

Primary Photochemical Processes in Silver Halides

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Introduction

The overwhelming majority of the modern concepts of the image formation in silver halides consists that this process is result of electron-ionic reactions in a solid lattice¹⁻³. In the basis of these models the Gurney-Mott principle lies, according to which the photolitic silver will be formed as a result consistently interleaved migration of photoelectrons and interstitial silver ions to certain local centres of a microcrystal. These so the named sensitivity centres, about biographic origin agreed by defects, play a important role in the theory of the photographic process and main ways of a property regulation in silver halide materials^{1,3} communicate with them. At the same time in radiating physics processes of defect formation and agregation in solids are known as a result of the electronic excitation desintegration in regular regions of a crystal^{4,6}. In works^{7,8} primary photochemical products were observed in nominally pure silver halide monocrystals by the method of the nanosecond laser photolysis. In the present paper a formation mechanism of such products is considered on the basis of the theory of the statistical interaction between electrons and defects in semiconductors⁴.

Results and Discussion

The spectra of induced absorption in silver halide monocrystals after action short-wave ($\lambda=347$ nm) laser pulse ($\tau=10^{-8}$ s), received by Tibilov⁸, have a important feature: the spectra are practically identical for AgBr and AgCl as at 77 K, as and at room temperature. This fact, as well as concurrence of kinetic curves of induced absorption decay has said about unity of a nature and formation mechanism of photochemical products at such light effect.

The nature of relatively long-life products ($\tau\sim 300$ ns), forming a induced absorption spectrum, communicates on one of the natural assumptions in paper⁸ with electrons seized by intrinsic defects in silver halides, in particular, by silver ions. However, the equilibrium concentration of Frankel defects (interstitial silver ions Ag_i^+ and vacancies V_{Ag^-}) consist of values 10^{14} cm⁻³ for AgBr and 10^{12} cm⁻³ for AgCl at room temperature². Such concentration obviously it is not enough for necessary absorption, as far as the formation of observable induced absorption spectra requires

participation of local states in a solid lattice with concentration 10^{17} - 10^{18} cm⁻³⁸.

At the same time the electronic excitation desintegration in wideband solids can result to occurrence of additional intrinsic lattice defects^{4,5}. Thus the defect formation communicates with desintegration of electron-hole pairs and autolocalized excitons. Autolocalized excitons were observed in AgCl at low temperatures^{5,9}, but in AgBr autolocalization of excitons is not executed⁵. At room temperatures in general it is inconveniently to speak about excitons in silver halides, therefore it is more really to consider defect formation processes with participation of electron-hole pairs. As far as photoconductivity of silver halides is determined basically by electrons^{1,2}, it is quite possible to be limited to consideration only of photoelectron participation in defect formation.

According to the theory of statistical interaction between electrons and defects in semiconductors after the occurrence of additional electron in a crystal a formation of intrinsic lattice defect, on which is located such electron, is more energetically suitably than formation of an electron at the bottom of a conductivity band or polaron⁴. Owing to increase of probability of the thermal defect formation with participation redundant electrons, excited in a conductivity band of by light, it is probably a essential increasing of intrinsic defect concentration. The temperature threshold of defect formation (T_{min}) is determined by the formula⁴:

$$T_{min} > (W + E_p - E_a) / k \ln(N^2 V / N_c), \quad (1)$$

where W - energy of defect formation; E_p - energy of polaron state; E_a - depth of a trap level; N - density of lattice units; N_c - density of states in a conductivity band; V - volume of a crystal.

The defect formation in a solids with the subsequent electron grab on its level depends on a energetics of intrinsic lattice defects. Electrons can occupy vacant levels of interstitial silver ions Ag_i^+ and under the formula (1) opportunity of realization of this process can be appreciated. The formation energy of Frankel defects make 1,35-1,40 eV for AgCl and 1,0-1,05 eV for AgBr¹⁰, and the level of a interstitial silver ion with trapped electron lies on a depth of the order 1 eV below the bottom of a conductivity band¹¹. In view of that $V=10^{-3}$ cm³, and usually $E_p=0,2$ eV and effective significances $N=3 \cdot 10^{23}$ cm⁻³, $N_c=10^{18}$ cm⁻³⁴, we receive the values $T_{min}=39$ K for AgBr and $T_{min}=125$ K for

References

AgCl. Thus the defect formation with participation of photoelectrons in silver halides begins at threshold temperatures, essentially below room.

It should note, that for epitaxial films the formation energy of interstitial silver ions is 0,21 eV for AgBr and 0,56 eV for AgCl¹. Then at a surface of a crystal the additional defect formation can occur practically at any temperature, since the valuations under the formula (1) give $T_{\min}=0$. Taking into account of fact, that used in work⁸ excitation light with $\lambda=347$ nm is basically absorbed in a nearsurface layer of a crystal because of large extinction factors, it is possible with reliance to say, that the considered processes of the defect formation are quite real in given conditions of experiment realization, i.e. at temperatures 77 K and 300 K.

Within the framework of the theory⁴ probability η of defect formation in a crystal called by thermal fluctuations with participation of electronic excitation can be appreciated: $\eta = 6 \cdot 10^{17} \text{ s}^{-1}$ for AgBr and $\eta = 10^{13} \text{ s}^{-1}$ for AgCl at room temperature. Hence, at nanosecond photoexcitation such channel of energy dissipation with formation of new interstitial ions in silver halides will be realized reasonably effectively.

It is also possible to evaluate concentration of formed defects⁴: we receive, that for the real significances of photoelectron concentrations 10^{15} cm^{-3} ⁸ at room temperature concentrations of new interstitial silver ions lie within the limits of 10^{17} - 10^{19} cm^{-3} in AgBr and 10^{15} - 10^{17} cm^{-3} in AgCl. These significances will well agree with mentioned above concentrations of local states, necessary for maintenance of observable in experiment induced absorption⁸.

Thus, the offered mechanism permits reasonably reliably to interpret experimentally observable on absorption spectra primary products of photolysis as formations of a silver nature in silver halide monocrystals. They are result of photoelectron trapping on levels of interstitial silver ions. That to evaluate the contribution of considered processes to photochemical sensitivity formation of real silver halide emulsion microcrystals, additional researches are necessary, as far as the defects of a biographic origin render doubtless influence on electronic and ionic processes as on first, as at the subsequent stages of photochemical conversions. First of all it should be determined a energy structure of local states in a forbidden band of a silver halide, which at synthesis of emulsions, as a rule, is strongly modified and, in essence, in each particular case we deal with a new semiconductor¹². But that the similar processes proceed and in real photomaterials, is confirmed by those fact, that the similar spectra of induced absorption are observed at nanosecond laser photolysis in small-grain holographic emulsions⁸.

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