THE KINETICS OF THE PHOTOLYSIS OF THIN FILMS OF TIN DIIODIDE

MINO GREEN and TITILAYO A. KUKU[†] Imperial College of Science and Technology, Department of Electrical Engineering, London SW7, England

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Abstract—The kinetics of photolysis of thin films of SnI_2 have been followed using a quartz crystal microbalance technique. The products of photolysis are iodine gas generated at the surface and tin formed within the SnI_2 (which appears as α -Sn even up to ~ 400 K). Rate as a function of extent of reaction, film thickness, light intensity and wavelength, temperature, doping agents and substrate and finally thin film microstructure have been investigated for both high and low temperature polymorphic forms of SnI_2 . The extent of photolysis, which always starts by being linear in time, goes via an intermediate regime to being proportional to $t^{1/2}$.

The kinetics of photolysis are similar to PbI_2 studied previously[1] and, as for that case, the photolysis mechanism is consistent with a rate determining anion motion.

1. INTRODUCTION

We have undertaken to study the mechanism and kinetics of the photolysis of several metal halides in thin film form. In each case the overall photochemical reaction of metal (M) halide (Hal.) is,

$$\mathbf{MHal}_{n} \xrightarrow{\mathbf{h}\nu} \mathbf{M} + \frac{n}{2} \mathbf{Hal}_{2}.$$
 (1)

While the choice of photolytic system has been dictated by possible utility in various device fabrication schemes it was nonetheless felt that several detailed investigations should be carried out so that one might see the way to useful generalisations about the photolysis of solids, or perhaps certain classes of solid. We have previously reported on the kinetics of the photolysis of thin films of lead iodide[1] and this work, which closely parallels the work reported here, will henceforth be referred to as (I). The literature on lead iodide, bromide and chloride was reviewed in (I) and requires little amendment[2, 3].

Tin diiodide (SnI₂), selected in the first instance for an application, is particularly interesting because among other things we have observed that it has two polymorphs. The polymorphic forms, differentiated by their colour, are the low temperature red α -SnI₂[4, 5] and a high temperature yellow β -SnI₂ which might be the same substance as reported by Desai and Rai[6]. But this polymorphism is not documented as such in the modern literature. We have studied the optical and structural properties of the polymorphs[8] and will be reporting them in due course. As for photolysis, which is the subject of this paper, there are no reported quantitative studies for pure SnI₂. There is a study[7] of the solid solution Sn_xPb(_{1-x})I₂(0.9 $\geq x \geq 0$) which is found to be more photosensitive than pure PbI₂.

2. EXPERIMENTAL

The investigation of the photolysis of thin films of SnI_2 is divided into two main parts, these are the production of thin films of SnI_2 and the subsequent *in situ* irradiation of the film with light of known intensity and spectral distribution. Photolysis was followed, as in (I), by using a quartz crystal microbalance housed in a special vacuum system as shown in Fig. 1 and reproduced here for convenience.

2.1 Preparation of SnI₂

 SnI_2 was prepared [8] by the reaction of HI with Sn. "Analar" grade hydriodic acid (66% w/v) and 150 $\mu\,m$ particle size tin of 99.75% purity were used. About 40 ml of hydriodic acid was placed in a three-necked flask which was being flushed with dry O2-free high purity nitrogen (<5 ppm O₂). The central neck contained a reflux condenser and a side neck was used for inserting aliquots of powdered tin, up to a total of 10 g. When all the metal had been added, the mixture was refluxed for 3 hr (still under a stream of N₂). The reflux apparatus was then converted to a distillation configuration and the excess hydriodic acid distilled off; the reaction flask was heated in a paraffin oil bath and the N2-gas flow kept up throughout. A mass of red crystals was produced in this way. During both the refluxing and distillation the glassware was kept wrapped in aluminium foil so as to protect the contents from being decomposed by light. The material was recrystallised from hot ethanol in an atmosphere of water free nitrogen. The mother liquor was removed by filtration on a sintered disc. The red crystals were stored under vacuum. Indexing the X-ray powder pattern of this material gave the same crystal structure as reported by Howie et al. [9].

2.2 Preparation of thin films

Thin films of SnI_2 were prepared by vacuum evaporation of the solid synthesised as above. The source "boat" for evaporation was merely a quartz tube 30 mm long

[†]Present address: Department of Electronics and Electrical Engineering, University of Ife, Ile-Ife, Nigeria.

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Fig. 1. Schematic plan view of the experimental arrangement for photolysis studies.

and 8 mm in dia., heated resistively. Snl₂ was placed in the boat, in air. The boat was then placed in the photolysis system which was forthwith evacuated. A source temperature between 520 and 670 K was found sufficient to give the desired evaporation rates (27–60 nm/min). Only the mid-fraction of material evaporated was used in preparing a film for experiment. The total pressure of the system rose to a maximum of 1.6×10^{-6} torr during evaporation.

The α -SnI₂ was prepared by deposition upon a substrate kept at 373 K. Determination of film density using a quartz crystal micro-balance method to determine mass and a multiple beam interferometric method to determine film thickness gave, to within 2%, the same density as reported in the literature, i.e. 5.30 g/cm³. X-Ray examination of the films gave the expected pattern[9] for α -SnI₂.

The α/β SnI₂ transition has been determined by us to be 381 K both for thin films and fine powders of SnI₂. The β -polymorph (yellow) has also been observed by us to be metastable near room temperature for long periods. Vacuum deposition of the film on substrates held at room temperature resulted in the yellow form, while subsequent gentle heating in vacuum changed the film to the red form which then went on to become yellow again as the transition temperature was traversed. This is the reason why films of the α -polymorph employed in this photochemical study were deposited on substrates kept at a temperature of 373 K and then adjusted to the desired photolysis temperature. Films of β -SnI₂ were obtained by deposition either on room temperature substrates or substrates kept at temperatures in excess of 381 K. Details of temperature control, quartz crystal holder, etc. are to be found in paper (I). Various minor improvements in the apparatus have been made, but do not warrant extensive discussion.

2.3 Photolysis arrangement

The films were deposited on AT cut 6 MHz quartz crystal substrates that had been coated with gold electrodes, necessary for the excitation of the crystals. In order to eliminate possible sensitisation of the photolytic reaction due to the presence of a metallic substrate, namely the gold electrode on the quartz plate, SiO_2 of about 200 nm thickness was sputtered over that part of

the electrode area that was subsequently exposed to stannous iodide vapour. The frequency change of the quartz crystal substrate (due to mass changes) either during film evaporation of film photolysis was compared with that of another crystal held outside the vacuum equipment and the difference in their frequencies was monitored on a commercial digital film thickness monitor (model FIM3, supplied by Edwards High Vacuum Ltd.). The quartz crystal was calibrated by an optical interference method, and gave a sensitivity of 1 Hz change in frequency equivalent to a mass change of 2.7×10^{-9} g. With our geometry this was equivalent to a loss of $1.94 \times 10^{13} I_2$ molecules cm⁻² or the same number of molecules of SnI₂ photodecomposed. The actual film area used in this work was 0.33 cm². Thus the quartz crystal microbalance technique enables us to know the as prepared SnI₂ film thickness (knowing SnI₂ density) and to follow the photolysis kinetics by means of the mass loss. Film thicknesses ranging from 400 to 1100 nm have been employed in this work.

The light source was a 650-W quartz-halogen lamp. The optical arrangement was as shown in Fig. 1. Light intensities were measured, usually after the experiment, by putting a photodiode type OSD-50-1 (Centronic Electro Optics Ltd.) in the same position where the film had been. Intensity readings, obtained from this diode were usually compared with a commercially calibrated photodiode of the same type. A range of light intensities, $17-650 \ \mu \text{ W cm}^{-1}$, has been employed in this study. The broad band radiation which we used was the spectral band obtained using copper sulphate solution as a filter, and we abbreviate this as B.B. The narrow band radiation, N.B., that we used was obtained using Barr and Stroud Ltd. interference filters (see Paper I).

The quartz crystal and film was maintained at the photolysis temperature for 2 hr or more prior to photolysis in order to stabilise the piezoelectric crystal and also to allow time for complete structural change in the film, especially near the phase transition temperature.

3. RESULTS

3.1 Reaction product

Some preliminary experiments involving the extensive photolysis of SnI_2 were carried out with the aim of

further characterising the tin produced as a reaction product. Thin films of both polymorphs of SnI₂ were evaporated onto clean soda glass substrates and their transmission spectra taken before and after photolysis. The data for β -SnI₂ are shown in Fig. 2: approx. 20% of a 500 nm thick SnI₂ film was photodecomposed in 1 hr at 140°C.

The photolysed film had an increased transparency on the high energy side of the absorption edge. Such an effect had earlier been reported by Kosarev *et al.*[7] for SnI_2/PbI_2 solid solutions, and for PbI_2 by Tubbs[10].

Thin films of both polymorphs of SnI₂ were also evaporated on soda glass substrates that were housed in a specially constructed jig which enabled vacuum photolysis of the evaporated films with unfiltered radiation. The photolysed films were subsequently removed and examined by X-rays, using a cylindrical thin film X-ray texture camera[11]. An unphotolysed film of both polymorphs was also examined by this method. Photolysis always produced additional lines. Table 1 shows our data for β -SnI₂ after photolysis. One set of additional lines has been identified as those of grey tin $(\alpha$ -Sn)[12] and there are also unidentified lines. We conclude that in the photolysis, which produces tin and iodine as reaction products, the tin is α -Sn: this is somewhat remarkable in view of the fact that the α/β -Sn transition temperature is 286.4 K (13.2°C). The tin must be present in the SnI₂ in the form of small clusters: but not so small that they do not give X-ray diffraction lines and not so large that they assume the thermodynamic properties of bulk white tin.



Fig. 2. Transmission spectra of β -SnI₂, before (× × ×) and after (...) photolysis. Film thickness 500 nm, ~20% photolysed at 413 K in 1 hr using unfiltered radiation. The origin of the peaks in the transmission spectrum of the film of unphotolysed β -SnI₂ is taken to be due to excitons and not to interference arising from multiple internal reflections. This latter assertion can be made because the separation between peaks is not an xth to (x + 1)th change given that at the first peak which is at 542.5 nm the real part of the refractive index is 3 and at the second peak at 625 mm the index is 6.

We have established that the tin is buried in the SnI₂ by carrying out the following experiments. Films of SnI₂ $\frac{1}{2} \mu m$ thick were deposited on the quartz crystal microbalance and were photolysed using B.B. radiation of 235 μ W cm⁻². This produced in the α -SnI₂ at 378 K a total of 1.4×10^{15} Sn atoms cm⁻² and in the β -SnI₂ at 393 K, 1.3×10^{16} Sn atoms cm⁻². In each case the films were exposed at the photolysis temperature for 1 hr to O₂ at a pressure of 10⁻⁵ torr after the light was shuttered off. Within the limits of experimental accuracy, i.e. 1 Hz or the equivalent of 3×10^{14} oxygen atoms cm⁻², no mass change was observed. Thus there was no oxygen adsorption at these elevated temperatures and so no exposed tin; i.e. just as for PbL₂, the photolytic metal must be produced within the SnI₂.

The reproducibility of the photolysis data was about $\pm 5\%$ for broad band photolyses, and $\pm 7\%$ for the narrow band experiments which involved lower photon fluxes. At the end of every run, i.e. when the light was shuttered off, there was observed a small reversal (~ 2 Hz at 110°C) in the resonant frequency of the quartz crystal plate as registered by the digital frequency monitor. This signified a small increase in the weight of the quartz plate, and was probably due to the adsorption of some of the iodine gas molecules on the film surface. This effect was not observed on a blank quartz crystal plate treated in the same manner.

3.2 Kinetic experiments

(a) Rate for various ranges of θ . Figures 3(a) and (b) show the time dependence of photolysis in units of θ , which is molecules of SnI_2 cm⁻²; as a function of temperature for a fixed set of conditions for both polymorphs. Long time photolysis data, giving rise to much more extensive reaction, are shown in Fig. 4. It will be seen that in every case there is an initial linear range, i.e. $(\partial \theta / \partial t)$ for a constant set of conditions is a constant. The approximate range of the linear regime is indicated by a dotted line in the case of the α -SnI₂ set. The linear range for β -SnI₂ is about ten times greater as can be seen on the log-log plot of Fig. 4. Figures 4 and 5 show that the linear regime is followed by a $\theta \propto t^n$ where $n = 3/4 \pm 1/8$, followed by a $\theta \propto t^{1/2}$ regime. Photolysis using narrow band radiation showed the same overall behaviour; Fig. 6 shows the linear region.

We would note that whereas photolysed PbI_2 goes black, photolysed SnI_2 goes from yellow or red to a midbrown-orange colour even for the most extensive photolysis.

(b) Film thickness dependence. Films of both polymorphs of varying thicknesses, between 400 and 650 nm were studied: no significant variation in rate or extent was found, an example is shown in Fig. 7. The thickness independence in the range studied is consistent with a high absorption coefficient; namely $\sim 10^5 \text{ cm}^{-1}$ for α -SnI₂ and $> 10^5 \text{ cm}^{-1}$ for β -SnI₂ for most of the wavelength range used for photolysis.

(c) Light intensity dependence. An abrupt change method, see (I), was employed to determine the dependence of photolysis kinetics upon light intensity using broad band irradiation. This method involved photolys-

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Line	Spacing, Å	Relative Intensity (%)	Features
1	2:360	30.4	SnI ₂
2	2.294	78	α-Sn
3	2.230	100	SnI2
4	2.203	35	?
5	2.168	17	SnI ₂
6	2.137	13	?
7	2.029	76	SnI ₂
8	1.956	63	α-Sn
9	1.847	17	SnI ₂
10	1.773	19	SnI ₂
11	1.744	26	?
12	1.705	11	?
13	1.667	34	SnI ₂
14	1.623	35	α~Sn
15	1.572	57	SnI ₂
16	1.551	54	?
17	1.470	72	SnI ₂
- 18	1.423	35	?
19	1.392	61	SnI ₂
20	1.323	13	SnI ₂ or a-Sn
21	1.235	11	?

Table 1. X-Ray data* for photolysed β -SnI₂

*Data obtained using texture camera⁽¹¹⁾



Fig. 3(a). Extent of α -SnI₂ photolysis (θ , molecules of SnI₂ cm⁻²) at various temperatures. (Thicknesses, 508 ± 10 nm; B.B., light intensity 230 ± 10 μ W cm⁻²).



Fig. 3(b). Extent of α -SnI₂ photolysis (θ) at various temperatures. (Thicknesses, 508 ± 10 nm; B.B., light intensity 230 ± 10 μ W cm⁻².)



Fig. 4. β -SnI₂ photolysis at 383 K for about 6 days, shown on a log-log scale. (Thickness, 517 nm; B.B., light intensity $225 \ \mu \text{ W cm}^{-2}$.)



Fig. 5. α -SnI₂ photolysis at 378 K on a log-log scale. (Thickness, 510 nm; B.B., light intensity 227 μ W cm⁻².)



Fig. 6. Initial behaviour in the photolysis of α - and β -SnI₂ using N.B. radiation of 507.9 ± 2.4 nm (α -SnI₂; thickness 1118 nm, intensity 73 μ W cm⁻²; temperature 368 K; β -SnI₂; thickness 795 nm; intensity 64 μ W cm⁻²; temperature 403 K.)

ing the film at one light intensity for some time and then abruptly changing to another value. The rate of reaction, for both intensities, at the point of interruption is obtained by extrapolating the kinetic measurements. The ratio of intensities were compared with the ratio of rates of photolysis. For the intensity range $87-650 \ \mu W \ cm^{-2}$ and over, an extent of reaction ranging from 1.0 to 9.5×10^{15} molecules of $SnI_2 \ cm^{-2}$, the rate was linearly dependent upon light intensity for both polymorphs.

(d) Wavelength dependence and quantum efficiency. The spectral dependence of the quantum yield in the linear regime for α -SnI₂ at 368 K and for β -SnI₂ at 403 K was determined and the results, corrected for reflection and incomplete absorption of light, are shown in Figs. 8 and 9. Reflection and absorption coefficients for both

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Fig. 7. α -SnI₂ photolysis of films of various thicknesses (B.B., light intensity 230 ± 10 μ W cm⁻²; at 363 K).



 α -SNI₂ for films about 1 μ m thick. (Arrows indicate centre wavelength of photolysing radiation.)



assumed to be associated with an undetermined error.)

polymorphs were determined experimentally [8] and were used in making the necessary corrections. Note there is only a weak wavelength dependence, and this is consistent with a free carrier diffusion length long compared with the film thickness.

(e) Temperature dependence. The data shown on Figs. 3(a) and (b) allow one to determine an activation energy

in the linear ranges for both polymorphs. The resulting curve is shown in Fig. 10. ΔH^4 for α -SnI₂ is 0.27 ± 0.02 eV and for the β -SnI₂ is 0.89 ± 0.18 eV. It is interesting to note that the cross-over of the activation energies is at 378 K, i.e. within 3° of the transition temperature. There is no sign of a saturation in rate with temperature as there was in PbI₂, see (I). If it is assumed that the quantum yield is ~5% at 403 K (see Fig. 9) for B.B. radiation and the activation energy is 0.90 eV then it is a simple matter to calculate that 100% yield should be obtained at 456 K. We could not reach this temperature experimentally because loss of SnI₂ by evaporation was noticeable beyond 413 K.

(f) Effect of doping SnI₂. Thin films of SnI₂ were doped by mixing the SnI₂ charge with small amounts of such dopants as CuI, AgI, PbI₂ or SnI₄. The films were evaporated with source temperatures between 620 and 670 K. Figures 11 and 12 show the effect of these dopants on α - and β -SnI₂. The extent of the doping is not known, the relative speed-up of the reaction by AgI or CuI may, therefore, be due to a comparative difference in their doping levels. The enhancement of the reaction rate by PbI₂, which forms a continuous series of solid solutions with SnI₂[9], has been reported previously[7]. Stannic iodide, SnI₄, on the other hand markedly suppressed the rate of photo-decomposition.

(g) Substrate effect. Kostyshin et al. [13] reported that metal substrates increased the photo-sensitivity of several metal halides. For this, and other reasons, we performed photolyses on tungsten. The tungsten substrate was prepared by vacuum depositing (evaporating) a thin film of tungsten on a previously SiO₂ coated quartz oscillator plate. The effect of the W substrate is shown in Fig. 11 and the speed-up in photolysis rate is consistent with the literature claims [13].

(h) Effect of microstructure. Scanning electron microscope studies of SnI_2 deposited at various rates and at various substrate temperatures have been carried out. The SnI_2 films were slightly etched (0.025 molar KI



Fig. 10. Temperature dependence of photolysis rate in the linear regime for both polymorphs.



Fig. 11. Effect of doping on the photolysis of α -SnI₂; included is the effect of the photolysis of undoped SnI₂ deposited on a thin film of tungsten. (Thicknesses, 511 ± 10 nm; B.B., light intensity, $230 \pm 20 \ \mu$ W cm⁻²; photolysis temperature 368 K; substrate temperature during film depositions, 373 K.)

solution for 10 sec at room temperature) in order to delineate grain boundaries and the mean grain size determined. The range of substrate temperatures investigated was 296-393 K and the range of deposition rates was 15-60 nm/min. The smallest mean grain size was 0.32 μ m and the largest 1.2 μ m. No experimentally significant effect of mean grain size on photolysis rate was observed. The high temperature films did not show the platelet structure evident with PbI₂ films.

4. DISCUSSION

The kinetics of the photolysis of thin films of α - and β -SnI₂ divide into three regimes. These are the initial,

linear, regime where $(\partial\theta/\partial t)_{T,\lambda,I}$ is a constant; the intermediate range where $(\partial\theta/\partial t)_{T,\lambda,I}$ is $\propto t^{n-1}$ $(n = 3/4 \pm 1/8)$; and the terminal regime which is by far the most extensive (see Fig. 4), where $(\partial\theta/\partial t)_{T,\lambda,I} \propto t^{-1/2}$. The overall photolytic behaviour of SnI₂ is strikingly similar to that of PbI₂ which has been fully reported in paper I. In view of this great similarity in photolysis kinetics we postulate the same phenomenological equations and the same sort of reaction mechanism. The proposed reaction scheme is recapitulated briefly making use of the representation shown in Fig. 13: but Kroger-Vink nomenclature is abandoned in favour of a, perhaps less rigorous but, generally more easily followed system.

We suppose that absorbed light creates electron-hole pairs in SnI₂. There is then the possibility of bulk recombination, surface recombination and photolysis of SnI₂. Photolysis is treated as an additional surface recombination process, since holes are consumed at the surface in the process of iodine evolution and tin is precipitated at sites initiated by Γ vacancies diffusing into the bulk from the surface. For both PbI2 and SnI2 the linear rate of photolysis is independent of the thickness of the iodide film for the common case that light is absorbed in a zone thinner than the thickness of the film (see Figs. 8 and 9). From this we conclude that the free carrier diffusion length (holes and electrons are treated alike) is long compared with the film thickness, in which case bulk recombination processes may be largely neglected and in our thick films we then take it that electron-hole pairs are lost by surface recombination and by photolysis.

(a) Photolysis mechanism (α/β change-over). The mechanism proposed for PbI₂, and now SnI₂, photolysis is that shown in Fig. 13 with a new possibility added. This new possibility, labelled α and β in the scheme, is that we may have to distinguish between sub-surface and bulk vacancy sites. This scheme is advanced with a view to accounting for the kinetic data at the α - to β -SnI₂ phase transition temperature which is shown in Fig. 10. In that figure we see that the α - and β -photolysis rates at the transition temperature are within experimental error identical. Yet the α -SnI₂ photolysis has an activation energy of 0.3 eV and the β -form has an activation energy



Fig. 12. Effect of doping on the photolysis of β -SnI₂. (Thicknesses 539 ± 2 nm; B.B., light intensity, 244 ± 1 μ W cm⁻²; photolysis temperature 393K.)

of 0.9 eV. We can only obtain equal rates in a sequential scheme if we compensate for increased activation energy by an increase in activity of the reacting species. We propose that in the special case of solid state phase change that the reaction schemes shown on Fig. 14 might apply. Thus there would be a large build-up in activity of $V_{1^-,sub}$ in the scheme for β -SnI₂, followed by rate determining bulk anion vacancy diffusion. We do not have enough reliable structural data to make an attempt at guessing the reaction coordinate for the proposed schemes, all we are proposing is that surface to subsurface exchange is the same in α - and β -polymorphs, while bulk diffusion is very different, but also the reverse surface reaction in both schemes has the same activation energy as the bulk diffusion in β -SnI₂. Using the usual assumptions of a consecutive set of reactions up to and including the forward part of the rate determining step we can write,

$$j_{\alpha} = \frac{kT}{h} [*V_{1,s}][I_{sub}] \exp(-F_{\alpha}^{+}/kT)$$
(2)

and

$$j_{\beta} = \frac{kT}{h} [V_{1^-, \text{sub}}] [I^-] \exp\left(-\Delta F_{\beta}^*/kT\right)$$
(3)

so that

$$\frac{j_{\alpha}}{j_{\beta}} = \frac{[*V_{1^-,s}][I_{sub}]}{[V_{1^-,sub}][I^-]} \exp\left(-\frac{\Delta F_{\alpha}^{\ t} + \Delta F_{\beta}^{\ t}}{kT}\right)$$
(4)

but

$$\frac{[^{*}V_{1^{-},s}][I_{sub}]}{[V_{1^{-},sub}][I^{-}]} = \frac{1}{K_{\alpha}}$$
(5)

where K_{α} is the equilibrium constant for the reaction step immediately preceding the rate determining step for β -SnI₂. The free energy for this reaction is such that,

$$K_{\alpha} = \exp - (\Delta F_{\beta}^{+} - \Delta F_{\alpha}^{+})/kT$$
(6)

so that

$$j_{\alpha}/j_{\beta} = 1. \tag{7}$$

There are two other points which we have noticed in the data that require further explanation. These are the variation of the range of the linear regime with temperature and the appearance of a fairly well defined intermediate regime.

(b) Extent of linear range. We suppose that deviation from a linear regime ($\theta = \theta_R$) sets in because the reaction product starts to influence the initial activities. This may simply be that some of the light is absorbed by reaction product thereby reducing the local activity of photogenerated electron/hole pairs: this is what was proposed



Fig. 13. Schematic of proposed mechanism of iodine and tin discharge in the photolysis of SnI_2 . The SnI_2 is taken to be an ionic solid. *I⁻ is an iodine ion on its normal lattice site adjacent to a tin ion vacancy. A subscript, s, denotes a surface species; sub., denotes sub-surface species in the top most "molecular-layer"; and no subscript indicates that the species is treated as a bulk species. *V_{1-s} is a missing *I_s⁻ and *I⁰ is a neutralised *I⁻ ion. *Sn²⁺ denotes a tin ion on its normal lattice site adjacent to an iodine vacancy.



Rate determining, bulk_diffusion



Fig. 14. Proposed potential energy-reaction coordinate representation for rate determining step in the photolysis of (a) α -SnI₂ and (b) β -SnI₂.

in I. We elaborate the proposal by suggesting that θ_{R} increases with temperature simply because there is a critical density of Sn atoms needed for Sn atom cluster formation and that tin reaction product is spread out over a greater depth with increasing temperature. Furthermore, in the first instance, no extra absorption of light starts until clusters are formed. The average depth of penetration of a photogenerated iodine ion vacancy before it participates in tin ion discharge will be related to the activation energy for bulk iodine ion vacancy diffusion and the cross-section for electron capture. In the case of α -SnI₂ this activation energy should be small, $\Delta H_{\alpha,D}$ (see Fig. 14a): a plot of $\ln \theta_R$ vs 1/T gives a good straight line with $\Delta H_{\alpha,D} = 0.2 \text{ eV}$, which is consistent with all preceding assumptions. The increased value of θ_R in β -SnI₂ is also consistent with the above hypothesis, but here we did not do enough long time experiments to get an activation energy plot with any precision. We have two points, θ_R (at 403 K) = 1.87×10^{16} cm⁻² and θ_R (at 393 K) = 1.1×10^{16} : these give $\Delta H_{\beta,D} \approx 0.4 \text{ eV}$ and it should be $\sim 0.9 \, \text{eV}$.

(c) Intermediate range. Suppose that at the end of the linear regime we had our full set of nucleation centres (quite near the surface) and that from θ_R onwards the centres would simply grow in size. We suppose that each centre scatters light either because it is Sn or because it has created a hole in the SnI₂, in either event we are in the Rayleigh scattering region where the amount of light scattered, S, is proportional to the sixth power of the

radius, a, i.e. $S \propto a^6 \propto \theta^2$. At a fixed set of conditions

$$\theta = Lkt, \tag{8}$$

where L is the flux of light used in photolysis at any time, k is a rate constant and t is time. But some of the initial photolysing light flux, L_0 , is lost by back scattering when $\theta > \theta_R$, whence

$$L = L_0 - \frac{1}{2}SN \tag{9}$$

where $\frac{1}{2}S$ is the amount of back scattered light per centre and N is the number per unit area of such centres, equal to θ_R . Since $S \propto \theta^2$ we get for $\theta > \theta_R$ that,

$$L = L_0 - \gamma (\theta - \theta_R)^2 \tag{10}$$

so that for $t > t_R$,

$$\theta = tk(L_0 - \gamma(\theta - \theta_R)^2). \tag{11}$$

This is clearly not-some simple power law. But we have tested eqn (11) for the data of Fig. 5, using the 150 min point to evaluate γ_k and get the following sort of fit: at 57 min we calculated 55 min; at 80, calc. 72; at 105, calc. 94. We advance this piece of work because we think that light scattering is important and not because we claim to have a good quantitative description. It was not the object of this experimental study to examine the intermediate regime and we would suggest that much remains to be done.

5. SUMMARY AND CONCLUSIONS

Apart from some interesting variations arising from the polymorphic transition of the photolysed material and the unsuspected allotropic form of the tin, the photolysis of SnI_2 is similar to that of PbI_2 . If one considers the broad features associated with the photolysis of these two substances and adds what can be gleaned from the literature it would seem a reasonable extrapolation to say that the chlorides, bromides and iodides of Zn, Ga, Ge, As, Cd, In, Sn, Sb, Hg, Tl, Pb and Bi, at the very least, must have broadly similar photolytic behaviour. By the phrase "broadly similar" we mean the following:

(i) Photolysis occurs when $h\nu \ge E(\text{optical gap})$. (This is because we require an electron/hole pair to effect photolysis.)

(ii) Bulk electron-hole recombination can often be ignored when compared with surface recombination. (Large band substance, $E(gap) \ge 1.8 \text{ eV}$, usually have long life times.) This means that photolysis and electron-hole surface recombination are in competition.

(iii) The rate determining step for photolysis will involve vacancy motion and for most substances this will be anion vacancy motion. Thus there will be a close correlation between electrical conductivity and photolysis efficiency, both of which will rise exponentially with temperature.

(iv) Impurities, or solid solutions, which increase the

anion vacancy concentration will increase photolysis efficiency.

(v) The halide (or non-metal) is generated at the surface and the metal atom, via cluster complexes to precipitate, is formed within the bulk.

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1. Albrecht M. G. and Green M., J. Phys. Chem. Solids 38, 297 (1977). We take this opportunity to point out a confusing error that appeared in this paper. Figures 2, 3, 4, 6, 8 and 9 have an inset on them in which are specified, amongst other things, the light flux employed in the experiment, as so many μ W cm⁻²: this is incorrect and the values should be multiplied by 20. However, it must be stressed that *everything else remains unchanged*. Thus consider Fig. 2 we reassert that the extent of reaction in molecules of photolysed Pbl₂ molecules per square cm was as indicated but that this was brought about by 400 μ W cm⁻².

The photon efficiencies indicated in Fig. 5 of course remain unchanged. The error on the insets came about because the PIN diode set-up that we used gave a read out in total received power and we had an aperature of 0.05 cm^2 , the figures from the experiments were inadvertently copied onto the diagrams although of course the data were correctly processed.

There is also a minor error in the abstract. Where we write $(\partial\theta/\partial t)_{T,\lambda,I} \propto T$ we should have written $(\partial\theta/\partial t)_{T,\lambda,I} = Const.$ Similarly on Figs. 2 and 3 we should have written $d\theta/dt = Const.$

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