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Low Temperature In-Situ Sequential Chemical Vapor Deposition of Ti/TiN
Ultrathin Bilayers for ULSI Barrier Applications

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ABSTRACT

With the emergence of ULSI technologies come increasingly restrictive demands on the properties and performance of barrier layers/adhesion promoters used in the metallization of integrated circuits. Accordingly, work by the present investigators has focused on the development of Ti/TiN ultrathin (<300Å) bilayers using a low temperature in-situ sequential chemical vapor deposition process with features designed for compatibility with cluster tool technology for emerging microelectronic applications. The Ti layers were deposited using a single source precursor, tetraiodotitanium (TiI₄), in conjunction with plasma assisted chemical vapor deposition (PA-CVD) in an argon and hydrogen plasma at low plasma density powers (0.03 to 0.16 W/cm²). Alternatively, TiN films were deposited from TiI₄ in a thermal CVD approach in the presence of ammonia, hydrogen and argon. The use of a single source precursor thus allows the in-situ formation of Ti/TiN bilayers by sequential deposition in a single reactor under a low temperature (<450°C) processing regime. This paper presents progress to-date from screening studies which focused on identifying optimum processing conditions and developing process parameters-properties-performance relationships. These studies led to the production of films with excellent step coverage, high purity, low resistivity, stoichiometric (1:1) TiN, and formation of a titanium/silicon alloy at the interface of deposited titanium film.

INTRODUCTION

Current microelectronics technologies employ barrier layers in the metal interconnect to prevent interactions between the metal layers and surrounding dielectric layers. These barrier layers must also serve as strong adhesion promoters, in addition to preventing interdiffusion. They also must possess low contact resistivity, be easy to etch, and be able to withstand repeated thermal processing.¹

Due to their highly desirable physical and chemical attributes, titanium and titanium nitride are considered among the most suitable materials for such applications in both present and emerging device generations. They are refractory metals with high melting points and excellent resistance to corrosion. They also possess good thermal and electrical conductivity, high specific strength at elevated temperatures, and significant mechanical, chemical, and thermal stability.² In addition, titanium serves as an ideal getter for oxygen, when used as intermediate between Si and TiN, thus providing stable ohmic contact to silicon, and as a "wetting layer" for subsequent aluminum or tungsten deposition, when used over TiN.³ This wetting layer enhances the mobility of aluminum or tungsten atoms and leads to improved step coverage.

Although physical vapor deposition (PVD) techniques of Ti/TiN films have successfully met the demands of very large scale integrated (VLSI) circuitry, they have not, as yet, demonstrated the ability to comply with the requirements of the sub-quarter-micron circuitry embodied in emerging ultra large scale integrated (ULSI) technologies. Even at the half micron level, PVD techniques result in non-conformal coverage, with significant thinning at via and trench edges and walls. This problem is often compounded by columnar growth and trapped sputter gases within the deposited films.⁴⁻⁶ Collimated reactive sputtering has produced improved step coverage, but also resulted in reduced throughput, undesirable particulate generation and increased sensitivity to processing conditions.⁷

In view of the limitations of PVD methods, the focus of much current research in Ti/TiN technologies has been on chemical vapor deposition (CVD). CVD has a proven ability to produce conformal coatings on large area substrates with complex topographies at industrially viable growth rates. In addition, in thermal CVD, the catalyzing role of the substrate might lead, under appropriate conditions, to selective film growth. However, most efforts to-date have failed to produce high purity Ti/TiN films with conformal step coverage for substrates having holes and trenches with diameter of 0.25 μm or less (aspect ratios of 4:1 or higher).

In the case of Ti, most efforts have concentrated on metal-organic CVD (MOCVD) using Ti sources such as tetra-nepentyl-titanium $(\text{Me}_3\text{CCH}_2)_4\text{Ti}$ and sila-nepentyltitanium $(\text{Me}_3\text{SiCH}_2)_4\text{Ti}$,⁸ as well as cyclopentadienyl-based compounds.⁹ However, these processes produced films with high resistivity and carbon and oxygen contamination in excess of ten atomic percent.

In the case of TiN, deposition has concentrated on thermal CVD from titanium tetrachloride (TiCl_4) and ammonia (NH_3).¹¹⁻¹³ The resulting films exhibited low resistivities (50 to 100 $\mu\Omega\text{-cm}$), good step coverage, and chloride contamination below one atomic percent. But the need for processing temperatures in excess of 650°C have prohibited the implementation of this process above the contact level. Other TiCl_4 -based CVD alternatives were explored, including plasma-assisted CVD (PA-CVD) using nitrogen and hydrogen, atmospheric pressure CVD (AP-CVD) with isopropylamine, and electron cyclotron resonance CVD (ECR-CVD) in nitrogen.^{14,15} The films thus produced exhibited poor step coverage of 30 to 70%, resistivities above 200 $\mu\Omega\text{-cm}$, and chloride contamination of several atomic percents. MOCVD of TiN involved testing dialkylamino derivatives of titanium, single source precursors such as $\text{TiCl}_2(\text{NHR}_2)(\text{NH}_2\text{R})$ ¹⁶ and $\text{TiCl}_4(\text{NR}_3)$,¹⁷ cyclopentadienyl based compounds,¹⁸ and diimine analogs of β -diketonates.¹⁹ All of these processes have resulted in films with poor step coverage (<70%), high resistivities (>200 $\mu\Omega\text{-cm}$), and high levels of contamination (up to 50 atomic percent hydrogen and several atomic percent carbon).

Clearly, a critical need exists for an integrated CVD process for the non-columnar growth of high purity Ti/TiN ultrathin layers with low resistivity and excellent conformality in 0.25 μm structures and which is compatible with cluster-tool based manufacturing for ULSI device fabrication. To meet this need, work by the present investigators has focused on the development of a low pressure, low temperature CVD process for the deposition of Ti/TiN bilayers using tetraiodotitanium (TiI_4) as the source precursor. The process is designed for the in-situ sequential deposition of titanium and titanium nitride from simple inorganic source precursors by smooth and easy variations in the processing conditions.

The strategy espoused is to use simple inorganic titanium complexes where the dissociation energy of primary bonds is relatively low and recombination can be interrupted by the presence of hydrogen or nitrogen to yield, respectively, titanium or titanium nitride. Tetraiodotitanium (TiI_4), which belongs to the same class of halide chemistries as TiCl_4 , was selected as the source precursor because of desirable energetic considerations. Its heat of formation is -92 kcal/mole, as compared to -192 kcal/mole for TiCl_4 , which implies that the dissociation of primary bonds in TiI_4 should occur at lower temperatures than TiCl_4 . This is in agreement with studies on related chemistry systems for Ti^{III} chemistries, where it was been observed that the threshold temperature for disproportionation decreases with increasing halogen, with

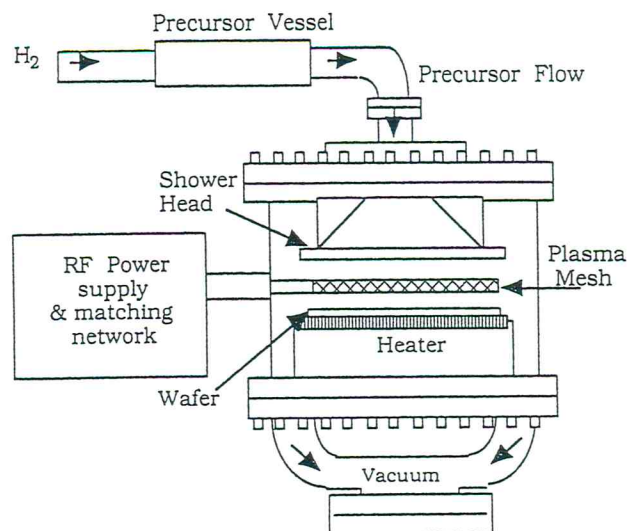
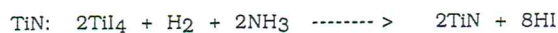


Figure 1: Schematic diagram of chemical vapor deposition reactor used for growth of Ti & TiN films.

TiI₃ disproportionating at 100°C lower than TiCl₃.²⁰ While the chemistry of Ti^{III} systems is not exactly analogous to that of Ti^{IV} systems, the disproportionation study summarized above presents additional clear indication of the ability of iodides to undergo dissociation and recombination reactions at temperatures considerably lower than chlorides and consistent with the energetics of the Ti-halogen bond energies.

In the case of TiI₄, it is expected that Ti-I recombination can be interrupted by the presence of hydrogen and/or nitrogen to form Ti or TiN as follows:



This paper presents progress to-date from screening studies which aimed at determining optimum processing conditions for Ti and TiN CVD and developing process parameters-properties-performance relationships. Results are presented from three separate, but complementary, activities. The first activity has focused on the successful identification of a process window for thermal CVD TiN from TiI₄ which extends existing high temperature TiCl₄-based CVD TiN technology to lower temperatures (375-450°C). The second activity was directed at developing a Ti PA-CVD processing regime which is compatible with TiN thermal CVD. Finally, results are presented from the demonstration of an in-situ sequential Ti/TiN CVD process which can be smoothly and reversibly changed between Ti and TiN by simple modifications in the processing conditions.

EXPERIMENTAL CONDITIONS

All TiN, Ti, and Ti/TiN bilayer depositions were performed in a customized designed, 8" wafer, warm wall stainless steel CVD reactor which is capable of both thermal and plasma-assisted CVD, as shown in figure 1. It is equipped with a

Table I. Optimum Deposition Conditions for TiN and Ti films

Material	TiN	Ti
Source	TiI ₄	TiI ₄
Process	Thermal	Plasma-Assisted
Working Pressure	200-350 mtorr	200-400 mtorr
Carrier Gas	H ₂ (20-60 sccm)	H ₂ (20-60 sccm)
Reactant	NH ₃ (400-600 sccm)	Ar (400-600 sccm)
Sublimation T	100-160°C	100-160°C
Substrate T	375-450°C	400-450°C
Plasma Power Density	0.0	0.15 W/cm ²
Growth Rate	300-500 Å/min	-----

Table II. Optimum Film Properties (TiN)

Property	Substrate T	
	<375°C	>375°C
Purity	O (5-30 at%)	> 99 at% TiN
As deposited ρ	up to 6700 $\mu\Omega\text{cm}$	44-288 $\mu\Omega\text{cm}$
Adherence	-----	Good on Si & SiO ₂
Color	Gold, Purple, Brown	Gold
Structure	(200)	(111)

parallel plate plasma (radio frequency of 13.56 MHz) configuration and a high vacuum load lock for sample transfer and handling. The substrate was placed on the heated bottom (ground) electrode, and a specially designed shower head provided uniform gas dispersion and reactant mixing. Electronic mass flow controllers were used to measure the flow rate of carrier gas, and process pressures were monitored with capacitance manometer gauges. A cryogenic pump system ensured reactor cleanliness, while a roots blower stack was used for process pumping during deposition runs because of the high flow and pressure conditions involved. Unpatterned Si and SiO₂ samples were employed for basic process and material characterization, while patterned substrates, with via and trench structures ranging from 0.25 μm (4:1 aspect ratio) to 0.8 μm (2:1 aspect ratio) were used for step coverage and conformality studies. Silicon substrates were precleaned with trichloroethylene, acetone, methanol, water, hydrofluoric acid solution, then water, and immediately loaded into the reactor. Silicon dioxide substrates were precleaned with methanol. After sample loading, a hydrogen plasma was used for in situ substrate cleaning prior to deposition. The substrate was heated to the desired deposition temperature, and film growth was initiated once the precursor vessel was heated to a preset temperature.

In the case of TiN, work focused on the identification of a process window for thermal CVD TiN from TiI_4 which extends existing high temperature ($>600^\circ\text{C}$) TiCl_4 -based CVD TiN technology to lower temperatures ($375\text{--}450^\circ\text{C}$). Accordingly, Table I summarizes the optimum deposition conditions for thermal CVD TiN from TiI_4 .

For Ti, work was directed at developing a low temperature Ti PA-CVD processing regime which is compatible with TiN thermal CVD. The corresponding optimum process window is summarized in Table I.

Finally, the two processing regimes described in Table I were combined to successfully demonstrate the in-situ sequential CVD of Ti/TiN by smoothly and reversibly changing between PA-CVD of Ti and thermal CVD of TiN by simple modifications in the processing conditions as shown in Table I.

The Ti and TiN films thus produced were metallic, continuous, silver (Ti) and gold (TiN) colored. Their structural and electrical properties as well as chemical composition, were thoroughly analyzed by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), Rutherford backscattering (RBS), four point probe, and cross-sectional SEM (CS-SEM). XPS measurements were performed using a Perkin-Elmer Physical Electronics Model 10-360 spherical capacitor analyzer. The gold $f_{7/2}$ line at 83.8 eV was taken as reference line and the analyzer calibrated accordingly. All spectra were obtained using a pass energy of 5 eV at a resolution of 0.8 eV. A primary x-ray beam (Mg $K\alpha$, 1274eV) of 15 keV and 300 W was employed. The analysis chamber pressure was in the 10^{-10} torr range, and the results were standardized using a sputtered TiN sample. All samples were sputter cleaned before data acquisition. The choice of a standard of composition and chemical environment and bonding similar to that of the CVD films allowed high accuracy in XPS analysis. The results are based on chemical and structural changes, if any, induced during the sputter cleaning process are basically the same in the standard and CVD produced films. Rutherford backscattering (RBS) spectra were taken using a 2 MeV He^{2+} beam, and calibrated with a bulk sample of silicon. Cross-section SEM analysis were carried out on a Zeiss DSM940 microscope, employing a 20 keV primary electron beam and a beam current of 4 μA . XRD studies were carried-out on a Scintag XDS 2000 with Cu $K\alpha$ radiation employed at an x-ray tube operating power of 1.8 kW (40 mA x 45 kV).

RESULTS AND DISCUSSION

1. Thermal CVD of TiN

Optimum film properties for the thermal CVD grown TiN films are summarized in Table II. In particular, XRD analyses of the TiN films grown at 400°C , as shown in Fig. 2 for a 1000Å-thick film on Si, showed a polycrystalline TiN phase with major diffraction peaks

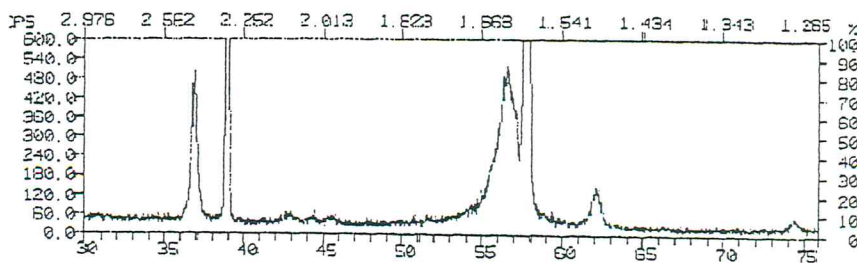


Figure 2 XRD diffraction spectrum of TiN film.

appearing at $2\theta=36.66^\circ$ (111), 42.59° (200), 61.81° (220), and 74.07° (311).

The XPS depth profile spectrum (Fig. 3) indicated that, within the detection limits of XPS, the TiN films were free of oxygen, carbon, and similar light element contaminants. The inclusion of the x-ray sensitivity factors in the peak-to-peak spectra of figure 3 yields an XPS atomic concentration profile which shows a stoichiometric TiN film. The presence of iodine concentrations, ranging from 0.4-1.5 at%, were detected in the films. Rutherford backscattering (RBS) spectra were taken using a 2 MeV He^{2+} beam, and calibrated with a bulk sample of silicon. The RBS results, shown in Fig. 4 for a 1000Å-thick TiN film on silicon oxide, confirmed the XPS findings that the CVD process yields TiN films with low iodine contamination (<1.5 at%).

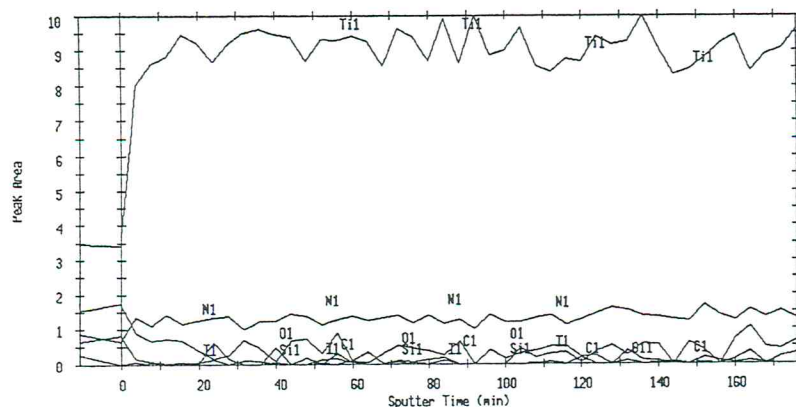


Figure 3 XPS depth profile spectrum of TiN from TiI_4 .

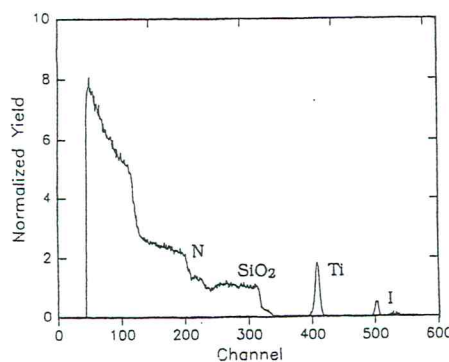


Figure 4 RBS spectrum of CVD TiN on SiO_2 .

Four-point probe resistivity measurements yielded film resistivities ranging from 44 to $288 \mu\Omega\text{cm}$ for film thicknesses from, respectively, < 300Å to 1000Å. Cross-section SEM analysis were carried out on a Zeiss DSM940 microscope, employing a 20 keV primary electron beam and a beam current of 4 μA . The SEM micrographs (Fig. 5) of TiN films in via and trench structures ranging from 0.25 μm (4:1 aspect ratio) to 0.8 μm (2:1 aspect ratio) show step coverage of better than 90%.



Figure 5 SEM micrographs of TiN film

2. *Plasma-Assisted CVD of Ti*

Optimum film properties for the PA- CVD grown Ti films are summarized in Table III. In this case, XRD analyses of the Ti films grown at 400°C, as shown in Fig. 6 for a 1000Å-thick film on Si, showed a hexagonal Ti phase. The XPS depth profile spectrum indicated that, within the detection limits of XPS, the Ti films deposited below 425°C (Fig. 7) contained up to 20 at% oxygen, while films deposited above 425°C were free of oxygen but exhibited significant interactions with the underlying Si substrate (Fig. 8). No carbon or any other light element contaminants were observed in the films, regardless of substrate temperature. The presence of I was detected at levels similar to those seen for TiN. RBS results confirmed the XPS findings concerning film purity and composition (Fig. 9). Four-point probe resistivity measurements yielded film resistivities in the range 75-91 $\mu\Omega\text{cm}$ for films produced below 400°C for film thicknesses of 100-250Å.

Table III. Optimum Film Properties (Ti)

Property	Substrate T	
	375<T<425°C	>425°C
Purity	O (<20 at%)	pure Ti (begins reacting with Si)
As deposited ρ	75-91 $\mu\Omega\text{cm}$	-----
Adherence	Good on Si & SiO ₂	
Color	Metallic Silver	Metallic Silver
Structure	hexagonal	hexagonal

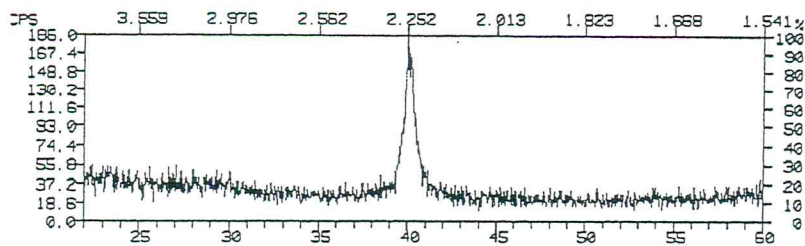


Figure 6 XRD of PA-CVD Ti.

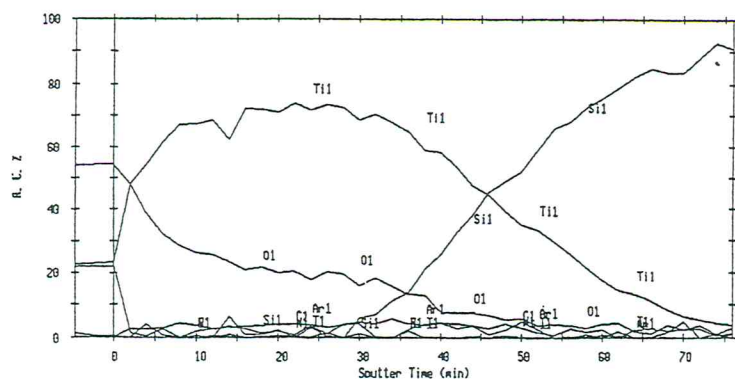


Figure 7 Typical XPS spectrum of PA-CVD Ti grown below 425°C.

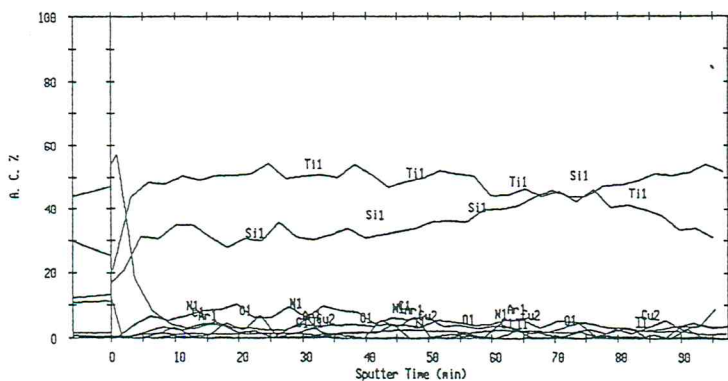


Figure 8 Typical XPS spectrum of PA-CVD Ti grown above 425°C.

3. PA-CVD Ti and Thermal CVD TiN Bilayers

A typical XPS spectrum of a Ti (~100Å)/TiN (~200Å) bilayer deposited on silicon is shown in figure 10. As can be seen in the figure, nitrogen concentration decreases within 200Å from film surface to below the detection limits of XPS indicating a smooth transition from a TiN phase to a Ti phase. As one continues ion sputtering, the Ti

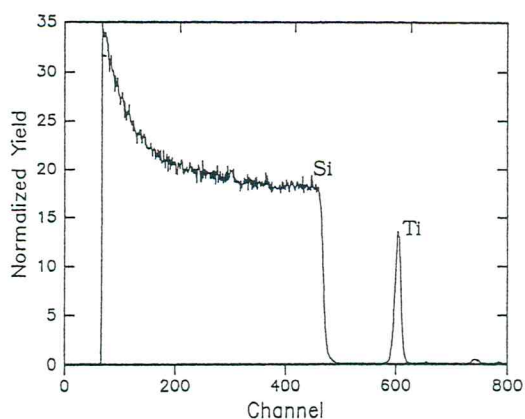


Figure 9 RBS spectrum of PA-CVD Ti grown below 425°C.

concentration similarly decreases within about 100Å from the Ti/TiN interface and is slowly replaced with a silicon signal from the substrate. Since the Ti films were deposited above 425°C, significant interactions are observed with the underlying Si substrate. No carbon, oxygen or any other light element contaminants were observed in the films. The presence of I was detected at levels similar to those seen for individual Ti and TiN films. Two dimensional XPS plots of elemental core level peaks confirmed the findings shown in figure 11 and indicated a clear shift from a TiN phase to a Ti phase within the bilayers. These results are summarized in figure 12 which shows a shift from a binding energy for the surface Ti of 455.2 eV, corresponding to TiN phase, to a binding energy of 454.4 eV, which corresponds to metallic Ti, within the bilayer.

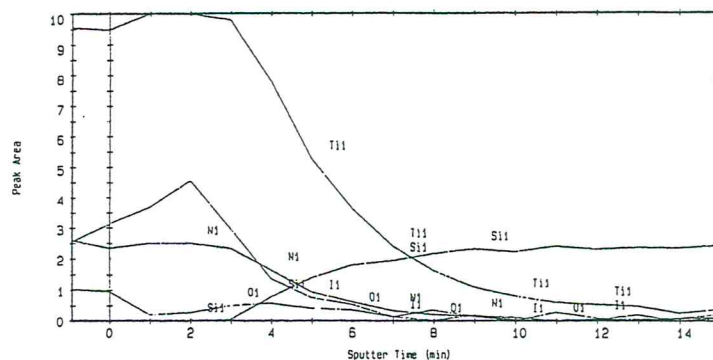


Figure 10 Typical XPS spectrum of in-situ sequentially grown Ti/TiN bilayers.

CONCLUSIONS AND FUTURE DIRECTIONS

In summary, Ti/TiN ultrathin (<300Å) bilayers have been successfully grown using a low temperature in-situ sequential chemical vapor deposition process with

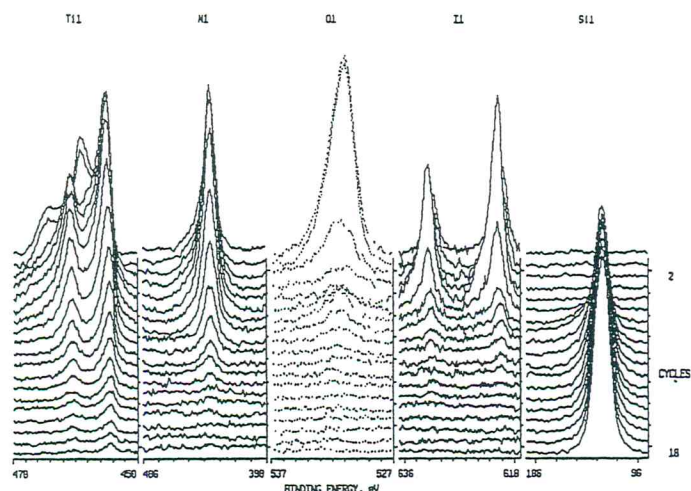


Figure 11 Two-dimensional XPS plots of core peaks versus film thickness for Ti/TiN bilayers.

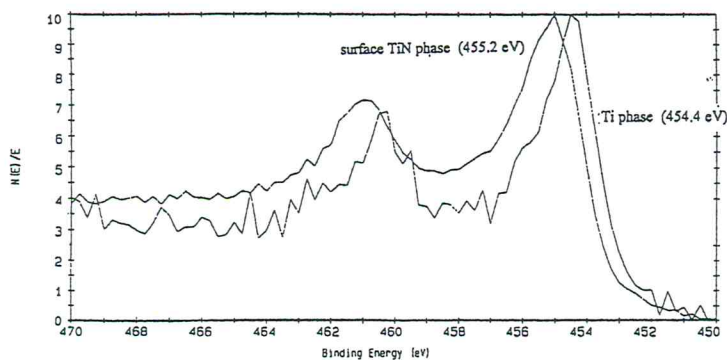


Figure 12 XPS core level peaks indicate a shift from a surface TiN phase to a Ti phase.

features designed for compatibility with cluster tool technology for emerging microelectronic applications. The Ti layers were deposited using a single source precursor, tetraiodotitanium (TiI_4), at substrate temperatures in the range 400-450°C in conjunction with plasma assisted chemical vapor deposition (PA-CVD) in an argon and hydrogen plasma at low plasma density powers (0.03 to 0.16 W/cm²). Alternatively, TiN films were deposited from TiI_4 in a thermal CVD approach in the presence of ammonia, hydrogen and argon at substrate temperatures in the range 375-450°C. The use of a single source precursor thus allows the in-situ formation of Ti/TiN bilayers by sequential deposition in a single reactor under a low temperature (<450°C) processing regime.

Further studies are presently underway to:

- Perform gas phase and surface mechanistic studies using Fourier-transform infrared spectroscopy (FTIR) and quadrupole mass spectroscopy (QMS) to

study the gas phase evolution of reactants and TiI_4 fragmentation patterns under real CVD processing conditions. The purpose is to develop mechanistic models for precursor decomposition and identify high yield pathways to the formation of pure Ti.

- Carry-out Design of Experiments and Modeling activities, using RS-1 Discover in conjunction with SPEEDIE, to develop optimized processing regimes for thermal and plasma-assisted CVD of Ti and TiN.
- Examine the effect of iodine on the electrical properties and performance of the ultrathin Ti/TiN bilayers and determine maximum allowable iodine concentration levels, if any.

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