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VOLATILE LIQUID PRECURSORS FOR THE CHEMICAL VAPOR DEPOSITION (CVD) OF THIN FILMS CONTAINING TUNGSTEN

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ABSTRACT

A new CVD process is described for depositing conformal layers containing tungsten, tungsten nitride or tungsten oxide. A film of tungsten metal is deposited by vaporizing liquid tungsten(0) pentacarbonyl 1-methylbutylisonitrile and passing the vapors over a surface heated to 400 to 500 °C. This process can be used to form gate electrodes compatible with ultrathin dielectric layers. Tungsten nitride films are deposited by combining ammonia gas with this tungsten-containing vapor and using substrates at temperatures of 250 to 400 °C. Tungsten nitride can act as a barrier to diffusion of copper in microelectronic circuits. Tungsten oxide films are deposited by adding oxygen gas to the tungsten-containing vapor and using substrates at temperatures of 200 to 300 °C. These tungsten oxide films can be used as part of electrochromic windows, mirrors or displays. Physical properties of several related liquid tungsten compounds are described. These low-viscosity liquids are stable to air and water. These new compounds have a number of advantages over tungsten-containing CVD precursors used previously.

INTRODUCTION

Chemical vapor deposition (CVD) is a widely-used process for forming solid materials, such as coatings, from reactants in the vapor phase. CVD processes can have many advantages: good step coverage, dense films, high deposition rates, scalability to larger areas and low cost.

CVD of tungsten is usually carried out using tungsten hexafluoride, WF_6, as the tungsten source.[1] However, the byproduct hydrogen fluoride is highly corrosive and can damage substrates. Residual fluoride contamination in the films can cause problems such as loss of adhesion, or diffusion of fluorine into gate oxides causing threshold voltage shifts.[2]

Tungsten hexacarbonyl, $W(CO)_6$, is another source for CVD which can avoid the problems with fluorine.[3] Gate electrodes of tungsten have been formed by CVD from $W(CO)_6$ on ultra-thin dielectrics needed for high speed/high density MOS and CMOS devices.[4] $W(CO)_6$ has also been used to deposit tungsten nitride, W_2N, with properties suitable for barriers to diffusion of copper in microelectronics.[5] CVD using both $W(CO)_6$ vapor and oxygen gas, O_2, has produced electrochromic films of tungsten oxide.[6]

However, tungsten hexacarbonyl does have some practical disadvantages. Sublimation from solid $W(CO)_6$ is not a reproducible source of vapor, since the surface area of a solid changes as the solid evaporates. $W(CO)_6$ is highly toxic and has sufficient vapor pressure at room temperature that toxic concentrations of vapor can be emitted from any spilled material. Also, the carbon monoxide byproduct from its CVD reactions is highly toxic and lacks any warning odor.

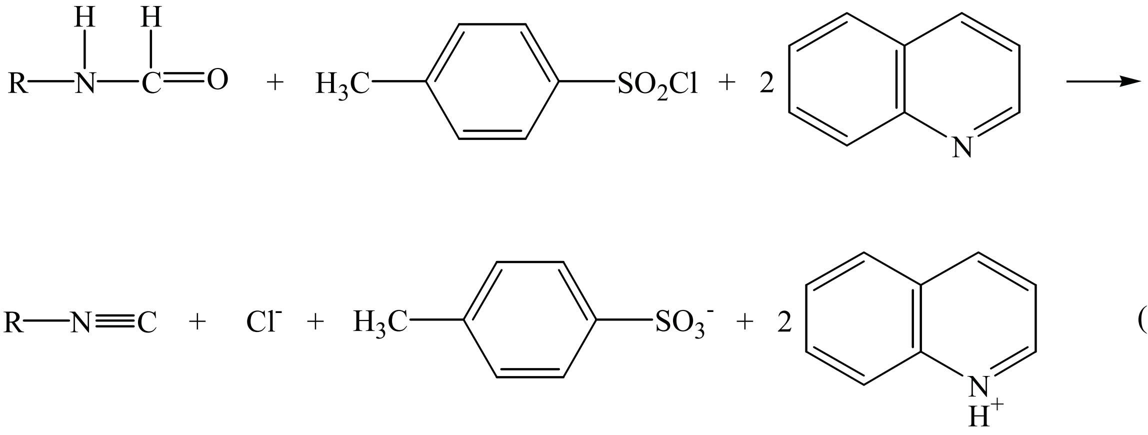
We have synthesized some new tungsten compounds that overcome the disadvantages of tungsten hexacarbonyl while maintaining similar capabilities for CVD of tungsten, tungsten nitride and tungsten oxide. The new compounds are formed by replacing one of the carbonyl ligands in tungsten hexacarbonyl by an alkyl isonitrile, RNC, where R is a hydrocarbon. With suitable choices of the alkyl group, these compounds are low-viscosity liquids at room temperature and can be vaporized and distilled at higher temperatures (typically 50 to 80 °C under vacuum). These liquids have negligible vapor pressure at room temperature, so they are safer to handle than tungsten hexacarbonyl. They are stable to air and water. Their CVD byproducts have a pungent odor even at low concentrations, so any failure of the exhaust scrubbing system can easily be identified before toxic concentrations of carbon monoxide are released.

SYNTHESIS OF VOLATILE LIQUID TUNGSTEN COMPOUNDS

The isonitrile ligands were synthesized in two steps from commercially available amines. First the amine is formylated by refluxing an equimolar mixture of the amine and ethyl formate:[7]

$$RNH_2 + HC(O)OC_2H_5 \longrightarrow RNHC(O)H + C_2H_5OH \qquad (1)$$

The resulting formamide is then dehydrated by reaction with p-toluenesulfonyl chloride and quinoline to form an alkyl isonitrile:[8]



(2)

The new tungsten compounds are readily synthesized by reacting the alkyl isonitrile with tungsten hexacarbonyl:

$$RNC + W(CO)_6 \longrightarrow RNCW(CO)_6 + CO \qquad (3)$$

The tungsten hexacarbonyl is dissolved in tetrahydrofuran, THF, and the liquid alkyl isonitrile is added dropwise with stirring at room temperature. A small amount of palladium oxide (0.1% by weight of the tungsten hexacarbonyl) is used to catalyze the reaction.[9] Carbon monoxide gas is evolved, and the reaction is complete within about 15 minutes. Slightly longer reaction times are needed for the isonitriles with larger alkyl groups. The solution is filtered to remove the palladium oxide, and the THF is removed under vacuum. The crude product is generally over 95% pure. Purification is then done by falling film molecular distillation[10] under high vacuum (typically 0.01 Torr).

This method is a considerable improvement on previous synthetic techniques for this type of compound. Previously, replacement of a carbonyl ligand with an isonitrile was done in refluxing toluene.[11] These conditions generally lead to considerable amounts of unwanted byproducts, such as bis- and tris-substituted isonitrile compounds, as well as cluster compounds containing two or more tungsten atoms.

During the reaction replacing carbon monoxide by isonitrile, the temperature of the solution stayed constant to within ± 0.1 °C. Thus the bond strengths of W-CO and W-CNR are practically identical. The reaction is driven to completion by the entropy generated by the release of the carbon monoxide gas.

Some physical properties of the new tungsten compounds are given in Table I.

Table I. Physical properties of some tungsten(0) pentacarbonyl alkylisonitrile compounds

Alkyl on Isonitrile	No. of carbons	M.P. of $LW(CO)_5$	Viscosity at 40 °C	Liquid Density	Mole-cular	B.P. of $LW(CO)_5$
	in alkyl group	°C	centiPoise	g/cc	Com-plexity	°C/Torr
isopropyl	3	58-61	solid		1.07	80/0.002
propyl	3	89-90	solid		1.07	
tert-butyl[11]	4	131-132	solid			
sec-butyl	4	43-44	solid		1.11	
isobutyl	4	47-49	solid		1.09	
n-butyl	4	34-36	6.85		1.09	115/1.2
2,2-dimethylpropyl	5	88-90	solid		0.93	
1,1-dimethylpropyl	5	74-76	solid		1.06	
1-ethylpropyl	5	33-34	7.68		1.04	
1,2-dimethylpropyl	5	31-33	10.13	2.02[12]	1.05	
isopentyl (isoamyl)	5	30-33	9.51		1.02	
2-methylbutyl	5	21-23	8.95	1.77	1.11	
1-methylbutyl	5	9	7.03	1.76	1.11	
n-pentyl (n-amyl)	5	-9 to -8	8.63	1.75	1.08	
1,3-dimethylbutyl	6	12-14	7.39	1.64	1.15	
n-hexyl	6	-10 to -9	9.91	1.64	1.00	
1-methylhexyl	7	2-4	9.49	1.62	0.95	
n-octyl	8	<20	10.35	1.62	0.88	

The last six compounds in Table I are liquids at room temperature, having melting points below 20 °C. All of the compounds with alkyl groups having 4 or fewer carbons are solids at room temperature. All of these compounds with alkyl groups having 6 or more carbons are liquids at room temperature. Of the 8 isomeric compounds with 5-carbon alkyl groups, 2 are liquid and the other 6 are solids with low melting points.

The molecular masses of these new compounds were determined by cryoscopy in p-xylene solution. Their "molecular complexities," defined as the ratio of the cryoscopic molecular mass to the theoretical monomeric value, generally fall between about 0.9 and 1.1. Thus the compounds are monomeric in solution.

The crystal structure (shown in Figure 1) verifies the monomeric nature of tungsten(0) pentacarbonyl 1,2-dimethylpropyl-isonitrile. The tungsten atoms have nearly perfect octahedral coordination by the six bonded carbon atoms. The tungsten-carbon bond to the isonitrile is 2.12 Angstroms long and the tungsten-carbon bonds to the carbonyls range from 2.03 to 2.05 Angstroms. These lengths are within the range of values previously observed for similar types of bonds.[13] The two enantiomers of the isonitrile ligand, whose chiral center is at carbon C2, appear to be disordered in the centrosymmetric crystal.

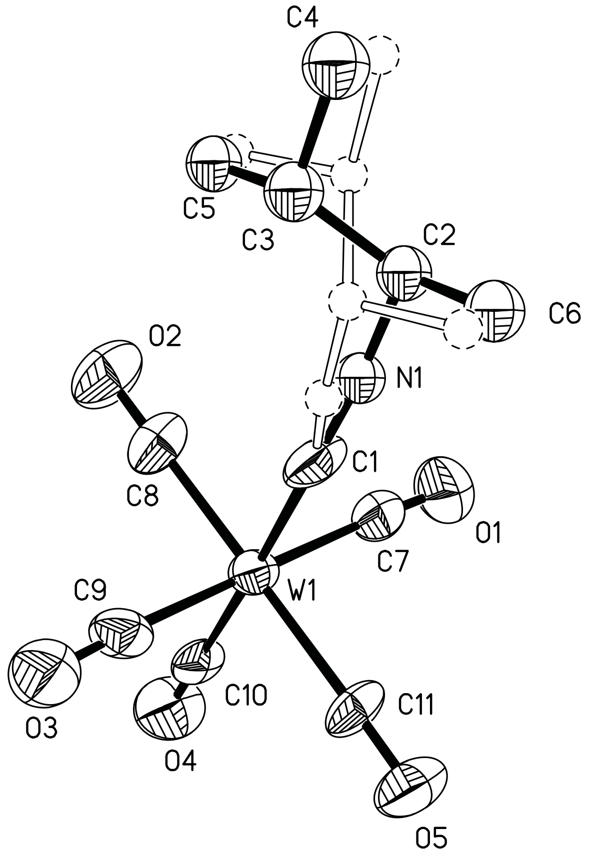


Figure 1. Molecular structure of solid tungsten(0) pentacarbonyl 1,2-dimethylpropylisonitrile.

These tungsten compounds are stable in contact with air and water at room temperature. Exposure to light, however, does cause gradual disproportionation into tungsten hexacarbonyl and tungsten tetracarbonyl bis-isonitrile and precipitation of dark tungsten cluster compounds.

CVD EXPERIMENTS

Tungsten(0) pentacarbonyl 1-methylbutylisonitrile was evaporated from a reservoir at 80 °C into a stainless steel vacuum chamber initially at 10^{-7} Torr. Tungsten metal films were deposited on silicon wafers, glass and glassy carbon substrates placed on a substrate holder heated to 500 °C. Rutherford Backscattering Spectroscopy (RBS) showed that the films were tungsten metal with about 1% molybdenum impurity derived from the starting tungsten hexacarbonyl. X-ray Photoelectron Spectroscopy detected some carbon and oxygen impurities. X-ray diffraction shows that the films are polycrystalline.

The precursors were also vaporized by flash evaporation. For this purpose, liquid tungsten(0) pentacarbonyl 1-methylbutylisonitrile was mixed with liquid mesitylene to lower its viscosity below about 3 centipoise. At this viscosity the solution could be nebulized easily into tiny droplets (less than about 20 microns in diameter) by a high-frequency (1.4 MHz) ultrasonic system.[14] The resulting fog was entrained by a flow of nitrogen and ammonia carrier gas at atmospheric pressure into a tube furnace with substrates placed on a heated aluminum substrate holder in the tube. The solid precursors could also be vaporized in this manner by dissolving them in mesitylene. Tungsten nitride films were deposited on substrates at 250 to 400 °C. RBS analysis showed that the films have a composition near to W_2N. X-ray diffraction showed that these films are amorphous.

Similar experiments with oxygen gas in place of the ammonia gave films of amorphous tungsten oxide. RBS analysis gave a composition $WO_{3.5}C_{0.025}$.

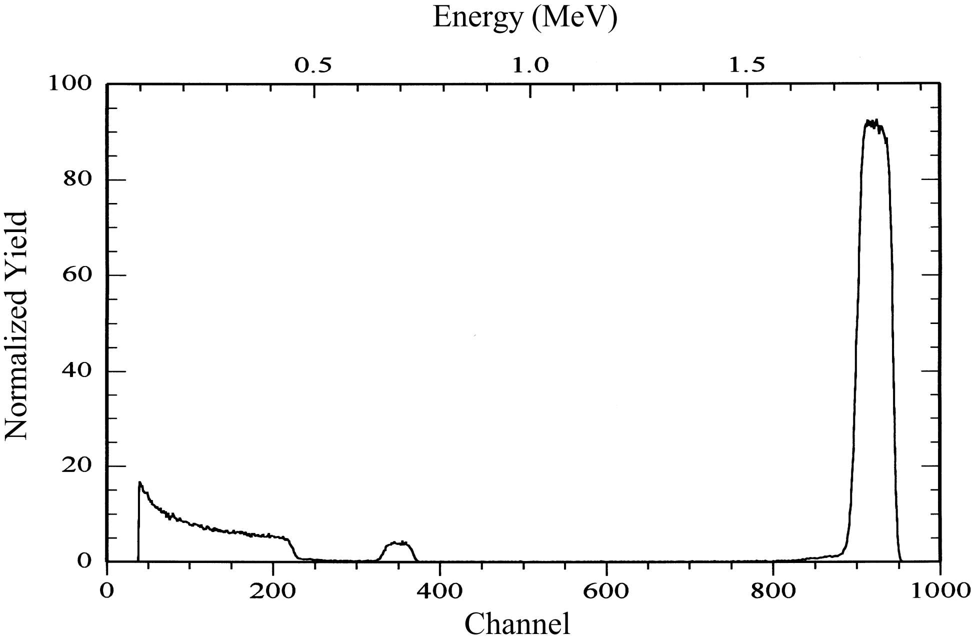


Figure 2. Rutherford Backscattering Spectrum of a CVD tungsten oxide film deposited on glassy carbon.

CONCLUSIONS

Six new liquid tungsten compounds have been synthesized and distilled under vacuum. These monomeric compounds have five carbonyl ligands and one alkyl isonitrile ligand octahedrally coordinated to the tungsten atom. The liquid with the lowest viscosity and highest volatility is tungsten(0) pentacarbonyl 1-methylbutylisonitrile. Eleven new solid compounds with similar structures were synthesized and sublimed under vacuum. Pure tungsten metal, tungsten nitride, or tungsten oxide can be deposited from their vapors.

ACKNOWLEDGMENTS

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