Estimation of hole conductivity of AgI through tarnishing studies of silver in iodine vapour at about room temperature

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This work reports the hole conductivity data of growing AgI film on silver both for the thicker (5500 to 30 000 Å) and thinner (< 6000 Å) ranges at about room temperature. Hole conductivity has been estimated through tarnishing studies of silver in iodine atmosphere and estimation has been based on the fundamental equation of Wagner relating the rate constant and the conductivity of the film. It is revealed that the thinner films show a higher hole conductivity than that of the thicker films under similar temperature and iodine pressure.

1. Introduction

The various parameters such as concentration, mobility, diffusion coefficient of positive holes in silver halides are of interest both because of their importance in the theory of the photographic process and because of a fundamental interest in the structure of valence band. It is known fact that the temperature-dependent number of free electrons and holes in thermal equilibrium in AgCl and AgBr is very small [1] and special methods are required to detect the small electronic charge transport [2, 3].

Electronic disorder can be introduced in two ways in these crystals: (1) by absorption of light quanta producing electron-hole pairs and (2) by incorporation of excess halogen into the crystal producing free holes. Predominant electronic conductivity (p-type) in silver halides has been noticed by several investigators [4–9] when the halide crystals are equilibrated with the corresponding halogen atmosphere. In this respect the initial work of Wagner [9] on the corrosion of silver by halogen is of major importance. According to him the halogen atoms adsorbed on the surface of the silver halide become halide ions by capture of an electron from the valence band, thus injecting a silver ion vacancy to preserve neutrality in the ionic lattice. The corresponding chemical reaction can be presented as:

$$\tfrac{1}{2} Br_2 = AgBr + Ag\square' + \oplus \qquad (1)$$
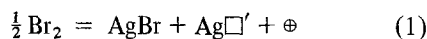
where $Ag\square'$ is a silver ion vacancy and $\oplus$ is a positive hole. From this, Wagner obtains the usual equilibrium relationship as:

$$C_\oplus = K_e(T) \cdot \frac{(p_{Br_2})^{\frac{1}{2}}}{C_{Ag\square'}} \qquad (2)$$

where $C_\oplus$ is the concentration of positive holes, p_{Br_2} is the bromine pressure, $C_{Ag\square'}$ is the concentration of silver ion vacancies and $K_e(T)$ is the equilibrium constant. If the concentration of silver ion vacancies introduced is small compared to the concentration of silver ion vacancies already present, the concentration of positive holes should be proportional to the square root of the halogen pressure and inversely proportional to the concentration of vacancies. These predictions have received experimental support by the data on the corrosion of silver by halogen [9, 10] and especially by the data on the excess conductivity of silver halides in halogen atmospheres [6–8]. The results of these excess conductivity measurements indicate that the excess conductivity (hole conductivity) is always proportional to the square root of the halogen pressure, and approximately inversely proportional to the impurity concentration

in the structure sensitive region, as aliovalent metallic impurities will have the mass action effect of lowering the hole concentration by adding to the vacancy concentration.

There are extensive studies on the properties of holes in AgBr crystals [4–6, 8, 9, 11–34]. The gap of knowledge for the AgCl system has been minimized by the initial work of Luckey [7] and by the recent contributions of Müller et al. [35] and van der Meulen and Kröger [36]. Quite a number of investigations [11, 37, 38] have already been made on the electrical conductivity of α-AgI, the stable form above 146° C. Conductivity values are also reported at room temperature as 1.1×10^{-5} S m^{-1} [39] for evaporated AgI and 1.65 $\times 10^{-8}$ S m^{-1} [40] and 0.9×10^{-8} S m^{-1} [41] for bulk AgI. Recently, Shiojiri et al. [42] studied the dependence of electrical conductivity of β-AgI films on temperature and on iodine pressure in the temperature range 35 to 130° C and in the pressure range 4.0 to 40.0 N m^{-2}. Their conductivity values lie approximately in the range of 3×10^{-5} to 10^{-6} S m^{-1}. From the observation of decrease of conductivity with iodone pressure they concluded that AgI films might have behaved as an n-type semi-conductor. At present there is little data on the properties of holes in AgI crystals. The only relevant work in this system regarding holes is that of Ilschner [11] on the determination of electronic conductivity by polarization and rate measurements and that of Jost and Weiss [37] on the calculation of transference number of electrons as a function of iodine pressure through rate measurements at 140° C. Ilschner's data at 174° C reveal that experimental values obtained through polarization measurements conform very nicely to the $p^{\frac{1}{2}}$ law in a plot of conductivity versus iodine pressure, but high pressure points from rate measurements do not fit into this law. From this he concludes that some deviations from the simple thermodynamic assumptions leading to this law occur in the case of AgI.

The aim of this investigation was, therefore, to obtain positive hole conductivity data of a film of AgI in contact with silver on one interface and iodine vapour on the other near room temperature. The hole conductivity was calculated with the help of the fundamental equation of Wagner relating the rate constant of tarnishing of silver in iodine vapour and the hole conductivity. The rate data already reported by us [43] were utilized for the estimation of hole conductivity. The effect of film thickness on the hole conductivity values was also reported in this work.

2. Results and discussions

The rate of the thinner and the thicker silver iodide film growth on silver in the temperature range 30 to 73° C and in the iodine pressure range 2.5 to 165.5 N m^{-2} was studied employing both the gravimetric and the electrometric techniques [43]. As with other workers [10, 11, 44] a parabolic growth law was followed under the above experimental conditions. Similar to our previous investigations [45, 46] on the Cu/CuI/I$_2$ system, we could also observe for the present system some deviations from the usual pressure dependent relation of the rate constant, i.e. $K_r \propto p_{I_2}^{1/2}$ that is expected according to equilibrium attainment at the phase boundaries of the halide film.

In the thinner film range (<6000 Å), the iodination rate constant was found to vary with iodine pressure as $K_r \propto (p_{I_2})^{1.5}$ at 60° C, whereas in the thicker range (5500 to 30 000 Å) the relation found was, $K_r \propto (p_{I_2}^{1/2} - p_{I_2}^{o\,1/2})$ at 35° C [43]. This type of pressure-dependent relation observed for the thicker film range was similar to that obtained by us for the Cu/CuI/I$_2$ system [45, 46].

Wagner's general relation [47] for the rate constant can be transformed into the following form for iodination of silver as

$$K_r = \frac{1}{F^2} \int_{\mu_I'}^{\mu_I''} t_\oplus \cdot t_{Ag} \cdot \sigma \cdot d\mu_I \qquad (3)$$

where K_r = rational rate constant in equivalents m^{-1} sec^{-1}, μ_I = chemical potential of atomic iodine in A sec V equiv^{-1}, μ_I' & μ_I'' = values of μ_I at the Ag/AgI and AgI/I$_2$ interfaces, $t_\oplus$ = transport number of positive holes, t_{Ag} = transport number of silver ions, σ = total electrical conductivity in S m^{-1}, and F = Faraday number in A sec equiv^{-1}. In the present case, transport number of holes, $t_\oplus$, instead of transport number of electrons, t_e, has been considered in Equation 3, since silver halides exhibit predominantly hole conductivity (p-type) when equilibriated with the corresponding halogen atmosphere [4–9]. Equation 3 can further be rewritten in the following form

$$K_r = \frac{RT}{2F^2} \int_{p_{I_2}'}^{p_{I_2}''} t_{Ag} \cdot \sigma_\oplus \cdot \frac{dp_{I_2}}{p_{I_2}} \qquad (4)$$

using the relations

$$\mu_I = \text{constant} + \tfrac{1}{2}RT \ln p_{I_2} \qquad (5)$$

and

$$\sigma_\oplus = t_\oplus \cdot \sigma \qquad (6)$$

where p'_{I_2} and p''_{I_2} = iodine pressure at Ag/AgI and AgI/I$_2$ interfaces respectively and $\sigma_\oplus$ = hole conductivity of the AgI film. In order to calculate K_r with the help of Equation 4, one has to know t_{Ag} and $\sigma_\oplus$ as a function of iodine pressure. This information is lacking at present for the experimental conditions employed here. On the other hand, $\sigma_\oplus$ can be calculated if K_r has been determined as a function of iodine pressure. Now differentiation of Equation 4 with respect to iodine pressure at the AgI/I$_2$ interface will lead to the relation

$$\sigma_\oplus = \frac{2F^2 p_{I_2}}{t_{Ag} \cdot RT} \cdot \frac{dK_r}{dp_{I_2}} \qquad (7)$$

It is also known that early experiments by Tubandt [48] and more recent ones by Kurnick [49] have established the transport number of silver ions in AgBr and AgCl to be unity for temperature ranging from 20° C to above 400° C. In the absence of any data on AgI, similar behaviour could be assumed for it. Hence, taking $t_{Ag} \approx 1$, it follows, that

$$\sigma_\oplus \approx \frac{2F^2}{RT} \cdot K_r \frac{d\ln K_r}{d\ln p_{I_2}} \qquad (8)$$

Now hole conductivity for the thicker films can be represented as

$$\sigma_\oplus = \frac{2F^2}{RT} K_r \left[\frac{1}{2} + \frac{A(p_{I_2}^{\circ 1/2})}{2K_r} \right]$$

$$= \frac{F^2}{RT} [K_r + A(p_{I_2}^{\circ 1/2})] \qquad (9)$$

when

$$\frac{d\ln K_r}{d\ln p_{I_2}} = \frac{1}{2} + \frac{A(p_{I_2}^{\circ 1/2})}{2K_r},$$

$A = 4.165 \times 10^{-12}$ equiv N$^{-1/2}$ sec^{-1}, being the proportionality constant between K_r and $(p_{I_2}^{1/2}) - p_{I_2}^{\circ 1/2})$ and $p_{I_2}^{\circ} = 13.67$ N m^{-2} [43]. The hole conductivity for the thinner films will have the expression

$$\sigma_\oplus = \frac{3F^2}{RT} \cdot K_r \qquad (10)$$

when

$$\frac{d\ln K_r}{d\ln p_{I_2}} = \frac{3}{2}.$$

The parabolic rate constant values as obtained by us [43] for thinner and thicker iodide film formation are presented in Table I. With the help of these rate constants and utilizing Equa-

TABLE I Rate constant values for both thinner and thicker iodide film growth on silver as a function of iodide pressure [43]

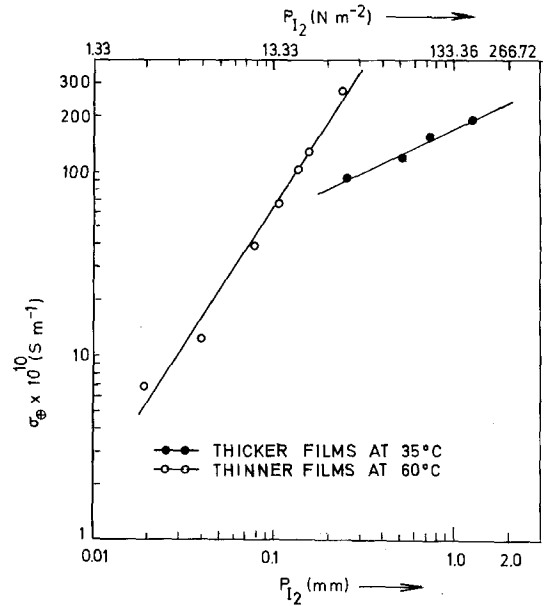| p_{I_2} (N m^{-2})	K_r (equiv m^{-1} sec^{-1}) $\times 10^{12}$ thinner films at 60° C	K_r (equiv m^{-1} sec^{-1}) $\times 10^{12}$ thicker films at 35° C
2.50	0.667	
5.20	1.205	
10.40	3.922	
14.14	6.572	
18.40	10.160	
20.80	12.920	
31.20	27.190	
33.50		10.20
68.60		17.66
95.40		26.75
165.50		36.81

Figure 1 Hole conductivity of AgI as a function of iodine pressure.

tions 9 and 10, the hole conductivity data of growing AgI films were calculated for the thicker and thinner ranges and are presented in Fig. 1.

From the nature of the plot of conductivity versus iodine pressure, it appears that non-equilibrium conditions prevail at the phase boundaries of AgI films. In the thicker range a modified $p_{I_2}^{1/2}$ dependence shows that a deviation from the equilibrium still exists at the Ag/AgI interface giving a value of $p_{I_2}^{\circ}$ much higher than the dissociation pressure of AgI in contact with silver, but a steady state condition is maintained at the outer phase boundary. The proportionality between K_r and $(p_{I_2}^{1/2} - p_{I_2}^{\circ 1/2})$ perhaps indicates that the hole con-

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centration at the metal/halide interface may not be negligible in comparison with that at the halide/halogen interface due to non-attainment of steady state conditions at that interface. Probably at a still higher thickness level, conductivity data will conform exactly to equilibrium considerations at the interfaces. But in the thinner film range, the deviation observed is much more than in the thicker range and this can be attributed to the comparatively faster rate of arrival of ions and holes at the interface or to the faster rate of consumption of the mobile species due to the thinness of the film.

Thus, the results demonstrate that hole conductivity of a growing AgI film is a function of the thickness of the film and the conductivity is much more sensitive to halogen pressure variation in the thinner than in the thicker film range.

Fig. 1 also reveals the interesting fact that at nearly similar conditions of temperature and pressure of iodine, the hole conductivity of the thinner films is on the higher side than that of the thicker films (at p_{I_2} 33.5 N m^{-2} and at 60° C, $\sigma_\oplus$ thicker $\approx 1.8 \times 10^{-8}$ S m^{-1} and $\sigma_\oplus$ thinner $\approx 2.7 \times 10^{-8}$ S m^{-1}) [43], which is an indication that compressive stress is much more in the thinner than in the thicker films. This statement receives support from the following discussions. There are studies on the ionic conductivity of AgBr [49] and AgCl [50] crystals under compression, showing a decrease in conductivity with compression. Similar behaviour could also be expected in AgI crystals. A decrease in ionic conductivity in silver halids could be correlated to a decrease in concentration of ionic defects, such as vacancies. A decrease in vacancy concentration will be reflected in an increase in concentration of positive holes according to Equation 2. Thinner films under higher compression might have lowered the concentration of vacancies and hence exhibit a higher hole conductivity than in the thicker films which are slightly relaxed compared to thinner films. This idea receives further support from the observation that annealed silver tarnishes at a faster rate than the deformed silver in iodine [43] as well as in chlorine [51] atmospheres. In case of AgI growth it was observed that at 18.4 N m^{-2} and at 60° C, the rate constants for annealed and 80% cold-deformed silver were 24.68×10^5 and 17.86×10^5 Å^2 min^{-1} respectively [43]. The corresponding hole conductivity values will be 102×10^{-10} and 74.2×10^{-10} S m^{-1} which means a lowering of conductivity by about 30% with an 80% cold-deformation. AgI film developed on already deformed silver will be in a slightly relaxed state compared to that developed on annealed silver because of comparatively less pronounced lattice mis-match between the silver substrate and the AgI film in the former case. Hence, films developed on annealed silver should, due to higher compression, show a lower ionic and a higher hole conductivity than that developed on cold-deformed silver substrate. From this result it can be concluded that isolated crystals of AgI in contact with iodine vapour will definitely show a lower hole conductivity in comparison with that in AgI film attached to silver substrate and exposed to the same iodine pressure.

Acknowledgement

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