Complex Formation and Photoreduction Processes in Sulphur Doped Silver Bromide *

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The dark conductivity of annealed silver bromide single crystals, containing trace amounts of silver sulfide, has been measured as a function of dopant concentration. At 21 °C the conductivity exhibited a more rapid than linear increase with silver sulfide concentration at levels below 8 ppm. At 4 ppm, the lowest level achieved, a limiting dependence of the conductivity upon the fourth pwoer of the dopant concentration was observed. The room temeprature conductivity of the annealed samples became constant at dopant levels above 10 ppm. The dark conductivity of these samples, measured at 21 °C after exposure to light at room temperature, dropped by more than an order of magnitude to constant levels typical of undoped silver bromide in the extrinsic range. This negative photoeffect could be largely reversed upon subsequent annealing. These results imply the formation of electrically active complexes incorporating several (~ 4) sulphur ions. The observed negative photoeffect is attributed to the photoreduction of interstitial silver ions to free silver. The relevance of the results to the photographic process is discussed.

Introduction

Pure and doped crystals of silver bromide (AgBr) were prepared in this laboratory for use in an investigation of the AgBr/aqueous electrolyte interface which is described fully elsewhere [1]. In order to adequately characterize the crystals they were sectioned to permit bulk conductivity measurements at various positions along their lengths. Results obtained for one crystal, doped with silver sulfide (Ag_2S), provide particularly significant information on the variation with dopant concentration of the ionic conductivity of AgBr. The results permit inferences concerning complex formation and photoreduction processes which are relevant for ionic conductivity studies of the silver halides generally, and for our understanding of the photographic process in particular. This work is incomplete in some respects since it is a byproduct of another investigation. It is reported here in the expectation that the results presented will be reproduced and extended by other workers for whom they are of more immediate interest.

It is well known that the dark conductivity of AgBr is ionic, arising from the migration of point defects of Frenkel type [2]. Doping with divalent cations, such as Cd^{++}, produces an excess of negatively charged vacancies, Ag_v^-, on the cation sublattice of AgBr [3]. Doping with divalent anions, such as S^{--}, generates an excess of positively charged interstitial silver ions, Ag_i^+ [4].

Experimental Method and Results

Three AgBr single crystals were grown under a nitrogen atmosphere by the Czochralski method [5]. The growing crystals were withdrawn from the melt at 2.0 cm/hr while being rotated at 16 rpm. One crystal, (U), was undoped. The other two, (Cd 15) and (S 16), were grown from melts containing 15 molar ppm $CdBr_2$ and 16 molar ppm Ag_2S respectively. After growth the crystals and residual melts were weighed. Then the crystals were cut transversely into sections, and the net crystal weight above the mid-point of each section (i. e., from the point of initiation of crystal growth to the mid-point of each section) was determined. Sections to be used for bulk conductivity measurements were carefully machined to the form of right circular cylinders, then silver electrodes were vacuum evaporated onto their end surfaces. Techniques of sample preparation and conductivity measurements are described in much greater detail elsewhere [1].

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[3] J. TELTOW, Ann. Phys. (6), **5**, 63, 71 [1949].

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Conductivity data are shown on a log plot versus reciprocal temperature in Fig. 1 for various samples sectioned from the sulphur doped crystal, (S 16). Data for a section from the undoped crystal are shown for comparison. To illustrate the nomenclature we observe that sample (S 16 – 22) was prepared from a section for which the total crystal mass above the mid-point was 22 gm. In the process of crystal growth this mass solidified prior to the mass comprising the lower half of the section and the remainder of the crystal beneath it. The total mass of melt used in preparing crystal (S 16) was 50.3 gm. The open symbols in Fig. 1 pertain to specimens which, after application of silver electrodes, were annealed in darkness under nitrogen at 210 °C for one hour, then slowely cooled to – 10 °C. Conductivity measurements were made upon warming in the dark.

Exposure to light at room temperature produced marked conductivity decreases in the Ag_2S doped specimens, as illustrated by the solid symbols in Fig. 1. Illumination sufficient to saturate the effect produced doped specimens with extrinsic conductivities lower than that of the undoped specimen illustrated. Thus exposure effectively eliminates sulphur as an electrically active impurity. Measurements on exposed specimens were made in darkness after exposure, again upon warming from – 10 °C. Similar measurements established that exposure had no effect upon undoped or $CdBr_2$ doped specimens.

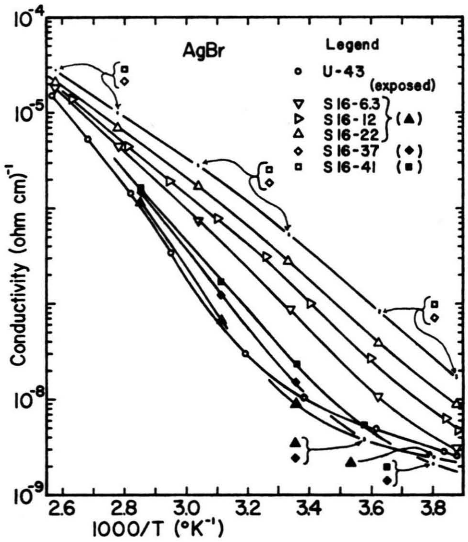

Fig. 1. Conductivity versus reciprocal absolute temperature is plotted for samples sectioned from a Ag_2S doped AgBr single crystal, with a sample from an undoped crystal included for comparison. Open and solid symbols pertain to annealed and to exposed samples respectively. Brackets and arrows are used to designate closely spaced points.

From Fig. 1 it is evident that the "exposed" conductivity of specimens (S 16 – 37) and (S 16 – 41) did not reach the low levels attained by the other specimens, except at the lowest temperatures. The negative photoeffect exhibited by these two specimens was, however, larger by reason of their higher conductivity in the annealed state. These specimens contained the highest concentrations of sulphur, and became quite opaque upon exposure. Their higher conductivity after exposure was probably due to insufficient internal illumination. Color changes from yellow-orange to green were observed upon exposure of all Ag_2S doped samples. This observation is consistent with optical absorption studies, such as those of VOLKE[6]. The color change is attributed to an absorption band arising upon formation of colloidal silver (the print-out effect).

Sample (S 16 – 12) was subjected to three cycles of annealing and exposure which established that its conductivity at room temperature in the fully exposed state was reproducible to within 4%. Its room temperature conductivity in the annealed state, measured relative to the initially observed value was lower by 6, 15, and 40% after successive cycles. This indicates a progressive loss of electrically active sulphur impurity with annealing. The loss may result from the precipitation of an electrically inert second phase, either internally or at the sample surfaces. A progressive dulling of the sample surface was observed. Qualitative observations of the annealing process established that the reversal of the negative photoeffect required one hour at 180 °C.

The distribution of impurities in a sample produced by "normal freezing" is given by[7]

$$C = k\,C_0 (1-g)^{k-1} \qquad (1)$$

where C_0 is the initial concentration of impurities in the melt, g is the fraction of the melt which has solidified at any given point in the freezing process, and C is the concentration of impurity which is being incorporated into the solid at that point. The distribution coefficient, k, is a constant equal to the concentration of impurity in the solid at the freezing interface divided by the concentration of impurity remaining in the melt. If the migration of impurities in the liquid is diffusion limited, as would be expected in the absence of stirring or convection, pro-

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[7] W. G. PFANN, Zone Melting, Second ed., John Wiley & Sons, Inc., New York 1966, p. 8.

nounced modification of the normal freezing curve given by Eq. (1) would result[7, 8].

If, for doped AgBr at a fixed temperature in the extrinsic range, we assume the conductivity to be proportional to the impurity concentration, then a log-log plot of the conductivity versus $(1-g)$ should yield straight lines with a slope of $(k-1)$ under conditions of normal freezing. Such plots of room temperature conductivity versus $(1-g)$ are presented in Fig. 2 for sections from each of the three crystals which we prepared. In crystal (S 16) the conductivity of sections in both the annealed and fully exposed states is shown. The data for both crystals (U) and (Cd 15) are well fit by straight lines with positive slope. From the slope of the line shown we obtain a value of 1.78 for the distribution coefficient of $CdBr_2$ in AgBr, which is within the range of values reported by SÜPTITZ[9]. He prepared AgBr crystals containing a variety of dopants using the Bridgman method. In this work relative dopant distributions were determined directly by use of appropriate radioisotopes. Süptitz studied the system $CdBr_2$ in AgBr thoroughly and noted some dependence of the distribution coefficient upon the crystal growth rate. The line through the data points for crystal (U) yields an effective distribution coefficient of 1.28 for the residual electrically active impurities. All AgBr used in these experiments was zone refined prior to use for growing crystals.

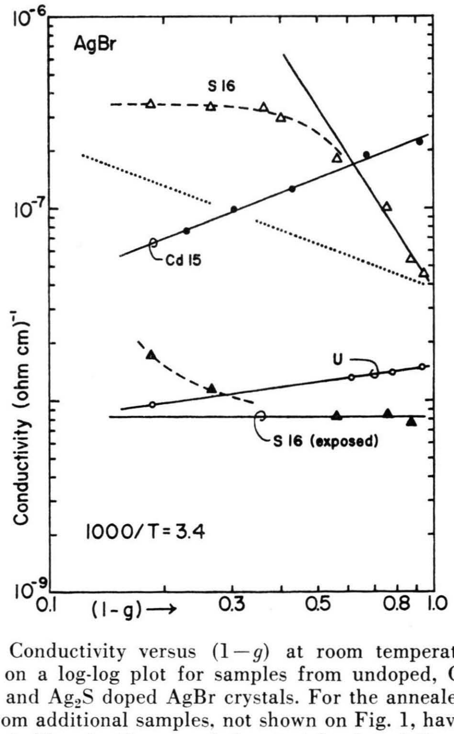

Fig. 2. Conductivity versus $(1-g)$ at room temperature is shown on a log-log plot for samples from undoped, $CdBr_2$, doped, and Ag_2S doped AgBr crystals. For the annealed case data from additional samples, not shown on Fig. 1, have been included. The significance of the straight dotted line is explained in the text.

Süptitz reports a value of 0.24 for the distribution coefficient of Ag_2S in AgBr. If the conductivity of Ag_2S doped AgBr were directly proportional to the concentration of dopant, then a straight line with a slope of -0.76 would have appeared on Fig. 2. A dotted line with this slope has been placed on Fig. 2 to permit direct comparison with the data actually obtained from annealed sections of our crystal, (S 16). These data, in the range of $(1-g)$ between 0.6 and 1.0, actually fit well a straight line of slope 3.0, implying that the conductivity increases with very nearly the fourth power of the Ag_2S concentration in this range. The conductivity then bends over and becomes constant for values of $(1-g)$ less than 0.3. From the distribution coefficient, and knowledge of the impurity concentration in the melt, we infer that the Ag_2S concentration in crystal (S 16) at the points where $(1-g)$ is equal to 1.0 and to 0.3 is 4 ppm and 10 ppm respectively. The conductivity of sections from crystal (S 16) after exposure is low and constant in the range of $(1-g)$ over which the rapid variation of conductivity was observed for the unexposed samples. At lower values of $(1-g)$ the conductivity of the exposed crystal rose rapidly, probably because of incomplete internal illumination.

The preceding analysis of the data for crystal (S 16) clearly presumes normal freezing. We believe this condition to have been well approximated for two reasons:

a) SÜPTITZ[9] obtained a normal freezing type of distribution of Ag_2S in AgBr crystals grown by the Bridgman method in which stirring of the melt is provided solely by convection. Additional stirring is provided by rotation of the growing crystal in the Czochralski method which we employed.

b) We have demonstrated a normal freezing distribution of $CdBr_2$ in AgBr crystals grown under identical experimental conditions.

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[8] W. A. TILLER, K. A. JACKSON, J. W. RUTTER, and B. CHALMERS, Acta Met. **1**, 428 [1953].

[9] P. SÜPTITZ, Ann. Phys. (7) **9**, 133 [1962].

An additional point in this regard is that, after these data were taken and analyzed, another crystal was grown from the residual melt which had been saved after the growth of crystal (S 16). This second crystal, which weighed 6 gm and incorporated all but 0.25 gm of the original melt, was sectioned for conductivity measurements. Though some anomalies were evident[1], the results for annealed samples indicated an extension of the range of constant conductivity to values of $(1-g)$ as low as 0.01. Under conditions of diffusion limited freezing, with conductivity proportional to dopant level, a sharp rise in conductivity should have been observed. Direct visual evidence of the accumulation of dopant at the lower end of the crystal was given by the observation of a deepening orange coloration there upon initial illumination of the cooled crystal after growth. Such a qualitative observation in itself does not distinguish between normal and diffusion limited freezing since an accumulation of impurities having distribution coefficients less than unity would be expected in either case. It does, however, substantiate our conclusion that the dark conductivity of annealed Ag_2S doped AgBr becomes independent of dopant level above 10 ppm, a conclusion based upon the assumption of normal freezing.

Discussion

The data presented above can be accounted for on the assumption of complex formation by a series of reactions of the form

$$(Ag_2S)^0 + (Ag_2S)^0_{n-1} \rightleftarrows (Ag_2S)^0_n \qquad (2)$$

with $n \geqq 2$. Here the basic unit, $(Ag_2S)^0$, consists of a silver and a sulfide ion on adjacent sites in the cation and anion sublattices respectively, plus a closely associated silver interstitial which renders the unit electrically neutral. Complexes of higher order are postulated to form by aggregation of such units. If none of the reactions in the series proceeds very far to the right, then, by the law of mass action, the concentration of the n-th order complex will vary in direct proportion to the n-th power of the concentration of $(Ag_2S)^0$, which will not differ significantly from the concentraiton of Ag_2S in the crystal. Conductivity attributable to complexes could result from reactions of the sort

$$(Ag_2S)^0_n \rightleftarrows ((Ag_2S)_{n-1}AgS)^- + Ag_i^+ \qquad (3)$$

in which silver interstitials are liberated by thermal activation. The conductivity produced by such interstitials would be proportional to their concentration, and hence to the n-th power of the Ag_2S concentration.

The negative photoeffect observed would result from the photoreduction of Ag_i^+ to free silver by the reactions

$$((Ag_2S)_{n-1}AgS)^- \xrightarrow{h\nu} ((Ag_2S)_{n-1}AgS)^0 + e^- \qquad (4)$$

and

$$e^- + Ag_i^+ \rightarrow Ag_i^0 \qquad (5)$$

in which a photoelectron, ejected from the complex, diffuses through the crystal lattice to an interstitial where it is trapped. If the neutral end products of reactions (4) and (5) are stable at room temperature, then given sufficient exposure to light, reactions (3), (4), and (5) will proceed to the right until all of the complex $(Ag_2S)^0_n$ has been transformed to $((Ag_2S)_{n-1}AgS)^0$. It is assumed that the sum of the concentrations of the three forms of complex are constant, being established by the equilibrium points of reactions (2) at temperature near the melting point of AgBr, where significant diffusion of S^{--} ions can occur. The total concentration of complexes is effectively "frozen in" at room temperature and at the annealing temperature used in our experiment.

Restoration of the unexposed state upon annealing probably proceeds in two steps, the first of which is

$$((Ag_2S)_{n-1}AgS)^0 + Ag_v^- \rightleftarrows ((Ag_2S)_{n-1}AgS)^-. \qquad (6)$$

Progression of the reaction to the right will be favored because elastic strain energy of the lattice will be relieved when a silver interstitial bound to the complex is able to occupy a normal site on the cation sublattice. The elevated concentration of thermally generated Ag_v^- at the annealing temperature will also drive the reaction to the right. Thermally generated Ag_i^+ will then drive reaction (3) to the left, restoring the original concentration of $(Ag_2S)^0_n$.

Our observation of a range over which the conductivity increases with the fourth power of the Ag_2S concentration suggests that $n=4$, i. e., that the predominant complex contains four S^{--} ions, which could be tetrahedrally arranged on the anion sublattice. This interpretation requires an additional assumption that silver interstitials are so strongly bound to complexes of lower order, in particular to $(Ag_2S)^0$, that their thermal dissociation is negligible. In addition it is possible that the fourth order complex is sufficiently stable that it is present in higher concentration than second and third order complexes. The saturation of the conductivity at high Ag_2S concentration is not explained by this model. It may be due to formation of larger, electrically inactive aggregates of Ag_2S at high dopant levels.

The results presented here appear to be particularly relevant to the photographic process. The reduction of silver ions to free silver by mobile photoelectrons was a basic feature of the first detailed theory of latent image formation, proposed by GURNEY and MOTT[10]. The role of sulphur in catalyzing the reduction of silver ions has been appreciated for many years. STASIW and TELTOW[11] discussed the possibility of photo-oxidation of S^{--} to S^-, with the subsequent reduction of Ag^+ to free silver. They noted further that this mechanism avoided the production of photoholes which could cause regression of the latent image if they did not escape rapidly enough to the surface. Stasiw and Teltow in fact envisaged precisely the sort of complex formation which has been discussed here. They took the point of view, however, that the complex was the site of the latent image. In the interpretation of our experiment no distinction can or need be made between this mechanism, and one in which the latent image forms upon photoreduction of silver ions at a site distant from the complex. Such a distant site could be a dislocation or other crystal imperfection, as considered by MITCHELL[12].

Conclusions

Using the electrical conductivity of Ag_2S doped AgBr as a probe, we have provided direct experimental evidence for:

a) The irreversible photoreduction at room temperature of interstitial silver ions to free silver, a process essential to latent image formation.

b) The existence and form of sulfide ion complexes which provide both interstitial silver ions and the photoelectrons which reduce them.

In view of the intense interest in this research area it is perhaps remarkable that the experimental facts reported here have escaped detection for so long. This can be understood, however, when it is recognized that these observations can be made only over a narrow range of Ag_2S impurity content. At dopant levels in the solid in excess of 10 ppm, saturation of the conductivity masks all effects. On the other hand, extrapolation of our data assuming a fourth power law indicates that the conductivity of unexposed samples will drop to levels characteristic of undoped AgBr when the Ag_2S concentration drops below 2 ppm.

The preceding discussion clearly implies that, for crystals grown from melts containing more than 40 ppm of Ag_2S, the lowest concentration of dopant in the crystal would be 10 ppm, and the effects which we have described would go completely undetected. Investigations of sulphur doping in AgBr with which we are familiar have generally involved dopant levels of at least 100 ppm. Investigators who may wish to reproduce and to extend this work would be well advised to employ lower dopant levels in the melt (~ 8 ppm) than we used. This would permit a full span of the range of variable conductivity for unexposed samples, thereby providing a more precise determination of its dependence upon the concentration of Ag_2S.

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