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A Mechanism for Selectivity Loss during Tungsten CVD

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ABSTRACT

We have investigated possible mechanisms for the loss of selectivity (*i.e.*, deposition on silicon dioxide) during tungsten CVD by reduction of tungsten hexafluoride and found strong evidence that selectivity loss is initiated by desorption of tungsten subfluorides formed by the reaction of WF_6 with metallic tungsten surfaces. Adsorption and disproportionation of the tungsten subfluorides on the silicon dioxide surface produces a reactive state of tungsten that can lead directly to selectivity loss. The key feature of the experimental setup is the ability to independently heat a tungsten foil and a nearby oxide-covered silicon sample in the presence of tungsten hexafluoride. With the tungsten foil at 600°C and the SiOy Si sample at \sim 30°C under a WF₆ ambient, a tungsten subfluoride was found to deposit on the SiO₂ surface. Auger electron spectroscopy was used to measure a F/W ratio of 3.7 ± 0.5. Heating this tungsten subfluoride overlayer resulted in disproportionation to yield gas-phase WF₆ and metallic tungsten which remained on the surface. With the tungsten foil at 600° C and the SiO₂/Si sample at 300°C in the presence of WF_6 , metallic tungsten deposited directly on the SiO₂ without stopping at the subfluoride adsorption step. The net effect of this tungsten subfluoride desorption-disproportionation mechanism is the transport of tungsten from tungsten surfaces to silicon dioxide surfaces as well as other regions in the deposition chamber. Extrapolated rates for this process are high enough to explain the magnitude of the selectivity loss seen at normal CVD temperatures.

Low pressure CVD of tungsten by reduction of WF₆ has many promising applications for the fabrication of VLSI devices (1-6). These applications include formation of diffusion barriers and planarization for multilevel interconnects. Tungsten CVD is attractive for most applications because of the selective nature of the deposition chemistry, i.e., deposition occurs on silicon and tungsten (and some other metals) but not on SiO₂ or other typical insulators. The selective nature of the deposition produces selfaligning structures and therefore significantly reduces the number of steps required for a metallization process. Unfortunately, it is not always possible to maintain selectivity indefinitely as tungsten may nucleate and grow on the insulator surfaces. The purpose of this study is to determine the fundamental mechanism(s) of selectivity loss (i.e., tungsten nucleation and growth on insulators) with hopes that this information will be useful for devising ways of enhancing selectivity.

Selectivity is the result of a deposition mechanism which is strongly controlled by heterogeneous processes. Dissociative chemisorption of hydrogen and tungsten hexafluoride are thought to be necessary heterogeneous steps in the deposition mechanism (2, 7). Several researchers have noted that selectivity loss usually first occurs on surfaces near, but not necessarily contiguous with, areas of tungsten deposition (5, 8, 9). This observation strongly suggests that a volatile reaction product, by-product, or intermediate is initiating selectivity loss. For deposition on silicon, the first reaction occurring is the silicon reduction of tungsten hexafluoride, *i.e.*, 3/2 Si(s) + WF₆(g) $\rightarrow 3/2$ SiF₄(g) + W(s). Several authors have postulated that silicon tetrafluoride or other silicon-bearing species produced by this

initial reaction may contribute to selectivity loss (5, 9). We note that if such a mechanism exists it could not explain the selectivity loss often observed during deposition when there is initially no exposed silicon. The primary reaction responsible for tungsten deposition is the hydrogen reduction reaction, *i.e.*, $3H_2(g) + WF_6(g) \rightarrow 6HF(g) + W(s)$, in which a large amount of hydrogen fluoride is produced. Hydrogen fluoride is known to react with silicon dioxide under some conditions and has also been suspected of initiating selectivity loss (8). However, our experiments investigating the role of HF failed to establish a definitive link between the HF partial pressure and the degree of selectivity loss. We have instead found convincing evidence for a mechanism that first involves the formation of volatile tungsten subfluorides (WF_x, x < 6) on tungsten surfaces. These subfluorides desorb from the tungsten surfaces and may diffuse through the gas phase. The adsorption and disproportionation of the tungsten subfluorides on SiO₂ surfaces then produces a reactive state of tungsten that can immediately catalyze the hydrogen reduction of tungsten hexafluoride.

When formulating an experimental approach, one is first confronted with the difficulty of detecting the species responsible for selectivity loss produced under actual CVD conditions. A very small surface concentration of "nucleation sites" can lead to a dramatic loss of selectivity, as illustrated schematically in Fig. 1. If an oxide surface were to become covered with "nucleation sites" to a density of 10⁸/cm² and tungsten particles were then grown at these sites to a thickness of 3000Å (or diameter \approx 6000Å), then approximately 25% of the surface would be covered with tungsten. Since a "nucleation site" is probably a very small



Fig. 1. Diagram illustrating the sensitivity of tungsten CVD to very small concentrations of "nucleation sites."

cluster of atoms, then even for this rather severe example there would be few if any techniques capable of detecting such a small initial concentration ($\leq 10^{-6}$ of a monolayer). One must use experimental conditions and procedures that increase the concentration of the critical species, and therefore accentuate the selectivity loss mechanism.

Experimental

These experiments were performed in a dual chamber vacuum system composed of a reaction chamber and a UHV analysis chamber (see Fig. 2). The analysis chamber was equipped with a cylindrical mirror analyzer (CMA) for Auger spectroscopy and a quadrupole mass spectrometer for TPD (temperature programmed desorption). This chamber was pumped with a turbomolecular pump to a base pressure of less than 2×10^{-10} torr. The reaction chamber was also pumped by a turbomolecular pump to a base pressure of $\approx 5 \times 10^{-9}$ torr. However, due to the large number of samples studied, the working base pressures as high as 300 mtorr were used during the CVD experiments, the turbopump for the reaction chamber was throttled to give a nitrogen pumping speed of ≈ 1.3 1/s.

The samples were 2 cm \times 1 cm \times 0.5 mm rectangular slices of 0.4 Ω -cm Si(100) which were covered with 400Å of thermally grown silicon dioxide. Samples were etched for 15s in a 20:1 NH₄F/HF solution and rinsed with distilled water. Cross-section TEM shows that \approx 270Å of oxide remains after this step. These samples were mounted on a long-throw manipulator by means of tantalum clips which allowed direct resistive heating to above 800°C. For temperature measurements, a Chromel-Alumel thermocouple was attached to the top edge of the samples with a small drop of ceramic cement (Aremco no. 516). By opening a straight-through valve, a sample could be moved from the reaction chamber into the UHV chamber for surface analysis within a few minutes after deposition is terminated.

A polycrystalline tungsten foil was also mounted in the reaction chamber about 3 cm upstream from the silicon

VACUUM SYSTEM SCHEMATIC



Fig. 2. Schematic of dual chamber vacuum system

sample and served as an independent source of reaction products and intermediates. This experimental arrangement proved essential for this study. The foil was heated resistively, and the temperature was measured with a Chromel-Alumel thermocouple spot-welded to the middle of the foil.

When performing AES on fluorinated tungsten species, it is particularly important to minimize electron beam damage. Low electron beam currents (1-2 μ A) were used and the beam was defocused until it was slightly less than the area analyzed by the CMA (~100 μ diameter spot). Since electron beams usually result in the desorption of fluorine from the surface, the fluorine region of the spectra were typically scanned first to obtain the highest possible fluorine signal.

Results and Discussion

The effect of hydrogen fluoride.—Our initial experiments focused on the possible role of HF as an initiator of selectivity loss. These experiments involved flowing additional amounts of HF through the reactor under otherwise typical CVD conditions to see if there was any noticeable increase in the amount of tungsten deposited on the oxide surface. No effort was made to quantify low densities of tungsten particles, but high densities are measurable with Auger spectroscopy. All experiments using additional HF(g) at pressures ranging from 1-100 mtorr failed to produce measurable tungsten coverages, *i.e.*, $\geq 1\%$ of a monolayer. The following experiment exemplifies this point. The SiO₂/Si sample was heated to 400°C in the presence of 5 mtorr WF_6 , 40 mtorr H_2 , and 100 mtorr HF at the aforementioned pumping speed. After 60 min, tungsten coverage was still below Auger detection limits (see Fig. 3). These experiments show that for the conditions studied HF plays no major role in the selectivity loss mechanism. During the experiments described in the sections that follow, no additional HF was injected into the reaction chamber.

Formation and disproportionation of tungsten subfluorides.-We then searched for possible reaction intermediates or by-products (other than HF) generated by tungsten surfaces in contact with the reactant gases. For these experiments, the additional tungsten foil in the reaction chamber proved invaluable. An Auger spectrum of the SiO₂ surface was first recorded to serve as a reference spectrum [see curve a, Fig. 4]. The silicon and oxygen peaks are indicative of SiO_2 , and the absence of carbon indicates the lack of significant hydrocarbon contamination. A very small fluorine signal is probably residual from the NH₄F/HF etch performed just before sample installation in the vacuum system. With the SiO₂/Si sample near room temperature while in the reaction chamber, WF₆ was introduced to a pressure of 5 mtorr and an approximate flow rate of 2 mtorr-liter/s. The tungsten foil was heated to 600°C for 90 min, then cooled and the chamber evacuated. While the foil was hot, the SiO₂/Si sample temperature would usually rise to 30°-40°C due to radiation and/or gas-phase conduction. Then the sample was transferred into the



Fig. 3. Auger spectra of: (a) initial SiO_2 surface, (b) surface after tungsten CVD conditions (see text) with additional 100 mtorr HF flowing in reaction chamber.

UHV chamber and an Auger spectrum recorded [curve b, Fig. 4]. Note the presence of tungsten and fluorine signals as well as the complete attenuation of the silicon signal. Quantification of the Auger signals indicates a WF_x stoichiometry of $X = 3.7 \pm 0.5$. This quantification was performed by measuring the WO₃ Auger spectrum and using the relative sensitivities of fluorine and oxygen to obtain the F/W ratio (10). This value would indicate the presence of a tungsten subfluoride, probably tungsten tetrafluoride or a mixture of such compounds. We know that the tungsten subfluoride(s) must originate at the tungsten surfaces because no accumulation of any such species occurs on the oxide surface when the foil is kept at room temperature for an otherwise identical experimental procedure. In retrospect, it is not too surprising to find the tungsten subfluoride(s) adsorbed on the oxide surface. Equilibrium calculations of the W/F2 system indicate a significant amount of



Fig. 4. Auger spectra of sample: (a) initially clean SiO₂ surface, (b) after deposition of tungsten subfluoride, (c) after heating subfluoride-covered sample to 500°C, (d) after tungsten CVD by H_2 -WF₆ reaction.

WF₅(g) present at temperatures as low as 230°C for an initial WF₆ pressure of 2.5 torr (11). Also, the experimental conditions described above are very similar to conditions used to synthesize WF₄(s) and WF₅(s). From the reaction of WF₆ with solid tungsten at temperatures of 500°-800°C, tungsten pentafluoride will condense on nearby surfaces at temperatures below room temperature (12, 13), while tungsten tetrafluoride will accumulate on surfaces held at 40°-60°C (14). We would not expect to observe adsorbed tungsten pentafluoride with Auger spectroscopy under our conditions because of its volatility and tendency to disproportionate into WF₆(g) and WF₄(s) around room temperature. The disproportionation of the pentafluoride is actually thought to be the principal source of the tetrafluoride formed under these conditions.

When the WF_x-covered SiO₂/Si sample was heated to 500°C while under vacuum, significant chemical changes in the overlayer occurred and tungsten hexafluoride was observed desorbing (to be discussed in next section). The Auger spectrum [curve c of Fig. 4] now shows that the remaining tungsten is much less fluorinated and but contains some carbon and oxygen. We believe that this residis formed by thermally ual tungsten induced disproportionation of the adsorbed subfluoride, e.g., $3WF_4(s) \rightarrow W(s) + 2WF_6$. This tungsten is in a lower oxidation state and more reactive towards background gases, thus explaining the carbon and oxygen signals. This reaction sequence is very analogous with the behavior of tungsten tetrafluoride, which is known to disproportionate into metallic tungsten and tungsten hexafluoride at 200°-330°C (15). Also note that the residual tungsten layer is very thin and/or nonuniform, which now allows a small SiO₂ Auger signal to be measured. Figure 5 displays a cross-section TEM micrograph of a thin tungsten layer ($\simeq 25$ Å) formed by two cycles of a similar procedure. The tungsten layer appears of nonuniform thickness and occasionally discontinuous.

After heating the subfluoride-covered SiO₂/Si sample to 500°C, it was moved back into the reaction chamber and heated to 400° C in the presence of 5 mtorr WF₆ and 100 mtorr H₂ under the same flow conditions. Visual inspection of the surface indicated that noticeable deposition occurred within 3 min and within 6 min the surface was completely covered with a metallic tungsten film. After 10 min, deposition was terminated and the reaction cell pumped out. The Auger spectrum [curve d of Fig. 4] then showed a large signal indicative of metallic tungsten, and the silicon signal was again completely attenuated. Profilometry measurement indicated a tungsten film thickness of $\simeq 1000$ Å. This experimental sequence indicates that the tungsten remaining after the disproportionation of the subfluoride(s), as observed in curve (c) of Fig. 4, causes very rapid nucleation and growth of tungsten on the SiO_2 surface under typical CVD conditions. Without the tungsten formed from the disproportionation reaction, no measurable (by AES) amount of tungsten appears on the oxide surface even after 30 min of the same CVD conditions.

TPD of tungsten subfluorides.-TPD experiments were performed to examine the volatile products evolved upon heating WF_x -covered SiO₂ surface. Starting with the subfluoride-covered surface described above [curve b, Fig. 4], the sample was heated at $\simeq 5$ K/s while the WF₅⁺ and WF₃⁺ mass spectrometer signals were recorded. For maximum sensitivity the resolution of the spectrometer was turned down and thus the individual isotopes of tungsten were not resolved. The resulting TPD spectrum is displayed in Fig. 6. The ratio of the WF_5^+ signal to the WF_3^+ signal remains constant over the spectrum, and that ratio is consistent with the known fragmentation pattern of $WF_6(g)$ (16) and that obtained from a calibration spectrum in our system. Tungsten pentafluoride produces no parent ion, WF_{5}^{+} , so we deduce that tungsten hexafluoride is the only gas-phase species observed (13). A major WF_6 peak is seen around 300°C and a weak shoulder at \approx 150°C. This observation again suggests that the adsorbed subfluoride(s) is primarily WF₄ because this subfluoride is known to yield WF₆(g) by disproportionation at 200°-300°C (15). Some de-



tails of the TPD spectra were not quantitatively reproducible, *e.g.*, the shoulder at \approx 150°C was sometimes more prominent and there was occasionally a small peak at 350°-400°C, but there was always a dominant peak at 300°-330°C. We believe the minor variations are due to small differences in the conditions under which the subfluorides were formed. Earlier reported TPD results were partially in error due to a faulty mass spectrometer which would sporadically lose all sensitivity for m/e values greater than 275 and therefore could not detect WF₅⁺ (17).

Tungsten subfluoride formation rate.—The tungsten subfluoride(s) examined in the experiments described above were produced with the tungsten foil at 600°C to enhance the production rate. Since most selective tungsten CVD is performed at temperatures between 250° and 400°C, it is important to know if tungsten subfluoride formation occurs at significant rates in this temperature range. We therefore measured the kinetics for this process from 600° to 940°C by using total and partial pressure drop methods we will now describe. A steady-state flow of WF₆ is established in the reactor with the tungsten foil at room



temperature. The tungsten foil is then rapidly heated to a higher temperature where some of the tungsten hexafluoride is converted into subfluorides. If these subfluorides have low vapor pressures, then they are essentially removed from the gas phase and the total pressure in the reactor will drop. This pressure drop, ΔP , is related to the WF₆ decomposition rate, R_d , by the expression

$R_{\rm d} = \alpha S \Delta P / A$

where S = pumping speed, A = tungsten surface area, and $\alpha =$ factor to convert pressure into density. An Arrhenius plot of total pressure drop results using a new tungsten foil is displayed in Fig. 7, curve a, and shows a nice, straight line with an activation energy $E_a = 23.9 \pm 0.9$ kcal/mol. It is highly suggestive, but maybe fortuitous, that this value agrees with the reported values for the heat of sublimation for WF₅(s) (23.4 and 22.2 kcal/mol) (12, 13). Extrapolation of the subfluoride formation rate down to 300° and 400°C gives values of 2×10^{11} and 3×10^{12} molecules/cm²-s, respectively. Since selectivity loss is considered severe with the ungsten particle densities of 10^8-10^{10} /cm², it is obvious that the tungsten subfluoride formation rate is very significant at normal CVD temperatures.

In order to test the validity of the assumptions (i.e., low volatility products) involved in the total pressure drop method, we made measurements by a partial pressure drop method also. A small amount of the gas is leaked from the reaction chamber into the UHV chamber were the mass spectrometer is tuned to the WF₅⁺ ion. As mentioned in section on TPD of tungsten subfluorides this ion serves as a monitor of only the WF₆ partial pressure. The upper curve of Fig. 7 displays data from both pressure drop methods taken simultaneously, and the agreement between the two types of data is excellent, thus supporting the volatility assumption. The foil used for this data set had become noticeably rougher, probably due to etching by WF_6 , and the pressure drops were about a factor of 4 larger (being consistent with a larger surface area) than those measured in the lower curve. Despite this change, the activation energy remained the same, $E_a = 23.1 \pm 1.2$ kcal/mol, within experimental error.

Direct deposition of tungsten on SiO_2 .—We have also investigated the effect of increasing the SiO_2/Si sample temperature while the tungsten subfluorides are being generated. If the oxide temperature were held at or above the temperature where WF₄ is known to disproportionate, one

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Fig. 5. Cross-section TEM of sample after two cycles of tungsten subfluoride disproportionation. Dark line is thin layer (~25Å) of tungsten.



Fig. 7. Arrhenius plot of total pressure drop and WF₆ partial pressure drop (both proportional to the tungsten subfluoride formation rate) for an initial WF₆ pressure of 5mtorr. Curve (a) is total pressure drop data. Curve (b) is total pressure drop (diamonds) and WF₆ partial pressure drop (triangles) data.

might expect a metallic or reduced form of tungsten to from on the oxide surface directly. To test this idea the tungsten foil was heated to 600°C and the SiO₂/Si sample was heated to 300°C for 10 min at the usual WF_6 pressure and flow rate. Visual inspection indicated a metallic tungsten film completely coated the oxide surface, and Auger spectroscopy [curve b, Fig. 8] supports this observation. Profilometry indicated a film thickness of $\simeq 200$ Å and resistivity measurements gave an average value of 21 $\mu\Omega\mbox{-}cm.$ This film, and all others we grew by this method, did not adhere well to the oxide surface and failed the "scotch tape" test. Thicker films (500-1000Å) were observed to spontaneously peel from the oxide surface during deposition. It is of interest to recall that these tungsten films were deposited only using $WF_6(g)$ and a tungsten foil, i.e., no H₂ (or HF) present. The net effect of this process is the transport of tungsten from the foil at 600°C to the oxide



Fig. 8. Auger spectra of: (a) initial SiO₂ surface, (b) surface after direct deposition of metallic tungsten at 300°C by the disproportionation of volatile tungsten subfluorides, presumably WF_5 .

surface at 300°C, via the subfluoride desorption-disproportionation mechanism

$$WF_6(g) + W(s) \rightarrow 6WF_5(g), T(W) = 600^{\circ}C: Desorption$$

 $6WF_5(g) \rightarrow 5WF_6(g) + W(s), T(SiO_2)$

= 300°C: Disproportionation

It is instructive to compare the subfluoride formation rate determined by the pressure drop methods with the apparent rate of subfluoride adsorption (oxide $T \simeq 30^{\circ}$ C) and metallic tungsten deposition (oxide $T \simeq 300^{\circ}$ C). If all of the tungsten subfluoride formed with a tungsten foil temperature of 600° C were to adsorb on the SiO₂ surface, then a growth rate of ≈ 0.5 Å/s would be expected based on the pressure drop data of curve b, Fig. 7. The actual subfluoride adsorption rate with the oxide temperature $\approx 30^{\circ}$ C can be determined approximately by monitoring the attenuation of the two SiO₂ Auger peaks at 72 and 1615 eV. This is achieved by stopping the deposition at 5-20 min intervals and recording an Auger spectrum. Using inelastic mean free path values of 7Å (E = 72 eV) and 31Å (E = 1615 eV) (18-19) we calculate a subfluoride adsorption rate of 0.02 \pm 0.004 Å/s, indicating that only a small fraction of the subfluorides formed adsorb on the oxide surface. We believe this is due to the fact that tungsten pentafluoride is the predominate subfluoride formed by the $WF_6(g) + W(s)$ reaction. The pentafluoride must disproportionate into the tetrafluoride (or even lower subfluoride) or it will sublime before the Auger spectrum can be recorded. This process occurs slowly at 30°C (12, 13), thus explaining the low apparent subfluoride adsorption rate measured by the Auger peak attenuation method. However, when the oxide temperature is raised to 300°C tungsten deposits at a faster rate of ≈ 0.3 Å/s, indicating that essentially all of the subfluoride formed disproportionates at the oxide surface to yield metallic tungsten.

Summary

We have shown that tungsten subfluorides are formed by reaction of $WF_6(s)$ and W(s) at temperatures between 600° and 940°C. These subfluorides will condense and/or disproportionate on SiO₂ surfaces at $T \simeq 30^{\circ}$ C to yield a WF_x overlayer of stoichiometry $X = 3.7 \pm 0.5$. Upon heating, this overlayer disproportionates around 300°C to yield gas-phase tungsten hexafluoride and a reduced, essentially metallic, tungsten layer on the oxide surface. This reduced tungsten is very reactive and can immediately catalyze the hydrogen reduction of WF_6 , thus initiating selectivity loss. Metallic tungsten may also be formed at a faster rate directly on the SiO_2 surface if the oxide temperature is raised to 300°C while the subfluorides are being generated. Extrapolation of the subfluoride formation rates to 300°-400°C indicates that significant quantities $(10^{11}\mathchar`-10^{12}\ molecules/cm^2\mathchar`-s)$ of these compounds are formed at metallic tungsten surfaces in this temperature regime. Even inefficient conversion of these compounds by disproportionation into a reduced state of tungsten could easily produce severe selectivity loss under typical CVD conditions.

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Plasma-Enhanced Chemical Vapor Deposition of TiN from TiCl₄/N₂/H₂ Gas Mixtures

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ABSTRACT

Thin films of TiN have been deposited on thermally grown SiO₂ using plasma-enhanced chemical vapor deposition. The films were obtained from gas mixtures of $TiCl_4/N_2/H_2$ at a total pressure of 1.1 torr and input power density of 5 W/cm² at 13.56 MHz. Auger spectroscopy, x-ray diffractometry, and electrical resistivity measurements were employed to characterize the films as a function of the substrate temperature and gas flow rates. It was found that while hydrogen is necessary for deposition to occur, too much hydrogen increases the chlorine content and resistivity of the film. On the other hand, increasing the nitrogen flow rate reduces the chlorine content and resistivity of the film with the end result being that low resistivity highly oriented polycrystalline TiN films can be deposited at a substrate temperature of 500°C.

Thin films of titanium nitride have been shown to be impermeable to silicon (1-3) and hence form an excellent diffusion barrier between silver and silicon (4-5) as well as a barrier between titanium and platinum in the Ti-Pt-Au system (6-7). This material has been deposited via reactive sputtering of titanium in an Ar-N₂ atmosphere (1-7) and evaporation of titanium in a nitrogen atmosphere followed by a high temperature anneal (8) as well as by dc plasma deposition from TiCl₄/N₂/H₂ gas mixtures (9). We will report on the RF plasma-enhanced chemical vapor deposition of TiN from TiCl₄/N₂/H₂ gas mixtures as a function of the gas flow rates and substrate temperature. We will show that while hydrogen is necessary for deposition under the conditions used here, too much hydrogen actually increases the chlorine content of the as-deposited films while additional nitrogen reduces the chlorine content of the film, allowing a good quality film to be deposited at 500°C. This result differs from that of Gleason et al. (10) who found that good quality TiN could be deposited from TiCl₄/NH₃ gas mixtures to 600°C.

Experimental Apparatus

The plasma-enhanced chemical vapor deposition system used in this work is seen in Fig. 1 and consists of a 16.5 cm diam Pyrex cross with two 11.5 cm diam stainless steel electrodes spaced 5.1 cm apart. The lower electrode is grounded while the upper electrode is driven by a capacitively coupled 13.56 MHZ RF power supply through a matching network. This electrode is also heated by a resistance heater where its temperature is monitored by an imbedded thermocouple.

The system is evacuated by a LN₂ cold-trapped diffusion pump to a base pressure of at most 5×10^{-6} torr before the gas flow is initiated. The hydrogen and nitrogen flow rates are electronically controlled and the gases are mixed in a ballast tank before being introduced into the system. The TiCl₄ flow rate is measured by a rotameter, and this gas is introduced separately into the system. It should be noted that we have not been able to detect any inhomogeneities in film thickness or composition using this particular gas introduction system. The pressure is read by a capacitance manometer, and for this particular work the total pressure was held constant at 1.1 torr as was the input power at 50W.

Substrates, consisting of 3000Å of thermally grown SiO₂ over silicon that are 2 by 2 cm, are placed in the center of the lower electrode, the gas flows are initiated, the substrate is heated to the appropriate temperature and the discharge is struck. After 15 min the discharge, substrate heater, and the TiCl₄ and nitrogen flows are all turned off. The hydrogen is permitted to flow until the substrate temperature is below 100°C, then the sample is removed.

The film's microstructure is analyzed by x-ray diffractometry and the electrical resistivity is determined by



Fig. 1. Schematic diagram of the discharge system and gas handling equipment used in these experiments.