The Thermodynamic Model of the Silver Halide Photolysis

Mikhail A. Goryaev and Vladimir S. Gerasimov
Central Design Bureau of Mechanical Engineering
St.Petersburg, Russia

Abstract

The model of the latent image formation in silver halides according to the stochatic mechanism of intrinsic defect formation after photoexcitation is discussed. A good agreement with experimental results on the AgHal laser photolysis is recieved. The contribution of a stochatic defect formation to the total photochemical process is shown to increase at the high light intensity. The dependence of the photographic reciprocity failure on the type of the silver halide and on the concentration of impurities are discussed according to considering model.

Introduction

The modern theories of photochemical processes in inorganic solids are considered these processes as result of electronic and ionic reactions in a lattice of a crystal.[1-5] First of all it concerns silver halides as the most known in a number of photochemical sensitive wide-band semiconductors . The models of AgHal photolysis are based on the Gurney-Mott principle,[1,6] according to which the silver will be formed at consistently interleaved migration of free carriers excited by light and interstatial silver ions to sensitivity centres of a crystal. These local centres are stipulated by defects of the biographic origin and the main formation ways of silver halide photographic materials communicate with regulation of such defects properties.[1,2]

At the same time the photochemical decomposition of silver halides occurs in perfect crystals,[1,7] and in radiating physics representations about processes of wide-band crystals decomposition due to the intrinsic defects formation and aggregation are advanced at desintegration of an electronic excitation in the regular areas of a solid.[8-10] Mechanism of the primary photochemical processes in silver halides due to the participation of intrinsic defects, appearing as a result of the photoexcitation energy dissipation is offered in works[11,12] within the framework of the theory of the stochatic electrons and defects interaction in semiconductors.[8] In the present work the model of intrinsic defects formation at photoexcitation and its application to the photochemical processes in silver halides are considered.

Stochastic model of defect formation

The formation of additional lattice intrinsic defects in wide-band solids can occur as a result of electron-hole pairs desintegration and autolocalized excitons desintegration.[8,9] A primary stage of photochemical processes in main inorganic semiconductors is an internal photoeffect,[1-6] in this connection it is possible to consider only defect formation processes with participation of electron-hole pairs. As far n-type photoconductivity is observed in silver halides,[1] it is quite possible to be limited only to participation of photoelectrons in defects formation.

According to the stochatic interaction theory of electrons and defects in semiconductors after occurrence redundant electron in a crystal formation of intrinsic lattice defect, on which electron is located, is thermodynamiccally more expediently than existence of an electron in a conductivity band or polaron.[8] The conditions of such defect formation are by minimization of free energy of a crystal.

Within the framework of the theory[8] two states are considered: 1 - (crystal + electron in a polaron state) and 2 - (intrinsic lattice defect + located on it electron). The free energy $F = E - TS$ is determined as by an internal system energy E, as by entropy of the system S at temperature T. Change of a crystal free energy at occurrence a nonequilibrum electron, forming a polaron (the state 1), will be[8]:

$$\Delta F_1 = - E_p - kT ln(N_c V), \qquad (1)$$

Where E_p - energy of a polaron state concerning the bottom of a conductivity band; N_c - density of states in a conductivity band; V - volume of a crystal.

The change of a free energy at formation of intrinsic defect, on which a nonequilibrum electron is located, is possible to write[8]:

$$\Delta F_2 = W - E_d + 2kT ln[(N_d V + 1)/(N_0 - N_d)V], \qquad (2)$$

Where W - energy of defect formation; E_d - depth of a electron capture level; N_d - equilibrum density of intrinsic defects at temperature T; N_0 - density of lattice units. Usually $N_d \ll N_0$ and then the difference in change of a free energy in states 1 and 2 will be:

$$\delta F = \Delta F_2 - \Delta F_1 = W + E_p - E_d - kTln(N_0{}^2V/N_c) \quad (3)$$

Usually $W > E_d$, therefore at the zero temperature a state 1 will be realized.

However the formation of an intrinsic lattice defect causes to a significant increasing an entropy S and at $T > 0$ a system free energy in a state 2 can be below, than in a state 1. Thus, at $\delta F < 0$ thermodynamic realization of a state 2 is more expedient, i.e. formation of an intrinsic lattice defect, on which a nonequilibrum electron is located, occurs. The temperature threshold defect formation, as it follows from the formula (3), is determined by a ratio:

$$T_{min} > \frac{W + E_p - E_d}{k\ln(N_0{}^2V/N_c)} \quad (4)$$

At temperatures higher T_{min} a concentration of intrinsic defects increases essentially. According to the theory[8] a concentration of additionally formed defects can be appreciated:

$$N_d = \left(\frac{\lambda_e\varphi N_0{}^2}{\gamma_f N_c}\right)^{1/3} exp\left(-\frac{W - E_d}{3kT}\right) \quad (5)$$

Where $\lambda_e\varphi$ - an electron concentration in a conductivity band at absorption of φ light quantums at a quantum yield of photoeffect λ_e; γ_f - a recombination speed of free electrons on a defect.

Thus, the opportunity of intrinsic defects formation and its efficiency at photoexcitation of a solid is determined by the energy of intrinsic defects formation in a crystal and the energy of these defect acceptor levels.

Photochemical processes in silver halide

The primary products of photochemical conversions with a life time ~ 300 ns in the nominally pure silver halide crystals were found in works[7,13] by the method of the nanosecond laser photolysis. These products have a important feature: the spectra and kinetic attenuation curve of induced absorption practically coincide for AgBr and AgCl as at 77 K, as at room temperature.[13] Under one of natural assumptions of work[13] the nature of such products communicates with electrons, seized by intrinsic defects in silver halides, in particular, by interstitial silver ions. However, the equilibrum concentration of Frenkel defects at room temperature are of the order 10^{14} cm^{-3} for AgBr and 10^{12} cm^{-3} for AgCl.[5] Obviously such concentrations are not enough for maintenance of observable absorption, as far as a concentration of local states in a solid lattice has to be 10^{17}-10^{18} cm^{-3} for formation of measured absorption density.[13]

Within the framework of considered model of the defect formation at desintegration of the electronic photoexcitation it is possible to evaluate conditions of interstitial silver ions occurrence. The energy of the Frenkel defects formation is 1.35-1.40 eV for AgCl and 1.0-1.05 eV for AgBr,[14] and the level of interstitial silver ions with trapped electron lies on a depth ~ 1 eV below the bottom of a conductivity band.[15] Crystals used in work[13] had V ~ 10^{-3} cm^{-3}, and usually E_p = 0.2 eV and

effective values N_0 = $3 \cdot 10^{25}$ cm^{-3}, N_c = 10^{18} cm^{-3},[8] we receive under the formula (4) T_{min} = 39 K for AgBr and T_{min} = 105 K for AgCl. At the surface of silver halides a defect formation is essentially more effective because of the energy of the interstitial silver ions formation decreases,[1] therefore in the subsurface of a crystal (where excitation light with λ = 347 nm is absorbed[13]) the additional defects can be formed practically at any temperature.[12]

Under the formula (5) it is possible to evaluate concentration of formed defects. Assuming for valuation γ_f = 10^7-10^{13} cm^3 c^{-1} [8] and using above signed parameters for silver halides, we receive, that for real significances $\lambda_e\varphi$ = 10^{18} cm^{-3} [13] at room temperature concentrations of appearing additional interstitial silver ions are about of 10^{18}-10^{20} cm^{-3} for AgBr and 10^{16}-10^{18} cm^{-3} for AgCl. Thus, the values designed on offered model will be agreeed with concentrations of defects, which are necessary for maintenance of experimentally observable optical density of induced absorption at nanosecond laser photolysis of AgHal.[13]

Valuation of the AgHal photolysis process evolution for formation of the stable silver latent image centres is made in work.[16] In view of aggregation processes of atoms and small-sized clasters there is shown the role of thermodynamic intrinsic defect formation increases, on the one hand, at small concentrations of impurity defects in initial crystals, and on other - at high intensities of exciting light.

It follows that stochastic model can be used to explain the reciprocity-law failure[17] for primitive emulsion (containing small amount of sensitivity centers). For primitive AgBr emulsion, the fact that the reciprocity law hold true can be explained by additional formation (at high light intensity) of latent image centers through stochastic formation of silver cations.

Note that the formation of latent image centers through stochastic formation of intrinsic defects provides the physical substantiation for Moisar model[18] that involves empirical correction for sensitivity parameters at different light intensivities in order to rationalize the reciprocity failure.

Conclusion

The considered mechanism of photochemical processes is alternate for known electron-ion process[1,6] in silver halides. Stochastic processes are very important first of all in designing modern photographic materials for rapid recording, where high intensity light sources are applied at short exposure intervals. The similar model also can be used to explain the photochemical processes in solids with different intrinsic defects (for example anion vacancies).[19]

References

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

2. M. A. Goryaev, Uspekhi nauchnoi fotografii, 24, 109 (1986).
3. J. F. Hamilton, Advances in Physics, 37, 359 (1988).
4. M. A. Goryaev, Zh. nauchnoi i prikladnoi fotografii, 38, 63 (1993); Engl. transl.: Scientific and Appl. Photography, 35, 95 (1994).
5. R. K. Hailstone, J. Phys. Chem., 99, 4414 (1995).
6. R. W. Gurney, N. F. Mott, Proc. Roy. Soc., 164A, 151 (1938).
7. S. G. Grenishin, A. A. Timokhin, S. S. Tibilov, Optika i spektroskopiya, 61, 1153 (1986).
8. V.L.Vinetsky, G.A.Kholodar, Statistical interaction of electrons and defects in semiconductors, Kiev, (1969).
9. Ch. B. Luschik, A. Ch. Luschik, Desintegration of electron excitation with formation of defects in solids, Moscow, (1989).
10. V. L.Vinetsky., Yu. K. Kalnin, et al, Uspekhi fizicheskyh nauk, 160, 1 (1990).
11. M. A. Goryaev, Proc. Intern. Symp. Silver Halide Imaging. Victoria, pg.148 (1997).
12. M. A. Goryaev, Zh. nauchnoi i prikladnoi fotografii, 43, 9 (1998); Engl. transl.: Scientific and Appl. Photography, 40, 125 (1998).
13. M. A. Goryaev, S. S. Tibilov, Phys. Processes in Light Sensitive Systems on Silver Salts, Kemerovo, 19 (1986).
14. J. Corish, J. Chem. Soc., Farad. Trans. II, 85, 437 (1989).
15. B. T. Plachenov, A. R. Sokolov, R. A. Evarestov, Fizika tverdogo tela, 28, 867 (1986).
16. M. A. Goryaev, Zh. nauchnoi i prikladnoi fotografii, 44, 34 (1999); Engl. transl.: Scientific and Appl. Photography, 41, 535 (2000).
17. P. A. Faelens, J. Phot. Sci., 33, 86 (1985)
18. E. Moisar, Photogr. Sci. Eng., 17, 86 (1973)
19. M. A. Goryaev, V. S. Gerasimov, Zh. fizicheskoi khimii, 78, 1902 (2004)

Biography

Mikhail A. Goryaev was born in 1949. In 1972 he graduated from the Leningrad University and joined the State Optical Institute. He received the Ph. D. degree in Physics from the State Optical Institute in 1977, the D. Sc. degree in Physical Chemistry from the Kemerovo State University in 2000. Since 1982 till 1987 he was Deputy Director and Director of the State Research Institute of Photochemical Industry (Leningrad Branch). Since 1988 till 1994 he was a senior and leading research specialist of the State Optical Institute again. Since 1994 he has been a Head of Laboratory in the Central Design Bureau of Mechanical Engineering. His research interests are in the area of the solid state photochemistry, spectral sensitization, photothermographic systems, electronic imaging, physical education and history of science. He has published about 110 papers and patents in these areas.