Journal of Photochemistry and Photobiology A: Chemistry 152 (2002) 259–265

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

The mechanism of the photochemical metal organic deposition of lead oxide films from thin films of lead (II) 2-ethylhexanoate

Laura S. Andronic, Ross H. Hill*

Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada V5A 1S6

Received 10 September 2001; received in revised form 18 December 2001; accepted 10 January 2002

Abstract

A mechanistic study of the photochemistry of thin films of lead (II) 2-ethylhexanoate is presented. Films of lead (II) 2-ethylhexanote can be cast on silicon solutions by spin coating. Spectroscopic evidence suggests that the molecules are polymeric within the thin film. Irradiation of the film with ultraviolet light leads to the fragmentation of the complex and the ejection of carbon dioxide, heptane and heptene from the film. The quantum yield for the reaction of the lead complex was found to be within error of one. A mechanism consistent with these results is presented. The composition of the film remaining on the surface is approximately that of lead (II) oxide. Annealing resulted in the formation of crystalline $PbO_{1.37}$.

Keywords: Photochemistry; Lead (II) 2-ethylhexanoate; Lead (II) oxide

1. Introduction

In this contribution we wish to report on the details of the photochemical metal organic deposition of lead oxide films from films of lead 2-ethylhexanoate. Lead oxide is of interest as a result of several of its properties. There are several phases of lead oxide which exhibit different levels of reflectance and thin films of lead oxide can be used as optical storage devices [1]. Lead oxide thin films also have applications as protective coatings for lead salt devices and gas sensors [2]. Lead oxide is also used as an adhesion promoter for thick films [3]. The preparation of lead oxide has received additional attention because lead oxide is a controlling factor in the quality of many lead-based ferroelectrics [4,5]. The preparation of these materials is often complicated by the high volatility of lead oxide at relatively low temperatures.

Thin films of lead oxide have been produced in a low-temperature, low-pressure metal organic CVD process using $Pb(C_2H_5)_4$ as a precursor [6]. Our own work [7] has demonstrated the production of amorphous lead oxide at room temperature by photochemical metal organic deposition.

Photochemical metal organic deposition is the process by which a thin film of a metal organic complex is constructed and photolytically converted to the metal or metal oxide. The metal organic complex is designed such that the photochemistry results in the expulsion of the organic components of the molecule from the film (Eq. (1)). When this process is carried out in the atmosphere air oxidation normally results in the formation of a metal oxide film.

$$ML_6 \xrightarrow{h\nu} M + 6L \tag{1}$$

In our previous report of lead oxide deposition lead 2-ethylhexanoate was used to construct the precursor film. By mixing lead 2-ethylhexanoate with other precursors we were able to demonstrate the deposition of lead titanate, lead zirconate and lead zirconium titanate [8]. We have also used this precursor to construct a variety of layered materials [9–11].

In a previous manuscript [7] we had established that the photolysis of thin films of lead (II) 2-ethylhexanoate led to loss of the organic components and the formation of an amorphous lead oxide film. This film was found to be free from organic contamination. The other products of the photolysis were not identified. It was also suggested, based on dose to print experiments, that the reaction was a chain reaction.

In this manuscript we present evidence concerning the mechanism of the reaction of the lead 2-ethylhexanoate film. In particular we investigate the fate of the ligands in the photoreaction and the nature of the lead precursor film. The determination of the order and efficiency of the photochemical reaction is also presented. In the earlier study a preliminary mechanism was suggested however we find that a measure

---

* Corresponding author. Fax: +1-604-291-3765.
E-mail address: ross@chem.sfu.ca (R.H. Hill).

1010-6030/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S1010-6030(02)00020-5

of the quantum yield has caused us to reevaluate that proposal. Finally we present a characterization of the lead oxide product and the effect of heat treatments on the PMOD produced lead oxide.

2. Experimental

2.1. Materials and instruments

The substrate used for the deposition of metal oxides was *n* type Si(1 0 0). The silicon wafers were obtained from Shin Etsu and were cut in house to the approximate dimensions of 1 cm × 1.5 cm. The UV–VIS absorption spectra were recorded with a HP 8452A diode array spectrophotometer with a range 190–800 nm. The substrates used for the electronic absorption spectra measurements were NaCl crystals purchased from Spectro Tech. Inc.

FTIR spectra were obtained using a Bomem Michelson 120 FTIR spectrophotometer at 4 cm^{-1} resolution. Auger electron spectra were obtained using a PHI double pass CMA at 0.85 eV resolution at the Surface Physics Laboratory, Department of Physics, Simon Fraser University. X-ray analyses were done with a Philips PW-1820 diffractometer using a monochromatized Cu Kα radiation at Department of Physics, Simon Fraser University. The mass spectrum was recorded using a HP 5958 GC/MS spectrometer with an electron impact ion source. The quality and the thickness of the film were determined using a Leitz optical microscope equipped with an interferometer.

The photolysis experiments were done using a 254 nm output Hg arc lamp in ambient conditions. The lamp intensity was measured with an International Light IL 1350 Radiometer with the sensor area of 2.835 cm^2. The power of the lamp was found to be 4.97 mW. This corresponds to an intensity of 3.72×10^{-9} E cm^{-2} s^{-1}.

2.2. Surface calibration experiments

A stock solution of lead (II) 2-ethylhexanoate was prepared by dissolving 0.1018 g lead (II) 2-ethylhexanoate in 2 ml *n*-butylacetate. A drop of this solution (0.0030 ml) was deposited on a silicon chip. After solvent evaporation, the FTIR spectrum was obtained. The same procedure was repeated for several successive drops. At the end of the experiment the area of the drop was measured to be 0.5024 cm^2. Each drop of the solution corresponds to the coverage of 3.71 molecules/Å^2. The absorbance at 1518 cm^{-1} was plotted against the coverage (molecules/Å^2) and the extinction coefficients (Å^2/molecule) were calculated from the slope of the line. The extinction coefficient ε_{IR} at 1518 cm^{-1} was found to be 0.00277 Å^2/molecule or 1.67×10^5 cm^2 mol^{-1}.

A single film was also used to measure the relative absorbance of the IR and UV absorptions. For a film spin cast on NaCl, the absorbance at 1518 cm^{-1} was found to be 0.092 while the absorbance at the irradiation wavelength, 254 nm, was 0.61. From this and the above extinction coefficient at 1518 cm^{-1} the extinction coefficient at 254 nm was calculated to be 6.7×10^5 cm^2 mol^{-1}. In a similar fashion the extinction coefficient of the absorption maximum at 248 nm was found to be 7.3×10^5 cm^2 mol^{-1}.

2.3. Quantum yield measurements

A thin film of lead (II) 2-ethylhexanoate was constructed as described above. The FTIR spectrum of the films was obtained. The film was then irradiated with the calibrated light source for 10, 20, 30, 40, 80, 120, 160, 240, and 320 min and the FTIR obtained after each irradiation. The decay of the band at 1518 cm^{-1} was used to monitor the concentration of the lead (II) 2-ethylhexanoate. This in conjunction with the calibration of the light source was used to calculate the quantum yield.

Following this photolysis the sample was investigated by Auger and X-ray diffraction experiments. The sample subjected to heat treatments and the X-ray diffraction spectrum was also obtained.

2.4. Characterization of the volatile reaction products

In a similar experiment a thin film of the lead (II) 2-ethylhexanoate was irradiated in a quartz container under a static vacuum. Following photolysis the atmosphere in the chamber was injected directly into the mass spectrometer and the mass spectrum obtained.

3. Results

3.1. Spectroscopic data for a thin film of lead (II) 2-ethylhexanote

Previous work [7] had utilized methylene chloride as a solvent. Films cast from methylene chloride suffered from a large number of optical defects. Films cast from *n*-butyl acetate were found to have less defects and yield optical quality films. Thin films of lead (II) 2-ethylhexanote used in this study were all cast from *n*-butylacetate.

The FTIR spectrum of a lead (II) 2-ethylhexanoate thin film is presented in Fig. 1. The most intense absorption bands appeared in the region 1550–1300 cm^{-1} and were associated with vibration of the carbon oxygen bonds. The band at 1518 cm^{-1} was assigned to $\nu_a(CO_2)$, whereas the bands at 1458 and 1414 cm^{-1} are assigned to $\nu_s(CO_2)$. These lower energy bands are presumably split as a result of coupling of adjacent carboxylate vibrations [22]. The difference between the symmetric and anti symmetric stretches associated with the carboxylate is 82 cm^{-1}, well within the expected range for a bidentate carboxylate group [12]. There is also a band observed at 1319 cm^{-1} which is considerably weaker than the other bands. This is presumably a result of a mixing of the carboxylate vibrations with those of the hydrocarbon portion.

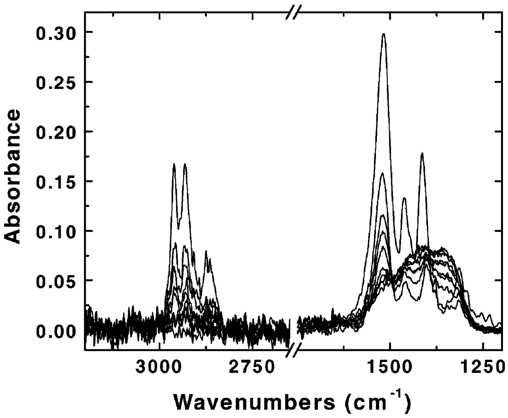


Fig. 1. Spectral changes accompanying the photolysis of a lead (II) 2-ethylhexanoate film for 0, 10, 20, 30, 40, 80, 120, 160, 240 and 320 min.

Table 1
FTIR spectral data for the lead (II) 2-ethylhexanoate films

Energy (cm^{-1})	Extinction coefficient (cm^2 mol^{-1})	Assignment
2964	0.94×10^5	ν(CH)
2933	0.92×10^5	ν(CH)
2874	0.45×10^5	ν(CH)
1518	1.67×10^5	$\nu_a(CO_2)$
1464	0.73×10^5	$\nu_s(CO_2)$
1414	1.00×10^5	$\nu_s(CO_2)$
1315	0.29×10^5	$\nu_s(CO_2)$

There were also apparent bands associated with the CH stretches of the aliphatic portion of the ligand. These bands were observed at 2964, 2933 and 2874 cm^{-1}. The data is summarized in Table 1.

Samples were also prepared by depositing known amounts of lead (II) 2-ethylhexanote in *n*-butylacetate on a silicon chip and allowing the solvent to evaporate. The deposit formed was not an optical quality film. Fig. 2 shows the overlaid spectra from samples made with different amounts of lead (II) 2-ethylhexanote in the film. The linear relationship between the FTIR absorbance at 1518 cm^{-1} and the surface coverage is also presented in Fig. 2. The extinction coefficient calculated from the slope of the line ε_{IR}, was 2.77×10^{-3} Å^2/molecule.

The UV–VIS spectrum of a thin solid film of lead (II) 2-ethylhexanoate was also measured. A single absorption band was observed in the region of 248 nm. This band was assigned as due to a ligand to metal charge transfer transition. The molar extinction coefficient was measured for the observed charge transfer band. The molar extinction coefficient for lead (II) 2-ethylhexanoate at 248 nm was 7.3×10^5 cm^2 mol^{-1}. In *n*-butylacetate solution this band appears shifted to higher energy, at 266 nm, probably due to sample solvent interactions [16]. A second charge transfer band was observed at 202 nm with an extinction coefficient in the thin film of 14.2×10^5 cm^2 mol^{-1}.

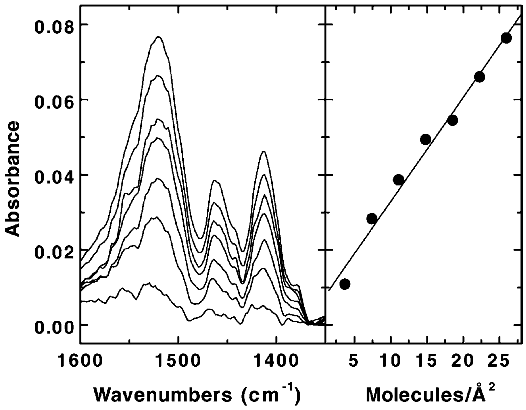


Fig. 2. Spectra of lead (II) 2-ethylhexanoate films consisting of 3.7, 7.4, 11, 15, 19, 22, and 26 molecules A^{-2}.

3.2. Solid state photochemistry of thin films of lead (II) 2-ethylhexanoate

A thin film of lead (II) 2-ethylhexanoate, spin coated from *n*-butylacetate, was exposed to the 254 nm output from a calibrated light source and the spectral changes monitored. The carboxylate bands at 1518, 1458, 1415 and 1319 cm^{-1} decreased in intensity as a result of the photolysis. Bands associated with the CH stretching modes at 2964, 2933, and 2874 cm^{-1} also decreased in intensity as a result of the photolysis. A single broad band was observed in the region of 1400 cm^{-1}. The results are shown in Fig. 1.

This results are indicative of the loss of the ligands from the complex and the formation of lead oxide. The single band observed in the product is believed to be associated with the formation of lead oxide [7]. These results are consistent with previous observations of this reaction in thin films [7].

A plot of the mole fraction of starting material remaining (calculated from the absorption band at 2964 cm^{-1}) versus irradiation time was made and is shown in Fig. 3. This

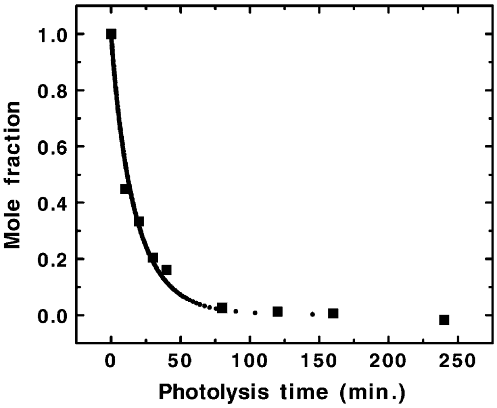


Fig. 3. Mole fraction vs. photolysis time for Pb(II) 2-ethylhexanoate where the squares represent experimental data and the points represent the numerical integration based on a quantum yield of 1.0.

line shows a significant deviation from a simple exponential decay. Previous studies have provided equations, which describe the time evolution of the amount of photoreaction as a function of photolysis time [20,21]. The mole fraction, X, of starting material is related to the photolysis time, t, incident light intensity, I^0, initial film thickness, c^0, initial and final absorbance at the irradiation wavelength, A^0 and A^f and quantum yield, Φ, by Eq. (2) [20]. Normally we have used these to describe a situation where the absorbance of the starting material and product is small and an analytical integration is possible. In the experiment described here, there is a significant absorbance associated with both the starting material and product at the irradiation wavelength. Under these conditions an analytical solution to Eq. (2) is not possible. A numerical integration was used with the quantum yield as the only variable in the fitting procedure. In Fig. 3 the simulation from this numerical integration is given. The resultant quantum yield was found to be 1.0.

$$\frac{\mathrm{d}x}{(A^0X/(A^0X + A^\mathrm{f} - A^\mathrm{f}X))\left(1 - \mathrm{e}^{-2.303(A^0X+A^\mathrm{f}-A^\mathrm{f}X)}\right)} = \frac{\Phi I^0\,\mathrm{d}t}{c^0} \qquad (2)$$

Similar experiments were conducted on films cast of methylene chloride. The spectral changes observed were in agreement with those found for the film cast from *n*-butylacetate. The only significant difference was that the film quality was generally of higher quality (i.e. optical) when cast from *n*-butylacetate.

3.3. Characterization of the reaction products

The photoproduced film was also investigated by Auger electron spectroscopy [7]. The Auger analysis indicated the presence of lead and oxygen in the film in the approximate ratio of 1:1 (Table 2). No carbon was detected within the film. X-ray investigations of the photoproduced lead oxide indicated that the film was amorphous.

Attempts were made to crystallize thin films of lead oxide. Samples with thickness in the range of 50–500 nm were annealed at different temperatures (200–700 °C). Our trials were not successful. This was probably due to the insensivity of measurements in the small quantities of thin films [1]. However, two peaks (Fig. 4) characterized the X-ray spectrum of a thin film of lead oxide sample annealed at 400 °C. The sample thickness was approximate 360 nm. The peaks were assigned according to JCPDS data cards as: (3 0 0) plane at $2\theta = 29.35$ and (1 1 3) plane at $2\theta = 31.23$ [13]. The position of these reflections and their relative intensity are consistent with the $PbO_{1.37}$ structure.

Table 2
Auger analysis of films produced by the photolysis of the lead (II) 2-ethylhexanoate with 254 nm light

Sputter time (s)	M %	O %	Composition (calculated)
0	55 ± 11	45 ± 9	Pb_5O_4
10	53 ± 10	47 ± 10	$Pb_{11}O_{10}$
20	49 ± 10	51 ± 10	PbO

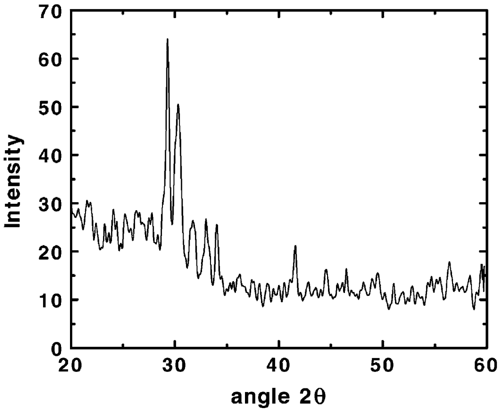


Fig. 4. XRD spectrum of lead oxide film annealed at 400 °C.

X-ray diffraction of PbO powder (massicot) heated at 280, 370, 440, 600 and 700 °C showed that besides the PbO (massicot) phase which existed throughout the temperature range, the Pb_3O_4 (minimum) phase appeared at 280 °C. The PbO_x phase with $x = 1.37$ appeared and Pb_3O_4 was no longer apparent at 370 °C. At 440 °C, PbO_x was no longer observed and red PbO (litharge) phase appeared in the diffraction pattern. Only at 600 °C yellow PbO (massicot) remains and at 700 °C, the yellow PbO melted [1]. Other researchers have found that lead oxide films deposited on silicon substrates participated in an interdifusion reaction. The reaction takes place in the temperature range of 400–450 °C and produces a silicate layer containing lead components [14]. Madsen and Weaver have observed that lead oxide produced by CVD on SiO_2-coated silicon wafer readily reacted with the underlying SiO_2 layer. In this deposition method, the substrate temperature was 515 °C. This effect was also observed for uncoated silicon substrates and was intensified by post deposition annealing [2].

3.4. Determination of the volatile products of the photoreaction of thin films of lead 2-ethylhexanoate

The technique employed for the identification of the volatile products produced during the photolysis of a thin film of lead (II) 2-ethylhexanoate, was electron impact mass spectrometry (EIMS). An amorphous film of lead (II) 2-ethylhexanoate, deposited on a silicon substrate, was placed in a sealed container and photolysed under a static vacuum. The container was then transferred to the mass spectrometer where the volatile photoproducts were passed through an inlet into an ionization chamber and bombarded with a beam of electrons. The interaction of the electric field of the electrons and the sample molecules will cause the ionization of the molecules, leaving them in highly excited energetic states. When the molecular ions relax, fragmentation of these excited states produces new ions and neutral particles. These ions are separated according to their mass to charge ratio and then recorded [15].

The mass spectrum has the distinctive features of the long chain saturated hydrocarbons [15]. Fragments appear at m/z values of 100, 98, 85, 71, 57, 44, and 43. The signal corresponding to the decarboxylation product, CO_2 has a strong intensity at $m/z = 44$. The molecular ions, C_7H_{16} and C_7H_{14}, are characterized by weak peaks at $m/z = 100$ and 98. The spectrum also indicates peaks corresponding to the fragmentation of the molecular ion at $m/z = 43$, 57 and 71. The distribution of the relative intensities of these ions is characteristic to saturated hydrocarbon chains, having the most intense peak at $m/z = 57$ (C_4 fragment). The peaks at $m/z = 43$ and 71 (C_3 and C_5 fragments) are also intense. Either side of this range, the ion intensities are less significant in both larger and smaller fragments.

Based on this result and the Auger electron spectroscopic characterization of the surface we can write a balanced reaction to describe the observed photochemistry. This is shown as Eq. (3).

$$\begin{aligned} &Pb(O_2CCH(C_2H_5)(CH_2)_3CH_3)_2 + \tfrac{1}{2}O_2 \\ &\quad \rightarrow PbO + 2CO_2 + C_7H_{16} + CH_3(CH)_2C_4H_9 \end{aligned} \tag{3}$$

4. Discussion

The FTIR of the precursor indicate that the 2-ethylhexanoate ligand coordinates as a chelating ligand. We also believe that in the film there must also be a further association of the lead (II) 2-ethylhexanoate.

The literature supports the suggestion that the lead (II) 2-ethylhexanoate is not monomeric in the thin film. Both crystallographic and solutions studies have demonstrated that many lead (II) carboxylates are associated. These may be held together by chelating carboxylate groups in which either one or both of the oxygen atoms also bridge to a further lead atom [17,18]. Lead (II) crotonate has a polymeric structure in which both oxygen atoms of a chelating crotonate ligand also bond to additional lead atoms [17]. Alternatively a bridging carboxylate may hold together a three dimensional network as found in lead (II) formate [19].

The FTIR data falling within the expected range for a bidentate carboxylate group suggests that the most likely mode of association within the solid film is via the carboxylate oxygen of a chelating 2-ethylhexanote ligand bridging lead centers. In this idealized structure both oxygen atoms of every second 2-ethylhexanoate ligand bridge lead atoms. This is analogous to the mode found in the lead (II) crotonate. The general features of the polymeric structure are illustrated in the schematic of the tetramer shown in Fig. 5. The length of the polymer within the film we have no estimate for although is would probably not be very monodisperse.

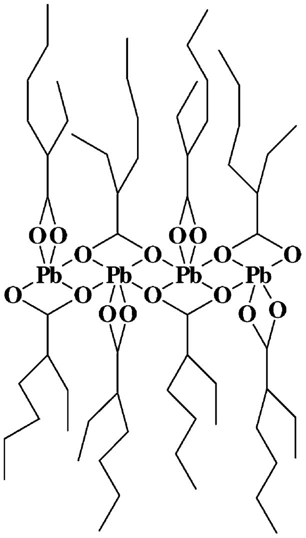
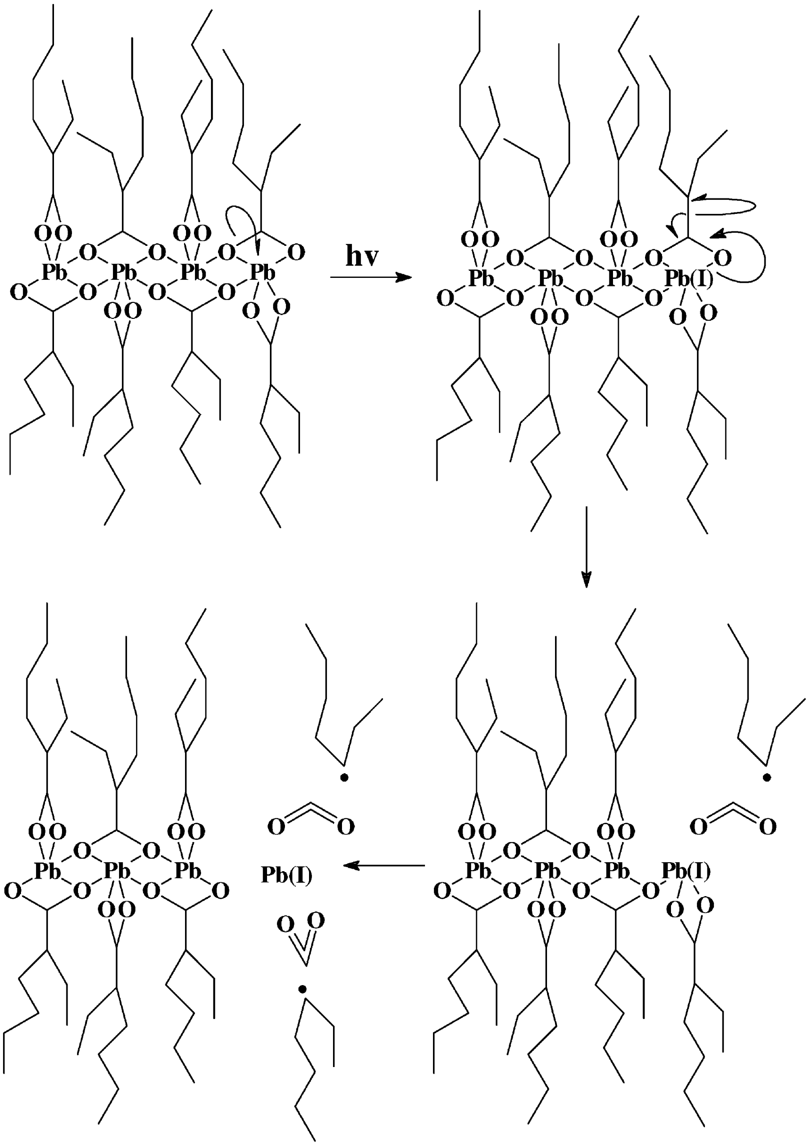


Fig. 5. Illustration of a four unit oligomer of lead (II) 2-ethylhexanoate showing the nature of the coordination expected for the polymeric structure within the film.

Upon photolysis the thin films of lead (II) 2-ethylhexanoate reacts to form lead oxide. A mechanism which accounts for the observed results is shown in Scheme 1. The reaction is initiated by the absorption of a photon which results in a ligand to metal charge transfer transition. In the scheme this absorption results in the transition occurring at a terminal position. The charge transfer transition results in the fragmentation of the carboxylate ligand and the formation of carbon dioxide and the 3-heptanyl radical. The lead, which was reduced in the charge transfer transition to lead (I) is not stable. The subsequent fragmentation of the lead (I) 2-ethylhexanoate complex generates a further carbon dioxide and 3-heptanyl radical.

The photoproduced lead is then oxidized by air to yield the observed lead oxide. The carbon dioxide diffuses from the film. The out gassed carbon dioxide was observed in the mass spectrum. The 3-heptanyl radical can react with a second 3-heptanyl radical as shown in Scheme 2. The radical abstracts a hydrogen from a second 3-heptanyl radical to yield heptane and heptene. Both of these products were observed in the mass spectrum. In Eq. (3) the formation of 2-heptene is shown to result by the abstraction of a hydrogen from the two position. We also expect that 3-heptene would be formed by the abstraction of the hydrogen from the four-position of the 3-heptanyl radical. Unfortunately the mass spectral data do not allow us to distinguish between these products.

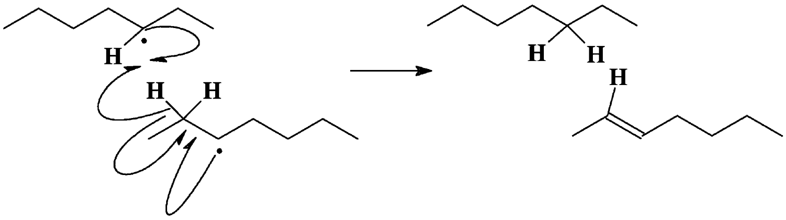
The mechanism illustrated shows the sequence of reactions for the terminal position of the oligomer. This position was chosen for illustrative purposes only. All of the steps in this mechanism could operate in interior positions in the oligomer or polymer which most likely makes up this film. This may also shed light on the low dose to print which was found for deposition of lead oxide in the past [7]. The



Scheme 1. Illustration of the proposed reaction mechanism on an oligomer of lead (II) 2-ethylhexanoate.

original suggestion was that the quantum yield in this system was possibly in excess of one and that the reaction was the result of a radical chain process. In this, more detailed study we find that the quantum yield does not provide evidence to support a radical chain process. In spite of this, the mechanism may provide insight into the low observed dose to print.

If the polymer chains within the film undergo significant reaction at internal sites in the polymer the average molecular weight of the polymer will decrease as a result of the exposure. The differential solubility, found in a dose to print measurement, may be an indication that the solubility of the polymer may be altered as a result of the molecular weight change. This result would be consistent with what is



Scheme 2.

commonly observed in organic polymer systems used in lithography [23].

5. Conclusion

The photochemistry of lead (II) 2-ethylhexanoate thin films has been elicidated. The films, formed by spin coating, are composed of polymeric lead (II) 2-ethylhexanoate. The photoreaction of this material is initiated by a ligand to lead charge transfer transition. The fit of the simulation of the time dependent concentration to photolysis time shown in Fig. 3 suggests that the quantum yield for the reaction is largely independent of the extent reaction for this process. Since the reaction must involve the shortening of the polymeric chain throughout this process, we can conclude that the quantum yield is independent of the chain length. The reaction proceeds by loss of the carboxylate ligand from the film in the form of carbon dioxide, heptane and heptene (through the intermediacy of the heptanyl radical). The air oxidation of the photoproduced lead results in the formation of lead oxide. Annealing of this material results in the formation of $PbO_{1.37}$.

Acknowledgements

We wish to thank Natural Sciences Engineering Research Council, EKC Technology Inc. and Simon Fraser University for financial assistance.

References

[1] S. Chao, Y.F. Fuang, Y.C. Chen, L. Yan, J. Phys. D 23 (1990) 955.
[2] L.D. Madsen, L. Weaver, J. Am. Ceram. Soc. 81 (1998) 988.
[3] M. Bersani, B. Morten, M. Prudenziati, J. Mater. Res. 12 (1997) 501.
[4] E. Hong, J.C. Shin, J. Choi, C.S. Wang, H.J. Kim, J. Mater. Res. 15 (2000) 1284.
[5] J.H. Kim, Y. Kim, A.T. Chien, F.F. Lange, J. Mater. Res. 16 (2001) 1739.
[6] R.S. Boorse, J.M. Burlitch, Chem. Mater. 6 (1994) 1509.
[7] S.L. Blair, C.W. Chu, R. Dammel, R.H. Hill, SPIE 3049 (1997) 829.
[8] R.H. Hill, S.L. Blair, ACS Symp. Ser. 706 (1998) 53.
[9] Y. Shi, G. Li, R.H. Hill, in: Proceeding of the Semiconductor Processing, Mater. Sci. 2 (1999) 297.
[10] G. Li, R.H. Hill, manuscript in preparation.
[11] L.S. Andronic, MSc. Thesis, Simon Fraser University, 2001.
[12] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th Edition, Wiley, New York, 1986.
[13] JCPDS-ICDD, file number 27-1202.
[14] W.G. Lee, S.I. Woo, J. Mater. Sci. 32 (1997) 815.
[15] E. Wayne, R.P. Wayne, Photochemistry, Oxford University Press, Oxford, 1996.
[16] G.L. Miessler, D.A. Tarr, Inorganic Chemistry, Prentice Hall, New Jersey, 1991.(Reference for the photodecay equation.)
[17] W. Clegg, I.R. Little, B.P. Straughan, Acta Cryst. C42 (1986) 1319.
[18] R.G. Bryant, V.P. Chacko, M.C. Etter, Inorg. Chem. 23 (1984) 3580.
[19] P.G. Harrison, A.T. Steel, J. Organomet. Chem. 239 (1982) 105.
[20] A. Becalska, R.J. Batchelor, F.W.B. Einstein, R.H. Hill, B.J. Palmer, Inorg. Chem. 31 (1992) 3118.
[21] M. Gao, R.H. Hill, J. Photochem. Photobiol. A: Chem. 97 (1996) 73.
[22] J.E. Tackett, Appl. Spectrosc. 43 (1989) 483.
[23] R. Dammel, Diazonaphthoquinone-based Resists, SPIE, TT11, Washington, 1993.