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## Laser-driven chemical vapor deposition of platinum at atmospheric pressure and room temperature from CpPt(CH<sub>3</sub>)<sub>3</sub>

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Photolysis of  $CpPt(Me)_3(Cp = \eta^5 \cdot C_5H_5, Me = CH_3)$  at room temperature and atmospheric pressure produces thin films and patterned structures of platinum metal on solid substrates. The platinum films are characterized by Auger electron spectroscopy, x-ray diffraction, and scanning electron microscopy. Substrates can also be prepatterned by laser irradiation and then developed into a shiny platinum deposit at a later time.

Thin films and patterned microstructures of platinum are of interest for applications to microelectronics because the metal has low resistivity and high stability. Thermal deposition of platinum from the vapor phase has been success-Pt(acetylacetonate)<sub>2</sub>,  $Pt(PF_3)_4$ , ful using and Pt(CO)<sub>2</sub>Cl<sub>2</sub>.<sup>1-3</sup> However, relatively high temperatures were required (200-600 °C) and the deposits were contaminated by heteroatoms from the ligands. The air-stable organometallic platinum compound  $CpPt(Me)_3$  has a high vapor pressure (0.052 Torr at 20 °C)<sup>4</sup> and has recently been reported to yield high quality thermally deposited films at 250 °C and 10<sup>-4</sup> Torr.<sup>5</sup> Photolysis offers a promising method of producing thin films and especially patterned microstructures at temperatures much lower than those possible in pyrolysis.<sup>6</sup> Laser-induced chemical processing for microelectronics takes advantage of both the specificity of the laser-induced chemistry and the ability of laser light to confine the reactions to the irradiated regions.7 We report here the room temperature atmospheric pressure photolysis of  $CpPt(Me)_3$  $(Cp = \eta^5 - C_5 H_5, Me = CH_3)$  to produce thin films and patterned structures of platinum metal on solid substrates.

 $CpPt(Me)_3$  was prepared by the published procedure.<sup>8</sup> Laser photolysis was carried out with the 308 nm line of a XeCl excimer laser and with the 351 and 364 nm lines of an argon ion laser. The irradiation was carried out in a glass flow cell with a quartz window. Crystals of the Pt compound in a small bulb were warmed to  $\sim$  56 °C (approximate vapor pressure 0.33 Torr)<sup>9</sup> and transported to the cell by flowing Ar at a flow rate of 2 cc/s. Hydrogen gas was introduced to the cell in proximity to the laser beam. Gas flow was parallel to the surface of the substrate. All photolyses were carried out at atmospheric pressure with the laser beam perpendicular to the surface. The substrates used in these studies included glass, fused silica, sapphire (1102), Si (001), and GaAs (001). The single-crystal silicon wafers were degreased by immersion in trichloroethylene and then rinsed in methanol and de-ionized water. The wafer was then twice etched for 2 min in a 1:4 solution of 30% hydrogen peroxide and concentrated sulfuric acid, rinsed in de-ionized water and blown dry in nitrogen.

The absorption spectrum of  $CpPt(Me)_3$  in the gas phase is almost identical to that of the compound in cyclohexane solution.<sup>10</sup> The lowest energy band has  $\lambda_{max}$  at 288 nm with an extinction coefficient of  $2.2 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>. The extinction coefficients at the wavelengths of irradiation are  $1.6 \times 10^3$ ,  $2.2 \times 10^2$ , and  $5.8 \times 10^1$  M<sup>-1</sup> cm<sup>-1</sup> at 308, 351, and 364 nm, respectively.

Photodeposition studies at 308 nm were carried out by irradiating a circle 1 mm in radius with 2.6 mJ/pulse at 10 Hz. Shiny deposits were formed in about 10 min. The resulting films were about  $10^3$  Å thick. Under these conditions, the rate of deposition is on the order of 100 Å per minute. The films were shiny when hydrogen was present but black in the absence of hydrogen. Photodeposition under cw conditions was carried out with fluences of 4-5 mW/mm<sup>2</sup> at 351 and 364 nm. Under the same conditions of flow rates and temperatures as used above, visible films were formed in about 10 min. The shiny or black deposits were similar to those produced with the pulsed laser. Photolyses were attempted by using the visible lines (488 and 514 nm) from the argon ion laser. No deposits were formed with laser fluences as high as 0.5 W/mm<sup>2</sup>. These results suggest that the deposition process depends critically on the absorption of light and involves a photochemical process rather than solely resulting from local heating of the substrate. However, the overall mechanism may also involve surface adsorption of a photointermediate followed by thermal reactions on the surface (vide infra).

The platinum films were characterized by Auger electron spectroscopy (AES). The films were wiped with acetone to remove contaminants introduced subsequent to the deposition, allowed to dry, and loaded into a sample treatment chamber. The films were then transferred to the analy-



FIG. 1. Auger electron spectra of (A) a shiny deposit and (B) a black film collected with a hemispherical analyzer. The Pt peaks are at 217, 237, and 253 eV. The C peak is at 274 eV.

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FIG. 2. Powder diffraction pattern of the shiny film. Peaks at  $39.7^{\circ}$ ,  $46.2^{\circ}$ , and  $67.4^{\circ}$  are from Pt crystallites. The broad peak between  $20^{\circ}$  and  $30^{\circ}$  is attributed to amorphous Pt.

sis chamber of a KRATOS XSAM 800 equipped with a scanning Auger microprobe that has a minimum electron beam diameter of ~ 3000 Å. AES data were collected with a primary beam energy of 5 keV and a constant peak to peak modulation voltage of 8 V. Figure 1 presents a comparison of the AES signal from a shiny surface and a black film after Ar ion removal of the surface contaminants to reveal the composition of the films. No contaminants other than carbon (C) were detected in either type of film. The C content of the shiny deposits was difficult to determine because of a sloping background in the C spectral region caused by energetically nearby Pt Auger transitions. An upper limit of 3.5 at. % C in the film is determined by assuming that the intensity difference between 262 and 274 eV is caused entirely by a C Auger signal. The actual C content is undoubtedly much lower because the Auger spectra of the shiny deposits are nearly identical to those collected from the surfaces of Pt films that had no C detectable by x-ray photoelectron spectroscopy (XPS). The photolytically deposited films were too small in area for XPS analysis in the KRATOS XSAM. The black film produced by photolysis in the absence of hydrogen contained approximately 20% C and degassed significantly during electron beam bombardment indicating that there may have been partially reacted starting material trapped in the black film.

X-ray diffraction characterization of the shiny deposits (Fig. 2) revealed a superposition of a broad band at  $2\theta = 26^{\circ}$  and platinum peaks at  $2\theta = 39.7$ , 46.2, and 67.4.<sup>11</sup> These results suggest that the shiny deposit consists of a mixture of amorphous and microcrystalline platinum. Inspection of the shiny deposits with a scanning electron microscope (SEM) revealed a smooth surface with traces of grain boundaries [Fig. 3(a)]. In contrast, the black deposits showed a well-developed structure with prominent cauliflower-like features [Fig. 3(b)]. These samples outgassed in the electron beam. The adhesion of the films to the substrates was qualitatively tested with adhesive tape. The tape did not pull off the shiny deposits whereas the black films could be removed from the surface.

The shiny deposits could be easily patterned by using a

mask and imaging the masked 308 nm laser beam with a 40 nm lens. In these experiments, the image was focused below the surface of the substrate in order to minimize the focus (and hence deposition) on the cell windows. At high laser fluences the patterns could be subsequently ablated. Typical patterns for study consisted of lines and crosses. No attempt to minimize the size of the patterned deposit was made. Typical widths of the platinum lines which were obtained were on the order of 100  $\mu$ m. No platinum deposition occurred in the unirradiated regions. Auger characterization of the patterned deposit showed that the composition is also > 96.5 at. % platinum.

During the course of the patterning studies, it was observed that the substrate could be prepatterned and "developed" at a later time. The imaged laser beam was used to irradiate the substrate for several minutes in the absence of hydrogen. No visible deposition occurred. (After longer irradiation times, the imaged black deposit was formed.)





FIG. 3. SEM photographs of the photodeposited films. (a) the shiny platinum surface deposited by photolysis in the presence of hydrogen. (b) the black deposit formed by photolysis in the absence of hydrogen.

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When the laser was turned off and hdyrogen and  $CpPt(Me)_3$ in argon allowed to flow through the cell, the shiny platinum deposit in the image of the mask was formed. In addition, in the presence of H<sub>2</sub>, thin visibly transparent films could also be further developed in the dark to produce reflecting films. This study shows that it is possible to specifically prepare well-defined regions of the substrate and develop them with platinum at a later time. The mechanistic implications of this discovery are under investigation.

The gas phase photochemical fragmentation pathway probably involves both associative and dissociative steps.<sup>12</sup> In solution, the primary photochemical step is Pt—CH<sub>3</sub> bond homolysis.<sup>10</sup> In a mass spectrometer, the elimination of methyl radicals is the dominant reaction path initiating the overall fragmentation.<sup>4</sup> In the presence of hydrogen, oxidative addition of H<sub>2</sub> and formation of  $\eta^3$ -C<sub>5</sub>H<sub>5</sub> followed by reductive elimination of methane may play an important role in the gas phase photochemistry. The two different types of films obtained in the presence and in the absence of hydrogen and the ability to prepattern the substrate in the absence of hydrogen and subsequently develop the shiny platinum deposit in the presence of hydrogen and additional  $CpPt(Me)_3$  support the hypothesis of both photochemical and thermal pathways. The formation of patterned platinum lines and films by the photolysis of  $CpPt(Me)_3$  at room temperature and atmospheric pressure in the presence of hydrogen is an interesting addition to the field of laser writing.

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