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# Organometallic chemical vapor deposition of tungsten metal, and suppression of carbon incorporation by codeposition of platinum

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Highly reflecting, amorphous, thin films of tungsten are obtained by the decomposition of bis-cyclopentadienyltungstendihydride, $(\eta\text{-}C_5H_5)_2WH_2$, in 1 atm of hydrogen at 350 °C. Auger depth profiling reveals that the carbon and oxygen content of the films are 25.1 and 3.1 at. %, respectively. Simultaneous chemical vapor deposition of tungsten with a small amount of platinum reduces the carbon and oxygen content of the film to 5.3 and 1.8 at. %. The platinum is deposited from cyclopentadienylplatinumtrimethyl, $(\eta\text{-}C_5H_5)Pt(CH_3)_3$, and its concentration in the film is 3.3%. Annealing at 750 °C in hydrogen converts the tungsten into a polycrystalline deposit which exhibits an x-ray diffraction pattern characteristic of the metal. The sheet resistivities of the amorphous films are $52 \pm 4$ $\mu\Omega$ cm.

There is great interest in depositing thin films of tungsten in microelectronics applications because of the high melting point and favorable resistivity of this metal.[1–3] The chemical vapor deposition of tungsten by the reduction of $WF_6$ in $H_2$ is a preferred method of filling vias in very large scale integrated circuits.[2–5] However, this process generates HF which is too corrosive for some applications, such as coating glass microspheres,[6] or for obtaining stable tungsten films on gallium arsenide.[7] As an alternative, several researchers have examined both the thermal and photoassisted decomposition of tungsten hexacarbonyl.[6,8] Films prepared from this precursor usually contain high percentages of carbon and oxygen. However, recently Singmaster and Houle[9] have shown that pure tungsten dots (10 $\mu$m in diameter) can be deposited from $W(CO)_6$ in high vacuum ($10^{-8}$ Torr) using a laser at 514 nm to heat the substrate to about 550 °C. This technique deposits tungsten at a very rapid rate, but requires a thin $WC_xO_y$ nucleation layer to initiate film growth.

We have explored the organometallic chemical vapor deposition of tungsten using hydrocarbon precursors, based on our success in depositing other transition metals in high purity.[7,10] There have been very few studies of organometallic sources for tungsten deposition.[11] Bis(benzene)tungsten has been attempted,[12] but this complex cannot be obtained in high yield.[13] Recently, Kirss and Chen[14] investigated the pyrolytic decomposition of tetraallyltungsten, $(\eta^3\text{-}C_3H_5)_4W$. They found that the material deposited from this compound contained large percentages of carbon and oxygen, and the sheet resistivity was characteristic of an insulator, i.e., $10^6$ $\mu\Omega$ cm. The precursor examined in the present study is bis-cyclopentadienyltungstendihydride ($Cp_2WH_2$) which is a relatively stable but air sensitive derivative. It can be sublimed at elevated temperatures to yield a sufficient vapor pressure for chemical vapor deposition.[15] In addition, we have examined the co-deposition of platinum from cyclopentadienylplatinumtrimethyl ($CpPtMe_3$) because platinum catalyzes the hydrogenolysis of the hydrocarbon ligands.[16]

The precursors, $Cp_2WH_2$ and $CpPtMe_3$, were prepared from $WCl_6$ and $K_2PtCl_6$ according to the literature methods.[15,17] The starting materials were purchased from Strem Chemical Co., Newburyport, MA ($CpPtMe_3$ may now be purchased directly from Strem). The depositions were carried out in a glass tube 2.5 cm in diameter. The $Cp_2WH_2$ was placed 5 cm upstream of the substrate, and was heated to 100–150 °C by a resistance heater located directly underneath. The vapor pressure of $Cp_2WH_2$ at these temperatures is ~0.01 Torr.[15] The section of the tube containing the substrates, about 3 cm long, was heated to $380 \pm 20$ °C by heating tape wrapped uniformly around the tube. For deposition of tungsten alone, hydrogen was fed to the reactor upstream of the precursor at 2 $cm^3$/min (at 23 °C). For deposition of tungsten with platinum, hydrogen was fed at 8 $cm^3$/min, and argon was fed at 16 $cm^3$/min. Before mixing with the hydrogen, the argon was passed through a glass frit containing $CpPtMe_3$ at 23 °C and became saturated with 0.045 Torr of the organometallic complex.[16] Both gases were purified by passing them through a deoxygenating catalyst (Oxysorb, Alltech Assoc., Inc.) and 13× molecular sieves. The films were deposited over a period ranging from 6 to 20 h.

The tungsten films were deposited on both glass and silicon (100) substrates. The glass was washed in ethylene chloride and methanol, rinsed in deionized water, and dried in air. The silicon wafers were washed in ethylene chloride and methanol, rinsed in deionized water, etched for 10 s in 10 vol % hydrofluoric acid, rinsed again in water, and dried in air.

The structure and composition of the W and W/Pt films were analyzed by x-ray diffraction, scanning electron microscopy, and Auger electron spectroscopy with depth profiling. The sheet resistivity was measured using a four-point probe. Film thickness was determined by the depth profiling measurement.

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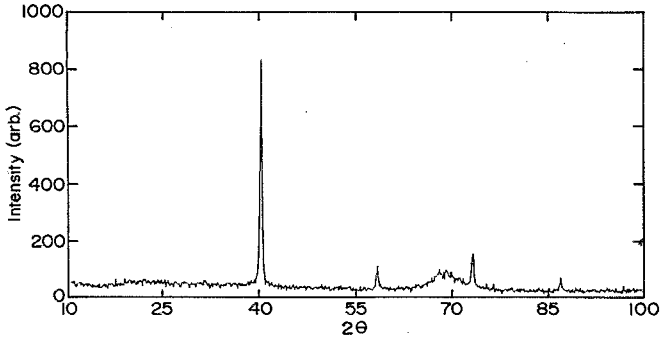

FIG. 1. X-ray diffraction pattern of tungsten film deposited on Si(100) after annealing in $H_2$ at 750 °C for 2.5 h.

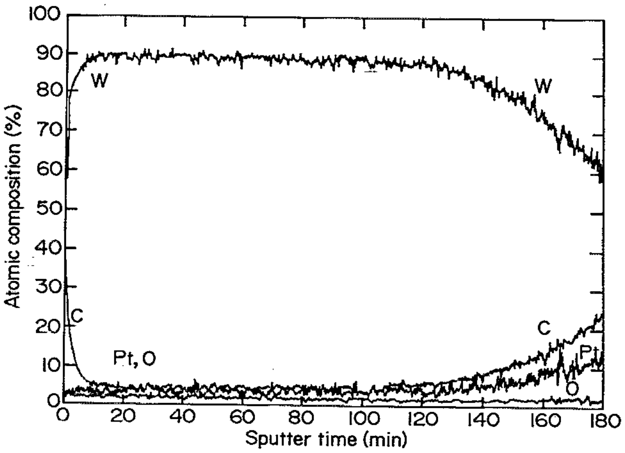

FIG. 2. Auger depth profile of tungsten/platinum film on Si(100).

We found that the tungsten decomposes more easily on the silicon (100) substrates than on the glass. After the 6 h deposition period, the glass surface is covered with a transparent brown layer of material. By contrast, the silicon is covered with a uniform, highly reflective, metal film. The W and W/Pt film thicknesses are 1450 and 3050 Å. Growth rates are estimated to be between 0.05 and 0.15 Å/s. The films show good adherence to the silicon: they could not be removed by cellophane tape.

After deposition the films are amorphous. Scanning electron micrographs reveal that the amorphous deposits are comprised of 100–500 Å clusters. Annealing in hydrogen at 750 °C, converts the clusters into microcrystallites. A diffraction pattern of the tungsten film is shown in Fig. 1. The sharp lines near $2\theta$ equal 40°, 58°, 73°, and 87° are due to W metal.[18] The broad peak at 69° is due to the silicon substrate. No peaks for tungsten silicide are present. The annealed W/Pt film also exhibits a diffraction pattern for W metal. Noticeably absent from this pattern are the lines for Pt metal. If platinum and tungsten are deposited one after another, the XRD pattern shows lines for Pt metal before annealing, and lines for both Pt and W metal after annealing. These results suggest that the platinum deposited simultaneously with the tungsten is dispersed throughout the metal layer even after annealing. The amount of platinum deposited with the tungsten is below the solubility limit of 5 at. %.[19] Further experiments are needed to determine the state of the platinum in these films.

The sheet resistivites of the unannealed W and W/Pt films average $52 \pm 4$ μΩ cm. This is much higher than the value for bulk tungsten metal of 5.6 μΩ cm.[20] The high resistivity of the films is probably due to the amorphous nature of the deposit and the poor contact between adjacent metal clusters.

An Auger depth profile of the W/Pt film is shown in Fig. 2. The bulk film is sputtered from 20 to 140 min, after which the Si signal appears due to sputtering of the silicon substrate. The atomic contribution from the silicon is not shown in the figure. The film contains 89.6% W, 3.3% Pt, 5.3% C, and 1.8% O. To our knowledge, this is the highest purity tungsten film ever produced from the thermal decomposition of an organotungsten precursor. The high purity appears to be a result of the catalytic hydrogenolysis of the hydrocarbon ligands by the co-deposited platinum.[16] Whitesides[21] has shown that hydrogenolysis of adsorbed alkyl groups on Pt is a very efficient process even at room

TABLE I. Atomic composition of films.

| Depth (Å) | Tungsten (%) | | Platinum (%) | Carbon (%) | | Oxygen (%) | |
|---|---|---|---|---|---|---|---|
| | W[a] | W/Pt | W/Pt | W | W/Pt | W | W/Pt |
| 0 | 44.9 | 54.6 | 1.9 | 46.2 | 39.0 | 5.9 | 4.2 |
| 190 | 66.6 | 88.6 | 3.4 | 24.6 | 5.7 | 3.5 | 2.0 |
| 380 | 67.3 | 89.8 | 3.6 | 24.5 | 4.8 | 3.4 | 1.6 |
| 570 | 67.4 | 90.9 | 2.3 | 24.9 | 4.8 | 3.4 | 1.8 |
| 760 | 66.7 | 90.9 | 2.6 | 25.5 | 5.1 | 3.2 | 1.5 |
| 950 | 65.7 | 88.9 | 4.2 | 26.2 | 4.8 | 2.2 | 1.8 |
| 1140 | 63.3 | 90.1 | 3.3 | 26.1 | 4.7 | 1.2 | 1.7 |
| 1330 | 39.5 | 88.9 | 4.0 | 11.3 | 5.1 | 3.3 | 1.8 |
| 1520 | 15.3 | 89.3 | 3.6 | 4.6 | 5.1 | 5.6 | 1.8 |
| 1900 | | 89.2 | 4.1 | | 4.7 | | 1.8 |
| 2280 | | 88.1 | 4.1 | | 5.9 | | 1.7 |
| 2660 | | 84.1 | 5.2 | | 8.9 | | 1.7 |
| 3040 | | 73.6 | 10.2 | | 13.8 | | 2.2 |
| 3420 | | 58.3 | 15.2 | | 24.2 | | 2.1 |

[a] Type of film.

temperature. The composition of the W and the W/Pt films are compared in Table I. When tungsten is deposited under the same conditions, but without platinum, the composition of the film is 71.8% W, 25.1% C, and 3.1% O.

This work demonstrates that small amounts of $CpPtMe_3$ can be fed along with other organometallic precursors to enhance the purity of transition metal films obtained by organometallic chemical vapor deposition. Experiments are underway to characterize the mechanism and kinetics of tungsten OMCVD from $Cp_2WH_2$, and to find out whether the purity of the films can be enhanced further.

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