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# Photostimulated spectral variations and photolysis in the epitaxy of silver iodomercurate on silver iodide

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It is demonstrated spectrally that when composite single crystals consisting of  $\text{Ag}_2\text{HgI}_4$  epitaxes on an  $\text{AgI}$  substrate are illuminated, photolysis will initially occur in the substrate only. When a certain critical saturation of  $\text{AgI}$  by photolytic  $\text{Ag}$  occurs, there is an irregular transfer of the latter to the epitax which by this time becomes disordered to the superionic state and hence has substantially greater space for  $\text{Ag}$  deposition.

Reference 1 describes changes in the absorption spectrum from the photostimulation of the phase transition in  $\text{Ag}_2\text{HgI}_4$  single crystals (SC) obtained by bulk crystallization in a thin gelatinous matrix that involves saturation of the matrix by  $\text{AgI}$  and  $\text{HgI}_2$  solutions in aqueous  $\text{KI}$ . The spectra reported in Ref. 1 demonstrated a  $\text{Ag}_2\text{HgI}_4$  phase transition from the nonsuperionic  $\beta$  phase to the superionic  $\alpha$  phase. Although the absorbed light will undoubtedly make a significant contribution to disordering of the cation sublattice (this is what photostimulation of the transition involves), the disordering itself is reversible and in darkness the lattice will relax to its initial cation-ordered state. The situation is analogous when the phase transition temperature is reduced in the same single crystals under irradiation by a strong electric field<sup>2</sup>; it is convenient to recall that essentially the same situation was observed in Ref. 3 where silver nonstoichiometry is established in  $\text{Ag}_2\text{HgI}_4$ .

Photolysis in  $\text{Ag}_2\text{HgI}_4$  SC, if it did in fact occur in Ref. 1, did not proceed beyond formation of particles that were so small and unstable that they could not serve as a channel for irreversible cation consumption. The present report considers the case of deeper photolysis without reversibility, i.e., essentially a different physical situation. The single crystals themselves were also different: By using different solubilities of  $\text{AgI}$  and  $\text{HgI}_2$  we selected the single crystal formation conditions in order to obtain high dispersion  $\text{Ag}_2\text{HgI}_4$  SC epitaxes on a more roughly disperse  $\text{AgI}$  SC substrate rather than a homogeneous  $\text{Ag}_2\text{HgI}_4$  SC population: Electron microscopy reveals a number of  $\text{Ag}_2\text{HgI}_4$  growths (bumps) on each  $\text{AgI}$  single crystal. Moreover, Ref. 1 employed an  $\text{He-Cd}$  laser whose radiation is absorbed solely by the iodine mercurate for the exposure process, while the present study uses the complete spectrum of an  $\text{Hg}$  lamp which is absorbed by both the epitax and the substrate. In these measurements we obtained information not only from the epitax absorption range but also from the equally interesting 370-450-nm range which contains such interesting absorption features of  $\text{AgI}$  at the exciton peak at 424 nm and the band  $\leq 400$  nm of the cluster  $\text{Ag}$  which the literature reports for  $\text{AgHal}$ .

Figure 1 shows the absorption curves of the composite single crystals at different stages of exposure. The large number of exposures normally employed for each specimen yields so many curves that it is virtually impossible to view all such curves on a single figure; hence we have limited our presentation to only 5 curves: The initial curve (prior to exposure) and the final curve (after sufficiently long exposure) and three intermediate curves.

Curve 1 is characterized by exciton peaks of nonsuperionic  $\text{AgI}$  and  $\beta\text{-Ag}_2\text{HgI}_4$  (424 and 483 nm, respectively). The absorption of  $\text{AgI}$  diminishes in the entire range below 410 nm during the initial exposure (curve 2); a broadband arises simultaneously with a maximum  $\sim 400$  nm, while the exciton peak shifts to 428 nm. The absorption of  $\text{Ag}_2\text{HgI}_4$  remains virtually unchanged during this period. Continuing the exposure (curve 3) strongly shifts the broadband towards shorter wavelengths (to  $\sim 375$  nm); changes also begin to appear in the absorption range of the iodine mercurate: The exciton peak shifts to 485 nm and the absorption band of superionic  $\alpha\text{-Ag}_2\text{HgI}_4$  reported in Ref. 1 appears near 540 nm. Further exposure (curve 4) has little effect on the exciton peak of  $\text{AgI}$ , although it does noticeably shift (up to  $\sim 390$  nm) and damps its broad band; the absorption of its  $\beta$  phase is damped significantly in the absorption range of  $\text{Ag}_2\text{HgI}_4$ ; this is accompanied by further enhancement of the

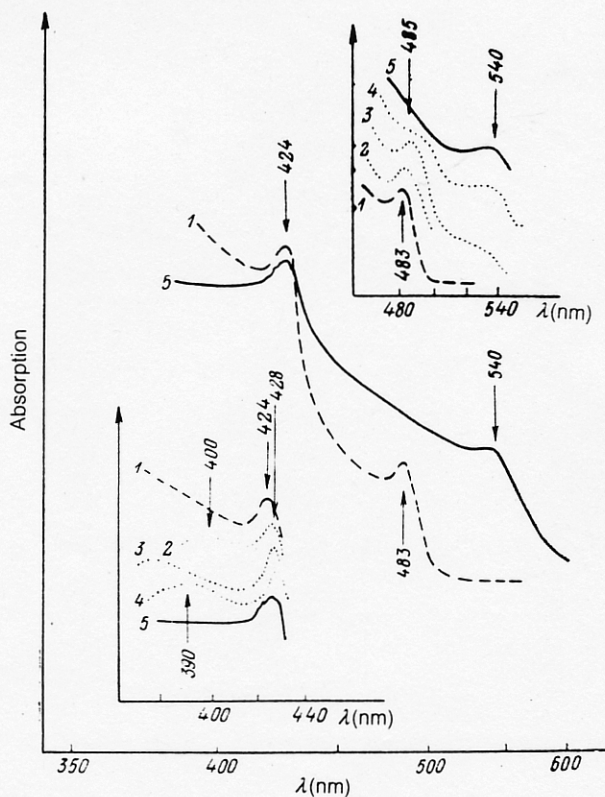


FIG. 1.



$\alpha$ -phase band. The same trends both with respect to the iodide absorption and the iodide mercurate absorption are conserved during further exposure: Specifically, the shift (to 395–400 nm) of the broad absorption band of the iodide and its damping continue, while the exciton peak shifts to 430 nm and the transition to the superionic state in the iodide mercurate continues. The final pattern (curve 5) shows complete superionicity of the epitax and the return of the iodide to its initial state (the peak again appears at 424 nm, while the broad band vanishes entirely).

We could surmise that the photolytic Ag remained in the AgI, yet was enhanced and its absorption shifted along the spectrum towards the shorter wavelengths which was masked by absorption of the iodomercurate. However observations of emulsions containing AgI single crystals without the iodine mercurate epitax have revealed that the photolytic Ag did not grow irregularly in any conditions as indicated in Fig. 1, but rather the spectral changes were continuous: The band expands gradually, initially covering the range near 450 nm (undetermined in our case) and subsequently spreading into the shorter-wavelength range. We intended to discuss this in detail: It is clear that the specimen shown in Fig. 1 is not consistent with such a picture either spectrally or (and more important) kinetically.

Exposure therefore transformed the epitax into a superionic without an analogous transformation in the substrate; photolysis occurred in the substrate, although its products were not retained, at least in the substrate itself. The appearance of a long-wavelength absorption tail on the epitax, which is similar to the colloidal band of Ag, and the change in the color of the specimens, indicating direct darkening, and other features suggest that photolytic Ag is present in the specimen and even though it does not appear in the substrate it will be localized in the epitax. A more comprehensive analysis of the picture represented by curves 1–5 is therefore advisable.

Data on the spectral band changes in the range 360–410 nm for silver and its salts (Ag particles in colored ultrafine-grained photoemulsions,<sup>4</sup> photolytic Ag with an adsorbed dye in photoemulsions,<sup>5</sup> particles in x-ray irradiated AgN<sub>3</sub>,<sup>6</sup> isolated Ag particles in an argon matrix,<sup>7</sup> and color centers in photochromic<sup>8</sup> and multichromic<sup>9</sup> AgHal glasses) revealed that this band does not belong to the colloidal-particle size class but rather to the cluster-particle size class, where the position of the maximum for such small particles responds to changes in size up to 1–1.5 nm (for example in Ref. 5). It would seem that this would be the range of particle sizes in the band < 400 nm shown in curves 2–4. Regarding the 424-nm peak, whose shift is always linked to the shift of the broad band, this likely represents an indirect reflection of the generation and growth of Ag on the atomic or atomic-cluster level: The spatial difficulties of Ag growth may cause a rearrangement of the lattice which would also influence exciton absorption. This is all the more likely as a specific form of disorder is characteristic of presuperionic AgI—polytypism, with the transition of one modification into another accompanied by approximately the same progression of the exciton peak<sup>10</sup> as in our curves: The long wavelength shift is greater the higher the excess Ag in AgI. Such an interpretation has been confirmed by other arguments as well as direct tests.

Therefore, when this Ag iodizes in the photolayer the

same broad absorption band (380 nm at 77 K and 385 nm at 295 K) and exciton peak at 426 nm appear as with nonsuperionic AgI; the position of the peak is again characteristic of the AgI obtained with excess Ag. We observed an even greater shift of the 424-nm peak (to 435 nm) in photoemulsion AgI SC obtained by conversion of the Ag through copper salt by the method from Ref. 11, i.e., again in excess Ag. Evidently the shift of the exciton peak of Ag<sub>2</sub>HgI<sub>4</sub> (see Fig. 1, compare curves 1 and 3) from the partial transformation of the iodomercurate to the superionic phase has a similar nature: this conversion is accompanied by, as would be expected, elevated cation levels at the interstitials.

The return of the AgI peak to its initial position is due to the disappearance of the band < 400 nm. Both occur simultaneously and irregularly, i.e., all forms of excess Ag in AgI—interstitial ionic, atomic and cluster—vanish simultaneously: A complete expulsion of the photolytic Ag from the substrate, where the spatial limitations on growth are strong to the epitax, which by this time is severely disordered and rich in cation cavities and, therefore, free space, occurs. Such expulsion in all likelihood corresponds to a certain critical size of the Ag particles and a critical supersaturation of the iodide with free Ag as well as a critical filling of the iodomercurate with cavities.

The question remains as to whether or not this fate of the photolytic Ag is the only fate and whether the quantity of Ag present in AgI corresponds to that subsequently detected in Ag<sub>2</sub>HgI<sub>4</sub>. Analysis on a semiquantitative level does not support complete agreement. Evidently (and this is also suggested by the short-wavelength shift of the band < 400 nm in the initial illumination period together with the monotonic long-wavelength shift during the entire exposure period) we cannot ignore the possibility that the Ag particles dissolve in the mercury from the iodomercurate, i.e., the same process that in its time represented the basis of the daguerreotype—the predecessor of modern photography.

These data therefore make it possible to understand the progression and final result of photolysis in a composite substrate—epitax single crystal with a superionic epitax. Photoemulsions with single crystals of such a structure have demonstrated in practice<sup>12</sup> preferential formation of photolytic Ag in the epitax zone regardless of the composition of the silver-containing epitax. This also confirms the general concepts<sup>13,14</sup> regarding the functions of the so-called sensitivity centers in AgHal-SC photoemulsions based on the superionicity of these centers.

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