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SPECTROSCOPIC ASSESSMENT OF THE RELIABILITY OF METAL/METAL OXIDE INTERFACES

Syracuse University

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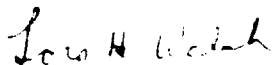
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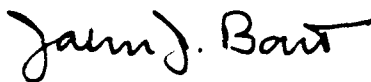
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Appendix II "Use of gas phase tetrakisdiethylaminotitanium reagents for simultaneous removal of impurities from substrate surfaces and chemical vapor deposition of TiO_2 ". to be submitted to J. Am. Chem. Soc. pp. 29-42

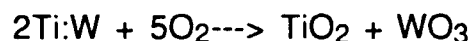
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Introduction

There is considerable interest in understanding the source of the electromigration resistance of the well known interconnect material, titanium tungsten(Ti:W). Measures of electromigration can be obtained with respect to a variety of parameters/physical properties. The variation of some parameters over time can be presumably associated with the increase in the probability of a electromigration related interconnect failure. In the simplest analysis, we immediately note that any metal in contact with the atmosphere oxidizes. Furthermore, the process is accelerated by increasing the temperature as is the rate of electromigration related failures. Therefore a rational basis exists to suspect that oxidation related chemistry can be related to electromigration related failure processes. This study probes the oxidation chemistry of this alloy on native oxide coated silicon. We report physical and chemical measurements on the interface between a ceramic and metal phase.

A recent study (Lytle, see appendix) of the oxidation of sputtered Ti:W films suggested that as the material ages, the Ti phase oxidizes independently of the W phase. The alloy oxidizes upon first exposure to the atmosphere such that the excess Ti is oxidized and the W phase is resistant. A Ti:W interconnect just exposed to the atmosphere quickly

becomes a mixture of a lower stoichiometry Ti:W phase and TiO₂. Over longer periods of time, at somewhat elevated temperatures, the earlier study gave results which could be interpreted simply on the basis of:



Interactions with the substrate, Si, or SiO_x, would not seem to be important. Furthermore, the earlier work was not able to distinguish intermediate steps in the oxidation chemistry. There are four known tungsten oxides and many stoichiometries/phases of titanium oxide. The mere fact that we cannot write a balanced equation involving a single "molecule" of Ti:W and oxygen leads us to suspect that the above *net* reaction occurs as a consequence of a *series* of elementary steps. It was the goal of this task to determine whether there is/are intermediate chemical interactions simultaneously involving Ti, W and oxygen which might be a step in the overall reaction stated above. Developing methodology for detecting the presence of any ternary compound involving those three reactants helps identify potential participants in the predominant failure mechanisms and reliability issues which are correlated with the progress of electromigration.

Because we are attempting to determine if there is the possibility of compound formation involving Ti, W, and oxygen on a silicon or silicon oxide substrate, it may not be most desirable to use conventionally sputtered Ti:W alloy films. In conventional sputtered Ti:W films, the compound(s) of interest may be formed in small quantities but exercise considerable influence on the aging of the film by virtue of some *catalytic* property. For this and other reasons we opted to produce an unconventional reaction mixture.

Our choice of system involved TiO₂ and tungsten clusters. By tungsten clusters, we mean globular particles of tungsten on the order of 10-10³ Å in diameter. Published TEM and SEM studies of electromigration affected areas suggest the possibility of a correlation between surface

irregularities like "hillocks" and the propensity for interconnect failure. Hillock formation has been observed in films which have considerable electromigration damage. Formation of electrically contiguous films with considerable surface irregularities is a characteristic of laser deposited films. Other reasons for the use of such films in this study will be presented.

This report will proceed with a description of the experimental strategy. A results section will follow which presents the data. These data are then discussed in the context of ternary compound formation on the stated substrates. Appendices, i.e. preprints of submitted papers, are included which give details and references relative to the chemical vapor deposition and laser chemical vapor deposition of the "reactant" films.

Strategy

We probe the interaction of tungsten clusters and titanium dioxide on a silicon oxide substrate using the following strategy and methods described below. A number of trials were carried out in which a series of four film "systems" were prepared and compared using a variety of methods. In each trial, the first two film systems were simply films of the separated reactants, i.e. tungsten clusters and TiO_2 , on the substrate of interest, i.e. native oxide coated Si. We deposit a film of titanium dioxide on a silicon substrate which has a freshly deposited native oxide layer using the hydrolysis of tetrakis dialkylaminetitanium as described in the appendix. We deposit a tungsten cluster film on a different piece of the same substrate material using the laser chemical vapor deposition(LCVD) methods described in the appendix. For the third "system", we deposit a film of titanium dioxide *on top* of a tungsten cluster film which was previously deposited on a native oxide Si. The fourth system consists of a ternary system in which the tungsten cluster film is put *on top* of the TiO_2 which is, in turn, on top of the native silicon oxide. These four films, and the uncoated native oxide substrate, are then

studied using Auger, SEM, TEM, FT-IR and Raman spectroscopy. These latter probes are directly sensitive to bond breaking/formation.

The deposition methods for the films/reactants were also chosen because we expected they would maximize the occurrence of chemical interaction, i.e. bonding, of Ti and W via oxygen. Since grain boundary phenomena are known to be the site of much electromigration related phenomena, it seemed rational to study a material with maximized grain boundary volume. For this, prenucleated films would seem to be an optimal choice, being produced by the deposition of gas phase clusters onto a cold substrate, such films have a substantial amount of void volume. We are inclined to associate void volume with grain boundaries. We have recently demonstrated the capacity to produce thin films from metal clusters using laser chemistry of organometallics. These clusters vary in diameter from 10^{-10} to 10^3 Å and were the form in which tungsten was included in the reaction mixture. The source of titanium was chosen to minimize the temperature of the overall processing. Moreover, since the sputtered material is apparently TiO_2 from the outset, it was acceptable that we could use the oxide as a reactant. We chose to deposit TiO_2 using a novel chemical vapor deposition route because it also has the effect of removing water, CO_2 and CO from the films.

Results

Figures 1-9 give representative Raman and infrared absorption spectra of the films used in this study. An infrared spectrum of the bare silicon substrate (International Wafer Service, p-doped, 110) is not included because a bare silicon substrate was used as the reference for all the spectra shown. To a large extent, the IR spectra are described in the appendices so they will be briefly reviewed here and the Raman spectra will be discussed in detail.

The IR spectra of the binary systems, i.e. the simple films, are easily compared to the literature, thus confirming the identity of the

materials. Consistent with the properties of laser chemical vapor deposition, $\text{CO}(\approx 1900 \text{ cm}^{-1})$ is easily seen in the nascent tungsten cluster films. A metal oxide region, $\approx 400\text{-}950 \text{ cm}^{-1}$, is seen to be stronger for the tungsten films than for the TiO_2 film. As can be seen in the appendix, the amount of oxidation which occurs upon exposure to the atmosphere is not enough to completely mask subsequent chemistry. The nascent tungsten cluster films are mostly tungsten with a thin oxide passivation coat. FT-IR spectra of the binary systems tend to have somewhat sloping baselines at the high wavenumber edge of the spectrum. We will return to this fact later.

The IR spectra of the composite films are different from each other or either of the binary systems. The order of film deposition clearly matters in determining the chemistry which occurs. When the tungsten is deposited first, the tetrakis reacts with the carbonyl impurity. When the tetrakis is deposited first, the carbonyl impurity is clearly present after the tungsten is deposited. The chemistry surrounding this observation is described in detail in an appendix. The appearance of the metal-oxygen stretching region for both composite films are sufficiently different to suggest that there is considerable interaction between the two metal atoms via oxygen.

Auger of the films showed the presence of titanium, tungsten and oxygen in a variety of stoichiometries. The distribution of the oxygen between the two metals is the main question. The Raman spectra are most useful in bearing light on this question. First, we note that while there is evidence for the presence of both anatase and rutile TiO_2 phases, the positions and extreme widths of the peaks ($\approx 500 \text{ cm}^{-1}$ region) are clearly suggestive of a wide range of forms being present. Of major importance is the lack of strong Raman activity in the 700-800 range. This region has two very strong peaks corresponding to the formation of WO_6 octahedra as in common bulk WO_3 . The lack of strong features in this region, together with the TEM and microelectron diffraction results detailed in an

appendix, clearly shows that tungsten is only present as metal or substoichiometric metal oxide clusters.

Finally we note a very curious observation regarding the $\approx 380\text{ cm}^{-1}$ Raman feature which can be seen to some extent in all the spectra, including the spectrum of the plain native oxide coated substrate. This feature is strongest for the plain substrate followed by the ternary systems and is much reduced for both the binary film systems. It would appear that this feature, which is clearly associated with the native silicon oxide of the substrate, is associated with a bonding mode which is more visible only when both the titanium and tungsten are present. This could occur for at least a few reasons. Some compound is formed involving titanium and tungsten which depletes the amount of each which is available to react with the native oxide. It is also possible that the titanium and tungsten react in such a way as to uncover the substrate thus making its Raman signal stronger. In either case, the Raman data clearly show that there is a chemical/physical interaction between the tungsten and the titanium.

Discussion

There are three sets of results which deserve discussion in the context of electromigration. The effect of the tetrakis reagent to remove water, CO_2 and CO could easily be the basis for a study of the effect of these impurities on the electromigration properties of sputtered Ti:W. Since Lytle showed that sputtered Ti:W already has a surface coat of TiO_2 it is only a minor perturbation to compare the electromigration behavior of tetrakis treated and untreated sputtered films.

The second point concerns the sloping baseline of the composite films. This could easily be indicative of the formation of a compound with a low lying optical absorption/bandgap. The increase in slope is difficult to observe and quantify and suggests that further IR/Raman studies in the near IR would clarify the situation. This observable is either less

sensitive to changes than is the 400-950 cm^{-1} region IR features, or the cause of the effect is independent of the order in which the films are deposited. This latter possibility would also be consistent with the possibility that the interaction is independent of the presence of all the other chemical species which are introduced in the process of constructing the composites. The main qualitative point is that there is evidence of chemical interaction between tungsten and titanium.

Indeed, the preponderance of results suggests that there is considerable mutual interaction between metal and metal oxides on a scale of individual molecules and on the scale of lattices, i.e. many atoms and molecules involving collective motions and reorganizations. In fact, there are probably at least a few processes, physical and chemical, in parallel in these composites. Some of the interactions, on both scales, are discussed in the appendices.

The final result which bears discussion involve the 380 cm^{-1} Raman feature. Silicides are known for titanium and tungsten of various stoichiometries and crystal habits. The appearance of a native oxide associated Raman feature which occurs concurrently with the growth of an apparently electronic feature strongly suggests that there is interaction between the substrate, the tungsten, the titanium and oxygen. This interaction would seem to be particularly significant with regard to electromigration. A material formed in the composite films could compete with separate formation of materials between each of the reactants and the substrate associated native oxide. Since the titanium is more oxophilic than tungsten, it seems reasonable to suggest that titanium serves the role of oxygen scavenger in the interconnect material. By "occupying" reactive oxygen containing species, the titanium could be promoting tungsten silicide formation. The chemistry between the titanium and the tungsten could be the link which would *dynamically* connect their individual and collective chemistry with the substrate. This in turn could lead to a more intimate *mechanical* connection between the tungsten and the substrate thereby imparting electromigration resistance.

Experiments which more delicately control and monitor the oxygen induced chemistry of the sputtered interconnect material would therefore be well advised. As suggested by the appendices, the present results are being prepared for publication.

Conclusions

Titanium, tungsten and oxygen on a native oxide coated silicon substrate form a complex reaction system at ambient temperatures. The diagnostics discovered as a part of this study will be useful bases for following the course of electromigration in other Ti:W samples. Future electromigration studies should not neglect the possibility of titanium promoted tungsten silicide formation.

7/17/91 TiO₂ on W on Si - dark current 15mW 3e-6 torr

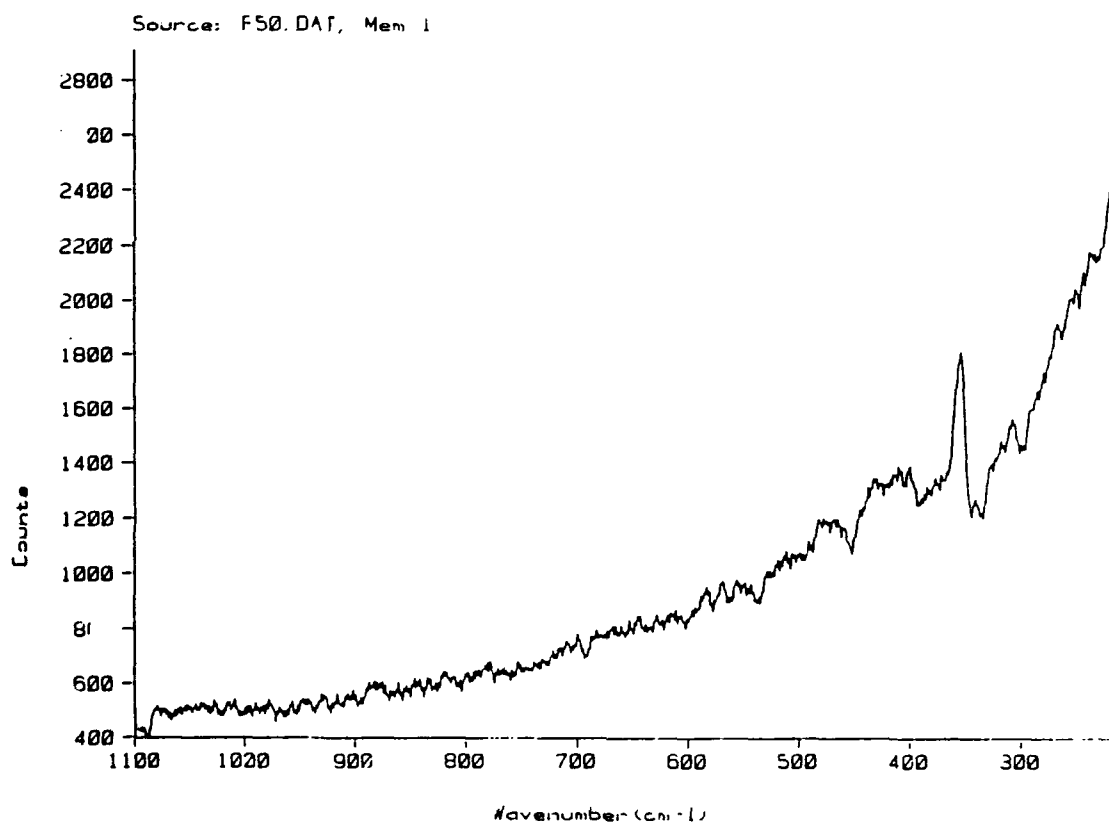


Figure 1. Raman Spectrum of typical TiO₂ film of Si substrate with W film in between

7/17/91 Si substrate - dark current 15mW 3e-6 torr

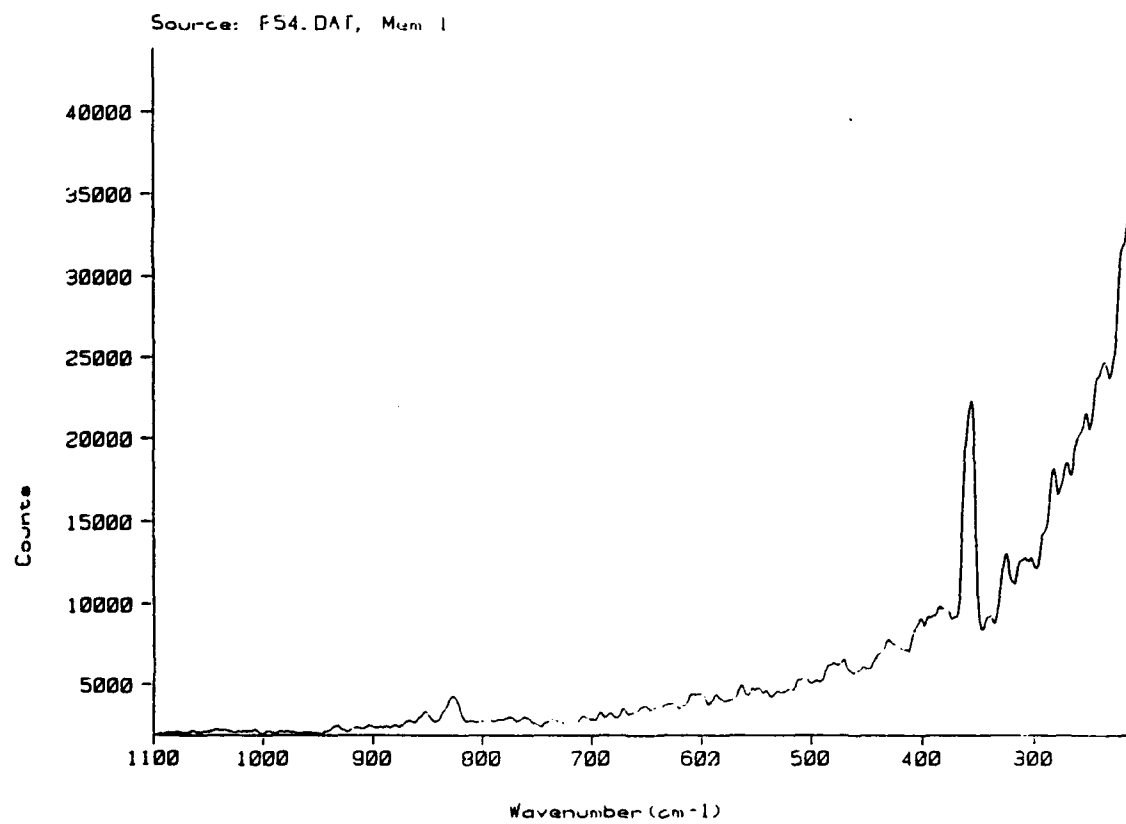


Figure 2. Typical Raman Spectrum of Si substrate

7/17/91 W on TiO₂ on Si - dark current 15mW 3e-6 W/cm²

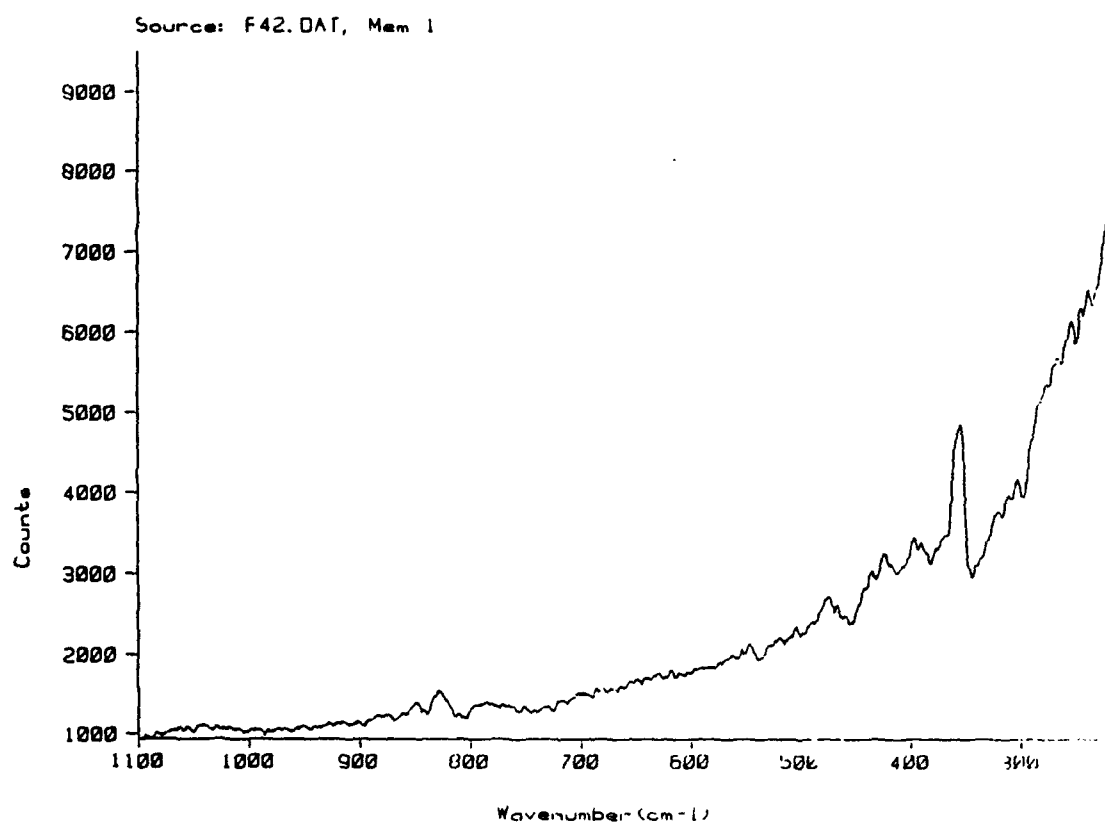


Figure 3. Raman Spectrum of typical W film on TiO₂ film on Si substrate

7/17/91 TiO₂ on Si - dark current 15mW 3e-6 torr

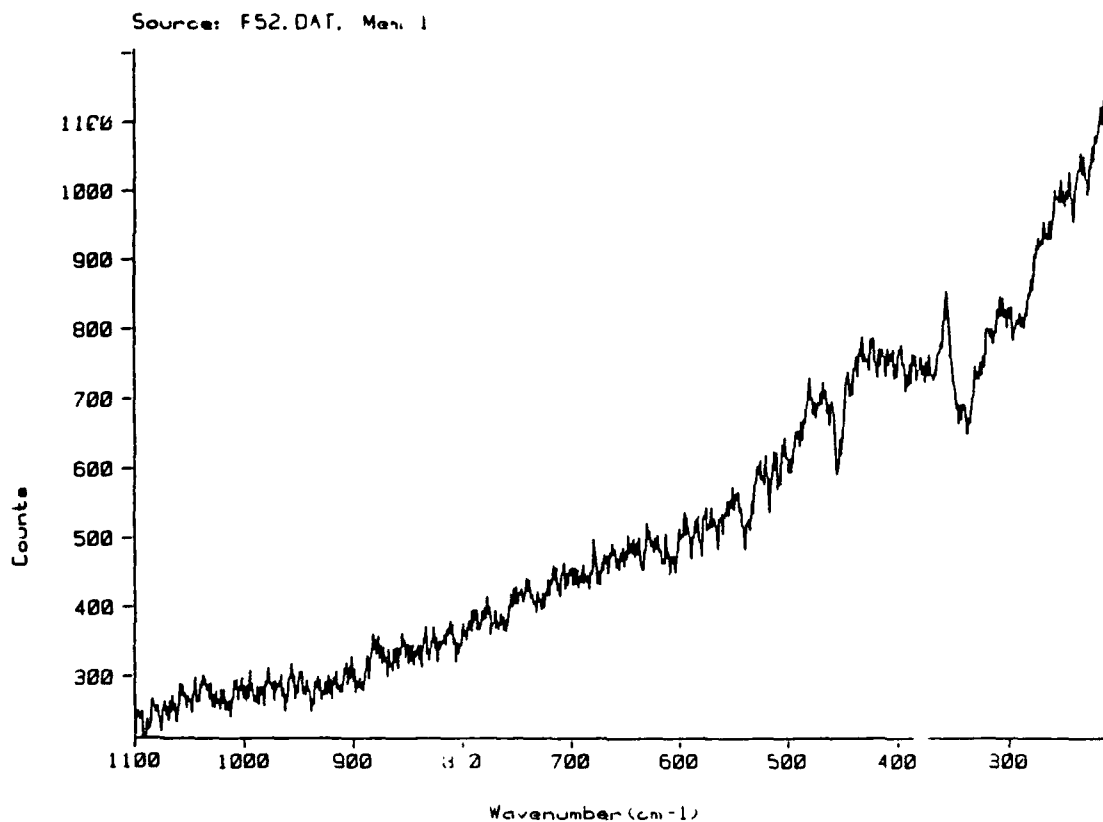


Figure 4. Typical Raman spectrum of TiO₂ film on Si substrate

7/17/91 W on Si - dark current 15nW 34.6 eV

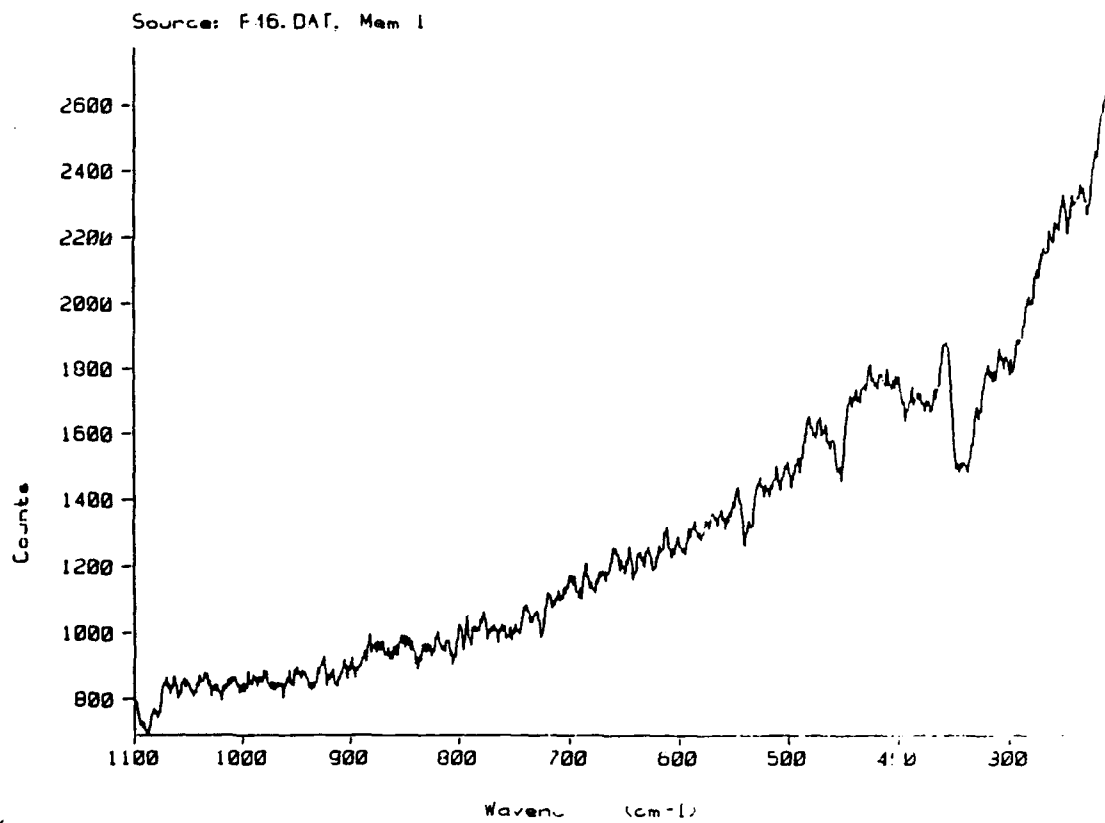


Figure 5. Raman spectrum of typical W film on Si substrate

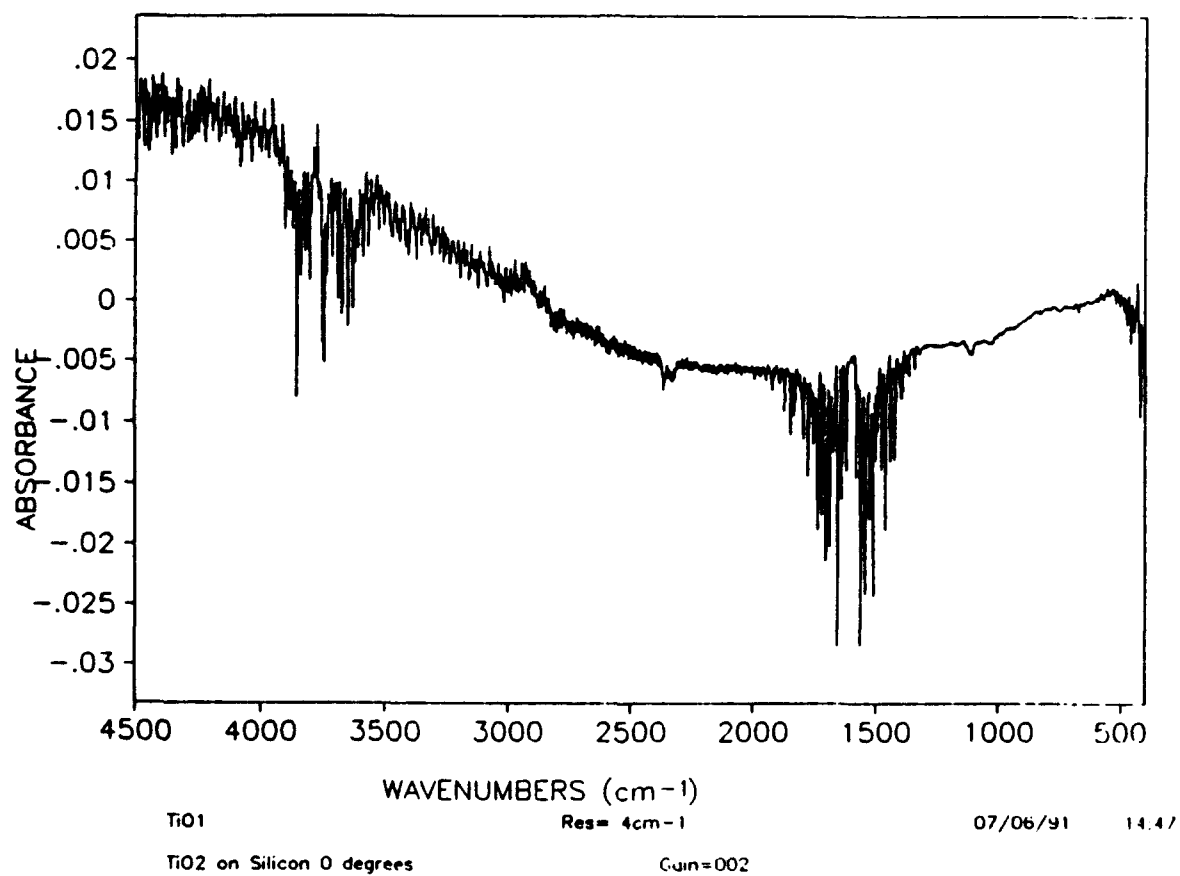


Figure 6. IR absorption spectrum

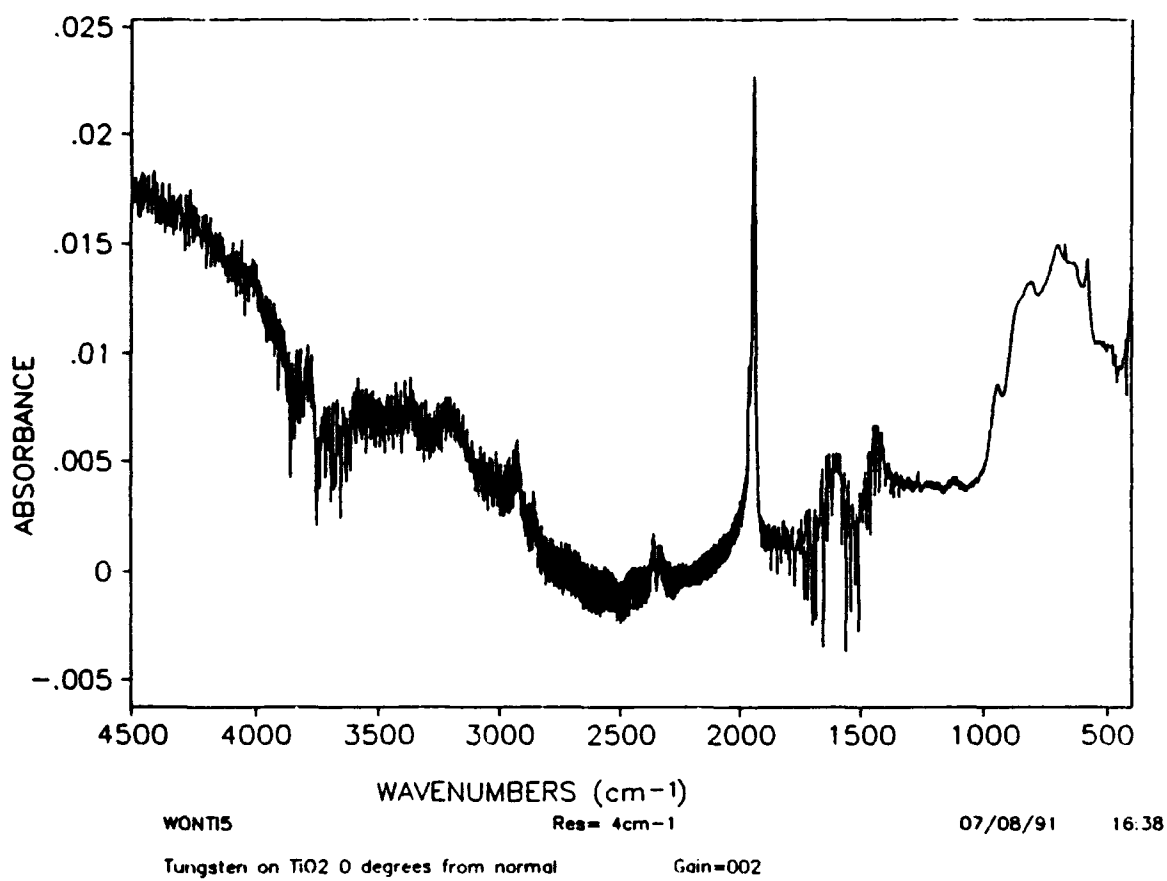


Figure 7. IR absorption spectrum

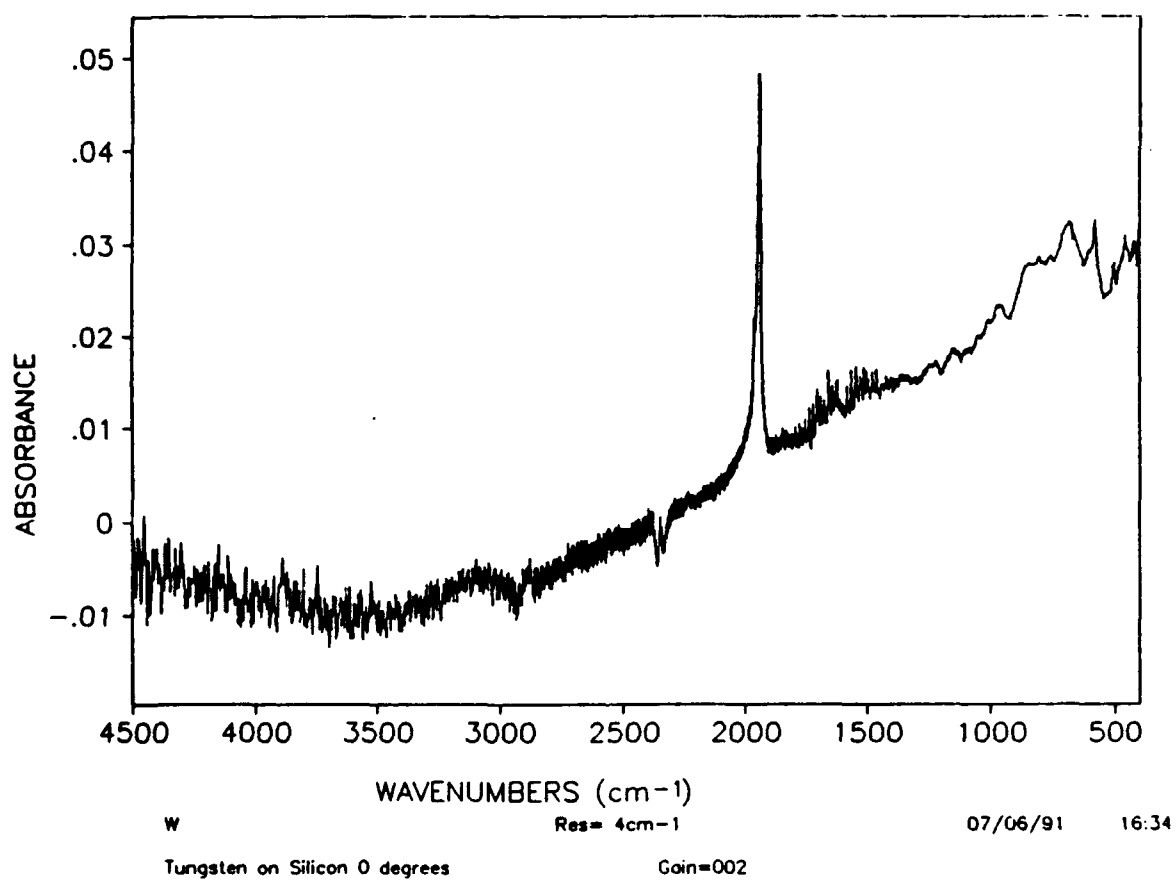


Figure 8. IR absorption spectrum

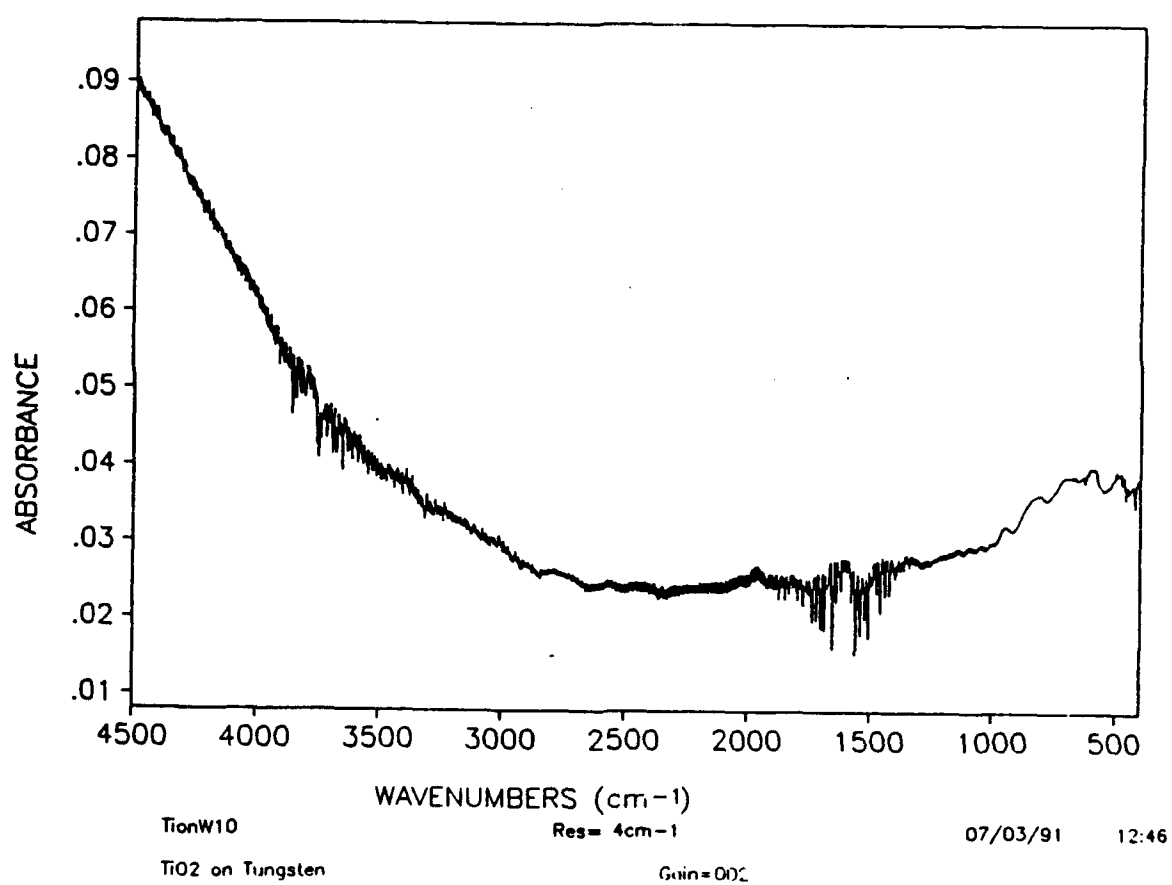


Figure 9. IR absorption spectrum

**Synthesis of Metal and Metal Oxide Cluster Films
Using Laser Chemical Vapor Deposition**

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Abstract

We present a transmission electron microscopy, electron diffraction, Auger, Raman, resistivity study of tungsten and tungsten oxide thin films produced on either quartz, metal grids, GaAs or Ge using laser chemical vapor deposition. We demonstrate the presence of metal and metal oxide clusters spanning the diameter range of 10^1 - 10^3 Å. We use FT-IR to show that carbonyl impurities are present only as terminal, i.e. surface bound, species.

Synthesis of Metal and Metal Oxide Cluster Films Using Laser Chemical Vapor Deposition

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A variety of theoretical studies support the expectation that metal clusters¹, metal oxide clusters², dielectric coated metal clusters³, and even dielectric coated voids⁴ in thin metal films will have an enhanced electrical polarizability compared to materials with the same chemical composition but without the submicroscopic physical features. Thin films of such materials should have enhanced photorefractive properties leading to applications⁵ in nonlinear optics, optical computing and related technologies. We have recently shown^{6,7,8} how to deposit thin films composed of platinum clusters using laser chemical vapor deposition(LCVD). Such films have the unusual optical/electrical property of being "transparent metal" electrodes suggesting various applications. We now present recent results demonstrating the synthesis of non-noble

metal and metal oxide clusters and thin films composed of such clusters. In the particular case we describe below, we use gas phase metal carbonyl precursors. As it turns out, we also demonstrate the unanticipated result that carbonyl impurities are localized on the surfaces, regardless of whether metal or metal oxide clusters are synthesized.

Although the present results relate to tungsten and tungsten oxide cluster films, the chemistry is directly applicable to other oxidizable metals. Puretsky and Demyanenko⁹ reported that gas phase clusters and ultrafine particles can be synthesized using excimer laser dissociation of all group six metal hexacarbonyls. Our earlier work on platinum clusters and our current results on other metals both suggest that the clusters which are present in our films are formed by gas phase processes. In fact, many^{10,11,12} have studied UV dissociation, in both single and multiphoton limits, of metal hexacarbonyls in the context of depositing thin films for microelectronic device fabrication. Incorporation of partially decarbonylated species and reaction products derived from these species is a disadvantage of LCVD of metallization patterns for microelectronic applications. We have recently shown⁸ that use of noncarbonyl precursors in laser chemical organometallic synthesis of platinum clusters also results in incorporation of organic impurities but that they can be removed and potentially utilized via postdeposition chemistry. Gas phase and postdeposition chemistry is limited by the tendency of the metal to oxidize which makes the results we now present quite distinct from our earlier LCVD platinum results.

A diagram of the basic apparatus used to perform LCVD has been presented elsewhere⁶. The tungsten hexacarbonyl was purified by sublimation before being loaded into a specially designed all stainless steel gas/reactant delivery system. This system utilizes a molecular sieve drying tube to remove water from whatever carrier gas is used to entrain the tungsten hexacarbonyl. A set of MKS capacitance manometers and isolable chambers of known volume were used to measure partial and total pressures and flow rates in the delivery system and in the deposition cell. Although this apparatus will be described in greater detail later¹³, for present purposes it suffices to point out that, utilizing a series of micrometer valves and lengths of tubing with various internal diameters, the total pressure, flow rate, gas stream composition and temperature could each be independently adjusted.

Figure 1a shows a TEM of a free standing tungsten film deposited by LCVD directly onto a TEM grid at x113,000 magnification; globular clusters are clearly visible. Figure 1b shows an electron diffraction pattern obtained from the conglomeration of clusters imaged in 1a). As is typical for diffraction patterns obtained from many such conglomerations, the near coalescence of the diffraction rings into spots presents an interesting comparison with the results of Mader¹⁴ and Aspnes.¹⁵ Observation of "implied" rings is consistent with the idea that our films are composed by condensation of clusters of varying sizes. The spacings between the rings were analyzed and only interplanar spacings of tungsten are evident¹⁶. These spacings would seem to be characteristic of the environment *inside* the clusters. The tungsten clusters are produced using 20 mtorr of tungsten hexacarbonyl at 62°C with argon added to produce a

total pressure of 70 mtorr in the deposition cell. This pressure is lower than the vapor pressure of bulk tungsten hexacarbonyl at the same temperature because we are working in a flowing cell. Figures 1c and 1d show essentially the same data obtained for tungsten oxide clusters. These clusters were deposited using the same partial pressure of tungsten hexacarbonyl but with the rest of the total pressure being composed using O_2 . For the oxide clusters, the diffuse quality of the rings suggests less order within the clusters as well as a distribution of sizes. Raman spectra of films composed of these clusters have extensive structure below $\approx 400\text{ cm}^{-1}$ but absolutely no hint of the well known, and extremely strong $700\text{--}900\text{ cm}^{-1}$ features indicative of the presence of WO_6 octahedra. Auger analysis (internally calibrated against authentic W, WO_2 and WO_3) of these oxide films reveals an average W:O stoichiometry 1:1.5 which is a factor of ≈ 10 below the gas phase ratio present during LCVD. The film W:O ratio varies widely from spot to spot on the film and can range from $\approx 1:2.5$ to nearly 1:1. Measurements of the temperature dependence of the resistivity of 200 nm thick films on quartz in air reveals irreversible changes occurring at temperatures as low as $\approx 100^\circ\text{C}$. The resistivity of nascent films, which are semiconductors, exceeds that of polycrystalline tungstate films although the implied band gap (.15 eV) is typical¹⁷.

Figure 2a shows an FT-IR spectrum of a nascent tungsten film deposited as described above onto a Ge substrate. There is evidence of W-O-W bonds¹⁸ and terminal W=O groups. Carbonyl stretches are clearly visible and occur at 1935, 1942, and 1962 cm^{-1} . All of these frequencies are too high to be characteristic of bridging carbonyls suggesting that the carbonyl does not exist in an environment conducive to bridging between

metal atoms. Although they could be shielded from the probing IR radiation by the presence of the metal, a lack of any bridging carbonyl whatsoever argues against an environment internal to the clusters. An FT-IR of the *same film* aged in air for nearly a year can be seen in Figure 2b and suggests that the carbonyls have reacted with airborne oxygen further suggesting that they were never buried deep in the cluster. The carbonyl stretching fundamentals are still clearly visible; they are only slightly shifted and still are not characteristic of bridging carbonyls¹⁹. Figure 2c shows a nascent film which was deposited under identical conditions for LCVD production of the metal oxide clusters. The carbonyl stretches (1969, 2008, 2106 cm^{-1}) are again clearly visible, nearly identically located with respect to the two other spectra, and not characteristic of bridging. The carbonyl features present in the nascent films decrease as the amount of oxygen present in the LCVD deposition cell increases. In both Figure 2b and 2c, the sharp FT-IR features just below 3000 cm^{-1} are as yet not unambiguously assignable. We currently believe they can be identified with formate formed by the coupling of water and CO which we believe could occur on the cluster surfaces. Although we are currently performing a variety of experiments to support this assertion, if our guess is correct, the water could be supplied from the substrate or the atmosphere.

The TEM results clearly demonstrate the existence of clusters. The electron diffraction, Auger, Raman and resistivity measurements together suggest that the oxide clusters are less stable to oxidation in air and are generally less ordered materials. The FT-IR results show that bridging carbonyls are never present in either nascent or films extensively aged in air. Reactions of the carbonyls associated with the films are indicative of

surface bound carbonyl. We are currently pursuing other chemical means of utilizing the carbonyl impurities as reactant for producing composite films from the nascent LCVD films we have shown here.

Acknowledgements

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Figure Captions

Figure 1 a) TEM image of tungsten cluster film deposited on copper grid using LCVD without any oxygen present during deposition. b) electron diffraction pattern of region shown in (a). c) TEM image of tungsten oxide films produced using LCVD with oxygen present during deposition. Total pressure present during deposition is identical for this film and that shown in (a) except that in this film excess pressure above that due to tungsten hexacarbonyl is due to oxygen. In (a) excess pressure is made up of argon. d) electron diffraction pattern obtained from free standing film shown in (c). Magnification of all TEM images is $\times 113,000$.

Figure 2 a) FT-IR spectrum(Ge reference) of tungsten film deposited on Ge without any oxygen present as in Figure 1a. b) FT-IR spectrum of same film after one year aging in ambient air. c) FT-IR spectrum of a film deposited on undoped GaAs(GaAs reference) under conditions identical to those obtained in Figure 1c.

Figure 1

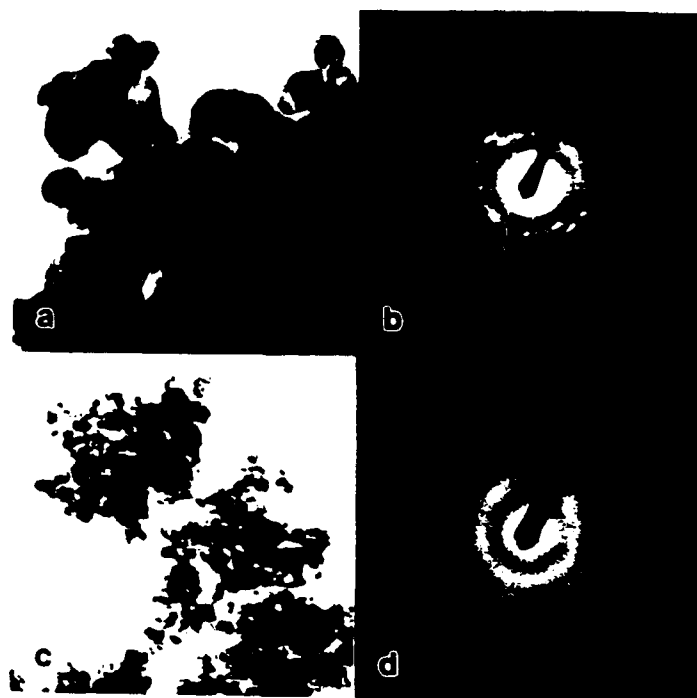


Figure 2a)

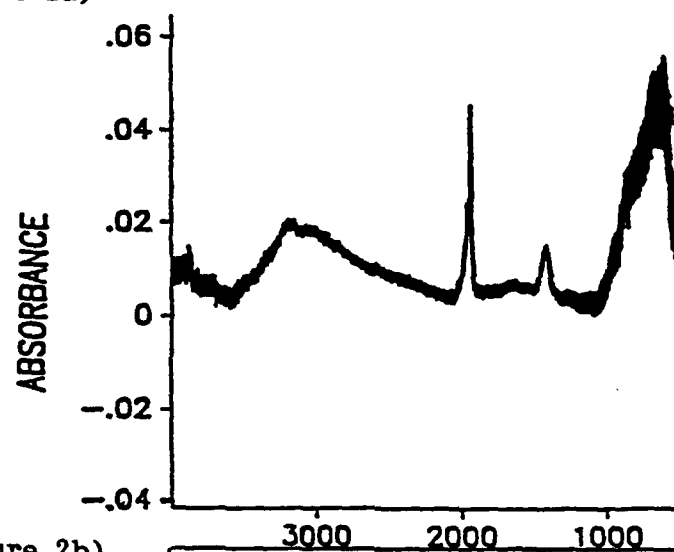


Figure 2b)

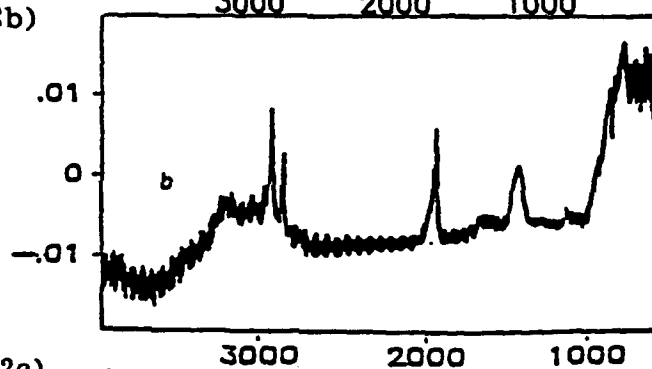
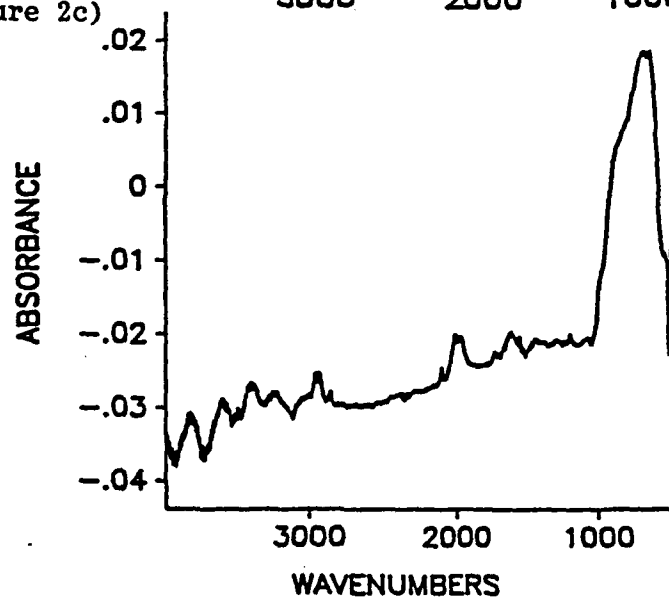


Figure 2c)



Use of gas phase tetrakisdialkylaminotitanium reagents for simultaneous removal of impurities from substrate surfaces and chemical vapor deposition of TiO_2 .

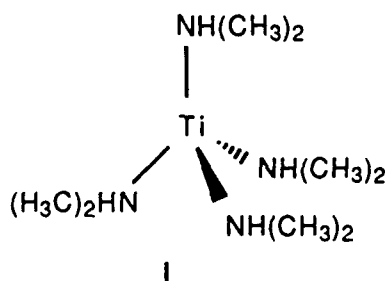
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Laser chemical vapor deposition(LCVD)^{1,2} of thin films, clusters and ultrafine particles offers many unique opportunities in materials synthesis. As precursors for LCVD of pure metal films, metal carbonyls have the advantage of high vapor pressure and their use has been thoroughly studied³. One major disadvantage of metal carbonyls as LCVD and even conventional CVD precursors is that carbonyl ligands or fragments thereof are invariably incorporated into the reaction products so the metal films produced are not suitable/optimal for microelectronic device fabrication. We report a novel method for removal of carbonyl, water, carbon dioxide and other related impurities from such films when they are intended to be one component of a composite film.



The essence of the method is to expose the desired substrate to I, gaseous tetrakis(dimethylamino)titanium, which immediately reacts with whatever water, carbon dioxide, and carbon monoxide may be present. Whatever water is present, or is purposely introduced into the system, results in deposition of TiO_2 . The novel element of the study we report here is the ability of this and similar reagents to leach the system/substrate of the other unwanted species listed above.

Although this class of precursor has been recently reported⁴ in the context of a gas phase reactive CVD nitriding reagent, the well known oxophilicity of titanium⁵ leads to deposition of TiO_2 and is an obvious result. The ability of a Ti-N moiety to incorporate carbonyl, carbon dioxide and related species is well preceded in the literature⁶ but apparently has never been applied to the problem at hand. We present a definitive demonstration of the relevant chemistry and characterize its fundamental aspects in the context of this seemingly unusual application. It has occurred to us that use of similar chemistry involving different reagents may be in use but we find no evidence in the literature supporting this suspicion. In fact, the chemistry we describe can also be used to provide protective and optically useful TiO_2 coatings⁷ on a variety of substrates while simultaneously removing the impurities noted above. As another extension, the niobium, tantalum and zirconium analogues present opportunities for waveguide and other integrated optic fabrication applications.

One synthetic thin film target is the Ti:W alloy in widespread use as an electromigration resistant interconnect and barrier metal in microelectronics⁸. In the context of silicon based devices, tungsten is well known to form a stable silicide and low temperature reactive CVD tungsten silicide deposition chemistry is well known⁹. Although the basis for this particular material's superior properties is currently not completely clear, a recent study suggested that conventional sputtered Ti:W films under application relevant chemical and physical conditions contain substantial amounts of TiO₂ if only near the surface. In an effort to study the earliest and intermediate stages of interaction between the W and TiO₂ phases in such films, we synthesized films which were TiO₂:W composites using a combination of LCVD and CVD. We planned to deposit W and TiO₂ films separately and examine the interaction of the two films at their mutual interface. We fully anticipated that carbonyl would be present at such interfaces if the W phase were deposited using LCVD but, as part of the overall electromigration study, we included such samples precisely to examine/maximize the presence and failure inducing effect(s) of impurities.

Chisolm and Extine and others¹⁰ thoroughly investigated the CO₂ solution chemistry of tetrakisdiethylamine metal compounds with regard to their promotion of various reactions. The gas phase chemistry is suitably summarized in Figure 1. Throughout the mid-IR there are no less than 7 isosbestic points(981, 1415, 1261, 1234, 1056, 930, 599 cm⁻¹) which correspond to complex equilibria involving the tetrakis precursor, CO₂ and H₂O. We have conducted extensive studies which will be presented elsewhere, involving D₂O, ¹³CO₂ and H₂¹⁸O to unravel these isosbestic

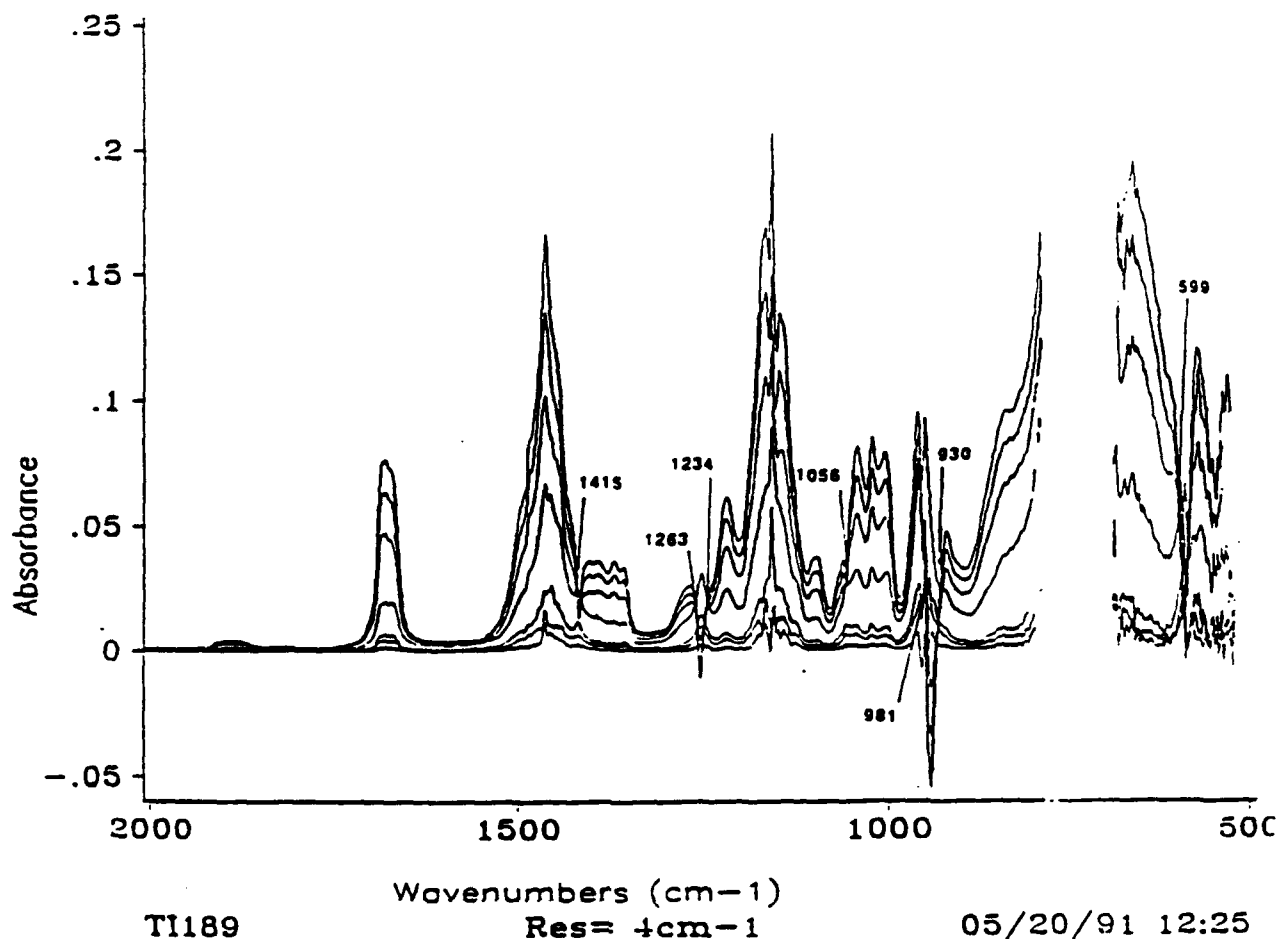
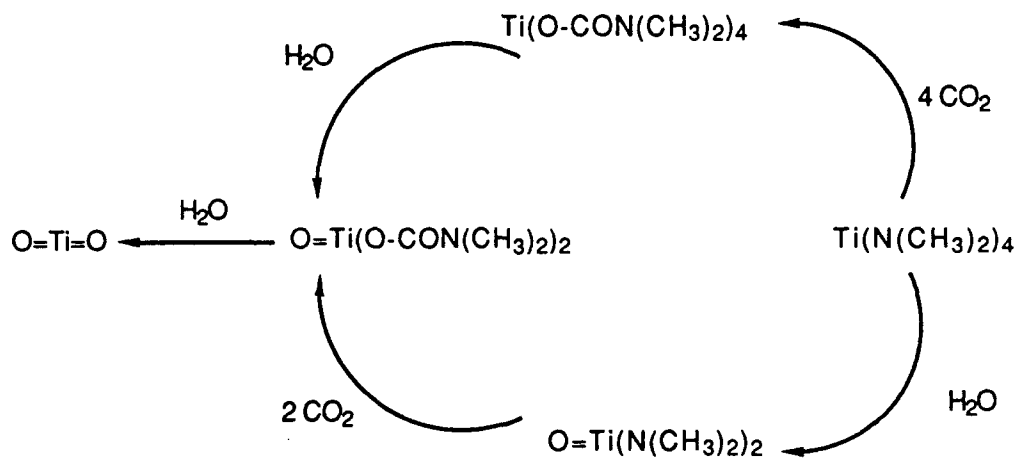
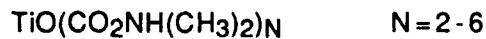
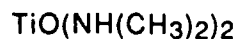
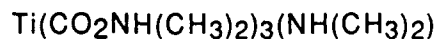
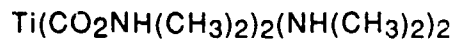
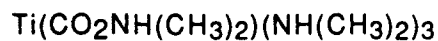
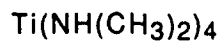


Figure 1: Consecutive FT-IR spectra used to follow the gas phase reaction of tetrakisdimethylaminotitanium (TTK) with water and CO_2 . Several isosbestic points are easily seen and are indicated in the figure. The spectra correspond to addition of successive aliquots of water. The reference spectrum for the whole set shown was that obtained when the TTK was initially added to the cell. Therefore, when the absorbance drops below zero it means that the absorbance at that wavelength is mostly due to unreacted TTK or some species which is equilibrium with TTK before reactants are *purposely* added to TTK (see Chisolm references with regard to 'fortuitous' CO_2 and water). In our hands, it is virtually impossible to completely remove all water and CO_2 before adding the TTK. Thus there is some amide and TiO_2 immediately formed upon addition of the TTK to the cell. However, the equilibria associated with reaction of TTK with these species are shifted far toward TiO_2 and the amides. In agreement with the analysis of Chisolm and Extine, we find that an amido ligand can be bidentate or monodentate bound to the titanium depending on the ratio of CO_2 and free amine in the gas phase. The feature at 1678 is particularly important in this regard. Experiments with the isotopically substituted reagents D_2O , H_2^{18}O , C^{18}O_2 and $^{13}\text{CO}_2$ have allowed us to map out the reactions designated in this Figure. Stoichiometry of net reaction, gross kinetics, and discrimination between various reactants, products and fortuitous reaction participants were accomplished using numerous plots of normalized incremental absorbance change versus amounts of added reactants or products. UV-visible spectra are substantially less complicated, i.e. at this point in our on-going study, only showing a single isosbestic point near 400 nm.

points. A simplified scheme is diagrammed below in which a number of the necessary intermediates are not shown. Some of these are listed below.

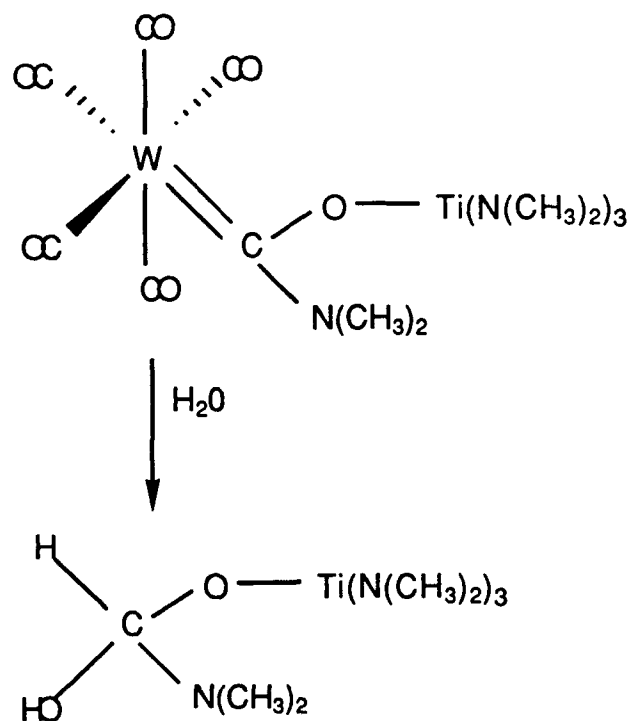


The scheme proposed above is actually very complex with only representative species being shown. Some of the partially reacted species involved but not shown above are listed below.



We have also clearly shown that the TiO_2 deposition chemistry results from reaction of the tetrakis compounds with H_2O and not O_2 . The gas phase equilibria evident in the Figures clearly shows the tendency for the precursor to form a variety of volatile *gas phase* intermediates. Figure 2 shows a set of transmission IR spectra of various thin films on silicon. The native oxide was not removed and its presence is evident by the interference fringes in all the spectra. The CO incorporation in a tungsten film deposited by LCVD using $\text{W}(\text{CO})_6$ is unmistakable in spectrum A. There are no bridging CO ligands¹¹ and most CO would seem to be present in the form of $\text{W}(\text{CO})_5$ and $\text{W}(\text{CO})_4$. Auger electron spectra clearly demonstrate the presence of tungsten in the films and the broad blended feature between $\approx 1000\text{ cm}^{-1}$ and 650 cm^{-1} corresponds to various W-O vibrational modes¹².

Figure 2B shows a transmission IR spectrum of the same LCVD tungsten film used to obtain Figure 2A after treatment with tetrakisdimethylamino titanium. The absorption features due to CO are now almost completely missing. For comparison, spectrum 2C shows a composite film which was prepared using the same CVD and LCVD chemistry but in reverse order. In this case, the CO ligands are introduced after the tetrakis treatment and they are obviously present. Comparison of all the spectra in Figure 2, including 2D which corresponds to the same TiO_2 film in 2C before the LCVD tungsten film was added, shows the lattice vibrations of the composite films also to be a function of the order of the application of the different reagents.



Auger electron spectra reveal a net stoichiometry of the TiO_2 corresponding roughly to $\approx \text{TiO}_{1.5}$. Raman spectra of films deposited on quartz substrates suggests that they are roughly 50% rutile and 50% anatase and that they retain these percentages over a period of months even upon exposure to air. Optical microscopy demonstrates that continuous films, tens of Ångstroms thick, with superior optical quality can be deposited on quartz with substrate temperatures as low as 60°C . In fact, as was also reported by Hoffman and coworkers in the context of nitride CVD using the same tetrakis precursors, low substrate temperatures seem to favor deposition of high quality films. We believe this results from inhibition of deposition of thick films which have a tendency to crack and also because the formation of the TiO_2 lattice is highly exothermic. The exothermicity combined with a cooler substrate drives the deposition chemistry to completion.

There is precedent for reaction of tetrakisdiethylaminotitanium with free CO as well as with bound CO involving group six metals^{10,13,14}. In this regard the FT-IR spectra clearly show that *all* of the CO ligands ultimately react with the tetrakisdiethylaminotitanium. Assignment of the metal oxide stretching region strongly suggests that the reaction products are also hydrolyzed leading to TiO₂ incorporation.

In conclusion, it is clear that in addition to the obvious chemistry which results in deposition of TiO₂, tetrakisdiethylaminotitanium and related compounds have the very favorable characteristic of removing CO and CO₂ from previously deposited LCVD thin films. It has also been reported that carbonyl is dissociatively chemisorbed onto growing LCVD tungsten films. This potentially leads to incorporation of carbide and oxide into such films. To the extent that production of these species is reversible, and they therefore exist in equilibrium with carbonyl, the chemistry we describe could also result in their removal as well.

Acknowledgements

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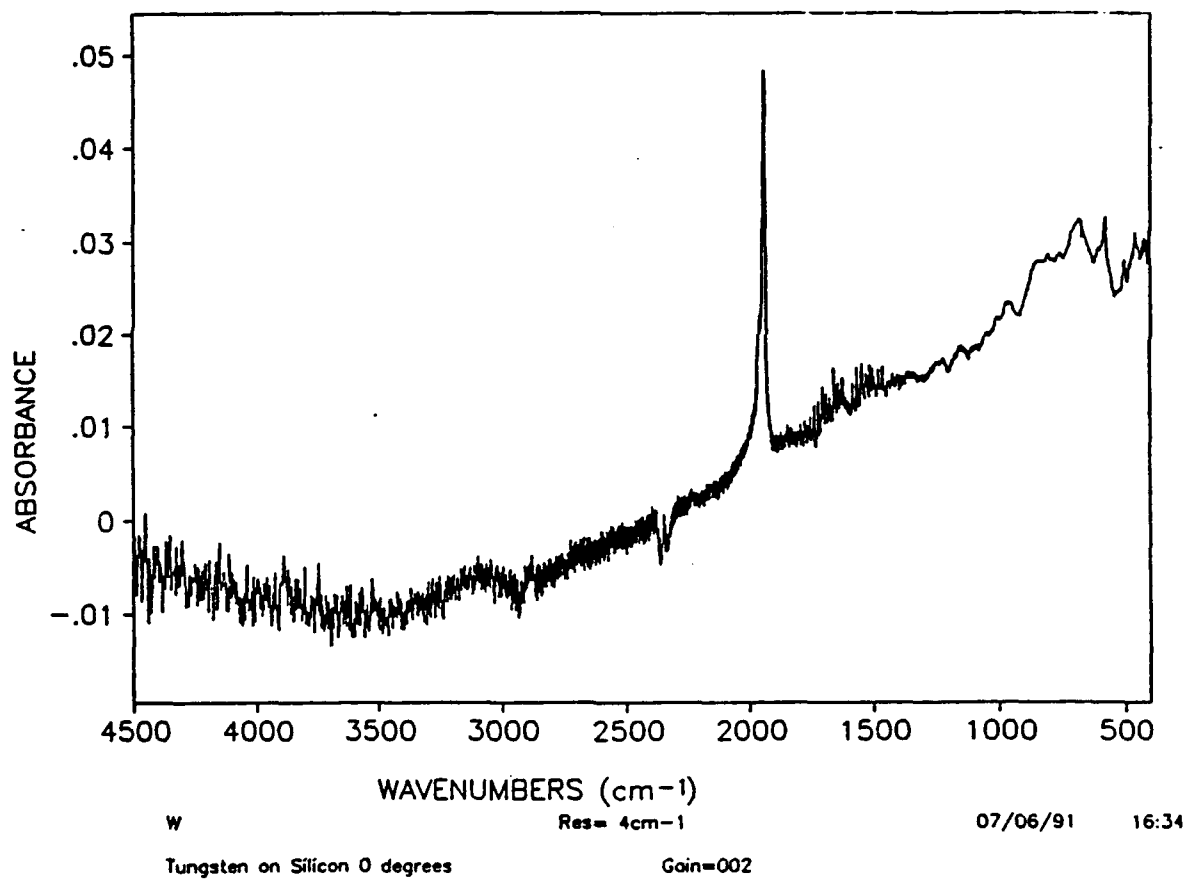


Figure 2A

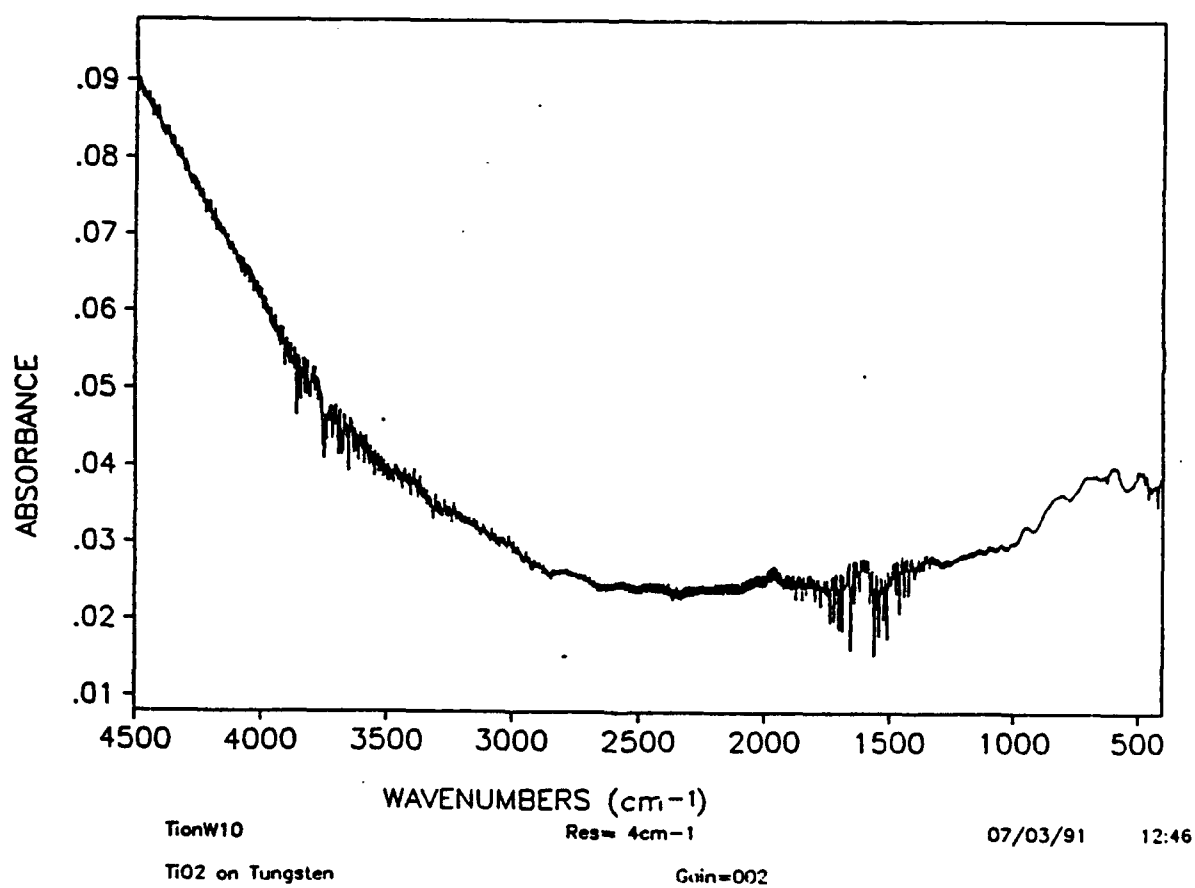


Figure 2B

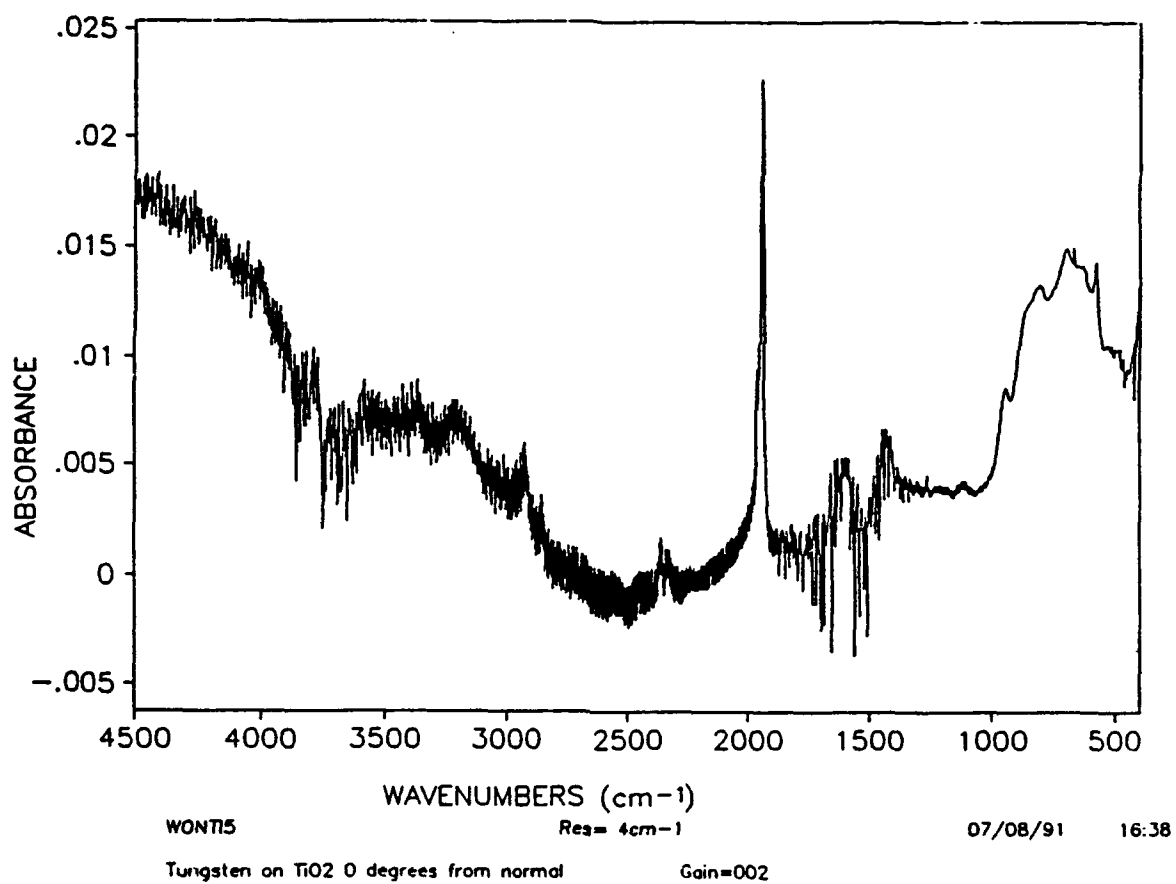
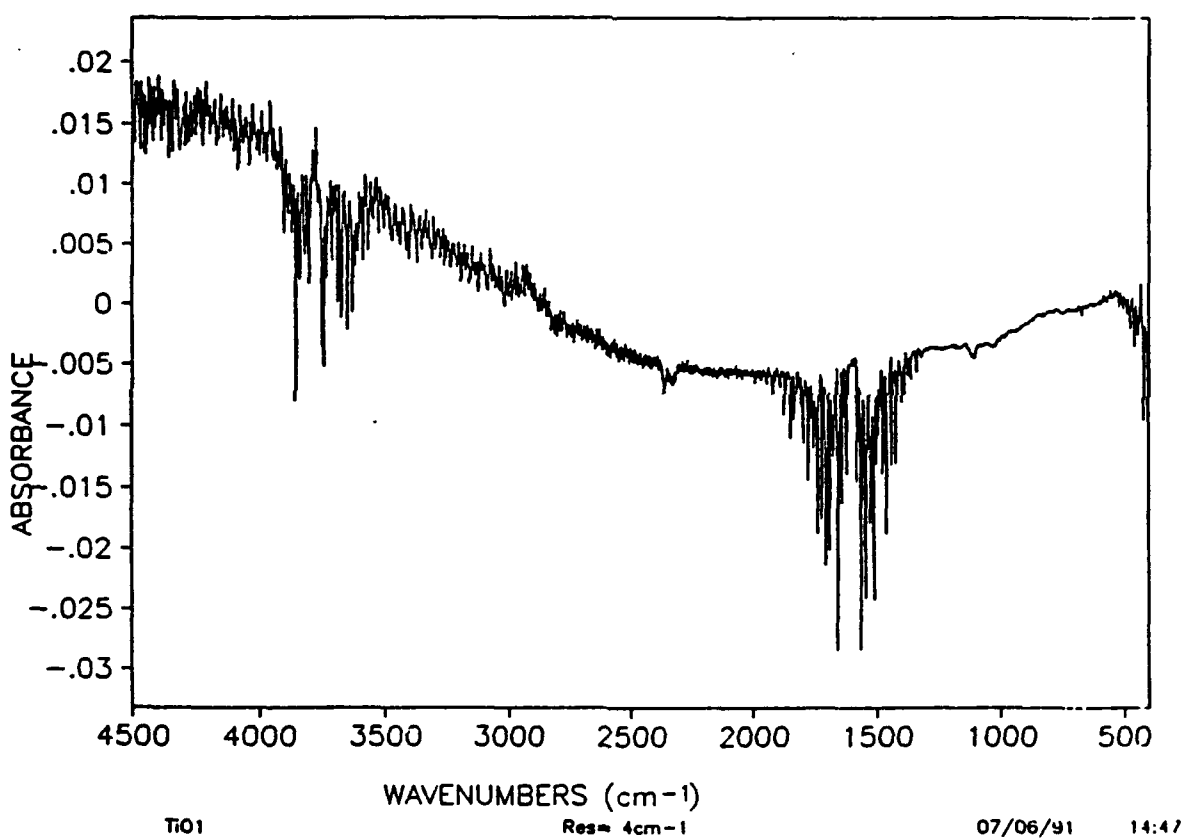


Figure 2C



TiO2 on Silicon 0 degrees

Gain=002

Figure 2D

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