N&G model is based.[5]

Computer Simulation

The computer simulations are based on the Monte Carlo technique in which the sequence of events in latent-image formation occur in random, but the sequence is weighted by the probability of each event.[6] The simulation uses a steady-state approximation for the reversible events and focuses exclusively on the irreversible events of light absorption, nucleation, growth, and recombination. Although highly successful, this simulation approach has a limitation in that spatial effects are accounted for in only a very indirect way. Thus, grain size effects and spatial effects in general cannot be studied, which is a major drawback. To remedy this situation a more sophisticated simulation scheme was developed and implemented on a parallel processor.[7]

The new simulation scheme is analogous to those used for semiconductor device simulation. The dimensions of the grain is an explicit parameter, as are those associated with the trapping/detrapping and atom formation/decay events. Also included are the parameters associated with the random walk movement of the carriers through the grain. A list of typical parameter values is given in Table I.

Example Application

The use of the new simulation scheme is best understood through an example. It is well known that blue light absorption in AgBr emulsion coatings increases linearly with increasing grain volume. It follows that speed should also increase linearly with log grain volume. This behavior is actually observed experimentally up to a certain grain volume, beyond which the speed increase is sublinear.[8] This is a well known feature of silver halides and presents a major impediment to designing high-speed films with good image quality. The region of sublinear dependence on grain volume is due to grain-size dependent inefficiencies, the precise nature of which is the subject of debate. Possible inefficiencies include dispersity,[8a-c] impurity-induced electron loss, internal

Table I. Typical parameter values used in the simulations.

Parameter	Value range
Time step	10^{-11}
Diffussion coefficient, electron	$5x10^8$ $\mu m^2/s$
Diffusion coefficient, hole	$5x10^4$ - $5x10^6$ $\mu m^2/s$
Trap depth	0.05 - 0.50 eV
Recombination radius	25 - 50 A
Trap radius	25 - 50 A
Atom formation time	10^{-5} - 10^{-7} s
Atom decay time	10^{-1} - 10^{-6} s
Trapped hole time	10^{-6} - 10^{-10} s
Number of traps	10^2 - $10^4/\mu m^2$
Exposure time	10^{-6} - 10^3 s
Number of photons	2 - 1024
Number of grains	400 - 1000

latent-image formation, and grain-size-enhanced recombination.

In an earlier study we explored this problem with the new simulation scheme.[9] Size-independent quantum sensitivity could be achieved in the grain size range of 0.1 to 0.95 μm cubic edge length. Thus, the dispersity inefficiency was not observed in this size range, which encompasses the range where sublinearity is observed. Since impurities and internal latent image formation were not incorporated in the designed simulation scheme, these inefficiencies were not observed. Finally, recombination was found to be independent of grain size. Thus, at this point the model is not consistent with the well-known grain-size dependent quantum sensitivity observed experimentally.

To bring the model closer to reality we have considered the effect of iodide, which is an ubiquitous impurity in AgBr. Iodide is a well-known hole trap and can therefor enhance recombination.[2] Because the number of iodide impurities/grain will increase with increasing grain size, the possibility of a size-dependent recombination inefficiency seemed probable and worthy of investigation.

The level of iodide impurity is taken as the upper limit of Aldrich specifications for KBr used in our emulsion preparations — 0.001 M% (10 ppm). Since iodide is isoelectronic with bromide, the hole trapping radius of iodide is taken as a lattice spacing. This is about 20% that of the surface hole traps which are assumed to be negative kink sites with charge -0.5*e*. However, after hole trapping at an iodide the recombination site has a +*e* charge with respect to the surrounding lattice, whereas the surface-trapped hole would present only a +0.5*e* charge. Because the recombination radius for a free carrier goes as the charge of the trap squared, the recombination radius presented by the iodide-trapped hole is taken as 4x that for a surface-trapped hole. Thus, internal iodide impurity is a poor hole trap, but a good recombination center once it does trap a hole. Implicit in this discussion is the assumption that ionic relaxation in the vicinity of the iodide-trapped hole is negligible

Ideally, the iodide impurity centers should be placed at random positions throughout the volume of the grain with a number density consistent with the impurity concentration. However, from prior experience it was known that this approach would consume significant computation time, particularly for large grains, since hole trapping and recombination would have to be checked for after every movement of the electron and hole. A more efficient algorithm is to build a core-shell structure as a model system with all the iodide impurity placed at the core-shell interface, and the traps due to sulfur-plus-gold sensitization at the surface. The ratio of core diameter to core-shell diameter is fixed at 0.75 and the number of iodides at the core is scaled with the total grain volume in accordance with the specified impurity level of 10 ppm. Grain edge lengths studied are 0.2, 0.4, 0.8, and 1.6 μm, providing more than a 500-fold change in grain volume.

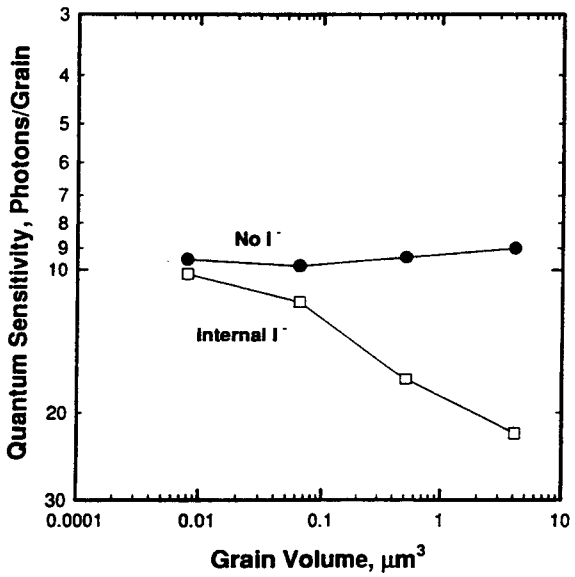

Fig. 1. Quantum sensitivity vs grain volume for control and iodide-containing grains. A minimum developable size of three atoms was assumed. Exposure time is 10^{-6} s.

Figure 1 shows how quantum sensitivity depends on grain volume for both the control simulation (no iodide) and with 10 ppm iodide. It is obvious that the effect of iodide impurity on quantum sensitivity increases with grain volume, as expected. Even though the iodide centers have a small trapping cross section for holes, their density, even at 10 ppm, is such that they have an effect on the total recombination when the grain volume increases. The

simulations also allow a determination of the location of the recombination. Figure 2 shows that the partitioning between surface and internal recombination varies with grain volume. For the 0.2 μm grain recombination is exclusively surface recombination, whereas in the 1.6 μm grain half the recombination occurs internally.

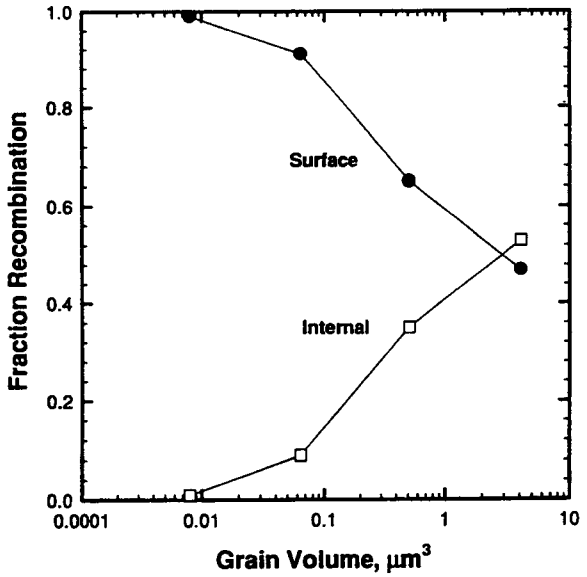

Fig. 2. Partitioning of recombination between surface and internal sites for the iodide-containing grains. Data taken from simulation results presented in Fig. 1.

Conclusion

This simulation example serves to illustrate the power and utility of the new simulation scheme. Such a study would have been impossible with the older scheme. In addition, the ability to study potential inefficiencies individually through simulation greatly simplifies the problem, leading to a clearer understanding of the phenomena.

These simulation studies have shown that iodide-induced recombination can have important consequences for speed-grain size relationships. However, this does not mean that it is the most important inefficiency. We have already eliminated dispersity as an inefficiency, but have not yet studied internal latent image formation. It is likely that this latter inefficiency is also an important factor in size-dependent quantum sensitivity, and, indeed, may be the dominant factor. This new simulation scheme could be used to study the relative importance of these two effects.

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