

Selective Chemical Vapor Deposition of Platinum and Palladium Directed by Monolayers Patterned Using Microcontact Printing

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High-purity platinum and palladium thin films can be deposited selectively by combining microcontact printing (μ CP) and metal–organic chemical vapor deposition (MOCVD). Printed patterns of octadecyltrichlorosilane thin films are used to direct the selective deposition of the metallic thin films from bis-(hexafluoroacetylacetonato)platinum(II), Pt(hfac)₂, and bis(hexafluoroacetylacetonato)palladium(II), Pd(hfac)₂, in the presence of hydrogen. This process has been used successfully to fabricate Pt and Pd patterns on substrates such as titanium nitride, indium tin oxide, silicon dioxide, and sapphire. Features with sizes as small as 1.5 μ m have been deposited by this combined μ CP–MOCVD method. The Pt and Pd films were found to be free of detectable impurities, as measured by X-ray photoelectron and Auger electron spectroscopies. Grain sizes in the deposits can also be varied. We found, for example, that the Pt film growth process yields heavily faceted deposits whose habits depend strongly on the temperature of the substrate during processing. Addition of water vapor to the reactor feed during platinum chemical vapor deposition increased the number of nucleation sites, thus reducing the grain size, but did not otherwise affect the deposition rate to a significant degree. We describe in this report how this photolithography-free process might simplify the patterning of metal and other thin films of interest in integrated circuit fabrication.

Introduction

Platinum and palladium are widely used in a variety of applications in microelectronics¹ and catalysis.² In particular, platinum is extensively used as the electrode material in nonvolatile ferroelectric random access memory devices and high dielectric capacitors due to its chemical inertness and low electrical resistivity at elevated temperatures.³ The patterning of fine Pt features using conventional plasma or wet etch processes, however, cannot be accomplished with the tolerances necessary for fine-scale integration, and this limitation greatly constrains the use of Pt films in integrated ferroelectric devices.^{3–5} The development of a method to effect the selective chemical vapor deposition (CVD) of Pt might greatly simplify the patterning process and in addition would make possible the conformal deposition of Pt on textured surfaces (i.e., those bearing high-aspect-ratio topological features).

The chemical vapor deposition of platinum^{6–20} and palladium^{20–22} films has been widely reported. Most of these studies describe the deposition of uniform films on flat surfaces, and most occur nonselectively. The hexafluoroacetylacetonate (hfac) complexes are among the few that

have been shown to effect surface-selective depositions. These precursors deposit Pt or Pd selectively on copper, for example, by means of a redox transmetalation reaction in which copper atoms are replaced by Pt or Pd.^{20–22,26} It would be of interest, however, to develop a more generally applicable method for selective metalization that did not depend on the presence of copper.

We recently reported a method for the selective deposition of copper by thermal CVD which yields high-quality fine line features; the microstructure formation in these depositions are in turn directed by self-assembled monolayers (SAMs) of octadecyltrichlorosilane (OTS) which are themselves patterned by contact printing.^{28,29} The patterned deposition thus is achieved without the use of photolithography or reactive ion etching. This method provides a wide process window for the selective CVD of copper on a variety of substrates and exploits the advantages inherent in CVD by carrying out the reaction

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under conditions of kinetic control: regions of the substrate modified with OTS SAMs are essentially inert while the unmodified regions are reactive. In this paper, we describe a two-step process for the selective chemical vapor deposition of high-quality platinum and palladium thin films directed by a closely related process.

Experimental Section

Monolayer patterning via the microcontact printing of OTS was performed using previously reported procedures.^{28–31} The substrates [titanium nitride (TiN), indium tin oxide (ITO), silicon dioxide on silicon (SiO₂/Si), sapphire, and borosilicate glass] were washed with high-purity deionized (DI) water, acetone, and 2-propanol and then dried in a stream of filtered argon. The dried substrates were placed in a UV/ozone generator for 5–10 min to remove trace organic contaminants (and in some instances to generate an oxide overlayer on the surface)^{32,33} immediately before printing with the OTS solution. A solution of OTS in dry hexane (10 mM) was used as the “ink”. The OTS solution was applied to the polydimethylsiloxane stamp using a photoresist spinner (3000 rpm for 30 s) and the inked stamp was dried in a stream of Ar for ~30 s. The stamp was brought into contact with the substrate (by hand) and held in place for ~30 s. This procedure routinely yields OTS thin films that are ~25–30 Å thick. Detailed structural characterizations of these films are reported separately.³⁴ The OTS-patterned substrates were cleaned with DI water and 2-propanol and finally dried with a stream of argon before being loaded into the CVD reactor.

The depositions of platinum and palladium films were carried out in a home-built, cold-wall stainless-steel reactor²⁸ with bis-(hexafluoroacetylacetonato)platinum(II), Pt(hfac)₂, and bis-(hexafluoroacetylacetonato)palladium(II), Pd(hfac)₂, as precursors.^{35,36} Both Pt(hfac)₂ and Pd(hfac)₂ are solids at room temperature with vapor pressures of 0.15 Torr at 70 °C¹² and 0.1 Torr at 60 °C,³⁷ respectively. The precursors were kept in a constant temperature water bath (40–70 °C). The substrates were heated during the deposition. The surface area of each substrate was ~4 cm², and the temperature of the susceptor was regulated to within ±2 °C.

After the samples were loaded, the CVD chamber was first evacuated to 1 × 10⁻⁶ Torr and two feed gas streams were then introduced via separate effusion-source lines. One gas stream consisted of the precursor in an argon carrier (5–100 sccm), while the other consisted of hydrogen (20 sccm). For our reactor, the optimum argon flow rates for reagent delivery were 50 and 20 sccm for Pt and Pd CVD, respectively. The chamber was dynamically pumped to maintain a specified pressure, as noted below. In some experiments, water vapor was added to the hydrogen stream via a reservoir attached to the hydrogen delivery line. The water reservoir was held at 40 °C, and a needle valve was used to control the water flow. The chamber pressure (0.1–5 Torr) during the depositions was regulated with a throttle valve. After the depositions were complete, the samples were allowed to cool to room temperature under vacuum.

Surface profilometry and scanning electron microscopy (SEM) were used to determine the film thicknesses. Reasonably good agreement was found between the two measurement methods. The surface morphology of the platinum and palladium thin films was investigated by SEM. X-ray photoelectron spectroscopy (XPS) and depth profiling Auger electron spectroscopy (AES)

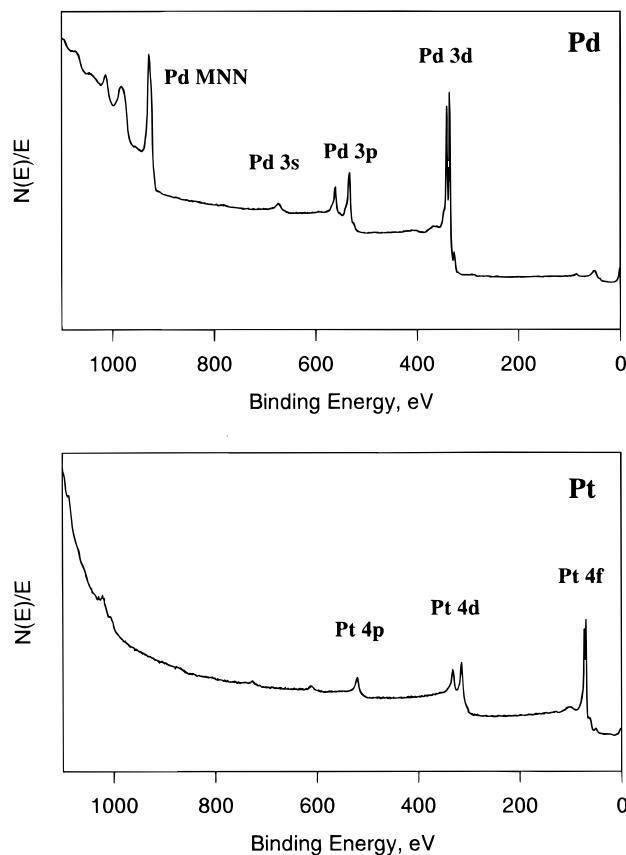


Figure 1. XPS survey spectra of CVD platinum and palladium thin films. The platinum film was deposited at 300 °C while the palladium film was deposited at 250 °C. These spectra were taken after 5 min of Ar sputtering to remove surface contaminants.

were used to determine the film composition. The film resistivity was measured with a four-point probe, and X-ray diffraction was used to determine the crystallographic orientation.

Results and Discussion

The platinum and palladium thin films selectively deposited in the presence of H₂ from Pt(hfac)₂ and Pd(hfac)₂ onto substrates patterned with SAMs of OTS are of exceptionally high purity. The selectivity of the thin film depositions and the noted purity of the metal thin films were maintained in the presence of hydrogen across a broad range of process temperatures, spanning ~175–275 °C for Pd and ~200–350 °C for Pt. The representative XPS survey spectra shown in Figure 1 demonstrate that the platinum and palladium films are relatively free of impurities: the carbon, fluorine, and oxygen contents (after removal of a contaminating surface film by sputtering) are largely below the detection limits (Figure 1). Depth-profiling AES spectra (not shown) further showed that significant levels of impurities were not trapped within the bulk of the deposit.

Of particular interest in this work is the spatial control which contact printing can exert over the deposition of Pt and Pd. This degree of control is, in fact, substantial. Figure 2 shows an optical micrograph of a representative palladium deposit (3000 Å) on a ITO substrate that had been patterned with OTS. The individual patterned features shown in Figure 2 range from 200 μm (large circles and squares) down to less than 5 μm. The printed patterns of OTS direct the deposition of the metal to regions not modified by the monolayer. The patterning thus is strictly a result of kinetic control, presumably because the reactive sticking probability of the precursor is lowered by the presence of the monolayer. The test pattern shown here also

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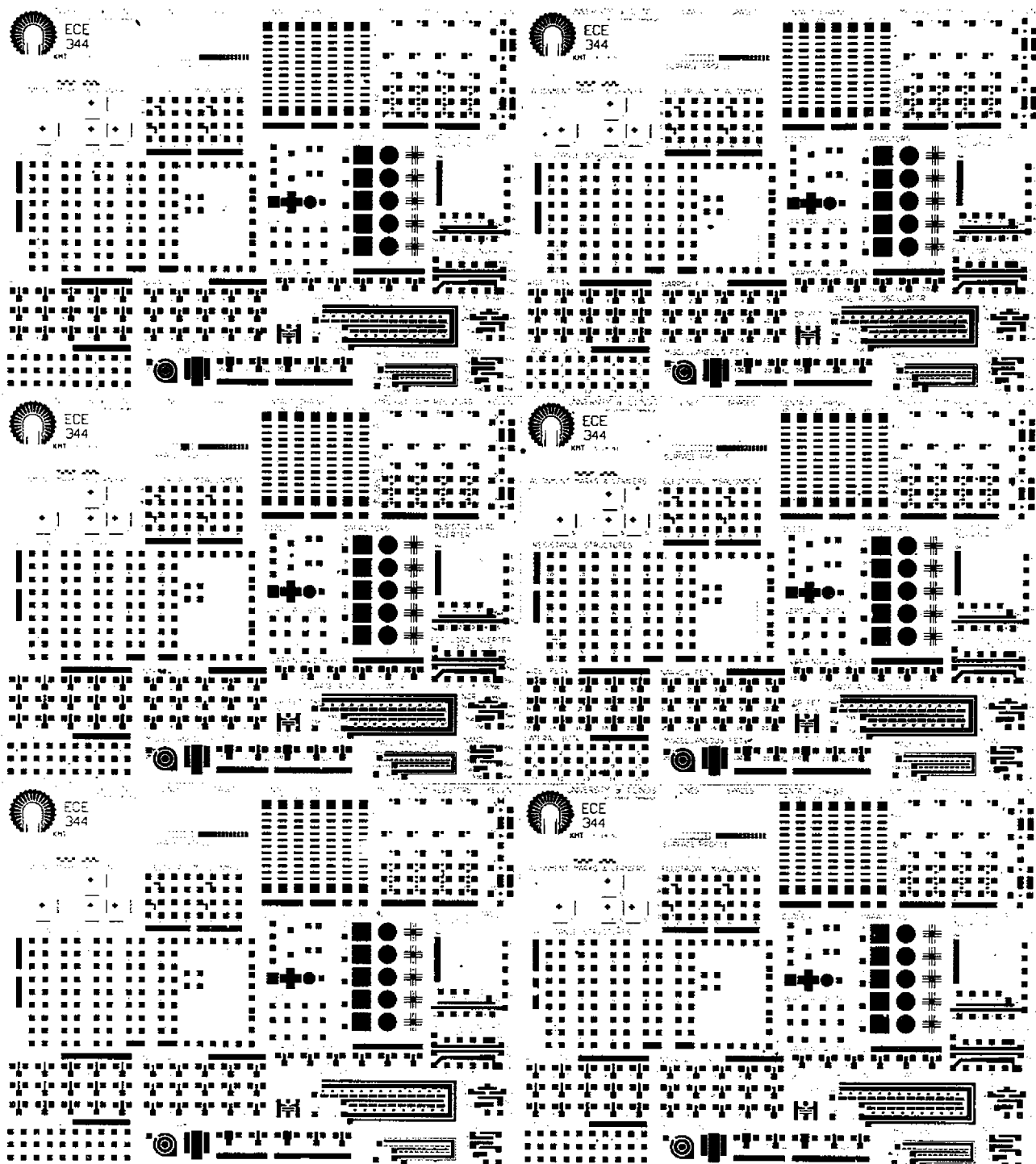


Figure 2. Optical micrograph of a palladium (3000 Å) thin film deposited selectively on an ITO substrate. The deposition was carried out at 250 °C with 10 sccm Ar and 50 sccm H₂ flows. The chamber pressure was maintained at 0.25 Torr. The feature sizes range from 200 to 5 μm.

demonstrates that printing-based patterning methods can yield features with a broad range of "pitches" and aspect ratios. The fidelity of the deposition is also very good and pertains more generally as similar results were also found for the platinum CVD system.

Selective deposition of platinum and palladium films have been carried out on substrates as large as 2 × 2 cm (dimensions limited only by the size of our sample holder). Platinum and palladium can also be deposited selectively on a variety of other substrates, including TiN, SiO₂/Si, and sapphire. All of the films are strongly adherent and could not be removed with scotch tape.

Selective deposition was achieved over a large range of processing conditions. A particularly important experi-

mental factor with regard to controlling selectivity was the absolute flux of the precursor impinging on the substrate. At relatively low precursor fluxes (low deposition rates), selective deposition occurred at all temperature and pressure ranges studied (temperatures between 175 and 275 °C for palladium and between 250 and 350 °C for platinum, with pressures of the Ar/H₂ mixture maintained between 0.1 and 5 Torr). Selectivity becomes more difficult to maintain, however, when the deposition rate is increased above about 400 Å/min (the flux dependence, likely, is coupled closely to other process parameters—such as gas composition and substrate temperature, for example—but these sensitivities have yet to be fully explored).

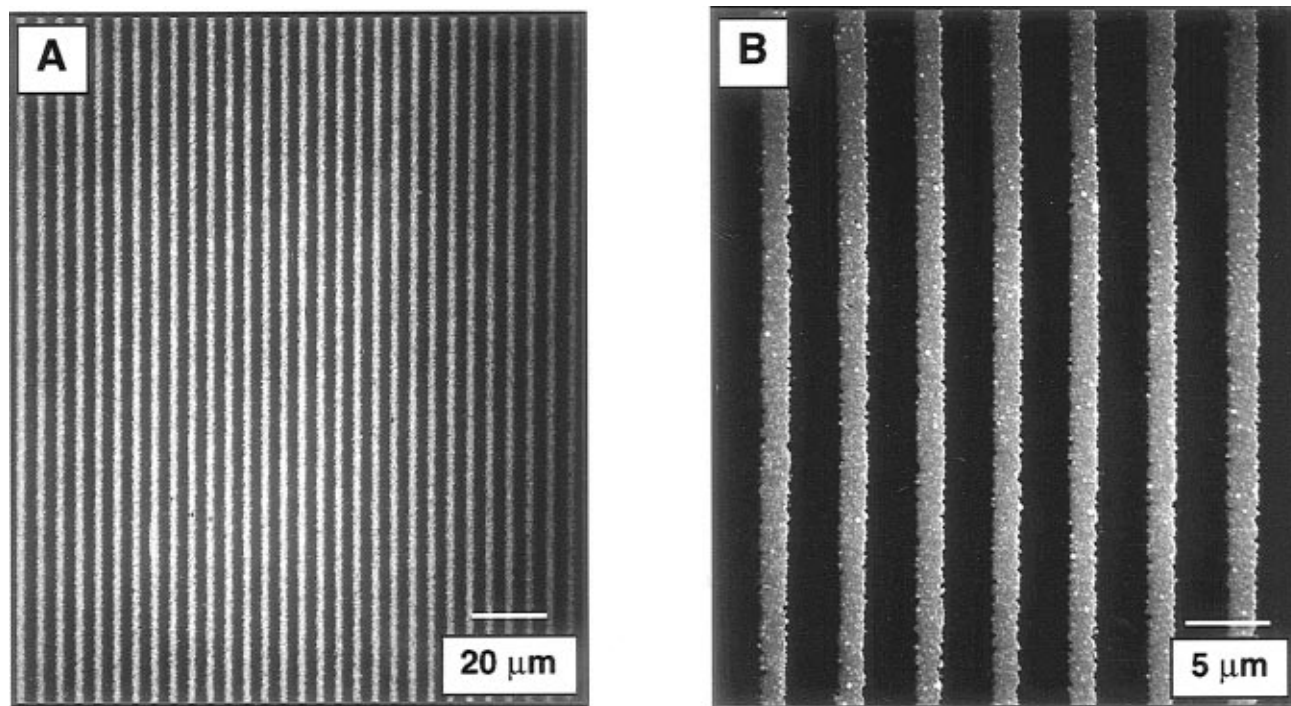


Figure 3. SEM micrograph of 3 μm wide Pd lines deposited selectively on SiO_2/Si (A) and 1.5 μm wide Pt lines deposited selectively on TiN (B). The substrates had been patterned by microcontact printing with a negative image template of OTS. The 3000 Å thick Pd and 3000 Å thick Pt were deposited at 250 °C and 300 °C, respectively. Both films were deposited in the presence of hydrogen.

We next explored whether micron-sized features could be deposited. Scanning electron micrographs of 1.5 μm wide platinum lines deposited selectively on TiN and 3 μm wide palladium lines on SiO_2/Si are shown in Figure 3. Thin films with these feature sizes could be reproducibly deposited by the combined μCP –MOCVD method. There is no obvious impediment to extending these results to the deposition of submicron features on wafer-sized substrates with the possible exception being that the line edge definition is limited by the grain sizes obtained with these CVD processes.

Of critical concern in the application of Pt as an electrode material in device architectures is the crystallographic orientation of the deposit. The X-ray diffraction pattern of a 3000 Å thick platinum thin film deposited on a sapphire (0006) substrate at 350 °C is shown in Figure 4. The film is strongly textured, showing a significant orientation along the (111) direction. This result is representative of the textures found for Pt and Pd thin films deposited on other substrates as well.

The morphologies of the platinum (A) and palladium (B) thin films deposited on TiN were investigated by SEM (Figure 5). Both films were deposited under identical conditions (substrate temperature of 275 °C, argon carrier gas flow rate of 50 sccm, and total chamber pressure of 0.5 Torr) but show drastically different grain shapes and surface morphologies. The platinum film consists of large, highly faceted columnar grains where the palladium film consists of smaller, smooth-walled columnar grains. These columnar grains appear to be ones characteristic of films deposited under mass transport limited conditions. That the Pt and Pd deposition kinetics were indeed mass transport limited is supported by the observation that our steady state deposition rate varied only weakly over the temperature range studied (175–270 °C for Pd and 200–350 °C for Pt): ~ 200 Å/min for Pd at 250 °C (Ar carrier flow rate of 10 sccm) and ~ 100 Å/min for Pt at 250 °C (Ar carrier flow rate of 50 sccm).

The selective CVD process yields films with nonoptimal, but still acceptable, electrical properties. The measured resistivities of the platinum and palladium deposits were

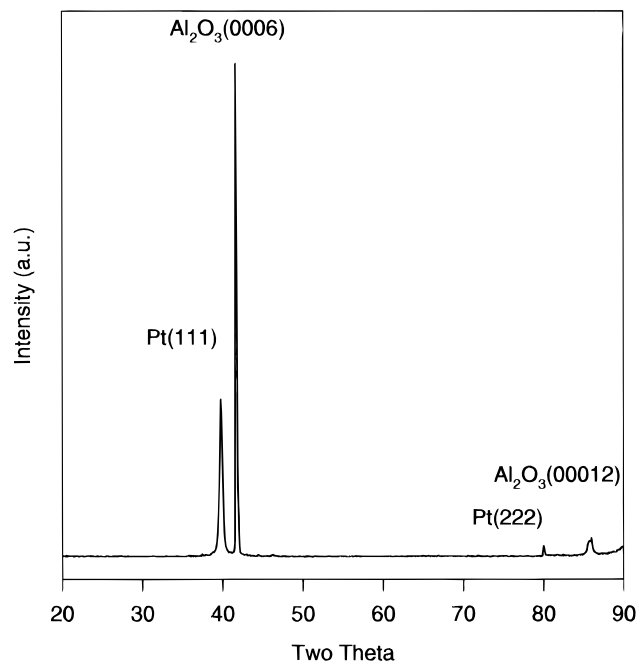


Figure 4. XRD pattern of 3000 Å thick platinum thin film deposited on sapphire (0006) at 350 °C. The processing conditions used are described in the text.

~ 30 and 25 $\mu\Omega\cdot\text{cm}$, respectively. These values are somewhat higher than the bulk values (10.6 $\mu\Omega\cdot\text{cm}$ for Pt and 10.8 $\mu\Omega\cdot\text{cm}$ for Pd). The higher resistivities may be due to the relatively coarse, disconnected grain structure evidenced in the micrographs shown in Figure 5.

As noted above, the platinum films deposited by MOCVD consist of highly faceted grains. For use as an electrode material in ferroelectric capacitors, however, it is important that the platinum films be smooth and uniform. The platinum films shown earlier are unsuitable for fabricating such electrodes because the roughness of the film (2000 Å) exceeds the total thickness of the (lead zirconium titanate) ferroelectric thin films that are used. We,

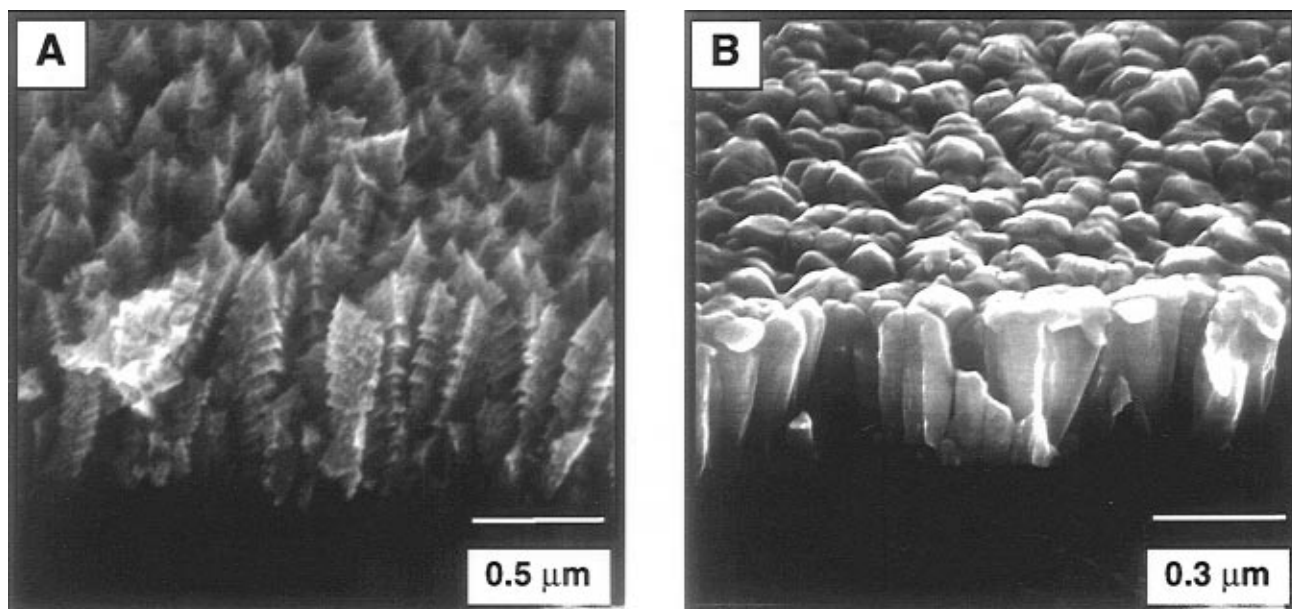


Figure 5. Cross-sectional SEM micrographs of platinum (A) and palladium (B) films deposited on OTS-patterned TiN at 275 °C. The processing conditions used are described in the text.

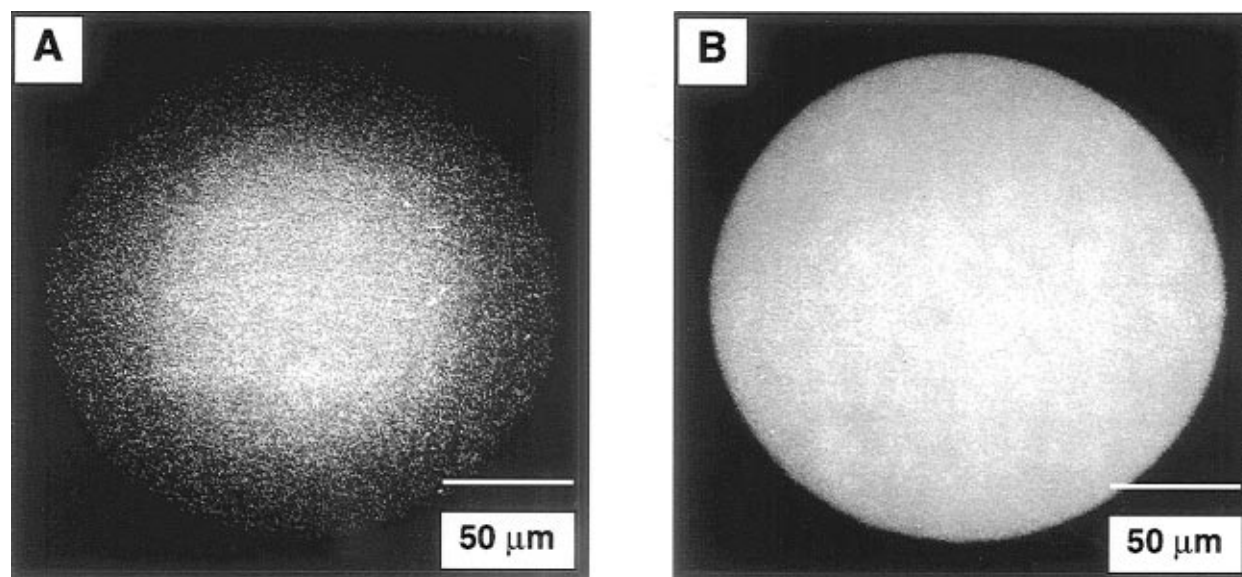


Figure 6. SEM micrographs of platinum thin films deposited selectively either without (A) or with (B) water vapor being present. A patterned area is shown in both micrographs, where the circular area is bare silicon with varying amounts of platinum growth and the dark region outside of the circle is stamped with OTS. Platinum growth is seen as white dots within the circle. The deposition was carried out on TiN under conditions identical to those described in the text. The micrographs were taken at an early stage of the deposition process, and the reaction time was held constant in each.

therefore, investigated whether the deposition conditions could be modified to improve the morphology of the CVD Pt films.

Effects of Water and Deposition Temperature on Pt Morphology and Deposition Selectivity. Studies of copper CVD from $\text{Cu}(\text{hfac})_2$ and $\text{Cu}(\text{hfac})(\text{vtms})$ precursors have shown that significant enhancements in the deposition and nucleation rates occur upon the addition of water vapor to the carrier gases.^{38–40} In addition, the presence of water during deposition often shortens induction times and affects the film microstructure.³⁹

We find that the addition of water vapor during CVD from $\text{Pt}(\text{hfac})_2$ significantly increases the number of nucleation sites while maintaining deposition selectivity

(Figure 6).⁴¹ As a result, the platinum grains were generally smaller when grown in the presence of water, but they were still highly faceted. This latter effect demonstrated little sensitivity to the nature of the substrate, since the film morphology obtained (especially the fiber texture growth habit, see Figure 5) was very similar on substrates such as sapphire, TiN, and SiO_2/Si , the latter two of which are not lattice-matched to Pt.

The morphology of the CVD platinum films is, however, strongly influenced by the substrate temperature. At low deposition temperatures (200 °C, Figure 7A), the film was not continuous and was made up of sparsely nucleated islands with highly faceted grains. At higher temperatures, more nuclei were present and the films were smoother ($T > 250$ °C, Figures 7B and 7C). Similar results have been observed in other CVD processes, and the

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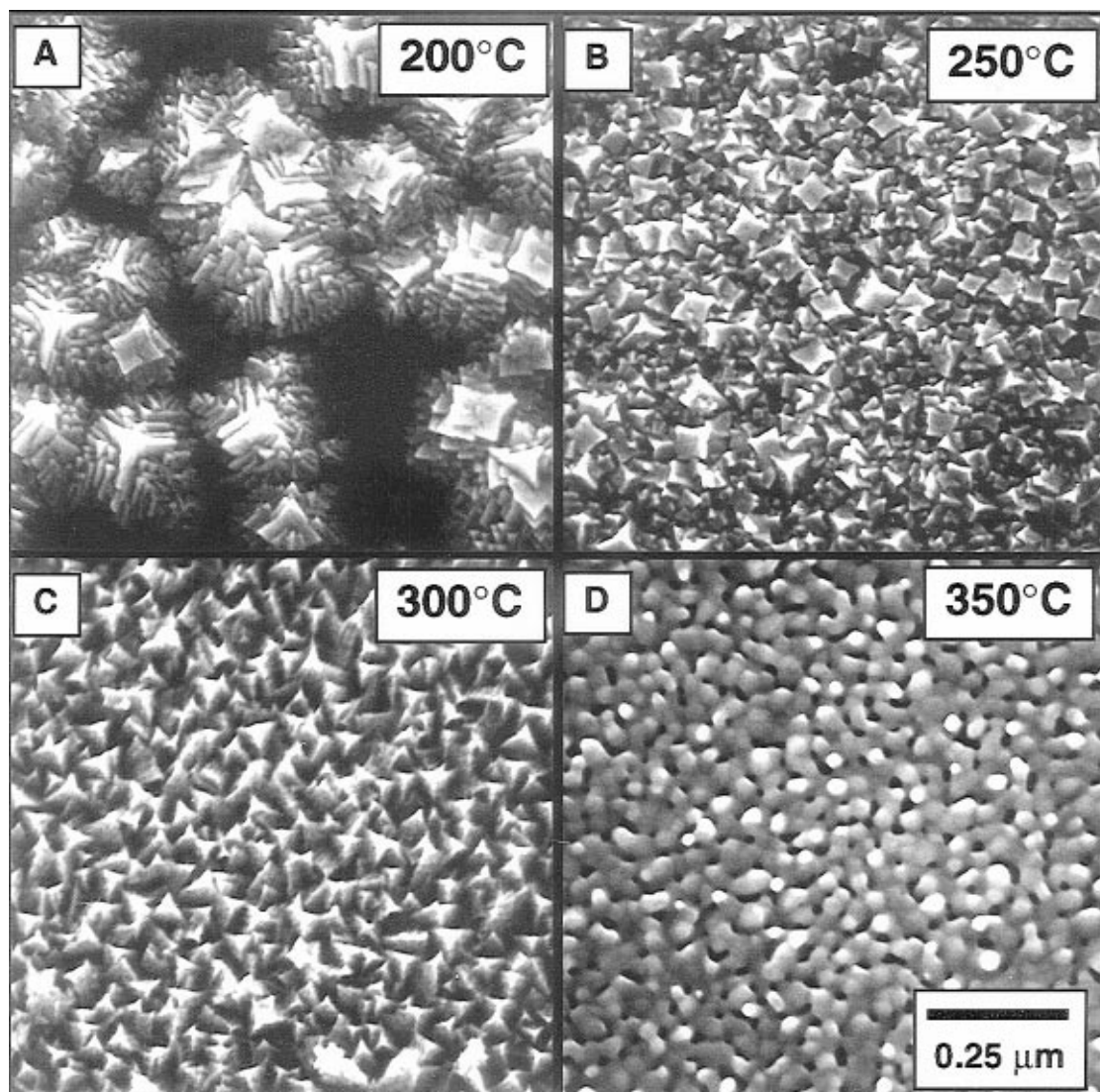


Figure 7. Scanning electron micrographs of platinum films deposited at different temperatures on TiN substrates. The Ar and H₂ flow rates were fixed at 50 and 20 sccm, respectively. All depositions were carried out in the presence of water vapor at a total chamber pressure of 0.5 Torr.

difference in number of nuclei seen likely reflects the faster nucleation kinetics occurring at higher temperatures.⁴²

Surprisingly, platinum films deposited above 325 °C (Figure 7D) consist of round grains with smooth surfaces, in sharp contrast to the faceted, rough surfaces seen below 325 °C. This phenomenon was universal in that identical results were observed for different substrates and irrespective of the presence or absence of water vapor in the feed. Of particular interest, though, is that the selectivity was maintained even at this extreme temperature. Taken together, the results suggest that selective Pt CVD processes might find application in fabrication schemes for advanced device architectures, but only after the nonoptimal features of the growth habits can be corrected. We are continuing to study ways to effect chemical control over the grain structure development of the CVD platinum (and Pd) films and to understand the mechanism behind the smoothing of the grains seen at the higher deposition temperatures.

Conclusion

High purity platinum and palladium thin films were deposited selectively by thermal CVD from Pt(hfac)₂ and Pd(hfac)₂ in the presence of hydrogen. The microcontact printing (μ CP) of octadecyltrichlorosilane (OTS) thin films,

when combined with MOCVD, provided an effective means for producing micron-scale Pt and Pd features on a variety of substrates. The patterned metal films deposit selectively on regions not modified by the OTS monolayer. The thin films were adherent and had resistivities of 25 and 30 $\mu\Omega\cdot\text{cm}$ for palladium and platinum, respectively. Features ranging from 1.5 μm to several hundred microns were reliably deposited in two steps without the use of photolithography or plasma etching. The presence of water vapor increased the number of nucleation sites but did not significantly change the morphology or film deposition rate. The approach described in this paper is a general one and should be applicable to other MOCVD precursors, templating SAMs, and substrate surfaces. This photolithography-free process has the potential to simplify the deposition of patterned thin films for use in the fabrication of microelectronic devices.

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