Two Models of the Latent Image Formation

Mikhail A. Goryaev
Central Design Bureau of Mechanical Engineering
St.Petersburg, Russia

Abstract

We have compared models of the latent image formation in silver halides according to the Gurney-Mott mechanism and the statistical mechanism of intrinsic defect formation. Physical parameters governing the latent image formation for these two mechanisms are discussed. A probability of primary photochemical processes with the participation of biographic sensitivity centers and a probability of the thermal defect formation with the participation of an electronic excitation are determined. The contribution of a statistical defect formation to the total photochemical process is shown to increase at the high light intensity. Mechanisms of the photographic reciprocity failure are discussed according to considering models.

Introduction

The majority of the modern theories of the photographic process in silver halides consider the image formation as result of electron-ionic reactions in a solid lattice.[1] The main models[2,3] of the latent image formation are based on the Gurney-Mott principle. According these models the primary photochemical product in AgX is a result of localization of the photoelectron and interstitial silver ion at the sensitivity center. At the same time the photochemical process takes place in nominally pure AgX monocrystals. In works[4,5] the statistical model of primary photochemical processes is proposed. This model has a good agreement with the experimental data on the nanosecond laser photolysis of AgBr and AgCl monocrystals.[6] In the present paper two models of the latent image formation are compared and physical parameters governing the primary photochemical processes are discussed.

Primary Photochemical Processes

Local states in the forbidden band of AgX, in particular electron traps N_t (Fig.1), play an important role in the first stage of the latent image formation according the Gurney-Mott mechanism.[7] The electron lifetime on these traps can be evaluated under the formula:

$$\tau_t = \frac{1}{S_n v N_c} \exp\left(\frac{E_t}{kT}\right) \qquad (1)$$

Here N_c is a density of states in a conductivity band, E_t is a trap depth, S_n is a trap cross-section, v is a thermal electron speed. At really probable values $S_n = 10^{-18} - 10^{-15}$ cm^2, $v = 10^7$ cm/s, $N_c = 10^{19}$ cm^{-3}, even for traps on a depth of 0.1 eV from the bottom of the *c*-band we receive at room temperature $\tau_t = 10^{-7} - 10^{-4}$ s. Such lifetimes are sufficient for participation seized electron in the subsequent stages of the image formation, since inertness of an electronic stage does not surpass 10^{-8} s.[7,8]

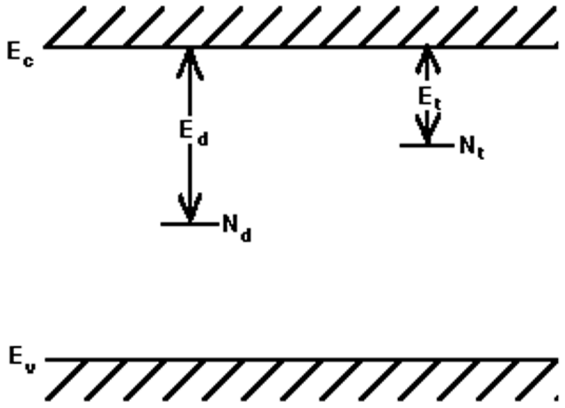

Figure 1. Energy structure of AgX with traps N_t and intrinsic defect levels N_d.

The probability of an electron capture at a trap is determined by the formula:

$$\eta_1 = N_t v S_n \qquad (2)$$

The statistical mechanism of primary photochemical processes[4,5] is based on the theory of statistical interaction between electrons and defects in semiconductors.[9] According to this theory after the occurrence of an additional electron in a crystal a formation of intrinsic lattice defects N_d (Fig.1), on which an electron is located, is thermodynamically more expediently than a formation of an electron at the bottom of a conductivity band. Owing to increase of a probability of the thermal defect formation with participation of electrons, excited in a conductivity band by light, it is probably an essential increasing of the intrinsic defect concentration:

$$N_d = \left(\frac{\lambda_e \varphi N^2}{\gamma_f N_c}\right)^{\frac{1}{3}} \exp\left(-\frac{W - E_d}{3kT}\right) \qquad (3)$$

Here $\lambda_e\varphi$ is an electron concentration in a band after the absorption of φ light quanta at a quantum yield of photoeffect λ_e; γ_f is a recombination temp of free electrons on defect; N is a concentration of lattice units; W is an energy of an intrinsic defect formation; E_d is a depth of a defect level.

The probability of the spontaneous intrinsic defect formation in a crystal, called by thermal fluctuations with the participation of an electronic excitation is determined under the formula:[9]

$$\eta_2 = \frac{a^3 v_0^2 N^2}{N_c} \exp\left(-\frac{W - E_d - E}{kT}\right) \quad (4)$$

Here a is a lattice parameter; v_0 is a frequency of jumps between neighbor sets of a crystal; E is an activation energy of a defect migration.

It is necessary to compare a probability of an intrinsic defect formation and a probability of an electron capture on biographic traps, to evaluate the contribution of the statistical defect formation to the photographic process. But that the processes of the statistical defect formation occur in real photomaterials, is confirmed by those fact, that at the nanosecond laser photolysis of holographic emulsions primary photochemical products are observed as well as in nominally pure monocrystals.[6]

Nucleation and Growth of Latent Image Centers

The final goal of any modeling of the latent image formation is the formation of silver clusters which are really developable. The main schemes consider nucleation (Ag_2 formation) and growth (formation of Ag_3 etc.) processes.[1–3] Fig. 2 shows processes of silver concentrating according two considering models.

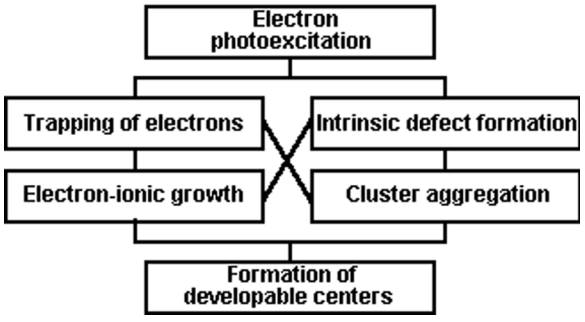

Figure 2. Schemes of the latent image formation.

The first model assumes the consequent migration of electrons and interstitial silver ions to a primary center.[2,3] The electron-hole recombination and losses linked with halogen formation can be accounted for these electron-ionic processes.

The other way is associated with the aggregation of interstitial atomic and molecular clusters for the formation of stable developable centers.[10] The main difficulties of such aggregation process are contradictions between a high speed of a silver atom aggregation into silver clusters (~10^{11} $Ag{\cdot}cm^{-3}{\cdot}s^{-1}$) and a low speed of a thermal atom generation (~10^7 $Ag{\cdot}cm^{-3}{\cdot}s^{-1}$). However this contradiction is absent if the statistical model of a defect formation is considered.[4,5]

Naturally the nucleation and the growth of latent image centers according both the Gurney-Mott mechanism and the statistical mechanism can be result of as electron-ionic reactions as the atomic cluster aggregation (Fig. 2). Therefore these processes must be accounted for a consideration of both models. For the choice of one alternative model of the latent image formation it is necessary at first to determine probabilities η_1 and η_2 according formulas (2) and (4).

Reciprocity Failure at High Intensities

The concentration of additional intrinsic defects N_d depends on an intensity of light according to the formula (3). Therefore the role of the statistical defect formation increases when the concentration of biographic defects is small and the exposure light intensity is large.

An absence of a reciprocity failure for primitive AgBr emulsions[11] is determined by the effective formation of latent image centers according a statistical mechanism. For a = $5.8{\cdot}10^{-8}$ cm, W = 1.05 eV, E_d = 1 eV, E = 0.15 eV, $v_0 = 10^{13}$ s^{-1}, N_c = 10^{19} cm^{-3} and N = 10^{22} cm^{-3} η_2 is equal 10^{13} s^{-1} for AgBr. Value of η_2 is equal about 10^8 s^{-1} for AgCl. Therefore there is a reciprocity failure at high intensities in primitive AgCl emulsions.[11]

Obviously processes of the latent image formation are reversible at every stages. Therefore one believes that the formation of the high concentration of unstable primary centers according a statistical mechanism determines a reciprocity failure at high intensities. For decreasing of such defect formation it is necessary to enter traps into a crystal, which would compete with these process. The ions Cd^{2+} create in AgBr electron traps with cross-section $S_n \sim 10^{-15}$ cm^2.[12] To be comparable a probability η_2 under the formula (4) with η_1 under the formula (2), traps concentration should be ~10^{20} cm^{-3}. Really after doping of thermally processed compositions on the basis AgBr by $CdBr_2$ with concentrations ~1 mol% the reciprocity failure of photothermographic films has essentially reduced at high intensities.[13]

Conclusion

The first semi-quantitative estimations show that the proposed statistical model of the latent image formation as the Gurney-Mott model may play an essential role in some real photographic systems. Further applications and the quantitative estimations of parameters are possible for different photographic processes by use for example of computer procedures according the work.[3]

References

1. T. H. James, The Theory of the Photographic Process, 4th Ed., New York, 1977.

2. N. Malinowski, J. Malinowski, *J. Imag. Sci*, **29,** 105 (1985).
3. R. K. Hailstone, *J. Phys. Chem.*, **99,** 4414 (1995).
4. M. A. Goryaev, *Proc. Intern. Symp. Silver Halide Imaging*, Victoria, 148 (1997).
5. M. A. Goryaev *Zh. nauchnoi i prikladnoi fotografii*, **43**, Nr 3, 9 (1998); Engl. transl.: *Scientific and Appl. Photography*, **40,** 125 (1998).
6. M. A. Goryaev, S. S. Tibilov, *Phys. Processes in Light Sensitive Systems on Silver Salts*, Kemerovo, 19 (1986).
7. M. A. Goryaev, *Uspekhi nauchnoi fotografii*, **24**, 109 (1986).
8. A. A. Benken, et al., *Pisma v Zh. tekhnicheskoi fisiki*, **10**, 569 (1984); Engl. transl.: *Tech. Phys. Lett*., **10**, 264 (1984).
9. V. L. Vinetsky, G. A. Kholodar, Statistical interaction of electrons and defects in semiconductors, Kiev, (1969).
10. A. G. Kovetsky, et al, *Fisika tverdogo tela*, **25**, 3698 (1983).
11. P. Faelens, *J. Phot. Sci.*, **33,** 86 (1985).
12. J. Malinowski, *Phot. Sci. Eng.*, **17,** 86 (1973).
13. M. A. Goryaev, T.B.Kolesova, *Zh. nauchnoi i prikladnoi fotografii*, **38**, 63 (1993); Engl. transl.: *Scientific and Appl. Photography*, **35,** 95 (1994).