Site Selective Copper and Silver Electroless Metallization Facilitated by a Photolithographically Patterned Hydrogen Silsesquioxane Mediated Seed Layer

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Introduction

The process of electroless deposition of thin metal films such as copper and silver onto nonconductive surfaces is of considerable importance in microelectronics fabrication. In the electroless process a chemical reducing agent provides the electrons for the heterogeneous reduction of metal ions to the ground state. Electroless plating solutions typically contain a metal salt of the metal to be plated, a suitable reducing agent, a base, a complexing agent to solubilize the metal salt, and special additives to control the solution stability and plating rate.[1−3] These plating solutions are stable until they come into contact with a catalytically active surface that initiates the thermodynamically favorable reduction of the metal salt to deposit a metallic thin film onto the surface. Typically, the surface catalytic species is a palladium colloid or a palladium/tin complex that is deposited prior to exposure to the electroless plating solution. The freshly plated metal surface then propagates itself in an autocatalytic manner to build thickness.

It is known that the silyl hydride functionality can be utilized as a single electron donor for the reduction of several transition metal halides to the ground state.[4] In one example, it was demonstrated that hydrogen silsesquioxane (HSQ) particles, and silicas coated with a thin layer of HSQ, were active for reducing silver and palladium salts to the corresponding ground-state metals.[5] Fry and co-workers have reported that silyl hydride functionalized silica and glass surfaces can be used to generate catalytically active surfaces by the reduction of palladium(II) and silver(I) cations.[6,7] They also reported that a silyl hydride generated catalytic layer can be used for electroless metal deposition onto glass surfaces.[8]

When prepared under controlled conditions, HSQ forms stable solutions in organic solvents and is used as spin-on-glass dielectric for microelectronics fabrication.[9] A feature of solvent-deposited HSQ thin films that has not been exploited is the abundance of reactive silyl hydride functionality on the film surface. This characteristic combined with its ease of processing presented the idea that thin films of HSQ coated onto nonconductive or conductive, but discontinuous surfaces could be used as a template onto which electroless metallization catalysts could be selectively generated by silyl hydride directed metal reduction.

Reports in the literature have described methodologies for specific electroless metallization of surfaces by site-specific catalyst deposition[10,11] or photolithographic patterning of preactivated surfaces.[12] HSQ films can be selectively masked using traditional photoresist technology, directly patterned by incorporating a photobase generator into the resin film,[13] or patterned by electron beam exposure.[14] The ability to specifically mask or pattern HSQ serves as a platform for examining silyl hydride site-directed metal seed layer formation and site-specific copper and silver electroless metal plating. In this report the results of feasibility trials toward selective electroless copper and silver metal deposition on patterned and nonpatterned HSQ thin films are described.

Experimental Section

Preparation of Substrates. Details for lithographic processing of HSQ films have been described previously.[13]

Thin films of HSQ on the surface of silicon wafer substrates were prepared by spin-coating Dow Corning solutions of FOx-14 (14 wt % HSQ in MIBK; 800 rpm for 0.6 s and 4000 rpm for 10 s) and FOx-16 (21.9 wt % HSQ in MIBK; 500 rpm for 3 s and 1700 rpm for 10 s) to give films with thicknesses of 0.2 and 0.5 μm, respectively.

Nonpatterned Partially Cured HSQ Films. *N*-Methylnifedipine (1 wt %) was dissolved into FOx-16 (1 wt % relative to resin) and spin-coated at 500 rpm for 3 s and then at 3000 rpm for 10 s. The film was prebaked at 80 °C for 1 min and then irradiated with broadband UV (4.8 mW/cm^2 at 254 nm) for 8 s in the absence of a photomask. Postbaking the film at 80 °C for 1 min and rinsing with toluene yielded a 0.4 μm thick blanket film.

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(9) FOx solution, processing conditions, and properties thereof are commercially available from Dow Corning Corp., Midland, MI. As the critical component for selective metallization is the silyl hydride functionality, silyl hydride containing resins from other sources may also provide similar results.

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Patterned HSQ Films. As described above, but with a photo-test-mask used in the lithographic step. Following development, 0.4 μm thick films with 5 μm and greater line and space features were obtained.

Partially Cured HSQ Film with a Patterned Resist Coating. OMS-83 negative resist from Tokyo Oka (60 cP) was spin-coated onto the partially cured nonpatterned blanket HSQ film at 500 rpm for 3 s and at 5500 rpm for 20 s. The film was prebaked at 80 °C for 5 min and irradiated with broadband UV (4.8 mW/cm^2 at 254 nm) for 2 s through a test photomask. After an 80 °C postbake for 1 min the resist image was developed by rinsing with toluene to yield a 0.3 μm thick patterned resist film on the blanket HSQ film.

Preparation of Solutions for Film Surface Activation. To prepare the $PdCl_2$/methanol solution, 0.12 g of $PdCl_2$ was dissolved in 100 g of methanol. To prepare the $PdCl_2/H_2O$ solution, 0.015 g of $PdCl_2$, 0.030 g of NH_4Cl, and a few drops of concentrated HCl were dissolved in 100 mL of distilled H_2O. To prepare the $AgNO_3/H_2O$ solution, 0.6 g of $AgNO_3$ was dissolved in 50 mL of distilled water. The solutions were filtered before use. Seed layer deposition onto the HSQ films was performed by immersion into the metal salt solutions. The samples were then washed with methanol or water and allowed to dry. In some cases the surface activated HSQ films were heat-cured in air with a Carbolite furnace model OAF 11/1 prior to electroless plating. The conditions for cure are described in the Results and Discussion section.

Preparation of Electroless Plating Baths. The copper electroless plating bath was prepared by mixing a solution of 0.43 g of $CuSO_4$, 3.0 g of EDTA−diammonium salt hydrate, 23 mL of a 25 wt % solution of TMAH in water, and 77 mL of distilled water. Just prior to use, a 37 wt % formaldehyde in water solution was added at a ratio of 1 part formaldehyde solution to 60 parts copper solution. This bath, with a pH of 12.5, was used at 50 °C. The silver bath was prepared by dissolving 0.62 g of $AgNO_3$ in 50 mL of H_2O. Prior to use, an equivalent weight of a mixture of 12 mL of concentrated ammonium hydroxide and 2 g of α-D-glucose was added to the aqueous $AgNO_3$ solution. This solution was used at a temperature of 40 °C. The silver and copper plating solutions were stable for a period of at least 3 h after their preparation. The plating was performed by adding about 3−4 g of electroless plating solution into a small glass sample bottle, equilibrating the solution to the desired temperature with a water bath and then full immersion of the sample film into the plating solution for a fixed period of time. Fresh plating solutions were utilized for each sample to ensure uniform conditions. After removal from the plating solutions, the films were washed with water and dried. Photomicrographs of the deposited metal films were obtained with a Polyvar optical microscope.

Results and Discussion

Preparation of Substrates. To prepare continuous films, HSQ in MIBK solvent was spin-coated onto silicon wafers. Discontinuous patterned films were prepared from HSQ/*N*-methylnifedipine formulations, according to literature guidelines,[13] to provide minimum features of 5 μm. Blanket irradiated HSQ/*N*-methylnifedipine formulations were used to prepare HSQ films resistant to organic solvents. A negative resist solution (OMS-83) was spin-coated onto the HSQ continuous film and lithographically patterned to give a 0.3 μm thick resist mask, exposing 5 μm and greater sections of the underlying HSQ film.

Silyl Hydride-Directed Catalyst Deposition. For electroless deposition studies three substrates were evaluated: a continuous film of HSQ, a directly patterned film of HSQ,[13] and a HSQ film selectively masked with a patterned negative resist layer. Two seed layers, metallic Pd and Ag, were evaluated for electroless deposition of metallic Cu and Ag films. To generate a thin Pd seed layer, two different salt solutions were considered: $PdCl_2$ dissolved in methanol and $PdCl_2$ dissolved in a mixture of H_2O, NH_4Cl, and a trace of HCl. To generate the active Pd seed layer, the HSQ films were fully immersed into the Pd salt solutions. Immersion into the methanolic $PdCl_2$ solution resulted in the rapid generation of a thin Pd film on the surface as evidenced by the appearance of a visible black coloration within 1 min of exposure. It was discovered during this step that HSQ films partially cured by photobase processing were more stable to the metal seed layer deposition process compared to noncured films, which suffered delamination and film breakage and were more easily scratched after exposure.

Pd metal deposition by substrate immersion into an aqueous $PdCl_2$ solution was slow compared to the methanolic solution and required substrate contact to a 90 °C solution for 10 min to attain a visible change in surface color. The deposition of metallic Ag as a surface catalytic species required contact of the HSQ films to a 90 °C aqueous $AgNO_3$ solution for 10 min to obtain visible surface deposition.

Films of HSQ with a surface seed layer of Pd metal generated by exposure to the methanolic palladium chloride solution were chosen as substrates for electroless metallization. As the goal of this work was to demonstrate feasibility, little effort was made toward optimizing or understanding the metal seed layer deposition process or the nature of the seed layer.

Electroless Copper Deposition onto Hydrogen Silsesquioxane Films. Copper is a very advantageous metal for microelectronics fabrication given its high conductivity and good electromigration properties. Electroless Cu typically shows a resistivity a low as 1.7 $\mu\Omega\cdot$cm.[15] Copper plating solutions typically constitute a solution of $CuSO_4$, $Cu(NO_3)_2$ or $CuCl_2$ as the metal salt with formaldehyde as the reducing agent. (Other reducing agents including hydrazines, dimethylborane, borohydrides, hypophosphites, and dithionites have been reported.[1−3]) NaOH is added to maintain a high pH (>12), and since Cu salts are insoluble above a pH of 4, complexing agents such as tartrate or ethylenediaminetetraacetic acid salts (EDTA) are added to the solution. To improve the utility of Cu plating solutions to a microelectronics processing environment, Shacham-Diamand and co-workers[15] have developed sodium-free plating solutions by replacing NaOH with tetramethylammonium hydroxide (TMAH).

Initial trials to deposit copper films on the surface of HSQ using a NaOH-containing bath were not entirely successful due to damage of the film and seed layer during the plating process. It was assumed that this was due to the susceptibility of the silica-based film to strong alkali. This problem was reduced by making two modifications to the plating process. The first modification was to replace the NaOH in the plating solution with the weaker base TMAH. The second modification was to subject the Pd-coated HSQ film to a prebake prior to electroless plating The prebake was to increase the cross-linking of the silica structure to improve its resistance to alkali. The baking condition has not been optimized, but for the sake of feasibility trials, prebake

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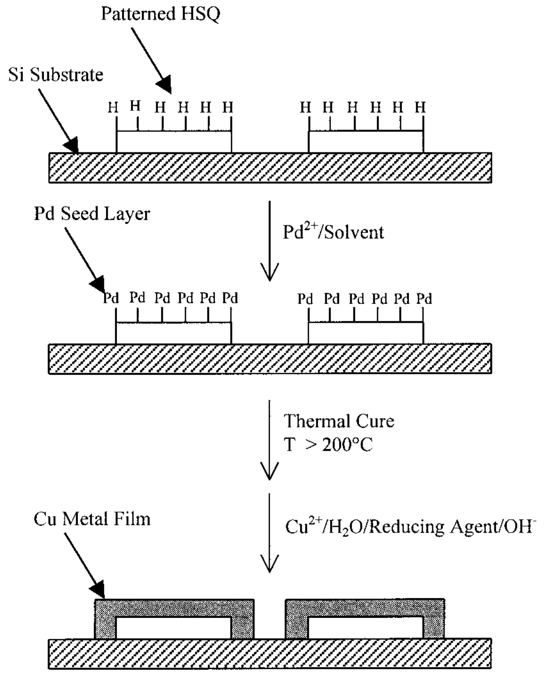

Figure 1. Illustration of the electroless copper metallization process using a silyl hydride directed Pd metal seed layer generated on the surface of a directly patterned HSQ film.

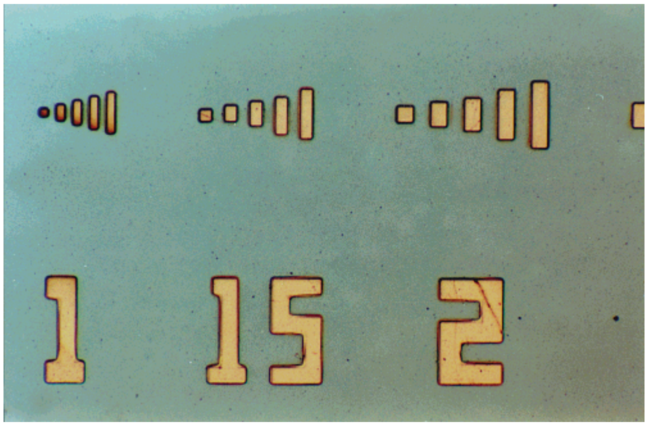

Figure 2. Photomicrograph of a directly patterned HSQ film selectively metallized with copper using a 1.5 min exposure to the copper plating solution. The widths of the line and space patterns are 10, 15, and 20 μm.

temperatures of 300 °C and above were found to offer sufficient performance to continue the study.

Electroless Cu deposition was attempted on the catalytically active Pd-coated films after a prebake at 300 °C for 1 h. Cu plating solutions differing in the type of Cu salt, the chelating agent, solution temperature and pH were examined. The best plating results were obtained from a solution containing $CuSO_4$, EDTA–diammonium salt hydrate as complexing agent, TMAH as base, and formaldehyde as the reducing agent. At a plating temperature of 50 °C a good quality Cu film with a metallic gleam selectively deposited onto the activated HSQ surface could be obtained in less than 2 min. Figure 1 illustrates the metallization process for a directly patterned HSQ film. Figure 2 shows a photomicrograph of a directly patterned HSQ film selectively metallized with Cu (1.5 min exposure to the electroless Cu plating solution). Qualitative observations of film growth indicated that the initial deposition occurred slowly but then accelerated as the film thickness increased. (The rate of H_2 gas evolution was used as an indicator.) Another observation was that Cu films with a thickness of >0.5 μm showed some delamination from the HSQ surface. In some cases, growth of the copper film was accompanied by a grainy surface texture that is characteristic of electroless deposition processes. Increasing the quantity of formaldehyde in the plating solution or increasing the bath temperature increased the rate of deposition; however, control and plating selectivity were reduced. Lowering the quantity of formaldehyde or utilizing a lower bath temperature reduced the rate of deposition and led to a more grainy surface texture.

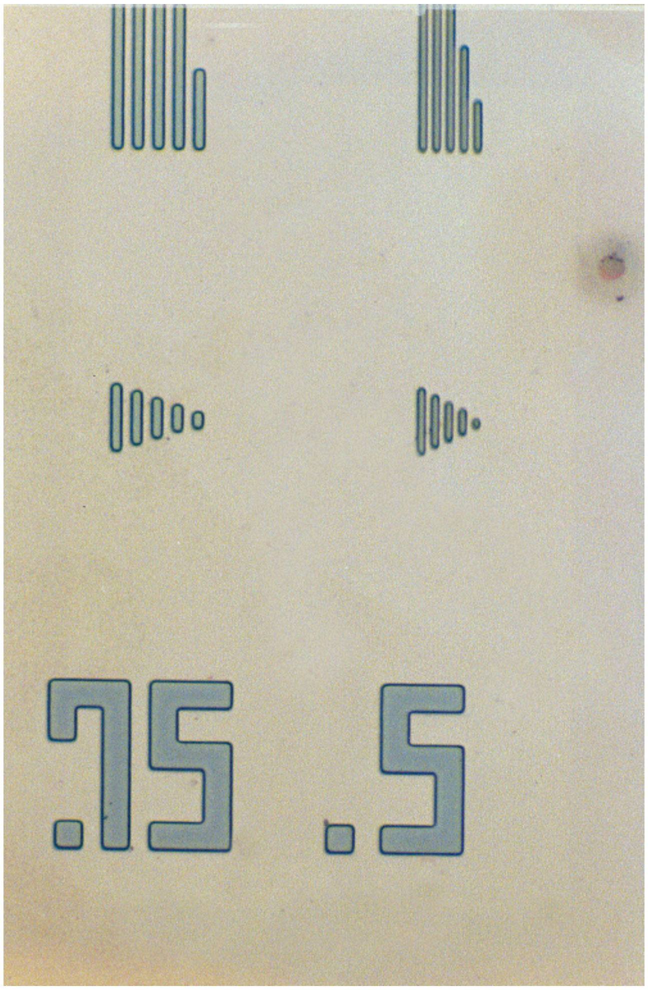

Figure 3. Photomicrograph of a Ag-metal-coated, directly patterned HSQ film (the white region corresponds to the silver-coated HSQ film and the dark areas to the silicon wafer substrate). The widths of the line and space patterns are 7.5 and 5 μm.

The same process was applied to a film of HSQ masked with a patterned resist film. The masked film was exposed to a methanolic solution of $PdCl_2$ to deposit the active Pd seed layer and then baked at 400 °C for 30 min. This resulted in cracking of the resist layer; however, its function was to direct Pd deposition, and its destruction thereafter was not expected to influence the results. Exposure of the film to the Cu plating solution resulted in selective deposition of Cu metal onto the original Pd-activated HSQ surface. No metal deposition occurred on the HSQ film originally masked by the photoresist.

Electroless Silver Deposition onto Hydrogen Silsesquioxane Films. Ag metal is typically plated from ammonical $AgNO_3$ solutions that contain a small amount of a reducing agent such as a sugar, formaldehyde, hydrazine, or dimethylamine borane.[2,13] (Silver amine complexes are potentially explosive if allowed to dry without neutralization.[2]) For this feasibility study, $AgNO_3$ was used as the metal salt with α-D-glucose as the reducing agent. Electroless silver deposition on a patterned HSQ surface activated with either a metallic Pd or Ag seed layer proved to be site specific, but the films grew slowly over several minutes while immersed in the Ag plating bath. The resultant Ag films were white in color and grainy in texture and lacked a metallic gleam.

It was later learned that Ag films could be selectively prepared from noncatalytically active HSQ surfaces (no initial Pd or Ag activation) by direct contact of the patterned HSQ film to the electroless Ag-plating solution. Immersion of a patterned HSQ film into a solution of $AgNO_3$, $NH_4OH_{(aq)}$, and α-D-glucose at 40 °C resulted in the rapid selective deposition of a Ag film with metallic gleam. Figure 3 shows a photomicrograph of a Ag-coated patterned HSQ film, where the white regions correspond to the silver-coated HSQ film and the dark areas to the silicon wafer substrate. The process occurs through an initial silyl hydride reduction of the Ag salt to deposit a seed layer that then propagates by autocatalytic electroless silver deposition. The rapidity of the one-step Ag deposition process suggests that there is some deactivation of the silver seed layer using the two-step process. According to the literature,[2] metallic Ag is only weakly autocatalytic; hence, it might be assumed that the washing and drying processes involved in generating the catalytic seed layer in the two-step process somehow reduced its catalytic activity.

A problem with the one-step Ag metallization approach was that deposition was so rapid that it was difficult to control. Selectivity was also reduced for electroless bath exposures of more than 30 s. The one-step Ag metallization process did not require a prebake of the HSQ film to enhance its resistivity to damage by the electroless plating bath. Presumably this is due to the lower pH of the Ag-plating bath and perhaps rapid Ag metallization that helps to protect the underlying HSQ film.

HSQ films prepared with a patterned resist layer were evaluated for selective Ag deposition on the exposed HSQ surfaces. Immersion of the resist patterned HSQ film into the electroless Ag plating solution resulted in rapid deposition of metallic Ag onto the silyl hydride exposed regions. Good control of the selectivity was maintained even with exposures as long as 2 min. This result suggests that the loss of selectivity observed above for the as-patterned HSQ films may be due to small residual amounts of HSQ resin remaining on the solvent-etched portions of the silicon wafer.

These results demonstrate the utility of patterned HSQ surfaces for directed electroless metallization of Cu and Ag metal features on nonconductive substrates patterned to dimensions of 5 μm and greater. Issues regarding the stability of the HSQ template to electroless deposition solutions, the mechanism and optimization of the catalytic seed layer, applicability to other metals, and the ultimate resolution of the metal deposition process provide grounds for future studies.

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