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Low-temperature organometallic chemical vapor deposition of platinum

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Impurity-free, polycrystalline films of platinum have been grown by the decomposition of cyclopentadienyl platinum trimethyl, $CpPtMe_3$, in hydrogen and a noble gas over silicon or glass substrates heated to 180 °C. The films contain less than 1 at. % of oxygen and carbon, and no other detectable impurities, as measured by x-ray photoelectron and Auger spectroscopies after argon ion sputtering. Sheet resistivities are 50% greater than sputter-deposited platinum.

Thin coatings of platinum have many uses. A few of these are metal contacts for microelectronic devices, 1,2 catalysts for electroless metal plating,³ catalysts for pollution control,⁴ and protective coatings for specialized instruments.⁵ Platinum is an attractive metal because of its low resistivity, high thermal stability, corrosion resistance, and high catalytic activity. Of the many processes for generating platinum films, chemical vapor deposition offers several advantages: it is a low-temperature process; complex objects can be covered uniformly; and the film can be confined to selected areas by using focused UV light to decompose the Pt source molecule.6 One of the disadvantages of chemical vapor deposition is that the films are not of high purity. Prior attempts to deposit platinum by this method have used Pt(acetylacetonate)₂, Pt(CO)₂Cl₂, or Pt(PF₃)₄.⁷⁻⁹ These precursors produce films contaminated with heteroatoms derived from the ligands. Recently, there was a report of using $CpPtMe_3$ ($Cp = \eta^5 - C_5H_5$, $Me = CH_3$), although no description of the process or of the quality of the film produced was given.¹⁰ Here, we report the deposition of impurity-free, polycrystalline platinum metal by decomposition of CpPtMe, in an atmosphere of hydrogen. These studies were prompted by an earlier experience in this laboratory¹¹ and in others¹² of the facile decomposition of organometallic complexes in the presence of H_2 .

We prepared $CpPtMe_3$ from $PtMe_3I$ and NaCp by a modification of the published procedure¹³: toluene was used instead of benzene as the solvent, and the reaction was started at -77 °C. The yield was 52% vs 32% reported earlier.

The platinum was chemically decomposed onto the substrates in a cold wall glass reactor. The substrates were mounted on a resistively heated pedestal and held at 180 °C during deposition. The complex was vaporized at atmospheric pressure and 25 °C into a stream of flowing argon at 25 ml/min. The vapor pressure of $CpPtMe_3$ is 0.05 Torr at 25 °C.¹⁴ Hydrogen was introduced through a separate port at 25 ml/min. The hydrogen, Pt complex, and argon flowed together horizontally over the hot substrate and reacted to form the Pt film.

Either glass slides or silicon wafers with (100) orientation were used as substrates. The glass slides were cleaned with acetone prior to use. The silicon substrates were degreased in trichloroethylene, acetone, and isopropanol, dipped in concentrated hydrofluoric acid, rinsed in de-ionized water, and gently dried under argon. The substrates were held at reaction temperature in H_2 atmosphere for 30 min prior to film desposition.

The structure and composition of the Pt films were analyzed by x-ray diffraction, scanning electron microscopy, and x-ray photoelectron and Auger spectroscopies. The sheet resistivity was measured using a four-point probe. Film thickness was determined with a Deptak II profilometer.

For the source feed conditions described above, the deposition rate is roughly 0.1 Å/s. Depositions were carried out for 1/2–3 h and resulted in films several thousand angstroms thick. Shown in Fig. 1 is an x-ray diffraction pattern of a Pt film deposited on silicon. Sharp lines are observed which are consistent with the powder diffraction pattern for polycrystalline platinum metal.¹⁵ A scanning electron micrograph of this film is shown in Fig. 2. The crystallites are cube shaped and approximately 1000 Å across. All of the films are visually bright and reflective.

X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy (AES) reveal that the surface of the Pt film is highly contaminated with oxygen and carbon after several days exposure to ambient conditions. Upon argon ion sputtering into the film, the oxygen content decreases below detection limits, while the carbon content decreases to less than 1 at. %. No other impurities are detected in the platinum. An XPS spectrum of a lightly sputtered sample is shown in



FIG. 1. Powder diffraction pattern of a 2000-Å-thick platinum film deposited on Si(100) at atmospheric pressure and 180 °C.

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FIG. 2. Scanning electron micrograph of a 2000-Å-thick platinum film deposited on Si(100) at atmospheric pressure and 180 $^{\circ}$ C (magnification is 50 000x).

Fig. 3. At the interface between platinum and silicon the only impurity detected is oxygen. The oxygen is due to the native SiO₂ remaining on the Si wafer. Our results may be contrasted with chemical vapor deposition of Pt using the $Pt(PF_3)_4$ source⁹: these films contain 10–20 at. % phosphorus near the surface and 1 at. % phosphorus at the interface.

The hydrogen is essential for reducing carbon contamination. In the absence of H_2 , nonreflecting deposits are produced, and AES analysis detects much higher concentrations of carbon inside the film.

Film resistivities are found to be in the range of 26–28 $\mu\Omega$ cm for several thousand-angstrom-thick films. These values are higher than the 18 $\mu\Omega$ cm resistivity obtained by Rand for Pt(PF₃)₄.⁷ Our higher resistance may be attributed to the poor contact between crystallites as evidenced by the electron micrograph shown in Fig. 1. Sputtered or evaporated metal films have resistivities between 15 and 20 $\mu\Omega$ cm.⁷

Further experiments are being conducted to determine



FIG. 3. X-ray photoelectron spectrum of the platinum film after sputtering away the top layer of contaminants (Al anode, sputter depth ~ 100 Å).

the effects of deposition conditions on film composition, morphology, contact resistance, and adherence.

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