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Nickel β-diketonate complexes as precursors for the photochemical deposition of nickel oxide thin films

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In this paper we report the utilization of amorphous films of Ni(II) diketonate complexes as precursors for the direct photochemical deposition of thin films of nickel oxides. The UV photolysis of amorphous thin solid films of $Ni(PhCOCHCOPr)_2$ results in the loss of all ligands from the coordination sphere. The acetylacetone derivative was chosen for the solid state photochemistry because the presence of the long carbon chains or highly branched hydrocarbons substituents, lowers the intermolecular interactions and allows the formation of high quality films upon spin-coating. The surface morphology of the films was observed by scanning electron microscopy and showed excellent quality without islands or other imperfections. The formation of NiO was determined by X-ray difraction and Auger spectroscopy analysis. The photochemical deposition of patterns of NiO was shown to be compatible with standard lithographic techniques by the lithography of 100 × 2 μm lines.

1. Introduction

Nickel oxide, is a material widely used in fuel cell electrodes, the manufacture of ferrites, electroplating, nonmetallic resistance thermometers or thermistors, etc. Thin films of nickel oxide have potential applications as components for high power ultra-capacitors, miniature batteries, and is one of the most promising electrochromic materials because of its large dynamic range, good durability and low material cost [1]. Also, because of its antiferromagnetic nature, alloys or multilayers of NiO with ferromagnetic materials have shown interesting magnetic properties in relation with the exchange anisotropy phenomenon and the giant magnetoresistance effect (GMR) [2–4].

Sputtering methods such as direct ion beam sputtering (IBS) [5], reactive magnetron sputtering [1, 3, 6], have been used for deposition of NiO films. One of the advantages offered by sputtering techniques over CVD and evaporation techniques, is the possibility of achieving epitaxy at lower substrate temperatures, which in turn minimize undesirable interactions at the substrate-film interface [6]. Thin films of nickel oxide have also been grown on different substrates by the technique of laser ablation from Ni metal targets in an atmosphere of molecular oxygen [7].

Although no photochemical deposition methods can be found in the literature related to the formation of nickel oxide films, Hill and co-workers have developed a method by which thin films of inorganic or organometallic precursors upon irradiation are converted to amorphous films of metals or oxides, depending on the reactions conditions [8, 9]. The development of this method requires that the precursor complexes form stable amorphous thin films upon spin coating onto a suitable substrate, and that photolysis of these films results in the photoextrusion of the ligands.

In this paper, nickel diketonate complexes are proposed as source materials for the direct photochemical deposition of nickel oxide thin films. The photochemistry of metal β-diketonate complexes has been widely investigated in the past. For example, copper and nickel complexes are known to photochemically react in solution, upon LMCT excitation or by sensitization with triplet aromatic ketones, to form metallic copper and nickel respectively [10–14]. Although the solid state photochemistry of these compounds has not been investigated, we have shown that irradiation of amorphous thin films of a copper diketonate complex allows the formation of high quality thin films of metallic copper or copper oxide [15]. These results also indicated that the best films are obtained with precursor molecules having bulky organic ligands. In this way the polar interactions between molecules which aid in crystallization are lessened, and therefore precursor complexes can be cast into amorphous films [14, 15].

2. Experimental procedure

The Si wafers were obtained from WaferNet, San Diego, Ca. The Si(100) surface was used in these studies and the wafers were p-type silicon with tolerances and specifications as per SEMI Standard M1.1STD.5 cut to the approximate dimensions of 1cm × 1cm. Prior to use the wafers were cleaned successively with ether, methylene chloride, ethanol, aqueous HF (50 : 1) for 30 seconds and finally with deionized water. They were dried in an oven at 110°C and stored in glass containers [16].

The FT-IR spectra were obtained with 4 cm^{-1} resolution in a Perkin-Elmer 1605 FT-IR spectrophotometer. UV spectra were obtained in a Hewlett-Packard 8452-A diode-array spectrophotometer. SEM analysis were performed on a JEOL 5410 scanning electron microscope equipped with EDX spectrometer, in the Electronic Microscopy Laboratory, Departamento de Ingenieria Metalurgica, Universidad de Santiago de Chile. 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. Grazing incidence X-ray diffraction patterns were obtained using a Siemens D5000 X-ray diffractometer, Department of Physics, Simon Fraser University. The X-ray source was a Cu K_α (1.54 Å) beam. The film thickness was determined using a Leitz Laborlux 12 ME S with an interference attachment.

The irradiation source was a 200 W high pressure Hg-Xe lamp in a Photon Technologies Inc. housing equipped with condenser lenses and filtered through a 10 cm water filter with quartz optics. For the photolitographic experiments a UVP Model UVS-28 (2 × 8 W) 254 nm lamp was used.

All β-diketones and its Ni(II) complexes were prepared according to published procedures [17], and were characterized by FT-IR spectroscopy and elemental analysis. Solvents were Merck (p.a. grade) and were distilled and dried before use.

2.1. Preparation of amorphous thin films

The thin films of the precursor complexes were prepared by the following procedure: A silicon chip was placed on a spin coater and rotated at a speed of 1500 RPM. A portion (0.5 ml) of a solution of the nickel diketonate complex in $CHCl_3$ was dipensed onto the silicon chip and allowed to spread. The motor was then stopped and a thin film of the complex remained on the chip. The quality of the films was examined by optical microscopy and in some cases by SEM.

2.2. Calibration of the FT-IR absorption on Si surfaces

A solution of $Ni[PhCOCHCOPr]_2$ in $CHCl_3$ (0.2038 g in 5.0 ml) was prepared. From a microsyringe, 4 μl of this solution was placed on the silicon surface and allowed to dry. The area of the dried drop was 15.2 mm^2 (1.52×10^{13} nm^2) and correspond to a coverage of 1.132×10^3 molecules/nm^2. The FT-IR of the surface was obtained. This process was repeated several times and the spectra collected with each additional drop (Fig. 1a). A plot of the absorbance at 1519.5 cm^{-1} vs coverage was linear as shown in Fig. 1b. This plot was used to determine coverage in films prepared for photodeposition.

2.3. Photolysis of complexes as films on Si surfaces

All photolysis experiments were done following the same procedure. Here is the description of a typical experiment. A film of $Ni[PhCOCHCOPr]_2$ was deposited on p-type Si(100) by spin-coating from a $CHCl_3$ solution. This resulted in the formation of a smooth, uniform coating on the chip. The FT-IR spectrum of the starting

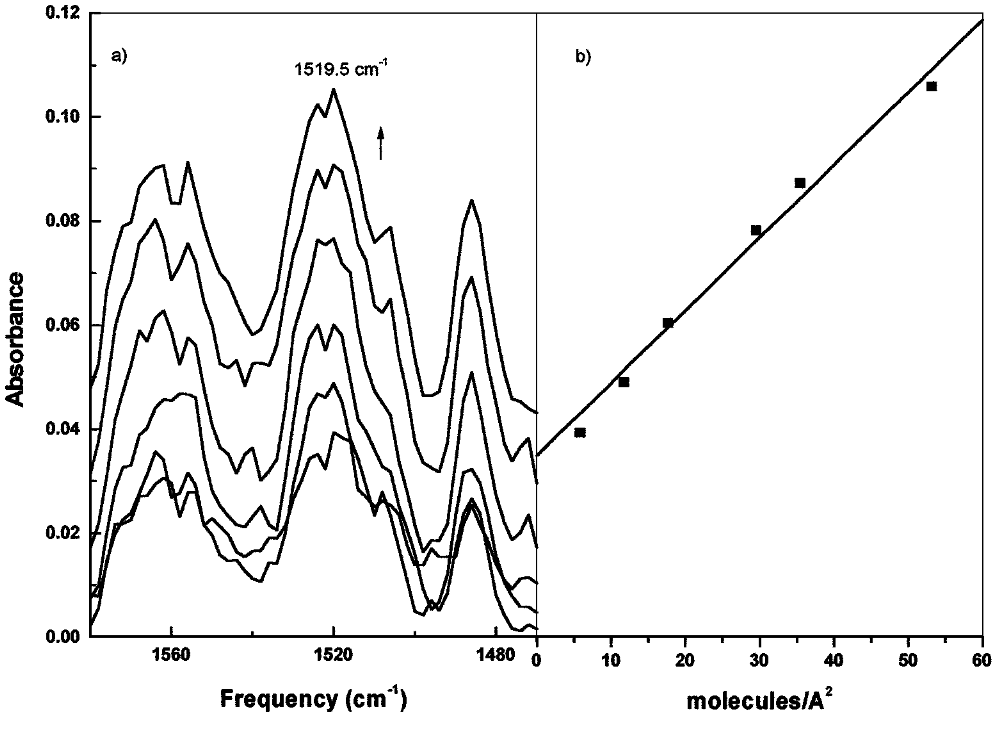

Figure 1 (a) FT-IR spectra of a film composed of 5.92, 11.84, 17.76, 29.60, 35.52 and 53.28 molecules/$Å^2$ of $Ni(PhCOCHCOPr)_2$ on a Si(100) surface. (b) Plot of the absorbance at 1519.5 cm^{-1} band of $Ni(PhCOCHCOPr)_2$ versus coverage.

film was first obtained. The chip was then placed on a brass sample holder in an optical bench equipped with an illumination system as described above. The 200 W Hg-Xe lamp was placed 40 cm from the film and a small cooling fan was used to keep the temperature of the sample below 30°C during irradiation. After the IR spectrum showed no evidence of the starting material, the chip was rinsed several times with dry acetone to remove any organic products remaining on the surface, prior to analysis.

2.4. Optical lithography

A thin film (∼400 nm) of Ni[PhCOCHCOPr]$_2$ was prepared on a silicon chip by spin coating from a CHCl$_3$ solution and irradiated for 72 hours through a quartz lithography mask. The sample was examined by optical microscopy and features were readily observed. Development consisted in rinsing the film with hexane which resulted in the loss of unexposed film from the surface. The resulting pattern was clearly visible by optical microscopy (1000× magnification).

3. Results and discussion

In this work, several different complexes of the general formula Ni(R^{1}COCHCOR^2)$_2$ (**I**: R^1 = phenyl, R^2 = *n*-propyl; **II**: R^1 = phenyl, R^2 = nonyl; **III**: R^1 = phenyl, R^2 = isobutyl; **IV**: R^1 = R^2 = isobutyl; **V**: R^1 = isobutyl, R^2 = *n*-propyl; **VI**: R^1 = methyl, R^2 = isobutyl, **VII**: R^1 = nonyl, R^2 = isobutyl) were investigated in order to determine if they formed good amorphous films upon spin coating. Although it was found that most of the above complexes form good quality films, the best results were observed with the complex **I** where R^1 = phenyl (Ph), R^2 = *n*-propyl (Pr). This compound can be spin-coated from chloroform onto a suitable substrate such as borosilicate glass or a Si(100) chip, forming amorphous films showing no sign of crystallization on examination under an optical microscope up to 1000× magnification. For comparison, the acetylacetonate derivative forms a powder upon spin coating. Furthermore, complex **I** showed the highest photosensitivity as a film, of all the β-diketonate derivatives. For further study we hence concentrated on this Ni complex.

Thin films of Ni(PhCOCHCOPr)$_2$ were prepared by spin-coating chloroform solutions of the complex on Si(100) chips. The FT-IR of one such sample is shown in Fig. 2. The spectra were similar to those found in the calibration curve and also comparable to those obtained for crystalline samples.

Irradiation of a thin film (∼400 nm) of Ni(PhCOCHCOPr)$_2$ under air atmosphere, led to the disappearance of the absorptions associated with the ligand, as shown by the FT-IR monitoring of the reaction (Fig. 3). At the end of the photolysis there are no detectable absorptions in the infrared spectrum. These results suggest that the diketonate groups on the precursor are photodissociated on the surface forming volatile products which are readily desorbed from the surface. The resultant film was analyzed by Auger spectroscopy. The only peaks observed in the spectrum

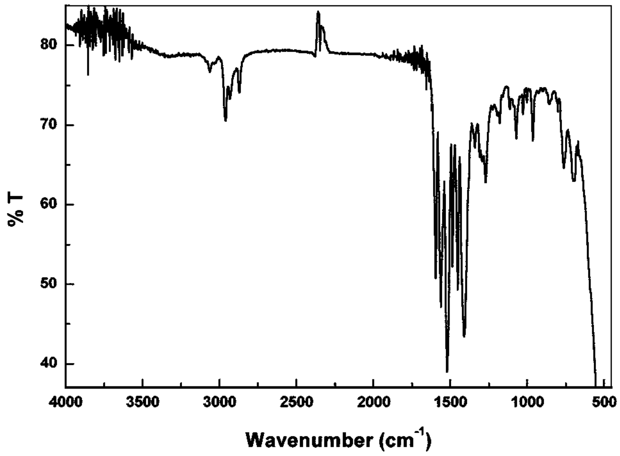

Figure 2 FT-IR of a Ni(PhCOCHCOPr)$_2$ thin film deposited by spin-coating of a CHCl$_3$ solution (on NaCl).

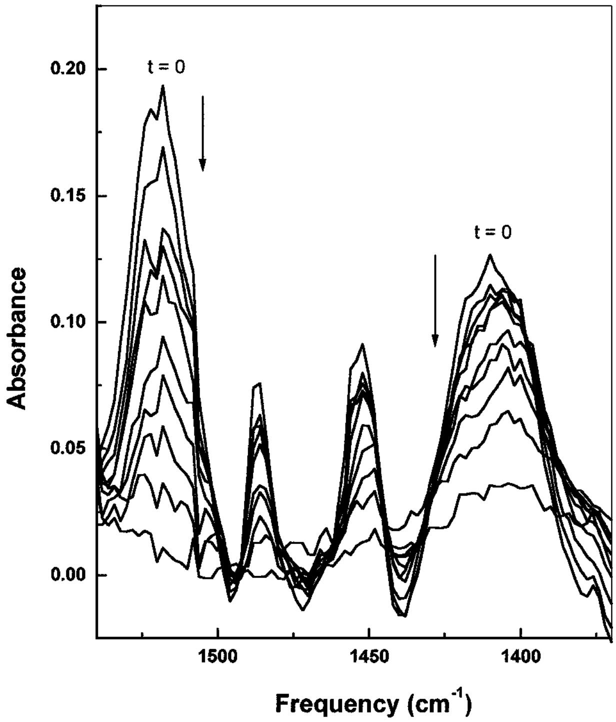

Figure 3 FT-IR spectral changes associated with the photolysis for 0, 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 min of a 400 nm film of Ni(PhCOCHCOPr)$_2$ deposited on Si(100).

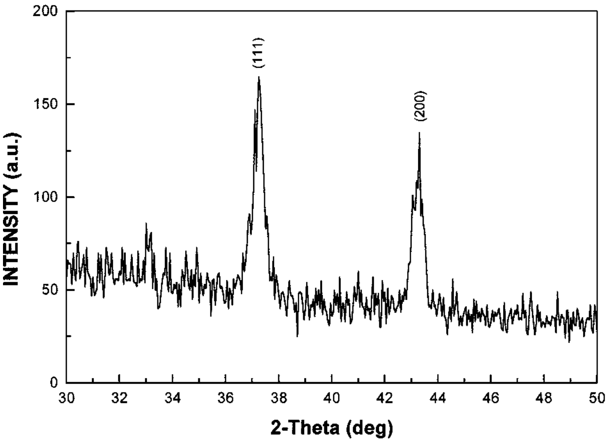

Figure 4 X-ray diffraction pattern of a film produced by the irradiation for 3.5 h of a thin film (400 nm) of Ni(PhCOCHCOPr)$_2$ on a Si(100) substrate after annealing at 650°C for 2 h.

were indicative of carbon (35.9%), nickel (48.2%) and oxygen (15.9%). Both the relative amounts of nickel and oxygen and the position of the nickel lines are indicative of NiO formation. The carbon content of the film is presumably a result of contamination rather than inefficient photochemistry. Sputtering of the surface with Ar^+ for 30 s results in a decrease of the carbon signal to 12.8% and a significant increase in the metal to oxygen ratio (84.3% and 2.9% respectively). This may be an effect of preferential sputtering of the oxygen.

In order to confirm the formation of NiO, the resultant films were analyzed by XRD. For this, a film was annealed in an air atmosphere at 650°C for 30 min in a Lindberg furnace and allowed to return to room temperature slowly. This led to the XRD powder pattern shown in Fig. 4. Peaks associated with the [111], [200], and [220] planes of cubic polycrystalline NiO are clearly discernible at 2θ angles of 37.28, 43.3 and 62.92 degrees, respectively [18], although precise specimen orientation cannot be inferred from this data.

The physical properties of the films change upon UV irradiation. The thickness of a $Ni(PhCOCHCOPr)_2$ film, measured by optical interferometry, changes from 400 nm before irradiation, to 273 nm after prolonged photolysis under air atmosphere. After

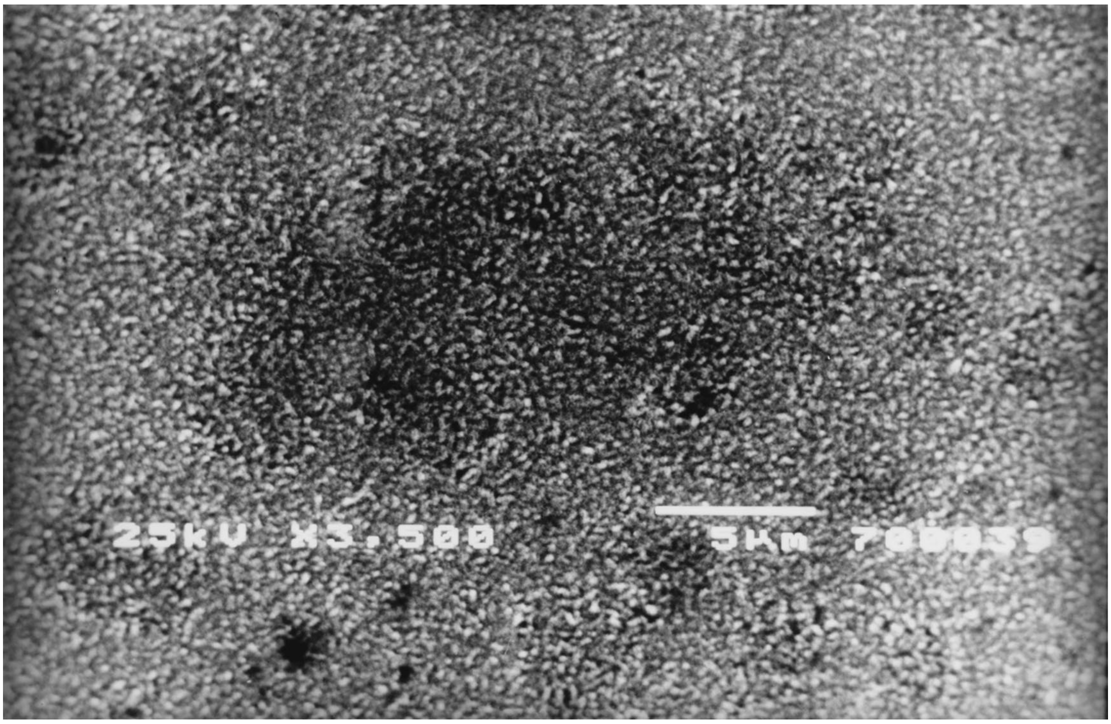

Figure 5 Scanning electron micrograph of a NiO film produced by the irradiation for 3.5 h of a thin film (400 nm) of $Ni(PhCOCHCOPr)_2$ on Si(100) substrate.

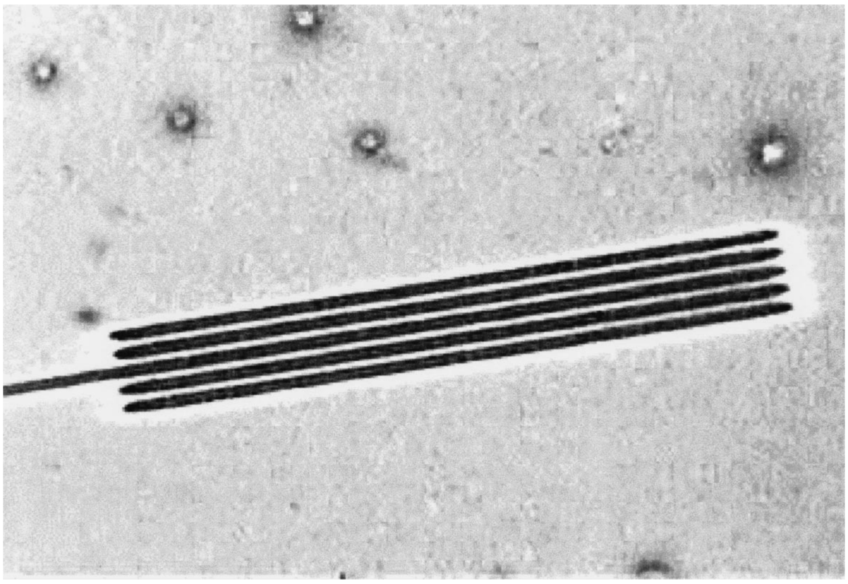

Figure 6 Optical micrograph (1000× magnification) of a pattern (100 × 2 μm) obtained by the photolitography of $Ni(PhCOCHCOPr)_2$ on a Si(100) surface.

annealing the film at 650°C for 30 min under air, the thickness drops to 164 nm. The surface morphology of the film was examined by SEM and showed excellent quality with no visible, islands or other imperfections (Fig. 5). Furthermore, all films showed strong adhesion to the silicon substrate as demonstrated by the "scotch tape test".

In order to demonstrate the utility of this process for the lithographic deposition of nickel oxide, photolitography experiments were conducted with amorphous films of $Ni(PhCOCHCOPr)_2$. A thin film (∼400 nm) of $Ni(PhCOCHCOPr)_2$ was prepared on a silicon chip by spin coating from a $CHCl_3$ solution and irradiated for 72 hours through a quartz lithography mask. When the resultant film was dipped in hexane, the unexposed region dissolved and the exposed region remained on the surface. The sample was examined by optical microscopy and features were readily observed. The resulting pattern was clearly visible by optical microscopy (1000× magnification) and is shown in Fig. 6. As can be seen from the image, the pattern of 2 μm lines obtained in a simple contact exposure is well resolved.

4. Conclusion

We have demonstrated that NiO could be formed as thin films in a photochemical process from simple precursors at temperatures of 20 K. This shows that optical radiation at the surface, in addition to fragmenting the precursor complex, promotes surface diffusion and the desorption of products from the surface. The deposition of patterned oxide films with excelent spatial resolution (<2 μm feature widths) demonstrate that direct photolithography of films composed of inorganic and organometallic materials provides an alternative route to the production of metal and metal oxide patterns.

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References

1. Z. XUPING and CHEN GUOPING, *Thin Solid Films* **298** (1997) 53.
2. R. P. MICHEL, A. CHAIKEN, C. T. WANG and L. E. JOHNSON, *Phys. Rev* **B58** (1998) 8566.
3. C.-L. LIN, J. M. SILVERSTEN and J. H. JUDY, *IEEE Trans. Magn.* **31**(6) (1995) 4091.
4. M. J. CAREY and A. E. BERKOWITZ, *Appl. Phys. Lett.* **60** (1992) 3060.
5. R. P. MICHEL, A. CHAIKEN, Y. K. KIM and L. E. JOHNSON, *IEEE Trans. Magn.* **32** (1996) 4651.
6. M. J. CAREY, F. E. SPADA, A. E. BERKOWITZ, W. CAO and G. THOMAS, *J. Mater. Res.* **6** (1991) 2680.
7. R. J. KENNEDY, *IEEE Trans. Magn.* **31** (1995) 3829.
8. R. H. HILL, A. A. AVEY, S. L. BLAIR, M. GAO and B. J. PALMER, *Mater. Chem. Phys.* **43** (1996) 233.
9. R. H. HILL, S. L. BLAIR, C. W. CHU, M. GAO, C. I. HORVATH and B. J. PALMER, *Trends in Photochemistry and Photobiology* **3** (1994) 331.
10. G. E. BUONO-CORE, K. IWAI, Y. L. CHOW, T. KOYANAGI, A. KAJI and H. HAYAMI, *Can. J. Chem.* **57** (1979) 8.
11. Y. L. CHOW, G. E. BUONO-CORE, C. W. B. LEE and J. C. SCAIANO, *J. Am. Chem. Soc.* **108** (1986) 7620.
12. Y. L. CHOW, X. E. CHENG and G. E. BUONO-CORE, *Organometallics* **6** (1987) 1126.
13. B. MARCINIAK and G. E. BUONO-CORE, *J. Photochem. Photobiol., A: Chem.* **52** (1990) 1.
14. Y. L. CHOW and G. E. BUONO-CORE, *J. Am. Chem. Soc.* **108** (1986)1234.
15. G. E. BUONO-CORE, M. TEJOS, J. LARA, F. AROS and ROSS H. HILL, *Material Research Bulletin* **34** (2000) 2333.
16. K. SAGA and T. HATTORI, *J. Electrochem. Soc.* **143** (1996) 3279.
17. J. T. ADAMS and C. R. HAUSER, *J. Am. Chem. Soc.* **66** (1944) 1220.
18. JCPDS-International Center for Diffraction Data, 4-835 (1993).

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