Photoresist-free lithography of 3 µm wide UO₃ lines from amorphous films of uranyl complexes

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The solid-state photochemistry of two uranyl complexes has been investigated with the purpose of developing methods for optical lithography of uranium oxide films. The complex, $UO_2(NCS)_2(OP(C_6H_5)_3)_2$, is photosensitive in the solid state, undergoing loss of both NCS ligands to yield $UO_2(OP(C_6H_5)_3)_2$ as the final photoproduct. Films of this material were easily patterned by photolithography. The complex, $UO_2(C_5H_7O_2)_2$, was also photosensitive and decomposed with no apparent intermediate to yield films of uranium oxide (δ-UO_3). This process was also shown to be compatible with optical lithography by the patterning of δ-UO_3 on silicon surfaces.

1. Introduction

X-ray lithography possesses considerable advantages over optical lithography, such as reduced diffraction far below deep-ultraviolet limits, and lower defect levels due to the relative insensitivity of organic contamination to X-rays [1]. In theory, X-ray lithography offers the ability to print sub-0.1 µm lines; however, this resolution has yet to be achieved owing to practical limitations [2,3]. Commonly, X-ray lithography masks consist of a low X-ray-absorbing substrate supporting a high X-ray-absorbing pattern, such as gold [1]. However, a uranium pattern is preferable because it possesses a higher X-ray-absorption cross-section than gold, permitting the use of thinner patterns, thereby reducing Fresnal diffraction [1, 4]. Optical lithography presents one means of fabricating patterned uranium films which are potentially useful as X-ray masks.

Here we explore the use of optical lithography to pattern uranium films from thin films of molecular precursors. In previous work we have shown that both inorganic and organometallic complexes of transition elements could be designed which would allow for optical lithography [5–10]. These studies explored the possibilities of direct photo imaging of metals and metal oxides on silicon surfaces. Typically, an amorphous film of the precursor complex is prepared and irradiated. The result of photolysis is to eject from the surface all but the metal, resulting in the formation of metal in the exposed areas. These ultimately may be of use for interconnect or device fabrication. For these uses, high-purity thin films are required. In the production of an X-ray mask, the requirements are somewhat different.

The choice of a material for an X-ray mask is not dominated by absolute purity, but rather other factors. The overall X-ray stopping ability is of most importance. The more common concerns such as stability are, of course, also important. In addition, purity becomes important if the impurities contained within the mask material are able to diffuse out over time. Here we address the problem of high X-ray stopping ability with the investigation of uranyl compounds which may be used to generate mask materials containing the uranyl group. In this process, the photochemistry required to obtain sufficient differential solubility for the production of a mask is also investigated. Finally we demonstrate for the first time, optical lithography to result in the patterning of uranium oxide lines. For these experiments silicon wafers are used as the substrate because they provide a reproducible flat surface.

2. Experimental procedure

The silicon wafers were obtained from Pacific Micro-electronics 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. Uranyl nitrate was purchased from Strem Chemical.

The Fourier transform–infrared (FT–IR) spectra were obtained with 4 cm^{-1} resolution using a Bomem Michelson 120 FT–IR spectrophotometer. The samples were held by an aluminium clip to an aluminium sample mount.

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

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.

2.1. Preparation of the uranyl complexes $UO_2(NO_3)_2(OP(C_6H_5)_3)_2$, $UO_2(NO_3)_2(P(C_6H_5)_3)_2$, $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ and $UO_2(C_5H_7O_2)_2$
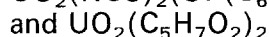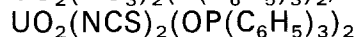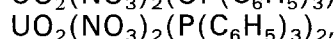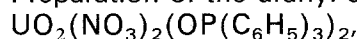
The complexes, $UO_2(X)_2(L)_2$, ($L = P(C_6H_5)_3$, $X = NO_3$; $L = OP(C_6H_5)_3$, $X = NCS$, NO_3) were prepared by published procedures [11]. The complexes were characterized by elemental analysis and FT–IR spectroscopy.

A literature preparation [12] was also used for the preparation of the uranyl complex, $UO_2(C_5H_7O_2)_2$ which was characterized by elemental analysis and FT–IR spectroscopy.

2.2. Calibration of infrared absorption on surfaces

A stock solution of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ (0.0072 g) was prepared in CH_2Cl_2 (2.0 ml). A drop (0.0038 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 0.64 cm². This corresponds to a coverage of 139 molecules/nm². This process was repeated several times yielding the spectra shown in Fig. 1a and the corresponding calibration curve of absorbance at 2050 cm⁻¹ versus molecules of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ is shown in Fig. 1b. From the slope of this line, 0.28×10^{-3} nm² molecule, the absorbance per monolayer is calculated as 2.1×10^{-4}/monolayer assuming a molecular volume of 1.540 nm³. The position and extinction coefficients of the other bands are reported in Table I.
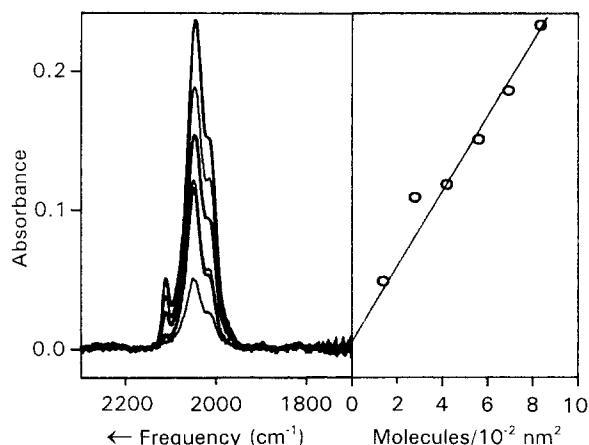

Figure 1 FT–IR spectra associated with 1.4, 2.8, 4.2, 5.6, 7.0 and 8.3 molecules of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ per 10^{-2} nm² on a silicon surface and a plot of absorbance of the 2050 cm⁻¹ band of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ versus coverage.

In the case of $UO_2(C_5H_7O_2)_2$, a similar experiment was conducted using 0.0035 g in 2.0 ml CH_2Cl_2. The areal coverage was 0.28 cm² and each drop was 0.004 ml in volume. The spectra are shown in Fig. 2a, and in Fig. 2b the calibration curve for the absorbance at 1522 cm⁻¹ is shown. The slope of this line, 0.33 $\times 10^{-3}$ nm²/molecule, and the estimated molecular volume, 0.350 nm³, may be used to yield an extinction coefficient of 6.6×10^{-5}/monolayer for this band. The energies and extinction coefficients of the other bands are reported in Table I.

2.3. Photolysis of complexes as films on silicon surfaces

All photolysis experiments were done following the same procedure. Here we describe a typical experiment. A film of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ was deposited on p-type Si(1 1 1) by spin-coating from a CH_2Cl_2 solution. 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 h and the FT–IR

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

Complex	Energy (extinction) (cm⁻¹ (monolayer)⁻¹)	Literature [11, 12] energy (cm⁻¹)	Assignments
$UO_2(NCS)_2(OP(C_6H_5)_3)_2$	2112 (0.000 03)	2052	NCS
	2050 (0.000 21)		NCS
	2021 (0.000 11)		NCS
	1137 (0.000 16)	1138	P=O
	1085 (0.000 10)	1085	P=O
	930 (0.000 11)		UO_2
$UO_2(C_5H_7O_2)_2$	1574 (0.000 056)	1570	C=O
	1524 (0.000 066)	1529	C=C
	1429 (0.000 016)	1437	C–H
	1362 (0.000 048)	1351	C=O
	1271 (0.000 020)	1277	C=C
	1015 (0.000 020)	1024, 1014	CH_3
	920 (0.000 086)	925	UO_2

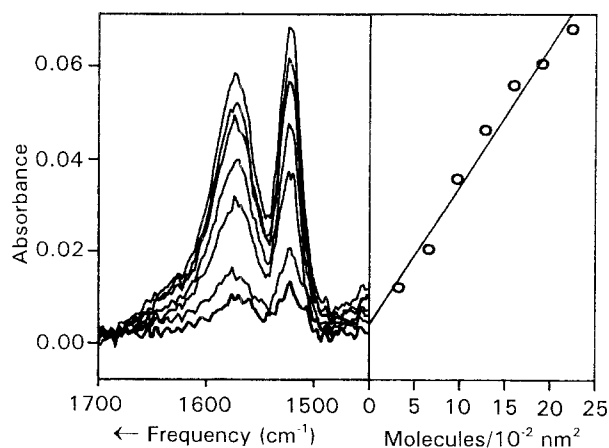*Figure 2* FT–IR spectra associated with 3.2, 6.4, 9.5, 12.7, 15.9, 19.1 and 22.3 molecules of $UO_2(C_5H_7O_2)_2$ per 10^{-2} nm^2 on a silicon surface and a plot of absorbance of the 1522 cm^{-1} band position of $UO_2(C_5H_7O_2)_2$ versus coverage.

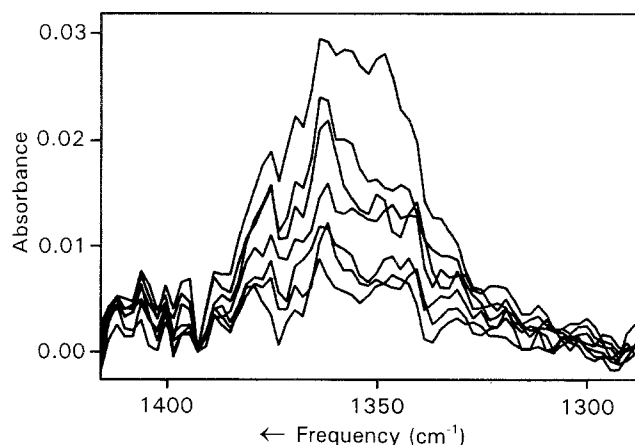*Figure 4* FT–IR spectral changes associated with the photolysis for 0, 23, 46, 95, 143, 189, and 237 h of a 700 monolayer film of $UO_2(C_5H_7O_2)_2$ deposited on Si(1 1 1). The peaks all decrease in intensity as a result of photolysis.

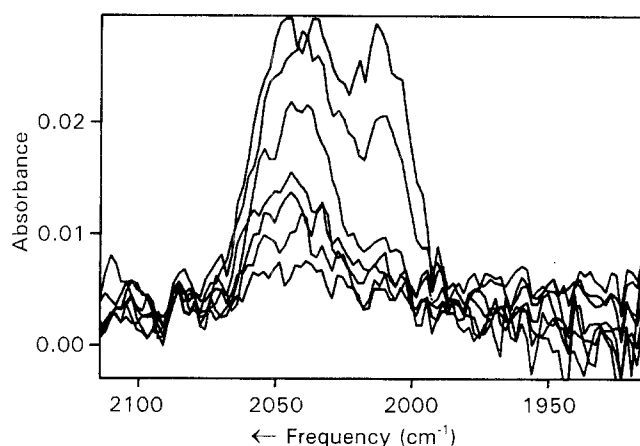*Figure 3* FT–IR spectral changes associated with the photolysis for 0, 15, 42, 80, 128, 176, 242 h of a 150 monolayer film of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ deposited on Si(1 1 1). The peaks all decrease in intensity as a result of photolysis.

spectrum obtained again. This procedure was repeated for the following photolysis times: 42, 80, 128, 176, 242 h. The results are shown in Fig. 3.

In the case of $UO_2(C_5H_7O_2)_2$ a similar experiment was conducted in which the photolysis times were 0, 23, 46, 95, 143, 189, and 237 h. The spectral data for this experiment are presented in Fig. 4.

2.4. Optical lithography

All experiments were done with the same procedure, varying only in photolysis times. A typical experiment is described below. A film of $UO_2(C_5H_7O_2)_2$ prepared on a silicon chip by spin coating from an ethanol solution and placed on a lithography mask. This sample was irradiated for 72 h from the bottom through the lithography mask. The sample was examined by optical microscopy and features were readily observed. Development consisted in rinsing the film with acetone and resulted in the loss of unexposed film from the surface. The remaining pattern was clearly visible by optical microscopy and is shown in Fig. 5.
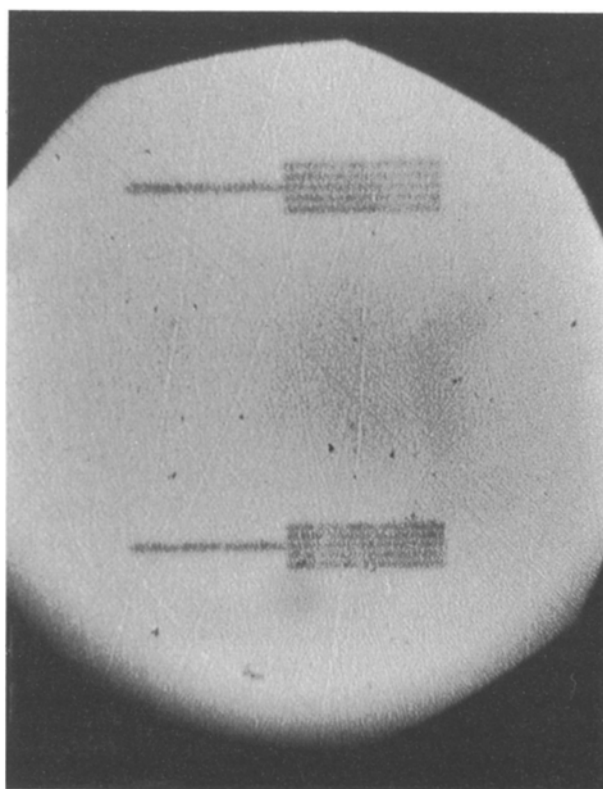

Figure 5 Image from optical microscope showing the surface obtained by the photolithography of $UO_2(C_5H_7O_2)_2$ on a silicon (1 1 1) surface following removal of unexposed $UO_2(C_5H_7O_2)_2$. Each short line is 100 μm long while each long line is 200 μm long.

3. Results and discussion

Several different complexes of the general formula $UO_2X_2L_2$ (X = NO_2, NO_3, NCS; L = $OP(C_6H_5)_3$ and XL = $C_5H_7O_2$) were examined to determine if they formed good amorphous films by spin-coating from organic solvents. Initial attempts indicated that the fabrication of the initial films for study was a limiting factor. It was found that only two of the above complexes formed high-quality amorphous films by spin-coating. These two complexes were $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ and $UO_2(C_5H_7O_2)_2$. For

further study we hence concentrated on these two species.

Thin films of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ were prepared by spin-coating methylene chloride solutions of the complex on silicon chips. The FT–IR spectra of one such sample is shown in Fig. 3. This may be compared with the spectra from the calibration experiment in Fig. 1. The relative intensity of the two bands associated with the NCS ligands is significantly altered. This presumably is a result of the environment created by the spin-coating procedure. Using the most intense band as an indication of the concentration, yields a film thickness of 120 monolayers for the spin-coated film. Photolysis of this sample with ultraviolet light resulted in the spectral changes shown in Fig. 3 for the isothiocyanato region of the spectra.

The intense absorption due to the NCS ligand at 2037 and 2014 cm^{-1} was found to decrease in intensity as a result of photolysis. The initial loss of the lower energy absorption may indicate loss of a single NCS ligand at short photolysis times. Longer photolysis resulted in the loss of both NCS ligands from the complex. The final absorption spectrum had a broad band at 923 cm^{-1}. This band indicates that the uranyl group was intact following the photoreaction. In addition, bands associated with the phosphine oxide were apparent throughout the spectra. Further confirmation of both the loss of NCS ligands and the retention of the phosphine oxide is obtained from the Auger analysis of the surface resultant after prolonged photolysis.

The Auger analysis of the films produced above indicated that the product contained significant amounts of uranium, phosphorus, carbon and oxygen. Of importance here is the intensity of the phosphorus signal. Following sputtering for 50 s a ratio of O:P:C of 1:1.2:17 was found. The ratio expected for $OP(C_6H_5)_3$ is 1:1:18. These results are certainly within error of retention of $OP(C_6H_5)_3$ intact within the film. Auger analysis also indicated that significant amounts of both sulphur and nitrogen remained on the surface.

The overall reaction is loss of the NCS ligand from the coordination sphere of the uranyl to form a species with the formula $UO_2(OP(C_6H_5)_3)_2$. The photoejection of halide and pseudo halides from uranyl complexes has long been known [13]. Ejection of the isothiocyanato ligand is also a well-established photoprocess [14]. In spite of the incomplete conversion to uranium oxide and low photosensitivity, the films were of high quality, so an attempt at lithography was made with this complex.

Optical exposure of thin films of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ through a lithography mask was conducted to determine if patterning could be accomplished. Following exposure for several days the sample was removed and the image in Fig. 6 obtained with an optical microscope. The pattern of lines is well resolved. Unfortunately, the adherence of the film is poor and attempted rinsing of the surface with hexane removed all patterning. We have not yet found a solvent in which the unexposed and exposed regions showed sufficient differential solubility to be of prac-
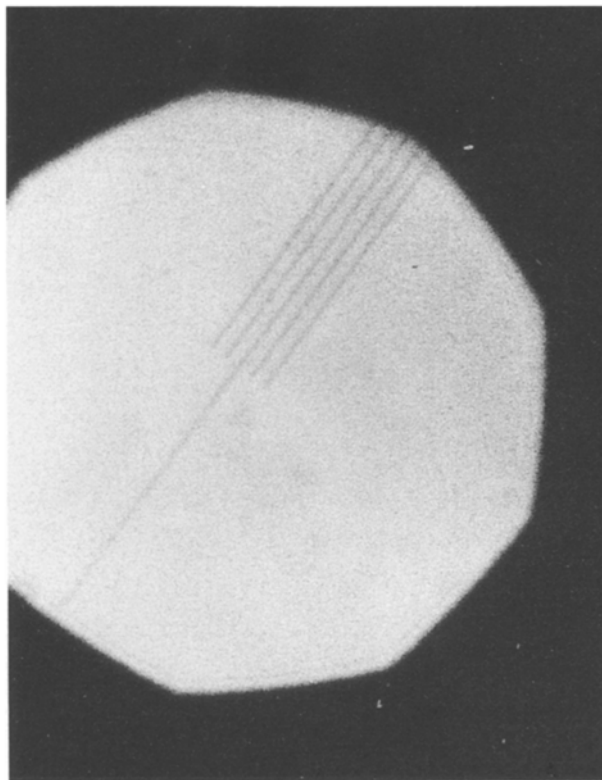

Figure 6 Image from optical microscope showing the pattern obtained upon exposure of a film of $UO_2(NCS)_2(OP(C_6H_5)_3)_2$ deposited on silicon surface to irradiation through an optical lithography mask. The single long line extends 100 μm beyond the other four lines.

tical value. In spite of this limitation, these results are encouraging, as the resolution obtained in a simple contact exposure is quite high.

Preliminary experiments were conducted on the various forms of $UO_2(C_5H_7O_2)_2$. Several attempts indicated that the anhydrous material could be most easily spin coated and was used for the remainder of the experiments. Spin-coated films gave similar spectra to those found in the calibration curve. These spectra are also comparable to those reported in the literature for crystalline samples. The spin-coating process was routinely used to fabricate films which were in the region of 700 monolayers thick. Because further experiments were conducted in both vacuum and under an air atmosphere, it is important to note that this is not a volatile complex. Previous studies have shown a limited volatility for these uranyl complexes, unlike the uranium (IV) derivatives of diketones [15,16]. It is also worth noting that a large amount of work has been done on the photochemistry of diketonates [17,18].

Photolysis of spin-coated thin films of $UO_2(C_5H_7O_2)_2$ also results in detectable photochemistry. In Fig. 4, the result of photolysis of this complex on a Si(1 1 1) surface is shown. Loss of bands associated with the acetylacetonato ligand at 1524, 1362 and 1271 cm^{-1} and the symmetric stretching of the uranyl group at 920 cm^{-1} are accompanied by the appearance of a single band at 923 cm^{-1}. This single product band is presumably due to uranyl oxide. The spectra of various forms of uranium oxide have been reported

[19–21]. The final spectrum we find is similar to that reported for δ-UO_3 by Hoekstra and Siegal [21].

Lithography of films of $UO_2(C_5H_7O_2)_2$ was also done. Attempts were made to pattern both glass and silicon substrates with images by photolysis of amorphous films of the uranyl complexes. Attempts at photoimaging with $UO_2(C_5H_7O_2)_2$ were more successful than reported above for $UO_2(NCS)_2$-$(OP(C_6H_5)_3)_2$. Initial exposure yielded good images. A photograph of the image following rinsing with hexane is shown in Fig. 5. In this case good differential solubility was found and the patterns could be deposited on both silicon and glass. The resolution was extremely sensitive to photolysis time. The best patterns were obtained after 4 days, and while no pattern was observed after 2 days, overexposure resulted after 5 days of photolysis. In spite of this problem, the result demonstrates that it is feasible to use solid films of uranium complexes as precursors for patterning.

4. Conclusions

The photoimaging from surface films of uranyl complexes has been demonstrated for the first time. The overall photosensitivity of these complexes is very low and although differential solubility was readily obtainable with the acetylacetonate derivative, the photolysis times required were less than satisfactory. Current work is concentrated on the design of a uranyl compound which will undergo the required photochemistry with higher quantum yields for a more efficient process.

Acknowledgements

References

1. I. W. BOYD and R. B. JACKMAN, "Photochemical Processing of Electronic Materials" (Academic Press, London, 1992) Ch. 4.
2. A. HEUBERGER, *Microelectron. Eng.* **5** (1986) 3.
3. *Idem, ibid.* **3** (1985) 535.
4. R. A. SERWAY, "Physics for Scientists and Engineers", 2nd Edn (Saunders College, 1986).
5. B. J. PALMER, A. BECALSKA and R. H. HILL, *J. Photochem. Photobiol. A Chem.* **57** (1991) 457.
6. B. J. PALMER, A. BECALSKA, R. HADER and R. H. HILL, *Polyhedron* **10** (1991) 877.
7. A. BECALSKA, R. J. BATCHELOR, F. W. B. EINSTEIN, R. H. HILL and B. J. PALMER, *Inorg. Chem.* **31** (1992) 3118.
8. B. J. PALMER, A. BECALSKA, T. W. H. HO and R. H. HILL, *J. Mater. Sci.* **28** (1993) 6013.
9. D. G. BICKLEY, R. H. HILL and C. I. HORVATH, *J. Photochem. Photobiol. A Chem.* **67** (1992) 181.
10. T. W. H. HO, S. L. BLAIR, R. H. HILL and D. G. BICKLEY, *ibid.* **69** (1992) 229.
11. F. A. HART and J. E. NEWBURY, *J. Inorg. Nucl. Chem.* **28** (1966) 1334.
12. A. E. COMYNS, B. M. GATEHOUSE and E. WAIT, *J. Chem. Soc.* (1958) 4655.
13. G. J. FERRAUDI, "Elements of Inorganic Photochemistry" (Wiley InterScience, New York, 1988).
14. A. D. KIRK, *Coord. Chem. Rev.* **39** (1981) 225.
15. H. I. SCHLESINGER, H. C. BROWN, J. J. KATZ, S. ARCHER and R. A. LAD, *J. Am. Chem. Soc.* **75** (1953) 2446.
16. H. GILMAN, R. G. JONES, E. BINDSCHADLER, D. BLUME, G. KARMAS, G. A. MARTIN, Jr, J. F. NOBIS, J. R. THIRTLE, H. L. YALE and F. A. YOEMAN, *ibid.* **78** (1956) 2791.
17. B. MARCINIAK and G. E. BUONO-CORE, *J. Photochem. Photobiol. A Chem.* **52** (1990) 1.
18. M. J. RAND, *J. Electrochem. Soc.* **120** (1973) 686.
19. K. OHWADA, *Spectrochim. Acta* **25a** (1970) 1035.
20. M. TSUBOI, M. TERADA and T. SHIMANOUCHI, *J. Chem. Phys.* **36** (1962) 1301.
21. H. R. HOEKSTRA and S. SIEGEL, *J. Inorg. Nucl. Chem.* **18** (1961) 154.