Highresolution electroless deposits on alumina from ultraviolet exposure of a Pt metalorganic

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Citation: Applied Physics Letters **60**, 2350 (1992); doi: 10.1063/1.107022
View online: http://dx.doi.org/10.1063/1.107022
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/60/19?ver=pdfcov
Published by the AIP Publishing

High-resolution electroless deposits on alumina from ultraviolet exposure of a Pt metalorganic

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(Received 18 November 1991; accepted for publication 12 March 1992)

Photochemical and electroless metallization techniques have been combined to create metal patterns on alumina (Al_2O_3). In this positive imaging process, small amounts of an ultraviolet (uv) sensitive metalorganic (MO) Pt compound are first applied to the surface of the alumina by spin coating. A quartz photomask is then used to selectively expose the Pt MO to uv light in the areas that are to be metallized. After a xylene rinse removes the Pt MO from the unexposed areas, the substrate and xylene insoluble Pt MO are fired in air at 450 °C for 5 min, followed by electroless deposition of Ni on the uv exposed surface. Total Pt consumption is to about 0.01–0.02 g/m^2 of metallized surface—no Pt or Ni was detected in nonmetallized regions. The uv exposure time is brief, $\leqslant$0.75 s, and 0.3-μm-thick Ni/B deposits can be patterned on 96% pure alumina with resolution of nearly 28 μm line/spaces.

Historically, there has been interest in reducing the size of hybrid electronics. Hybrid circuits placed on ceramic materials are often produced using silk screen technology. Because the best resolution available with that technology is about 125 μm, alternative processes are being examined for hybrid metallization. Subtractive photolithographic techniques[1] yield excellent resolution but use acid etches to remove portions of metal deposits. This is a drawback because of the requirements for recovery and disposal of the etchant. Therefore, we examined an additive approach towards obtaining high-resolution metal patterns on Al_2O_3 substrates that would lend itself to mass production.

Patterning techniques have been investigated in which precursors are directly decomposed into metals by lasers,[2–8] electron beams,[9] or ion beams.[10–12] Although all of these methods give excellent results, they do not lend themselves to rapid large volume production and all of them use complex costly equipment.

Electroless metallization[13] can be used to produce patterns on nonconductors if a catalyst (used to initiate the metallization) is either selectively deactivated[14,15] or is itself applied as a pattern through a photochemical reduction process.[16,17] An alternative to these processes, involving the photochemical formation of an intermediate with modified solubility, is given here. We make use of metalorganic decomposition (MOD)[18] and 254 nm ultraviolet light to convert a xylene soluble Pt metalorganic (MO) compound into a xylene insoluble derivative. A firing step decomposes the xylene insoluble derivative into active catalytic sites for electroless deposition onto 96% pure alumina. The Pt island catalysts thus produced catalyze electroless Ni/B deposits resolved to 28 μm.

The selective deposition process is shown in Fig. 1. The Pt MO used in this work, $[Pt(H_2NCH_2CH_2(NH_2)CH_3)_3]$ $[OC(O)CH(C_2H_5)(C_4H_9)]_4$, was prepared by Laing's method.[19] Pt MO solutions in xylene of 7 wt% were used. The viscosity of a typical solution was 1.23 centipoise at 23 °C. These solutions were filtered through a 0.2 μm filter after makeup and stored under air in colorless glass bottles at room temperature. The solutions were fairly stable for periods of up to two months, at which time the solutions had to be refiltered due to particulate buildup from gradual decomposition. The solution was applied to 2.5×2.5 cm 96% pure alumina (Coors Ceramics, Golden, CO) by spin coating. Spin speeds of 500–2000 rpm/20 s were examined.

A quartz mask with Cr patterns corresponding to the

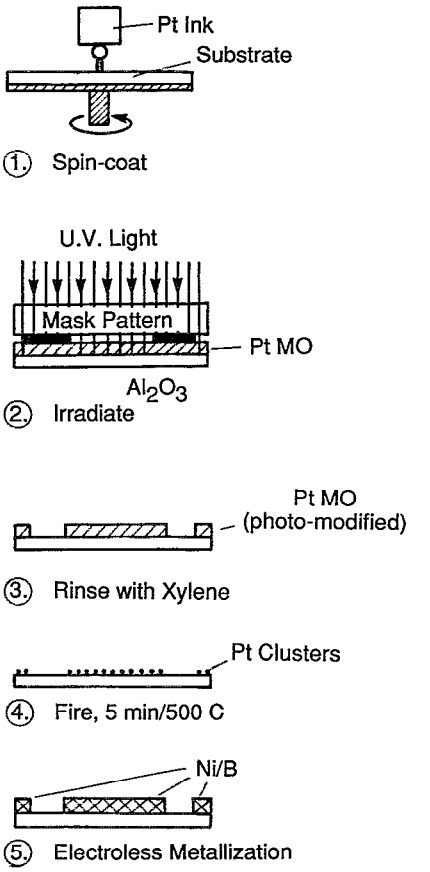

FIG. 1. Schematic of the process for using a light sensitive Pt MO to pattern electroless deposition.

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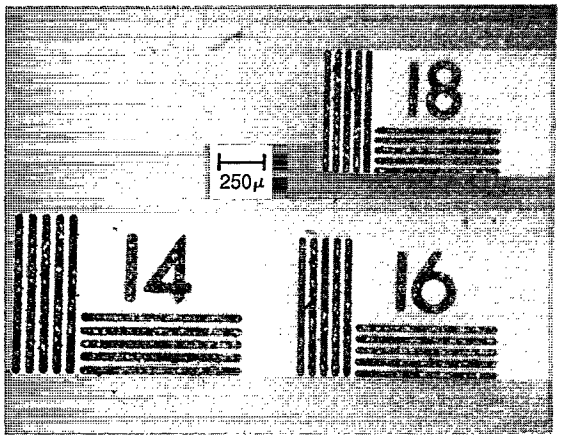

FIG. 2. 0.3-μm-thick Ni/B patterns on 96% alumina. Numbers in the pattern designate the number of cycles/mm: set 14 corresponds to line/spaces of 36 μm each (one cycle=72 μm), set 16 to 31 μm, and set 18 to 28 μm.

NBS resolution test chart 1010a was placed on top of the Pt MO coated substrate. High intensity uv light from a Fusion Systems Corporation (Rockville, MD) F 300 lamp/H-bulb was used to convert the compound into a xylene insoluble form. After single exposures, the original Pt amine (which was shielded by portions of the mask) was removed by soaking the sample for $\sim$10 s in xylene then rinsing for $\sim$5 s with xylene from a wash bottle, ultrasonically rinsing in xylene for 20 s, then rinsing again with xylene from a wash bottle. A xylene insoluble Pt compound remained on the uv exposed portions of the substrate. When the xylene had evaporated, the patterned alumina was fired for 5 min in air at 500 °C, then, after cooling, was immersed in the electroless metallization baths. Metallization was accomplished using Transene's nickel-B bath (Transene Co., Rowley, MA).

For a thickness of 0.3 μm Ni/B, a resolution of 28 μm line/spaces (the smallest available with the mask), can nearly be achieved (Figs. 2 and 3). At that resolution, the electroless deposit can be seen to be about 32-μm-wide and the spaces about 24 μm wide. Widening of the metal lines

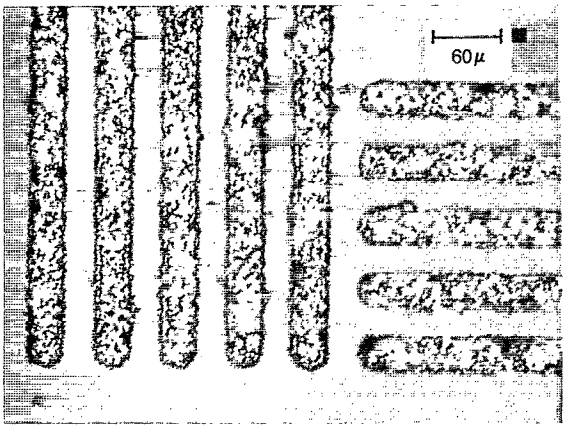

FIG. 3. The increase in size of metal deposits over spaces can be seen at the 28 μm feature level.

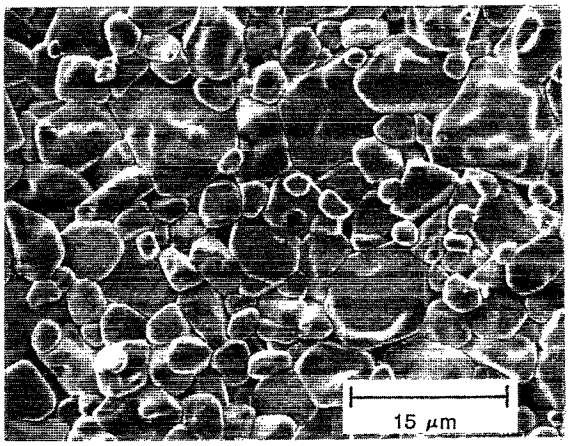

FIG. 4. SEM of 96% alumina.

is most likely due to light scattering at the rough 96% alumina surface and is probably not due to lateral growth of the Ni/B deposit since similar results were obtained with much thinner Ni/B deposits. Adhesion was good enough that no Ni/B could be scratched off with needles or pulled from the surface with transparent tape.

Surfaces with the fired Pt catalyst were quite stable. Indeed, after firing the patterned Pt, delays of a few days before electroless metallization created no problems—the catalyst remained active and resolution was maintained. However, delays of minutes or longer between other steps can degrade resolution. For instance, patterning is lost with delays of over 30 min between the spinning and uv exposure steps. The Pt compounds appear to anchor to the Al_2O_3 substrate, resulting in total coverage by the electrolessly deposited metal even after a thorough xylene rinse. Delays of a few minutes between exposure and rinsing limit resolution. We presume this is because a chemical produced during photolysis acts as a solvent for the degraded Pt MO material and causes it to diffuse into nonexposed areas. Tests revealed that the xylene insoluble Pt compound is soluble in polar solvents such as 2-propanol or 1,2-diaminopropane. It is likely that 1,2-diaminopropane is expelled from the Pt complex during photodegradation and acts as a solvent to mix the xylene soluble and insoluble Pt complexes. Immediate rinsing in xylene serves to remove the amine before resolution is lost.

Figure 4 shows the coarseness of the alumina substrates. Obviously, such a rough surface will scatter considerable light. It is likely that greater resolution would be possible on smoother substrates. In order to obtain optimum resolution, a balance had to be achieved between the concentration of Pt MO on the surface and the amount of light hitting the MO material. Table I shows how uv exposure time determines the amount of Pt on the surface when no mask is used and the spin speed is held constant (2000 rpm/20 s). Exposure times of 1.6 s worked best when a largely transparent mask with five 1 mil lines was used. When a negative of that mask was used, exposure times of 0.6–0.9 with spin speeds of 2000–4000 rpm were more effective.

TABLE I. Pt found on 96% pure alumina by x-ray fluorescence spectroscopy (XRF). Spun-on at 2000 rpm/20 s from a solution of 7 wt% Pt MOD in xylene. The specimens were ultrasonically cleaned with xylene after irradiation then fired for 5 min at 500 °C. Control specimens were coated with the MO material, but not irradiated or rinsed. One was fired and the other was tested without firing. Both of these showed [Pt] at 1.5 $\mu g\ cm^2$.

uv exposure time (s)	Pt concentration ($\mu g\ cm^2$)
0	<0.1
0.6	0.2
0.9	0.5
1.3	1.0
2.2	1.4
6.1	1.5

The author wishes to thank the following members of General Motors Research Laboratories, Analytical Chemistry Department, for their help: P. M. Hanley for the x-ray fluorescence analysis, C. A. Wong for scanning electron microscopy, and S. W. Gaarenstroom for helpful comments.

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