

Fig. 8. SEM image of aluminum film etched using copolymer mask. The etch mask has been removed.

MAA] copolymer mask. The Al lines are 2300Å thick. The final pattern is shown in Fig. 8.

#### Conclusions

We have developed a technique for patterning fine line features in aluminum using reactive ion etching. This approach avoids the use of carcinogenic gases like CCl4 and CHCl<sub>3</sub>. The use of three gases, Cl<sub>2</sub>, BCl<sub>3</sub>, and CH<sub>4</sub>, allows one to intentionally vary the etch rate based on the application. Statistically designed experiments were utilized to reach optimized etching conditions and to analyze the principal effects of each gas on the behavior of the etch. The anisotropy of the etch was shown to result from sidewall polymer layers using Auger spectroscopy. Anisotropic etching requires an organic etch mask and CH4 in the gas mixture.

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# Photochemically Generated Gold Catalyst for Selective **Electroless Plating of Copper**

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## ABSTRACT

The creation of surface-selective copper patterns was explored via the photochemical decomposition of dimethyl (1,3diphenyl-1,3-propanedionato) gold. UV irradiation of a substrate treated with the gold complex results in the formation of elemental gold, which in turn catalyzes copper metal plating from an electroless bath. Thus, a selective copper pattern can be formed in a simplified process as defined by patterned UV irradiation. The variables which are important to the process are discussed including the UV dose, wavelength, and the surface concentration of gold complex.

The metallization of circuit boards often requires the use of additive plating techniques (1). In a typical scheme, a dielectric substrate is coated with a photosensitive polymeric resist and exposed to ultraviolet (UV) light. The development of the photoexposed resist results in a surface relief pattern which will define the metal pattern or circuit (2). A catalytic treatment of the substrate is used to initiate electroless copper plating, the circuitry is plated to the desired thickness, and the lithographic stencil is removed. Electroless copper plating has been widely used with both negative and positive tone lithography for manufacturing circuitry via additive metallization processes (3).

Noble metals can be used to catalyze the initial plating of electroless solutions (4). Most commonly, additive metallization by electroless deposition is catalyzed by a palladium/tin colloid (5). The catalytic species has been found to consist of a palladium/tin core surrounded by an outer sphere of tin (II) (3, 6). Subsequent acid treatment removes the outer tin (II) shell leaving an active palladium/tin core. A second, similar method consists of sensitization with acidic tin (II) chloride followed by activation of the substrate with an acidic solution of palladium (II) chloride. During this procedure, the palladium (II) is reduced to metal while the tin (II) is oxidized to tin (IV) chloride (7). In both methods, photolithography is required to define the pattern for metallization prior to the catalytic treatment and electroless deposition of copper. Once copper is initially plated, the continued growth of copper results from the ability of copper metal to catalyze the electroless plating bath.

In this paper, a simplified method for the selective metallization of dielectrics was explored via the UV photoreduction of a gold complex. Insulating substrates were spin-coated with organic solutions of the gold complex and exposed to UV light patterned by a lithographic mask. Upon immersion in an electroless copper solution, the photoimage of gold metal initiates copper plating selectively in the UV-exposed regions (Fig. 1). The ability to photoselectively create a catalytic pattern, a replication of the mask image (*i.e.*, negative image), eliminates the need for polymeric resist materials and reduces the number of chemical processing steps required to form a circuit pattern. Selective metal plating from electroless solutions was previously achieved by the UV-induced oxidation of tin (II) colloids (8), photoreduction of palladium (II)-activated TiO<sub>2</sub> films (9), photoinhibition of active palladium-tin catalyst (10), or by the laser-induced decomposition of palladium (II)  $\beta$ -diketonates (11). To our knowledge, this is the first report of photoselective electroless plating from a photochemically generated gold catalyst.

## Experimental

Dimethyl (1,3-diphenyl-1,3-propanedionato) gold complex (1) was prepared by reacting dimethyl gold bromide dimer with the potassium salt of the 1,3-diphenyl-1,3-propanedione (Aldrich Chemical Company) in a mixture of hexane/methanol. The recovered product was recrystallized from hexane to obtain fluffy, white needles; IR and NMR spectra matched the literature values (12). Thermal analysis (DSC) exhibited a melting endotherm at 116°C



Fig. 1. Schematic diagram for creating patterned copper films via UV irradiation of the gold complex and electroless copper plating: (i) the sample is spin-coated with a solution of gold complex, (ii) irradiated with UV light through a lithographic mask, and (iii) selectively plates copper in the UV irradiated regions.

and a decomposition exotherm beginning at 118°C ( $\Delta H_{\rm d} = 23 \pm 1$  kcal/mol). A UV-visible absorbance spectrum was obtained on a Hewlett-Packard diode array spectrometer (Model 8415A). The solution spectrum (hexane) is shown in Fig. 2 and exhibits maxima at 210, 260, and 360 nm. The substrates consisted of 36 mm squares of highgrade alumina (Al<sub>2</sub>O<sub>3</sub>) or dye-colored glass-epoxy coupons. The substrates were rinsed with isopropanol, acetone, and blown dry with nitrogen prior to spin-coating. The solutions of gold complex were made with reagent-grade solvents which had been dried over activated molecular sieves (Aldrich Chemical Company). The solutions were filtered through a Gelman Sciences 0.2 µm Acrodisc filter prior to spin-coating to remove any gold particles or insoluble salts which might interfere with the selectivity of the photoprocess. The solution of gold complex was dispensed onto the sample and the sample was spun for 60s on a conventional lithographic spinner. Thin films of the gold complex were irradiated with an Optical Associates exposure tool (Model 780) equipped with a 500W Hg/Xe deep UV lamp. UV exposure doses were measured using an Optical Associates (Model 270) power meter equipped with several broad-band probes. Typical lamp emissions were measured as 8 mW/cm<sup>2</sup> at 254 and 26 mW/cm<sup>2</sup> at 365 nm using the broad-band detectors. The UV radiation was passed through either a chrome-on-quartz or chrome-on-Pyrex lithographic mask. The quartz transmittance was measured as 80% at 250 nm. The Pyrex transmits roughly 20% at 300 nm with no measurable transmittance at 254 nm. After UV exposure, substrates were plated in a freshly prepared Dynachem electroless plating bath (835 medium copper). Elemental analyses of spin-coated alumina substrates were performed by Galbraith Labs, Knoxville, Tennessee. Digestion of the substrates in acid was followed by atomic absorption spectroscopic analysis. The gold content determined by this analysis represents the surface

#### **Results and Discussion**

concentration of gold complex achieved by spin-coating

and is reported as  $\mu g/cm^2$  (Fig. 3).

Dimethyl (1,3-diphenyl-1,3-propanedionato) gold, **1**, is soluble in a number of organic solvents, but a 50:50 solution of tetrahydrofuran (THF) and 2-butanone (MEK) provided excellent spin-coating properties on several substrates. Dried solvents are critical in minimizing the decomposition of the gold complex in solution. Also, solutions of the gold complex should be stored in a freezer and protected from light. Otherwise, slow thermal and photochemical decomposition of the gold complex occurs, producing gold particles which cause a loss of selectivity and resolution of the copper-plated patterns. Thus, filtered solutions of the photoactive gold complex were used to obtain reproducible results throughout this study.

Although other dimethyl gold  $\beta$ -diketonate complexes can be used with the same success, **1** was chosen for several reasons. This gold complex is less volatile at room temperature (<1 mtorr pressure) when compared to the



Fig. 2. Chemical structure and UV spectrum of dimethyl (1,3-diphenyl-1,3-propanedionato) gold in hexane. Concentration was  $8.9 \times 10^{-5}$ M,  $\epsilon_{260} = 1.8 \times 10^5$ , and  $\epsilon_{360} = 1.88 \times 10^5$ .



Fig. 3. Plot of gold surface concentration vs. the spin-coat velocity for two solutions of different gold complex concentrations. The quantity of gold was determined by atomic absorption analyses of the digested samples.

other dimethyl gold  $\beta$ -diketonate complexes used for gold deposition (13) and thus, is better for forming thin films of known concentration. Also, 1 exhibits a strong UV absorption at 360 nm and it was hoped that photoreduction to gold metal would occur at this wavelength.

Electronic transitions in metal  $\beta$ -diketones consist of  $n \rightarrow \pi^*$ ,  $\pi \rightarrow \pi^*$ , ligand-to-metal (LMCT) and metal-toligand charge-transfer (MLCT) states. Solution-phase UV irradiation results in reduction of the metal center for several metal  $\beta$ -diketonates (14) and a similar reaction is observed for dimethyl (2,4-pentanedionato) gold in solution (15). The LMCT states are high in excitation energy and thus, require deep UV (<300 nm) wavelengths to induce the electronic transition. For copper bis ( $\beta$ -diketonates), the electronic transition at 250 nm has been assigned to the LMCT state ( $\sigma_L \rightarrow d_{xy}$ ) based on Huckel MO calculations (16) and is responsible for copper (II) reduction.

Irradiation (254 nm) of dimethyl (2,4-pentanedionato) gold in solution results in reductive elimination of ethane and liberation of the  $\beta$ -diketone moiety (15b). The mechanism of photochemical decomposition exhibits substantial free-radical character via a postulated charge-transfer excited state. The photodecomposition of a thin film of 1 may occur by a similar reaction pathway. Vapor-phase UV photodecomposition of dimethyl (2,4-pentanedionato) gold was found to produce carbon-contaminated films of gold metal; x-ray diffraction patterns indicate that crystalline gold particles (400-1900Å diam) are dispersed in an amorphous carbon matrix (17). It was also experimentally determined in this study that substrates coated with gold (I) chloride would not catalyze the electroless plating of copper under identical conditions.

The formation of copper-plated patterns via the photoreduction of 1 was studied as a function of irradiation wavelength. UV excitation at 254 nm was found to produce images on both alumina and glass-epoxy substrates that induced copper plating with doses of 1.0 J/cm<sup>2</sup>. Using the chrome-on-Pyrex mask, which transmits only 300 nm and longer wavelengths, the exposure dose had to be increased to 10 J/cm<sup>2</sup> to induce similar copper plating. Thus, the efficiency for photoreduction of 1 to gold metal is an order of magnitude greater at 254 when compared to longer wavelengths (*i.e.*, 365 nm). Since the molar absorptivity for 1 is the same order of magnitude at 260 and 360 nm ( $\epsilon = 10^5$ ), these observations are indicative of a higher energy charge-transfer (LMCT) excited state for 1 at 254 nm.

Samples of alumina were spin-coated with solutions of 1 and analyzed by atomic absorption analysis to determine the surface concentration of gold vs. the spin velocity and the concentration of 1 in solution. As shown in Fig. 3, the gold surface concentration ( $\mu g/cm^2$ ) exhibits an inverse correlation to spin velocity and a direct correlation to the solution concentration of 1. The surface concentration of 1 and the UV exposure dose will determine the amount of gold metal produced upon irradiation. The plating activity of the electroless copper bath is directly proportional to gold metal surface concentration, analogous to that found for conventional palladium catalysts (18).

A series of experiments was performed to determine the exposure dose necessary to induce copper plating from a fresh electroless bath. Using solutions that were 1% in gold complex concentration, substrates spin-coated at 2000 rpm showed excellent plating results after exposure to 1 J/cm<sup>2</sup> at 254 nm. The gold surface concentration for these samples was determined to be 2.7 µg/cm<sup>2</sup>. For higher surface concentrations of 1, the exposure doses can be lowered. For a solution that was 2% in gold complex concentration and spin-coated at 2000 rpm, a dose of 0.85 J/cm<sup>2</sup> was sufficient to induce similar copper plating. This surface concentration corresponds to 6.1 µg/cm<sup>2</sup> of gold on the substrate surface. For faster spin velocities, lower surface concentrations resulted and higher exposure doses (1-2 J/cm<sup>2</sup>) were needed to induce copper plating. It was determined that a surface concentration of  $<2.0 \ \mu g/cm^2$  would not produce uniform copper films after UV exposure, even at increased doses.

The exposure dose can also influence the resolution of the patterned image. For a given surface concentration, the higher UV doses result in wider copper-plated features when compared to lower UV doses. This effect is quite common in photoimaging technologies (2). Thus, for applications where the ultimate resolution is critical, the UV dose should be optimized; the UV dose must be large enough to induce copper plating but minimized to obtain the optimum resolution of features. With this process, it was possible to produce 30  $\mu$ m line and space features for thin copper-plated films (0.35  $\mu$ m thickness).

Typically, electroless plating of copper is an isotropic process (19) and the initial copper-plated image will grow three dimensionally. For example, a copper pattern that is plated to a thickness of  $5 \,\mu m$  will exhibit an increase in linewidth of 10 µm at the base. Thus, the final width of the plated copper feature will increase by twice the thickness of the copper-plated feature. Using the technique described, copper-plated patterns on glass-epoxy substrates exhibit good resolution of features and excellent copperto-epoxy adhesion. For alumina samples, a loss of resolution was observed and this result is currently not well understood. As shown in Fig. 4, the resolution of 100  $\mu$ m wide lines on glass-epoxy can be easily achieved for copper films of several microns thickness. Lastly, the ability to plate holes in the glass-epoxy was observed as shown in Fig. 5. Although this was somewhat unexpected, the diffuse UV light may be reflected into the hole and result in photodecomposition of the gold complex. Further studies are necessary to better understand this effect.

It should also be noted that the removal of the gold complex is easily achieved in organic solvents. Cleaning the



Fig. 4. Scanning electron micrograph of a copper-plated pattern which was produced on a glass-epoxy substrate via the described process. Vertical copper lines on the right side are 100  $\mu$ m in width.



Fig. 5. Scanning electron micrograph of a copper-plated through-hole on a glass-epoxy substrate. Marker denotes 100  $\mu$ m dimension.

substrate before or after the initial plating of copper may be necessary for several reasons: the resolution of the plated pattern may be better preserved because the gold complex can slowly decompose to gold metal upon prolonged exposure to sunlight or via thermal decomposition at temperatures >120°C. In the work described here, substrate cleaning was not employed. However, under typical manufacturing conditions (i.e., chip bonding, solder reflow), the gold complex must be removed. Thus, a specific application may necessitate the removal of gold complex to ensure electrical integrity of the plated pattern.

#### Conclusions

The formation of gold nucleation sites, which result from the photoreduction of a thin, surface layer of dimethyl (1,3-diphenyl-1,3-propanedionato) gold, catalyzes the selective plating of copper from electroless copper baths. Excellent copper patterns have been produced on glass-epoxy composites and display good adhesion. The UV dose combined with the surface concentration of the photosensitive gold complex will determine the plating activity of the photoimages. Although UV exposures at 365 nm catalyze copper plating, the use of deep UV wavelengths (254 nm) provide a higher efficiency for the photoreduction process.

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