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50 nm linewidth platinum sidewall lithography by effusive-source metal precursor chemical deposition and ion-assisted etching

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Vertical platinum sidewall structures 50 nm thick and 700 nm tall have been fabricated by Pt deposition from the thermal decomposition of tetrakis-(trifluorophosphine)-platinum using an effusive gas source followed by ion-assisted etching. Scanning electron microscope micrographs show that the sidewalls have high uniformity, very fine grains, and very sharp contours, demonstrating a high degree of conformal deposition. Scanning Auger microscopy confirms the presence of platinum only in the sidewalls. X-ray photoelectron spectroscopy analysis of the as-deposited platinum film reveals no detectable impurity and Scotch tape test shows good bonding of the film. The method is suitable to large-scale processing.

Nanometer linewidth metal features are of great interest in the field of micro and nanoelectronics. Nanometer-size (below 0.1 μm) metal etch masks can be used advantageously in the fabrication of submicron-size electronic devices of the future by lithographic techniques in large-scale processing because they are in general more durable in high annealing temperatures than organic resist materials. Other applications for nanometer linewidth metal features include interconnects, vias, and contacts for future generation multilevel ultra-large scale integrated components, for quantum wires, field-emission cathodes, etc. Some of the obvious limiting factors to the fabrication of such structures by film deposition are the degree of conformal deposition, the grain size, uniformity, and purity of the metal film.

Recently, in this laboratory, we have employed thermal decomposition deposition of a platinum precursor molecule using an effusive gas source in conjunction with the method of vertical sidewall formation. Previous methods for fabricating vertical sidewall structures on microcircuit substrates are found mainly in patent literature.[1-8] Significant, new aspects of our fabrication method compared with previous works on vertical sidewalls are (1) the deposition of a pure metallic platinum sidewall, (2) employing the *thermal decomposition* of a metal-containing precursor molecule, and (3) using a low-pressure effusive source. The superior material properties and morphological qualities of the resulting Pt sidewall structures can be attributed to the choice of the gas precursor and substrate starting materials and the experimental conditions employed in our work.

The starting structures are photolithographically fabricated 0.7 μm tall, vertical-walled amorphous silicon "buttress" structures above a 0.75-μm-thick SiO_2 layer thermally grown on top of a polycrystalline Si(100) substrate. The top views of these "buttresses" are in the shape of squares and octagons with overall dimensions of 9.2 and 4.5 μm across opposite sides, respectively. These starting structures were prepared by the National Nanofabrication Facility at Cornell. Amorphous silicon has been chosen for the buttress material because its small grain size (and thus high nucleation site density) leads to the deposition of uniform and small-grained platinum films. The substrate was cleaned by dipping in a concentrated sulfuric acid-30% hydrogen peroxide mixture, followed by repeated ultrasonication in triply distilled water and drying in a stream of argon. The native oxide was intentionally not removed to inhibit platinum silicide formation. The platinum metal precursor, tetrakis-(trifluorophosphine)-platinum, $[Pt(PF_3)_4]$, was synthesized at NRL by Berry using a known preparative method.[9] Rand has shown that among several known Pt precursors, $Pt(PF_3)_4$ gives the highest quality chemical vapor deposition Pt film when grown under one atmosphere total pressure (mostly hydrogen carrier gas). However, growth at one atmosphere total pressure produces films which suffer from phosphorus contamination.[10]

In this work we used a vacuum chamber that was pumped by a liquid nitrogen trapped, 6 in. diffusion pump, with a base pressure of 4×10^{-8} Torr. The resistively heated 1×1 cm substrate, attached to a Varian manipulator, was first heated to 500 °C in vacuum for 15 min. After cooling to and stabilizing the temperature at 290 °C, the substrate was moved 3 mm from and normal to the end of a 12-mm-diam dose tube. A 1:10 $Pt(PF_3)_4$:H_2 mixture, at a total pressure of 2.2×10^{-5} Torr as monitored on an ionization gauge in the chamber, was flowed onto the substrate. Typically the $Pt(PF_3)_4$ gas flow was stopped after 5 min of deposition time while H_2 gas flow continued. After 30 min, the substrate temperature was cooled slowly to room temperature, the hydrogen was shut off, and the chamber evacuated. At this point all the horizontal and vertical surfaces on the substrate were coated with a thin Pt film.

The substrate was then manipulated into a position with its surface normal to the beam axis of a Perkin–Elmer sputtering ion gun. After establishing a steady-state flow of Ne at a chamber pressure of 5×10^{-5} Torr, we used a 1.0 keV Ne ion beam with a beam diameter of approximately 0.5 cm at the substrate at a beam current of 20 μA to sputter remove the Pt film from the horizontal surface of the buttress structures and the surrounding substrate.

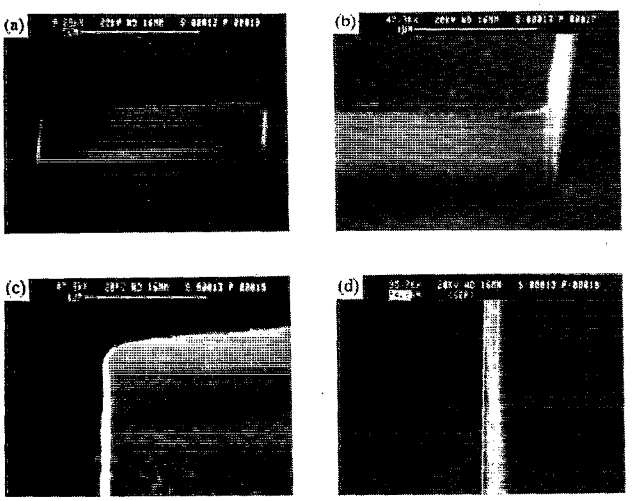

FIG. 1. Scanning electron microscope micrographs of platinum vertical sidewall structure and details above silicon dioxide substrate viewed at 82° tilt from substrate normal. (a) Square structure 9.2 μm on a side and 0.7 μm high. Details of (b) lower right corner and (c) upper left corner of structure. (d) Top view of left edge of structure showing linewidth of less than 55 nm.

Next, XeF_2:Ne, at a 1:6 ratio, was dosed concurrently onto the same spot on the substrate. The ion-assisted etching step was continued typically 30–45 min. We anticipate that anisotropic reactive ion etching (RIE) will also work as well, and may actually be more appropriate for processing conditions.

Since the starting buttress structures were spaced at about 100 μm apart, the ion beam spot encompassed many of these structures. Figure 1(a) shows the scanning electron microscope (SEM) micrograph of a square vertical sidewall structure made by the above method. Figures 1(b) and 1(c) show the details of the lower right and upper left corners of the same structure. Figure 1(d), an image of the left edge, is used to demonstrate the structure linewidth. Several observations are apparent. The vertical "crease" at the corner in Fig. 1(b) was likely present in the original buttress structure; its reproduction in the resulting vertical sidewall reflects the very high degree of conformal deposition by this method. Second, no grain structure is detectable on the sidewalls as shown in Figs. 1(b) and 1(c), suggesting that the grain sizes are probably less than 10 nm. Third, the slight jaggedness of the top horizontal edges shown in Figs. 1(b) and 1(c) is likely due to sputtering and ion-assisted etching. Optimizing or even using a different etching process can be expected to produce an improvement in this regard. The height of the vertical sidewall is about the same as that of the original buttress structure, suggesting that Pt is quite resistant to ion-assisted etching by XeF_2 under the conditions used, and can be used as an etch-mask material. Finally, and most importantly, Fig. 1(d) shows that the linewidth is not more than 55 nm, and possibly less than 50 nm, considering the nature of SEM imaging and that this tilted top view includes contributions from any distortion from the entire 0.7 μm height of the sidewall. We have observed linewidth measurements as low as 45 nm on other sample substrates using the same SEM imaging procedure. The linewidth can be further reduced by shortening the time of deposition, decreasing the precursor pressure, or lowering the deposition temperature. The ultimate lower limit of the linewidth will be determined by the Pt grain size which in turn is determined by factors controlling film nucleation and crystal grain growth such as the surface nucleation site density.

The following tests and observations have been made on the fabricated structures. The results will be published in a much expanded format in another paper. (1) The vertical Pt sidewall structures were analyzed by scanning Auger microscopy (SAM). SAM line scans revealed Pt only on the sidewalls and absence of Pt elsewhere. (2) Some of the Pt films were subjected to *ex situ* x-ray photoelectron spectroscopy analysis prior to Ne ion beam treatment. After 15 s of Ar ion sputtering to remove surface contaminants, no detectable impurities were found. The absence of carbon, phosphorus, fluorine, and even oxygen is significant. (3) X-ray diffraction of the as-deposited Pt film showed it to be polycrystalline. (4) Scotch tape tests showed no peeling of the Pt film from the substrate. Additional tests such as resistivity and stress will be carried out in the near future.

The high degree of conformal deposition, high film purity, and uniformity of the prepared structures can be attributed to using thermal decomposition of the $Pt(PF_3)_4$ precursor under effusive flow conditions which afford nearly free access of the fresh precursor gas to the surfaces, surface diffusion of the precursor molecule prior to decomposition, and the unimpeded escape of decomposition products such as PF_3. In contrast, under the atmospheric pressure deposition conditions used by Rand,[10] decomposition products experience many orders of magnitude more collisions and are therefore much more likely to be incorporated into the film, thus resulting in the observed phosphorous contamination. The very small grain size observed in our work likely results from the favorable nucleation conditions of the amorphous silicon buttress material as well as the choice of the $Pt(PF_3)_4$ precursor molecule.

In conclusion, we have developed a lithographic method for fabricating 50 nm linewidth Pt patterns using the thermal decomposition of a Pt precursor molecule from an effusive source in conjunction with a vertical sidewall technique. The resulting Pt line structures exhibit very desirable properties such as highly conformal deposition, ultra-narrow linewidth, high uniformity and purity, and small grain size. The resistance to oxidation and the high melting point of the Pt film are advantageous in preventing reliability problems such as loss of conductivity and electromigration. The method is a general one and should be applicable to the fabrication of nanometer linewidth structures of other metals, of metal alloys, insulators, semiconductors, ferroelectric, and magnetic materials. The properties of the resulting film structures will depend much on the suitable choices of the precursors and buttress materials to be used under effusive flow conditions.

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