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PLASMA-ASSISTED CHEMICAL VAPOR DEPOSITION OF GOLD FOR ULSI MULTILEVEL METALLIZATION SCHEMES

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ABSTRACT

A hydrogen plasma-assisted chemical vapor deposition (PA-CVD) process was employed to deposit device quality thin gold films for multilevel intra- and inter-chip interconnect schemes. The precursor employed in the PA-CVD process was dimethyl gold acetylacetonate, DMG(acac). A low power density hydrogen plasma was employed to provide reactive hydrogen species to cleanly and efficiently decompose the gold precursor. The PA-CVD process was carried out at a chamber working pressure of 1.2 - 1.6 torr, sublimator pressure of 26 torr, hydrogen carrier gas flow rate of 1000 -1300 cc/min, substrate temperature of 170 °C, sublimation temperature of 60°C, and plasma power density of 0.2 W/cm^2. The PA-CVD gold films were characterized by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Rutherford backscattering (RBS), and four point resistivity probe. As deposited resistivities of the PA-CVD gold films on silicon substrate with a titanium barrier layer were as low as 2.76 μΩ-cm. XPS analyses indicated that the films were free from carbon and oxygen contaminants.

INTRODUCTION

As the dimensions of integrated circuit devices decrease, research towards replacement of currently used metallization materials and techniques are receiving significant attention. Gold shows promise as a multilevel inter- and intra-chip interconnect metal for ultra-large scale integration (ULSI) applications. Gold has a low bulk resistivity of 2.44 μΩ-cm, excellent corrosion resistance as compared to tungsten, aluminum and copper, and enhanced electromigration resistance compared to aluminum.[1] Also, if gold is used both in inter-chip interconnect and via fill schemes, it will not suffer from the contact resistance problems encountered when two different types of metals are used.[2] Accordingly, work in this report focuses on the development of a plasma-assisted CVD (PA-CVD) process for gold films for multilevel interconnect schemes.

PROCESS DESCRIPTION

Chemical vapor deposition (CVD) techniques are quite advantageous compared to traditional "line-of-sight" physical vapor deposition (PVD) techniques for ULSI multilevel metallization schemes. The advantages include better step coverage, complete filling of aggressive via and trench structures, high growth rate, and the ability to grow pure films with high degree of compositional control. Also, CVD involves the substrate surface in the growth process, which can lead to conformal, planarized blanket or selective deposition.

Blanket and selective thin gold films have been grown by laser induced,[3,4,5,6,7] thermal,[8,9,10] and plasma-enhanced[11] CVD techniques. The present investigators employed instead a PA-CVD process for the deposition of gold films. The PA-CVD process uses a low plasma power density of approximately 0.2 W/cm^2 to generate relatively high concentration of atomic or ionic hydrogen species. These atomic or ionic hydrogen species are key in the clean and efficient reduction of precursor molecules.

The precursor employed in the PA-CVD process was dimethyl gold acetylacetonate, DMG(acac). The present investigators employed a synthesis method that was developed by Brain and Gibson,[12] with some modifications. The complex $pyAuCl_3$ (py=pyridine; vide infra) was carefully reacted with MeMgI in diethyl ether under nitrogen. The reaction mixture was quenched, extracted with hexane and the combined organic extracts treated with ethylenediamine (en) to precipitate $[Me_2Au(en)]I$. The precipitate was re-dissolved in water and the desired $[Me_2AuI]_2$ was freed by addition of concentrated HCl. The $[Me_2AuI]_2$ was converted to DMG(acac) with commercially available K(acac)·1/2H_20 rather than the highly toxic Tl(acac) of the Brain and Gibson method. DMG(acac) is white, needle-like, air stable, crystalline solid. It has vapor pressure of 9 mTorr at room temperature. The precursor is light sensitive, although it is highly stable if stored in dark areas near 0 °C.[3]

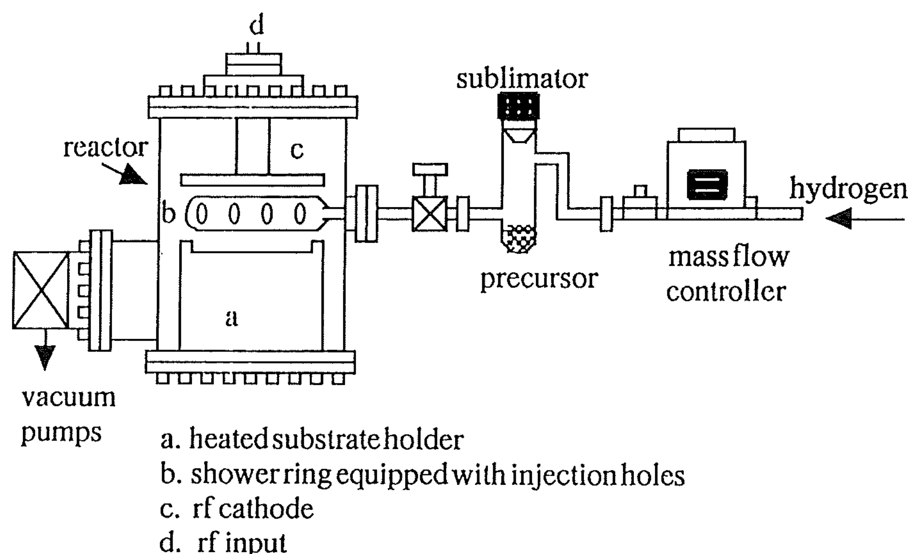

Figure 1. Schematic diagram of a gold PA-CVD reactor.

The design of the cold-wall PA-CVD reactor used to deposit gold films on five inch bare silicon and silicon with titanium barrier layer is shown in figure 1. The reactor is a stainless-steel parallel plate configuration, equipped with rf plasma capability. Between the substrate and plasma electrodes, a Pyrex gas ring, with holes specially designed to uniform gas dispersion and reactant mixing was inserted. A capacitance manometer gauge and mass-flow controller were used to measure, respectively, the pressure of the chamber and the flow rate of the hydrogen carrier gas. Prior to deposition, fifteen minutes of *in-situ* pre-deposition substrate cleaning with hydrogen plasma power density of 0.5 W/cm^2 was performed. After the plasma cleaning, the PA-CVD process was carried out with the process conditions indicated in Table I.

Table I. Process conditions for PA-CVD gold films.

Process Parameter	Value
Sublimator temperature	60°C
Substrate temperature	170°C
Pressure of sublimator	26 torr
Pressure of reactor	1.2 - 1.6 torr
Flow rate of carrier gas	1000 - 1300 cc/min
Plasma power density	0.2 W/cm^2
Growth rate	32 Å/min

The PA-CVD gold films were characterized by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), Auger spectroscopy (AES), Rutherford backscattering spectroscopy (RBS), and four point resistivity probe.

RESULTS AND DISCUSSION

X-ray Diffraction

XRD analyses of the PA-CVD gold films on Si with titanium as a barrier layers were performed utilizing a Scintag XDS 2000. Cu Kα radiation was employed at an x-ray tube operating power of 1.8 kW (which corresponds to a primary current and voltage of, respectively, 40 mA x 45 kV). Figure 2 shows XRD spectrum of the film's reflections corresponding to $2\theta = 38.3^{o}$ (111), 44.5° (200), 64.7° (220), 77.7° (311), 81.8°(222). The diffractions peaks were well matched with standard Au powder diffraction patterns, thus indicating a polycrystalline gold phase.

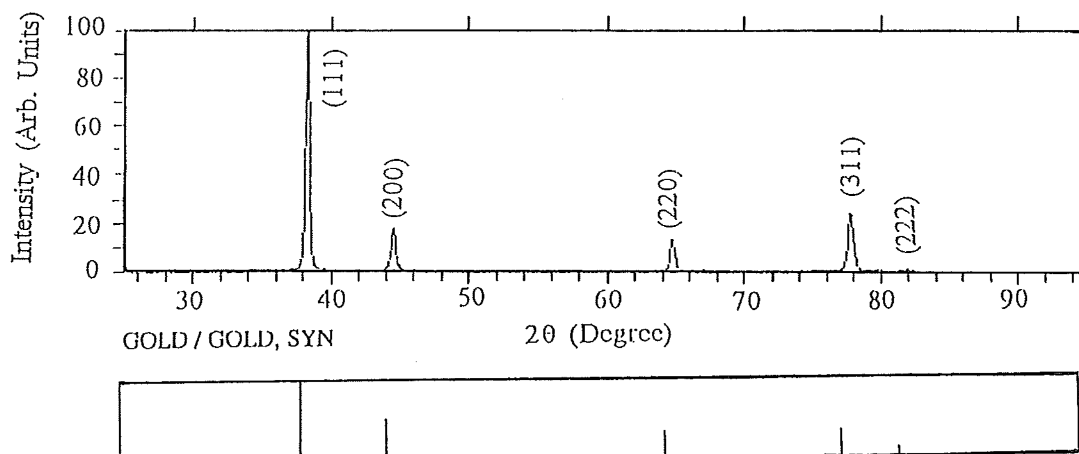

Figure 2. XRD pattern of PA-CVD gold films grown on silicon with titanium as a barrier layer indicate that the films are polycrystalline.

X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy

XPS analysis was done with Perkin-Elmer Physical Electronics Model 10-360 spherical capacitor analyzer. A Mg Kα (1253.6 eV) x-ray source at 15 KV and 300 W was used for data acquisition. Figure 3 shows typical XPS survey scan (0 - 800 eV binding energy) of PA-CVD gold film after sputtering to remove surface contaminants. The PA-CVD gold films show no oxygen and carbon contamination within the sensitivity of XPS when compared to a bulk gold standard. Auger electron spectroscopy (AES) confirmed our XPS results concerning the existence of a pure gold phase without any light element contaminants (figure 4).

Rutherford Backscattering

The 4.5 MeV Dynamitron accelerator at The University at Albany-SUNY was employed to conduct RBS experiments with a 2 MeV He^{+} beam. The calibration of the RBS data were done with a bulk gold standard. RUMP, a simulation program, was used for data reduction and simulation. Figure 5 shows an RBS spectrum confirming XPS and AES analyses that the gold film deposited on silicon with a titanium barrier layer is free from any detectable contamination. A Signatone four-point-probe was employed to measure film resistivity. The as-deposited PA-CVD gold film resistivity deposited on silicon with a titanium barrier layer was

as low as 2.76 μΩ-cm, compared to gold's bulk resistivity of 2.44 μΩ-cm. Typical PA-CVD gold film properties are shown in Table II.

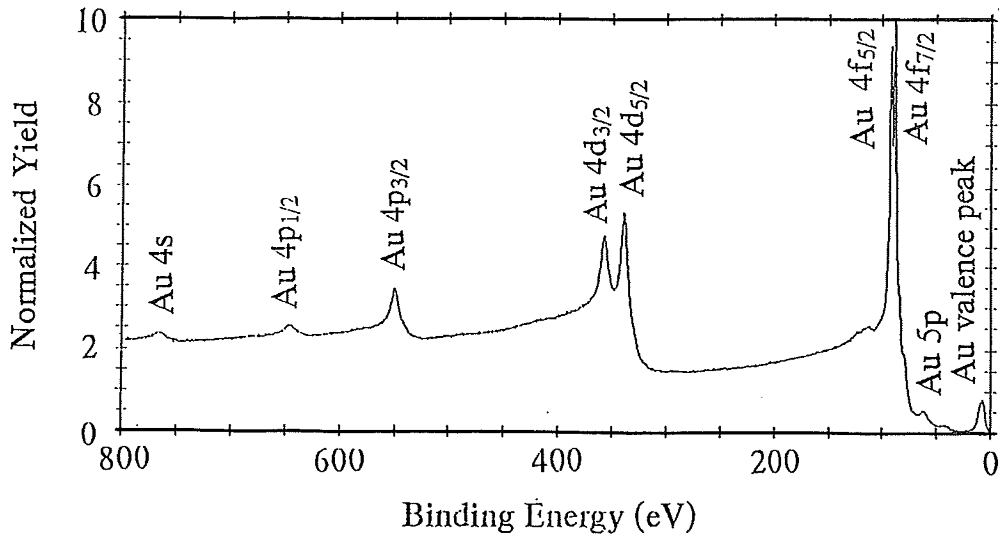

Figure 3. XPS spectrum of PA-CVD gold films grown on silicon with titanium as a barrier layer indicates that the films are pure, with no carbon or oxygen contamination.

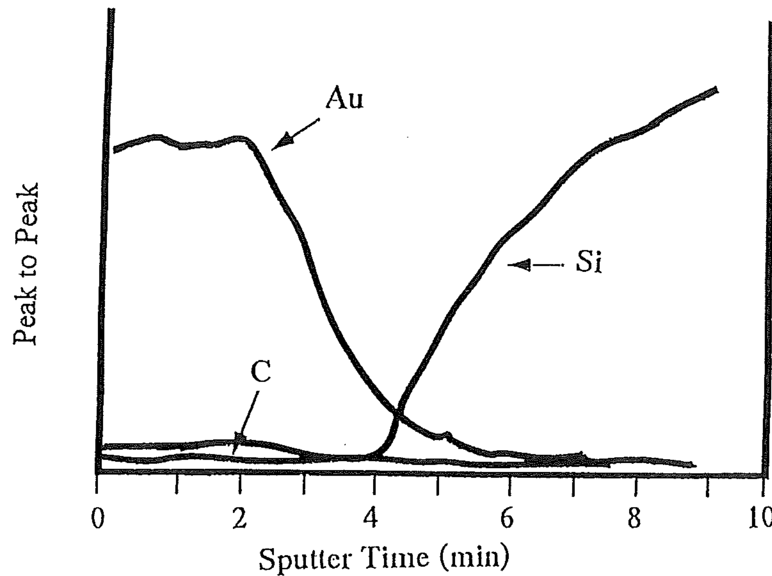

Figure 4. AES spectrum of PA-CVD gold films grown on silicon with titanium as a barrier layer confirm the XPS findings concerning film purity.

SUMMARY

In summary, a PA-CVD gold process has been developed for multilevel intra and inter-chip interconnect schemes. A low plasma power density of approximately 0.2 W/cm^2 was employed to provide reactive hydrogen species to cleanly and efficiently decompose the gold precursor. The gold films deposited on bare Si or Si with a titanium barrier layer were pure, specular, continuous, exhibited polycrystalline microstructure, and possessed a deposited

resistivities as low as 2.76 μΩ-cm. However, additional development work is required to identify an optimized processing window for the growth of gold films at more industrially acceptable growth rates (>2500Å/min).

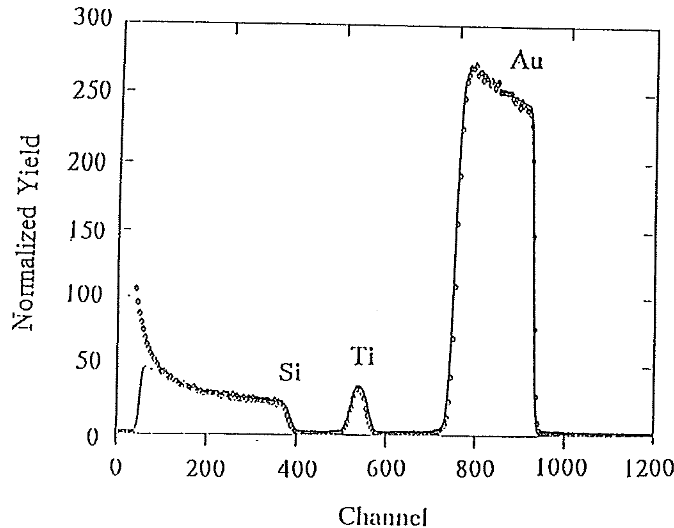

Figure 5. RBS spectrum of PA-CVD gold films grown on silicon with titanium as a barrier layer confirms the XPS findings concerning film purity, and demonstrates the lack of any gold-substrate inter-diffusion.

Table II. Typical quality of PA-CVD gold films.

Purity	> 99%
Best as deposited resistivity	2.76 μΩ-cm
Crystal structure	Polycrystalline
Thickness	0.27 -0.60 μm

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