JOURNAL OF MATERIALS SCIENCE 29 (1994) 2143–2146

Solid-state photochemistry of platinum(II) methylazide complexes as thin films on Si (1 1 1) surfaces: photolithography of platinum films

S. L. BLAIR, J. HUTCHINS, R. H. HILL*
Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6
D. G. BICKLEY
Department of Physical Sciences, University College of the Cariboo, P.O. Box 3010, Kamloops, British Columbia, Canada V2C 5N3

The solid-state photochemistry of $L_2Pt(Me)(N_3)$ ($L = PPh_3$, PEt_3, dppe/2) have been investigated on Si (1 1 1) surfaces. Photolysis of an amorphous thin film of $L_2Pt(Me)(N_3)$ results in the loss of all ligands. This occurs via a single photon process with no detectable thermally stable intermediate. The resultant films are primarily platinum metal although some phosphine-containing impurity remains. The final analysis leads to formulations of the films as $Pt(dppe)_{0.06}$, $Pt(PPh_3)_{0.12}$ and $Pt(PEt_3)_{0.07}$. The thicknesses of the platinum films ranged from 150 nm to less than 25 nm. This process was shown to be compatible with standard lithography methods by the production of 3 μm wires on Si (1 1 1) by photolithography.

1. Introduction

Recently there has been a great deal of interest in processes that may be used to direct the deposition of metal films on to surfaces [1]. This is, in part, a result of the requirement in the electronics industry for lithographic fabrication of both interconnect materials and devices. Within this context, platinum is useful for the fabrication of Schottky diode contacts to both silicon and gallium arsenide [2]. The deposition of platinum by both chemical and photochemical vapour deposition has been investigated by a variety of workers [2–5]. Our group has pursued studies of the photochemistry of surface films of molecular precursors as a method to produce metal films [6–11]. With this approach, mild processing temperatures have been demonstrated; however, both purity and efficiency remain a problem. In the present work, we addressed the problem of efficiency in the context of designing a system that is predicted to have no stable intermediate. Here we report the photochemical reactions of some $L_2Pt(Me)(N_3)$ complexes as films deposited on the surface of Si (1 1 1).

Our interest in these specific complexes is, in part, a result of earlier studies in which we investigated some diazide complexes of platinum. In these earlier studies we demonstrated that $(COD)Pt(N_3)_2$ [10] and $(dppe)Pt(N_3)_2$ [11] lost all azide ligands photochemically and yielded reasonably pure platinum films. Each of these complexes decomposed in a stepwise process as outlined in Reactions 1 and 2. The first photochemical step was loss of an azide to form a stable Pt(I) intermediate, as shown in Reaction 1. The thermally stable monoazide complex was in turn photosensitive as shown in Reaction 2.

$$L_2Pt(N_3)_2 \xrightarrow{h\nu} L_2Pt(N_3) + N_3 \qquad (1)$$

$$L_2Pt(N_3) \xrightarrow{h\nu} 2L + Pt + N_3 \qquad (2)$$

The requirement of a photon to decompose the Pt(I) intermediate is not desirable because it presents a limitation on the efficiency of the deposition process. Such a limitation on reaction efficiency is undesirable if these processes are to be implemented industrially. In spite of this drawback, the initial reactions of the azide, shown in Reaction 1, were efficient as expected from solution studies [12–15] and solid-state studies [8, 9].

In this research, we investigated the use of mono azide complexes as precursors for platinum films. The single azide ligand was utilized as the initial photoreactive ligand that underwent efficient photoinduced azide loss. This initial reaction then leads to an intermediate containing a Pt(I) metal centre as was found in earlier studies [10, 11]. The formulation of this intermediate in the studies reported here was expected to be $L_2Pt(Me)$. The substitution of the azide by the methyl was expected to result in reduced thermal stability of the Pt(I) intermediate. If the intermediate is sufficiently unstable, the decomposition of $L_2Pt(Me)$ will proceed thermally, eliminating the requirement for a second photon. This will result in a more efficient process because thermal decomposition may occur quickly at room temperature.

2. Experimental procedure

The silicon wafers were obtained from Pacific Microelectronics Center, Canada. The Si (1 1 1) surface was used in these studies and the wafers were p-type silicon with tolerances and specifications as per SEMI Standard M1.1.STD.5, cut to the approximate dimensions of 1 cm × 1.5 cm in-house. The CaF_2 crystals were obtained from Wilmad Glass Co. Inc.

The Fourier transform–infrared (FT–IR) spectra were obtained with 4 cm^{-1} resolution using a Bomem Michelson 120-FTIR spectrophotometer. The samples were held in an aluminium sample mount within either a NaCl or a CaF_2-faced vacuum dewar.

The photolysis beam was a 100 W high-pressure mercury lamp in an Oriel housing equipped with condenser lenses and filtered through a 10 cm water filter with Pyrex optics. Alternatively, a 75 W high-pressure xenon lamp was used.

Auger 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. Film thickness was determined using a Leitz Laborlux 12 ME S with an interference attachment.

2.1. Preparation of $L_2Pt(Me)(N_3)$

All methyl azide platinum complexes were prepared by the displacement of cyclooctadiene from $(COD)Pt(Me)(N_3)$ [16] by addition of the appropriate amount of phosphine in methylene chloride solution. The complexes were recrystallized from methylene chloride:hexane solutions. A combination of ^1H and ^{31}P NMR spectroscopy indicated a trans stereochemistry for the PEt_3 and PPh_3 ligands.

The complex $(COD)Pt(Me)(N_3)$ was prepared from (COD)Pt(Me)Cl [17] by metathesis with NaN_3 [16].

2.2. Calibration of absorption on the surface

A stock solution of $(dppe)Pt(Me)(N_3)$ (0.0155 g) was prepared in CH_2Cl_2 (25 ml). A drop (0.0045 ml) of this solution was then deposited on the surface of a silicon wafer. The solvent was allowed to evaporate and the FT–IR spectrum obtained. The area of the drop was found to be 0.5 cm^2. This corresponds to a coverage of 51 molecules/nm^2. This process was repeated several times yielding the spectra shown in Fig. 1a and the corresponding calibration curve of absorbance versus molecules/nm^2 of $(dppe)Pt(Me)(N_3)_2$ is shown in Fig. 1b. The slope of this line yields an absorbance of 0.00031 nm^2/molecule. Assuming, a molecular volume of approximately $(0.8\ nm)^3$, this corresponds to an absorbance of approximately 0.0039/monolayer.

Similar experiments were conducted with $L_2Pt(Me)(N_3)(L = PPh_3, PEt_3)$ which yielded absorbances of 0.000 20 and 0.00018 nm^2/molecule. Making the above assumption about molecular volume yields absorbances of 0.0026 and 0.0023/monolayer, respectively.

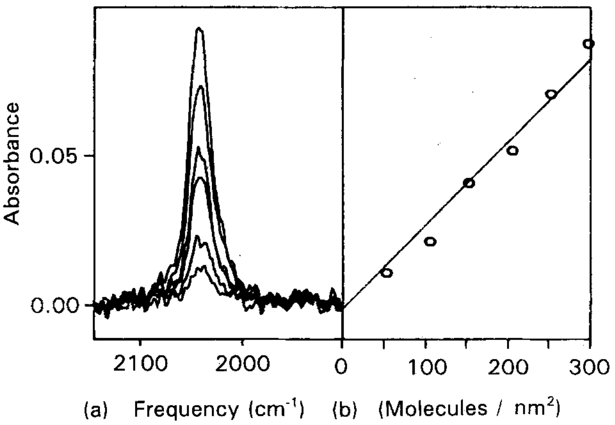

Figure 1 (a) FT–IR spectra associated with 51, 100, 150, 200, 250 and 310 molecules of $(dppe)Pt(Me)(N_3)/nm^2$ on a silicon surface. (b) Plot of absorbance of the antisymmetric N_3 stretch of $(dppe)Pt(Me)(N_3)$ versus coverage, data from (a).

2.3. Photolysis of complexes as films on silicon surfaces

All photolysis experiments were done in the same manner, A typical experiment is described in this section. A silicon surface was prepared with $(dppe)Pt(Me)(N_3)$ by spin coating with a drop of a CH_2Cl_2 solution (~ 5 mg/2 ml) on a silicon chip. This resulted in the formation of a smooth, uniform coating of the chip. The chip was then transferred to a vacuum dewar. The system was placed under vacuum and the FT–IR spectrum obtained. The sample was then irradiated for 15 s and another FT–IR spectrum was obtained. This procedure was repeated for the following (accumulated) photolysis times: 25, 30, 40, 60, 90, 180 and 300 s.

The samples were then examined under the optical microscope yielding film thicknesses ranging from 25–100 nm $(Et_3P)_2Pt(Me)(N_3)$; 25–150 nm $(dppe)Pt(Me)(N_3)$, 50–67 nm $(Ph_3P)_2Pt(Me)(N_3)$. The samples were then moved to the Auger spectrometer for elemental analysis of the surface.

2.4. Lithography

A $(dppe)Pt(Me)(N_3)$ film 150 nm thick was prepared on a silicon (1 1 1) surface, as above, and placed on a lithography mask. The sample was irradiated from below through a water (10 cm) filter and the mask using a 150 W Xe high-pressure lamp. Following 44 h photolysis, the sample was removed and rinsed with acetone. The image presented in Fig. 2 was obtained with a scanning electron microscope.

3. Results and discussion

3.1. Spectroscopic data for the complexes

The FT–IR spectrum of the antisymmetric azide stretch of $(dppe)Pt(Me)(N_3)$ on a silicon surface is shown in Fig. 1a. Note that a little change in appearance is observed over a coverage range from 50–300 molecules/nm^2. This range corresponds to approximately 2.6–23 monolayers. At these coverages no apparent thermal chemistry occurs upon deposition. This is confirmed by the linear plot of absorbance versus

Figure 2 Scanning electron micrograph of a surface obtained by the photolithography of (dppe)Pt(Me)(N_3) on a silicon (1 1 1) surface (image obtained at a 45° angle).

TABLE I FT–IR spectral data for relevant complexes on Si(1 1 1)

Complex	$\nu_a(N_3)$ (cm^{-1})	Absorbance ($monolayer^{-1}$)
(dppe)Pt(Me)(N_3)	2043	0.0039
$(Ph_3P)_2$Pt(Me)(N_3)	2041	0.0026
$(Et_3P)_2$Pt(Me)(N_3)	2037	0.0023
(dppe)Pt$(N_3)_2$	2050, 2045	0.0088
(dppe)Pt(N_3)	2033, 2000	

coverage shown in Fig. 1b. The energy of the antisymmetric azide stretch and its absorbance are summarized in Table I.

Similar spectra are found for all monoazide complexes discussed in this paper. All spectra are summarized in Table I. Also included for comparison in Table I are spectral data of other platinum phosphine mono and diazides that have previously been reported on surface films [11]. The position of the absorbances are similar to those of previously reported complexes on silicon surfaces. The absorbance intensity of the mono azides studied are approximately half the intensity of a previously reported platinum phosphine complexes containing diazides.

Before describing the photochemistry of the films, it is worth considering the approximate film thickness. If the molecular volume is estimated as approximately $(0.8\ nm)^3$ then the film is composed of ~ 640 monolayers of (at a coverage of 0.1 molecules/nm^2). The resultant thickness of such a film is approximately 500 nm. Because this thickness is near the wavelength of light used, the film will be irradiated throughout its thickness. In the photolysis experiments described below, all films were less than 500 nm thick.

3.2. Photochemistry of $L_2Pt(Me)(N_3)$ in the solid state

Photolysis of ten monolayers of (dppe)Pt(Me)(N_3) on a silicon surface under vacuum with ultraviolet light results in loss of the absorbance due to the azide at 2043 cm^{-1} (Fig. 3). No new absorbance band appeared that would indicate the presence of an intermediate. Similar spectral results are found for the other complexes, L_2Pt(Me)(N_3) L = PPh_3, PEt_3. In no case was there any absorbance indicative of the formation of an intermediate.

The above result is consistent with loss of the azide resulting in the decomposition of the complex. In order to demonstrate that no thermally stable intermediate was formed in these reactions, two samples of each complex were prepared and irradiated. When the azide was no longer observable in the FT–IR spectrum (~ 10 min) one of the samples was removed from the light and the second was irradiated for an additional 12 h. The final films, produced as above, were removed and transferred to the Auger spectrometer. Analysis was then conducted by Auger spectrometry.

The results of this analysis are shown in Table II along with the photolysis times. The results were dependent upon the phosphine donor ligand used. The complexes $(Ph_3P)_2$Pt(Me)(N_3) and (dppe)Pt(Me)(N_3) both gave analyses consistent with the formation of primarily platinum films contaminated with some remaining ligand. In these two complexes the proportion of ligand was such that approximately 0.12 phosphorous donor per platinum atom remained. The experiments conducted on $(Et_3P)_2$Pt(Me)(N_3) yielded a significantly lower retention of donor ligand. In this case, however, the retention was still close to 0.07 phosphorous atoms per platinum atom. This represents an upper limit and in each case the amount of ligand present is based on the amount of phosphorous detected. The amount of carbon detected is consistent with the formulation of these as retaining the phosphorous containing ligands. The only significant variation from this is in the photolysis of

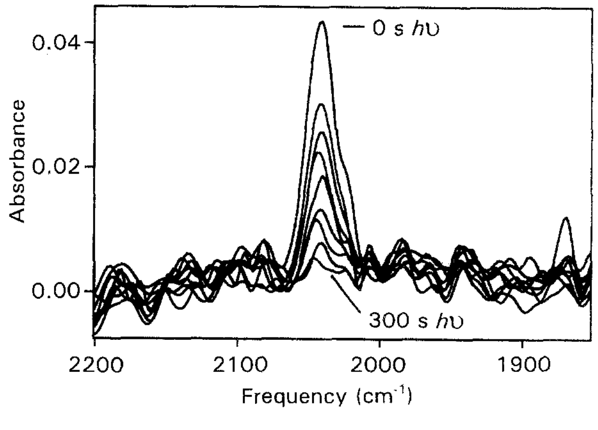

Figure 3 FT–IR spectral changes associated with the photolysis for 0, 15, 25, 30, 40, 60, 90, 180 and 300 s of a 170 monolayer film of (dppe)Pt(Me)(N_3) deposited on Si (1 1 1).

TABLE II Results of Auger analysis of the surfaces following a 30 s sputter with 3 kV Ar^+ ions

Complex	Photolysis time	Pt (%)	P (%)	N (%)	O (%)	C (%)
(dppe)Pt(Me)(N_3)	11 min	37.8	4.7	0	0	57.4
(dppe)Pt(Me)(N_3)	20 h	39.6	4.6	1.2	0	54.4
$(Ph_3P)_2Pt(Me)(N_3)$	9 min	30.3	3.9	0	0	65.8
$(Ph_3P)_2Pt(Me)(N_3)$	20 h	34.4	3.9	0	0	61.7
$(Et_3P)_2Pt(Me)(N_3)$	7 min	67.8	4.2	0	3.8	24
$(Et_3P)_2Pt(Me)(N_3)$	17 h	47	3.8	2.5	7.9	38.9

$(Et_3P)_2Pt(Me)(N_3)$ for 17 h. The final amount of carbon was in excess of that expected if it was all associated with the remaining PEt_3. This excess carbon is due to surface contamination. In separate experiments it was demonstrated that sputtering a surface containing excess PEt_3 ligand led to a surface with excess phosphorus rather than carbon. From this result it can be concluded that the carbon in the latter sample must arise from contamination.

No significant difference was found between those samples irradiated for ~ 10 min and those photolysed for longer periods. This shows that at the point when the azide is no longer detectable in the FT–IR spectrum, the reaction is complete. This result is not consistent with the formation of a thermally stable intermediate of formula L_2PtMe.

The results may be explained in terms of Reactions 3 and 4. The initial photochemical reaction is shown in Reaction 3, where the photon results in loss of a single azide. There is precedent for this reaction occurring in amorphous films [10, 11]. The punitive Pt(I) intermediates are not thermally stable and decompose to yield the final platinum films, Reaction 4

$$L_2Pt(Me)(N_3) \xrightarrow{h\nu} L_2Pt(Me) + N_3 \qquad (3)$$

$$L_2Pt(Me) \xrightarrow{\Delta} Pt + 2L + Me \qquad (4)$$

The azide radical [18, 19] is not observed, presumably due to its decomposition to nitrogen gas. This initial reactivity is similar to the reactivity reported in solution for $(Ph_3P)_2Pt(N_3)_2$ [20, 22] and as surface films for a variety of diazido complexes [8, 9] including some of platinum [10, 11].

Finally, we demonstrated the compatibility of this method to standard lithography procedures by irradiating a sample through a standard mask. The result of this procedure is shown in Fig. 2. Clear formation of lines 3 µm thick are visible.

4. Conclusion

It was found that the surface reaction of $(L_2)Pt(Me)(N_3)$ could be monitored by FT–IR. The complexes are all photosensitive and result in a single photon decomposition to platinum metal. The remaining impurities are consistent with some of the phosphorus donor ligand being retained intact. The important point is, however, that greater than 85% of the ligand is lost in each case. The resultant films produced in this way may be constructed in thicknesses ranging from < 25–150 nm thick. This overall procedure has been shown to be compatible with standard photolithography methods.

Acknowledgement

We thank B. Heinrich and K. Myrtle, Surface Physics Laboratory, SFU, for the Auger spectra, and NSERC (Canada) and the S.A. Committee (U.C.C) for financial support.

References

1. M. J. ALMOND, D. A. RICE and C. A. YATES, *Chem. Br.* **24** (1988) 1130.
2. M. J. RAND, *J. Electrochem. Soc.* **120** (1973) 686.
3. R. KUMAR, M. RASHIDI and R. J. PUDDEPHATT, *Polyhedron* **8** (1989) 551.
4. N. H. DRYDEN, R. KUMAR, E. OU, M. RASHIDI, S. ROY, P. R. NORTON and R. J. PUDDEPHATT, *Chem. Mater.* **3** (1991) 677.
5. H. H. GILGEN, T. CACOURIS, P. S. SHAW, R. R. KRCHNAVEK and R. M. OSGOOD, *Appl. Phys. B* **42** (1987) 55.
6. B. J. PALMER, A. BECALSKA and R. H. HILL, *J. Photochem. Photobiol. A Chem.* **57** (1991) 457.
7. B. J. PALMER, A. BECALSKA, R. HADER and R. H. HILL, *Polyhedron* **10** (1991) 877.
8. A. BECALSKA, R. J. BATCHELOR, F. W. B. EINSTEIN, R. H. HILL and B. J. PALMER, *Inorg. Chem.* **31** (1992) 3118.
9. B. J. PALMER, A. BECALSKA, T. W. H. HO and R. H. HILL, *J. Mater. Sci.* **28** (1993) 601.
10. D. G. BICKLEY, R. H. HILL and C. I. HORVATH, *J. Photochem. Photobiol. A Chem.* **67** (1992) 181.
11. T. W. H. HO, S. L. BLAIR, R. H. HILL and D. G. BICKLEY, *ibid.* **69** (1992) 229.
12. E. F. V. SCRIVEN, (ed.), “Azides and Nitrenes” (Academic Press, Orlando, FL, 1984).
13. J. L. REED, F. WANG and F. BASOLO, *J. Am. Chem. Soc.* **94** (1972) 7137.
14. C. BARTOCCI and F. SCANDOLA, *J. Chem. Soc. Chem. Commun.* (1970) 531.
15. J. F. ENDICOTT, M. Z. HOFFMAN and L. S. BERES, *J. Phys. Chem.* **74** (1970) 1021.
16. M. J. SHAW and D. G. BICKLEY, unpublished results (1988).
17. H. C. CLARK and L. E. MANZER, *J. Organomet. Chem.* **59** (1975) 411.
18. R. TIAN, J. C. FACELLI and J. MICHL, *J. Phys. Chem.* **92** (1988) 4073.
19. C. R. BRAZIER, P. F. BERNATH, J. B. BURKHOLDER and C. J. HOWARD, *J. Chem. Phys.* **89** (1988) 1762.
20. H. HENNIG, R. STICH, D. REHOREK, P. THOMAS and T. J. KEMP, *Inorg. Chim. Acta.* **143** (1988) 7.
21. H. HENNIG, R. STICH, H. KNOLL and D. REHOREK, *Z. Anorg. Allg. Chem.* **576** (1989) 139.
22. H. KNOLL, R. STICH, H. HENNIG and D. J. STUFKENS, *Inorg. Chim. Acta.* **178** (1990) 71.

Received 11 May
and accepted 19 October 1993