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THE CHEMICAL ANALYSIS OF THIN FILMS AT SANDIA NATIONAL LABORATORIES

MASTER

D. R. Tallant and E. L. Taylor

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ABSTRACT

The characterization of thin films produced by chemical and physical vapor deposition requires special analytical techniques. When the average compositions of the films are required, dissolution of the thin films and measurement of the concentrations of the solubilized species is the appropriate analytical approach. In this report techniques for the wet chemical analysis of thin films of Si:Al, $P_2O_5:SiO_2$, $B_2O_3:SiO_2$, TiB_x and TaB_x are described. The analyses are complicated by the small total quantities of these analytes present in the films, the refractory characters of these analytes, and the possibility of interferences from the substrates on which the films are deposited. Etching conditions are described which dissolve the thin films without introducing interferences from the substrates. A chemical "amplification" technique and inductively coupled plasma atomic emission spectrometry are shown to provide the sensitivity required to measure the small total quantities (micrograms to milligrams) of analytes present. Also the chemical analysis data has been used to calibrate normal infrared absorption spectroscopy to give fast estimates of the phosphorus and/or boron dopant levels in thin SiO_2 films.

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INTRODUCTION

Chemical and physical vapor deposition techniques allow the production of micrometer and sub-micrometer films of some relatively refractory materials which are of interest to both weapons and energy programs at Sandia Laboratories. An unfortunate characteristic of these deposition techniques, at least in their current state of technology, is the inability to accurately predict the composition of the thin films from the deposition conditions. Hence, the approach has been to characterize test batches of the films by physical and/or chemical analysis in order to determine what deposition conditions will yield the desired composition(s).

For those instances in which the average composition of the film is important and in which the application of instrumental analytical techniques is complicated by the nature of the film and/or its substrate, the preferred analytical technique is selective dissolution of the film from its substrate, followed by wet chemical analysis. Certain films produced by the Microelectronics Technology Department (2140) and the Metallurgy Department (5830) are in this category and have been the subject of recurrent requests to the Materials Characterization Department (5820) for chemical analysis. As can be seen from Table I, the submitted materials include films of

Table I

<u>Film Composition</u>	<u>Film Thickness (micrometers)</u>	<u>Substrate Composition</u>	<u>Deposition From</u>	<u>Program</u>
0-3 wt.% Si in Al	~1	Si	Al, Si (vapor)	Microelectronics Dev. (2140)
0-16 Mole% P_2O_5 in SiO_2	0.2 - 0.8	Si	SiH_4, PH_3, O_2	Microelectronics Dev. (2140)
0-15 Mole% B_2O_3 in SiO_2	~0.4	Si	SiH_4, B_2H_6, O_2	Microelectronics Dev. (2140)
TiB_x ($x \approx 2-6$)	25 - 90	Graphite	$TiCl_4, BCl_3, H_2, Cl_2$	Tokamak Improvement Program (TIPP, 5830)
TaB_x ($x \approx 1.4-3$)	10 - 30	Graphite	$TaCl_5, BCl_3$ or B_2H_6, H_2, Cl_2	BASIC Energy Sciences (BES, 5830)

aluminum-silicon alloys, phosphorus- and boron-doped glasses, and metal borides.

The programs in which these materials are involved include the development and production of microelectronic devices (Al:Si, $P_2O_5:SiO_2$, $B_2O_3:SiO_2$), development of improved wall coatings for Tokamak devices (TiB_x) and improvement of the corrosion and wear resistance of coatings for hostile environments (TaB_x).

The analysis of these materials presented two major problems: how to selectively etch the thin film off its substrate without attacking the substrate, and how to measure the small amounts of material thus solubilized. As can be seen from Table II, the etching problem was solved using a variety of etchants suited to specific thin film/substrate combinations.

Table II

Thin Film/Substrate Composition	Etchant	(Representative) Total Mass of Thin Film/ area of film
Si:Al/Si (coated w/ Si_3N_4)	1N NaOH	5 mg/20cm ²
$P_2O_5:SiO_2$ /Si	0.5% HF	3 mg/20cm ²
$B_2O_3:SiO_2$ /Si	0.5% HF	2 mg/20cm ²
TiB_x /Graphite	6M HNO_3	5 mg/0.25cm ²
TaB_x /Graphite	Conc. HNO_3 + Conc. HF	15 mg/0.75cm ²

Except for the highly corrosive solution required to solubilize TaB_x , selective etching of the metal borides off the graphite substrate was relatively simple. Loss of boron due to volatilization in acid solutions in the presence of fluoride was considered a potential complication [1] but did not occur. Selective removal of boron- and phosphorus-doped glassy layers from silicon substrates was found to occur with negligible attack on the substrates as long as oxidizing agents were excluded from the 0.5% HF etch solution. The most difficult problem in selective etching occurred with the Si:Al thin films on silicon substrates. The Si:Al film was completely solubilized by a relatively long (18 hr.) contact with 1 N NaOH. However, excessive solubilization of substrate silicon occurred unless the substrate was coated with a protective layer of silicon nitride (Si_3N_4) prior to deposition of the Al:Si film.

Within the thin films the elements of interest are present as major (1-100%) and minor (.01-1%) constituents [2]. However, the small total quantity of analyte present in the thin films (see Table II) places this work in the category of microanalysis [2], which requires the application of trace techniques to the measurement of the solubilized analyte. The standard gravimetric and titrimetric techniques for aluminum, boron, phosphorus, silicon, tantalum, and titanium are not sufficiently sensitive to measure trace quantities. Further, these elements tend to form refractory oxides in standard analytical flames at temperatures of a few thousand degrees centigrade. The sensitivity and accuracy of flame atomic absorption, atomic

emission, and atomic fluorescence for these elements is relatively low. Thus special chemical preparation and/or measurement techniques had to be applied. Silicon dissolved in 1N NaOH was determined by an "amplification" technique [3] coupled to flame atomic absorption. Silicon dissolved in hydrofluoric acid (which interferes with the "amplification" technique), boron, phosphorous, tantalum and titanium were determined by measuring their atomic emission from a radio-frequency argon plasma, which, by operating at an estimated torch temperature of 10,000°C or more, decomposes refractory compounds into their substituent elements and provides orders of magnitude greater sensitivity for the analytes of interest.

In the following sections the wet chemical analysis of the thin films listed in Tables I and II are described under three categories: Al:Si alloy films, phosphorus- and boron-doped glassy films, and metal boride films. For the glassy films the wet chemical analysis results are compared to infrared absorption data obtained before the films were dissolved. Infrared absorption spectroscopy is evaluated as a fast, approximate method of quality control for the phosphorus and boron content of glassy films.

1. Analysis of Al:Si Alloy Films

1.1 Introduction

One aspect of microelectronics fabrication technology [4,5] (Dept. 2140) involves metallization of integrated circuits with a thin layer (1 micrometer) of aluminum [6] containing a

small amount of silicon, which helps prevent diffusion of the aluminum into the substrate [7]. Quality control of the metallization process necessitated development of a technique for the determination of silicon (0 to 3 weight percent) in a thin aluminum layer on a silicon substrate. The application of instrumental techniques, such as x-ray fluorescence and electron microscopy, to this determination is complicated by their tendency to sample silicon in the substrate as well as in the thin aluminum film and by the similarity in the x-ray spectra of silicon and aluminum. Emphasis was therefore placed on developing a wet chemical technique by which the thin aluminum films could be selectively etched without sampling the silicon substrate and by which the 5 to 150 micrograms of solubilized silicon could be reliably determined.

Early on it was recognized that neither common acid nor basic etchants would solubilize the metallic film without attacking the substrate silicon. However, by depositing a thin coating of silicon nitride on the silicon substrate prior to the deposition of the silicon-containing aluminum film, a chemically-resistant (i.e. passive) substrate was formed from which the aluminum layer could be selectively etched. Other passive coatings (e.g. gold) could have been applied to the substrate, but the silicon nitride coating is considered most convenient and most similar to the actual integrated circuit surfaces on which aluminum films are subsequently deposited. The silicon nitride coating is not normally part of this specific microelectronics fabrication procedure, but is applied to those samples which are to be chemically

analyzed and therefore require a passive substrate.

Using a basic etchant which is compatible with the "amplification" technique [3] employed for measurement of the solubilized silicon, aluminum films have been analyzed for as little as 8 micrograms of silicon.

1.2 Experimental

1.2.1 Sample preparation

All materials used in sample preparation were of electronic grade purity. The silicon substrates were in the form of circular wafers of 5 cm diameter and approximately 0.4 mm thickness. These substrates were coated on all surfaces with 0.2 to 0.3 micrometers of silicon nitride by reacting silane and ammonia in a chemical vapor deposition apparatus. The deposition temperature was approximately 750°C. On one face of the silicon nitride-coated substrates were deposited thin films (about 1 micrometer thick) containing about 5 milligrams of aluminum and 5 to 150 micrograms of silicon. These films were applied by physical vapor deposition in a vacuum deposition apparatus from a heated crucible containing an aluminum-silicon mixture. The amount of silicon in the aluminum film depended on the composition of the aluminum-silicon mixture added to the vapor deposition apparatus. When no silicon was added, aluminum "blanks" were produced which were used to assess the chemical passivity of each batch of silicon nitride-coated substrates. In order to avoid loss of chemical passivity of the silicon nitride coatings due to air oxidation, the aluminum films were deposited within a day after the silicon nitride was applied.

1.2.2 Sample Etching

All etching and subsequent chemical processing were carried out in a clean bench rated to provide a Class 100 environment. The samples were placed in small plastic containers with the aluminum film facing up. The etchant solution, 3 mL of 1N NaOH (from electrolytic pellets filtered after dissolution), was pipetted onto each sample and spread so as to cover the entire aluminum film. Surface tension will hold the etchant "bubble" to the metallized side of the sample if sudden movement of the sample is avoided. The samples were covered to prevent evaporation and left in contact with the etchant solution overnight (16-18 hours). After etching was completed, the samples were rinsed into plastic separatory funnels with deionized water.

1.2.3 Silicon Measurements

To avoid silicon contamination from glassware, plasticware was used exclusively in the chemical processing. "Ultrex" [8] reagents were used where available and reagent grade chemicals otherwise. The silicon determination followed the procedure developed by Kirkbright et al., [3] although similar methods [4-13] also appear applicable. In this procedure the etchant solution is acidified with hydrochloric acid, and then ammonium molybdate solution is added to form silicomolybdic acid $\text{H}_4\text{SiO}_4(\text{MoO}_3)_{12}$, which is extracted into n-butanol. The organic phase is then analyzed for the twelve molybdenum atoms associated with each silicon atom (hence the name "amplification" technique) by flame atomic absorption spectroscopy. Standards were prepared by doping known amounts of silicon from a solution standard into

3 mL of 1N NaOH containing 5 mg of aluminum. These standards were then processed identically to the sample etchant solutions. The total mass of the aluminum film was measured by weighing the sample before and after the etch. Weight percent silicon was calculated according to the relation $\frac{\text{silicon found}}{\text{sample weight loss during etch}} \times 100\%$. The masses of the aluminum films ranged from 4.5 to 6 milligrams. The "silicon found" is the total silicon in each sample etchant solution as determined by the above procedure less any silicon present in etchant solutions from aluminum "blanks" etched and analyzed coincidentally with the samples.

1.3 Results and Discussion

The determination of silicon in thin aluminum films by the above procedure has been performed on over a hundred samples. The silicon content of samples ranged from 8 micrograms (~ 0.2 weight percent) to 130 micrograms (~ 2.5 weight percent). Since samples are typically submitted in duplicate, with only a few triplicates available, a formally-defined precision is difficult to establish. However, the range of replicate samples was typically less than 0.1 weight percent (or about 5 micrograms) of silicon for samples containing 0.2 - 1.5 weight percent silicon. In most of the instances in which this range was exceeded, the masses of the aluminum films from replicate samples varied by more than 10 percent. In these cases a weighing error may have occurred or the replicate samples may have experienced significantly different deposition conditions.

In the analytical procedure the dissolution of the aluminum thin film is allowed to proceed overnight partly for convenience and partly to assure complete dissolution of the silicon in the aluminum film. A comparison of silicon recoveries using different dissolution procedures (Table III) establishes the requirement for a relatively long dissolution time. A special run of nine replicate samples estimated to contain 2 to 3 weight percent silicon was divided into three groups of three samples. Three samples were etched for an average of 23 minutes and then the etchant was removed and analyzed. Another three samples were etched for an average of 12 minutes. Then the etchant solutions were rinsed from the samples and stored overnight at a basic pH to allow any particulate silicon rinsed from the sample to dissolve. Typically, the aluminum in the thin layer dissolved in less than 10 minutes. The third set of three samples was etched overnight as in the standard procedure. Three sets of aluminum "blanks" were etched by the same procedures and the etchant analyzed to provide silicon blank values. It is obvious from Table III that sufficient etchant-sample contact time is critical to efficient silicon recovery. Further, it appears that undissolved silicon particles resist being rinsed off the sample as was attempted in procedure 2 (Table III). The overnight etch is believed sufficient contact time since a 12 minute contact recovers about half as much silicon as the 18 hour contact and a 23 minute contact recovers 20 percent more than the 12 minute contact. Silicon powder was found to dissolve in 1N NaOH with complete recovery in less than 72 hours. This powder consisted

of particles primarily in the 40 to 100 micrometer size range. Since any silicon particles in the aluminum films will be considerably smaller than the 1 micrometer film thickness, an 18 hour etchant-sample contact time can be expected to solubilize essentially all the silicon in a film.

The chemical passivity of the silicon nitride coating to the NaOH etchant was found to be a function of its age and the method by which it was applied to the substrate. Table IV lists the mass of silicon recovered from aluminum "blanks" etched and analyzed at different times after the silicon nitride coatings and the aluminum films were applied. The silicon nitride coatings were chemical vapor deposited as described in the Experimental

Table III

Effect of Etching Procedures on Silicon Recovery

<u>Procedure</u> ¹	<u>Contact Time</u> ²	<u>Weight Percent Silicon</u> ³ (Average)
1. Short etch	23 min.	1.48, 1.49, 1.55 (1.51)
2. Short etch - Overnight dissolution	12 min.	1.28, 1.23, 1.28 (1.26)
3. Overnight etch	18 hrs.	2.05, 2.44, 2.56 (2.36)

1.) See text.

2.) Time that etchant solution was in contact with sample surfaces.

3.) Based on total silicon found less silicon found in aluminum "blanks" divided by the mass of the aluminum film as determined by difference weighing.

section (1.2.1). Over a period of months, the silicon in these coatings became more labile and appeared in the etchant in increasing amounts. Silicon in silicon nitride coatings deposited on the substrate from a radio-frequency plasma was found to be excessively labile. Even with coatings aged less than two weeks, 10 to 60 micrograms of silicon were found in the etchant solutions after an overnight contact with aluminum "blanks" on plasma-deposited silicon nitride. Substrates for a set of samples and aluminum "blanks" should therefore be coated with silicon nitride by chemical vapor deposition at the same time and under the same conditions.

Atomic absorption analysis of the molybdenum in the extracted silicomolybdic acid is sufficiently sensitive that the detection limit for silicon in the aluminum thin films of samples is determined by the variation in the silicon blank values. From the results of Table IV a few micrograms of silicon should be detectable if the "age" of the samples and aluminum "blanks" is two months or less. The aluminum "blanks" are essential to the success of the analysis, since they monitor both the chemical passivity of the silicon nitride coating and the environmental silicon contamination introduced during the analysis.

Prior to the use of a class 100 environment for the etching and chemical processing procedures, environmental silicon contamination (especially during dust storms) sometimes yielded erratic results and high silicon "blank" values. Etching and chemical processing in a "clean" environment have increased the reliability of the analysis. Occasional erratic sample

Table IV
Aging of Silicon Nitride Coatings

<u>Age</u> ¹	<u>Micrograms of Silicon Found</u> ²	<u>Number of "Blanks" Analyzed</u>
less than 2 weeks	1.6 $\pm$ 0.8	4
2 months	4.3 $\pm$ 0.6	6
3 months	10.9 $\pm$ 2.5	3

- 1.) Age from deposition to analysis.
- 2.) Average micrograms of silicon found in etchant solutions after overnight contact with aluminum "blanks" and estimated standard deviation of the results.

results and high silicon "blank" values are now suspected to be due to variations in the passivities of the silicon nitride coatings. The passivities of these coatings may be controlled by unknown factors in the chemical vapor deposition process, an area which could profit from further investigation.

2. Analysis of Glassy Films

2.1 Introduction

Glassy films of submicron-thick silicon dioxide, chemical vapor deposited on silicon substrates, are employed as insulating layers in microelectronic devices. Phosphorus, as phosphorus pentoxide (P_2O_5), may be codeposited with the silicon dioxide.

to form a phosphosilicate ($\text{SiO}_2:\text{P}_2\text{O}_5$) glass. Phosphorus oxide reduces the mobility of sodium and potassium in the glass and lowers its flowing temperature so that the glass conforms as closely as possible to the contours of the substrate. Likewise boron as boron trioxide (B_2O_3) forms a borosilicate ($\text{B}_2\text{O}_3:\text{SiO}_2$) glass, which is being evaluated in a developmental effort concerning integrated circuit field oxides. The properties of the phosphorus- and boron-doped glasses are a function of their composition.

Wet chemical methods were developed to analyze the thin film glasses for their phosphorus and boron contents. An etchant solution of dilute hydrofluoric acid was found to dissolve the glassy films without significantly attacking the silicon substrate so long as oxidizing agents were not added to the etchant. After dissolution the etchant solutions were analyzed for their phosphorus (or boron) and silicon contents by inductively coupled plasma atomic emission spectrometry.

A relatively fast, nondestructive method for the estimation of the phosphorus content of glassy films by infrared absorption spectrometry [14] was also evaluated. This technique provides approximately correct results and may be useful for quality control at a microcircuit production facility. Infrared absorption spectrometry also appears to be applicable to the analysis of borosilicate films.

2.2 Experimental

2.2.1 Sample preparation

The phosphosilicate thin films were vapor-deposited on 5 cm diameter <100> and <111> silicon wafers (approximately 0.4 mm thick) at 450°C from a phosphine-silane-oxygen mixture diluted with nitrogen. The phosphorus content was adjusted by varying the phosphine composition of the gas mixture. Deposition was carried out in two different apparatus: one with horizontal gas flow over a resistance-heated wafer in a quartz tube; the other with resistance-heated wafers moving under a manifold from which the gas mixture flowed down onto the wafers. No further heat treatment was carried out after the initial deposition. The preparation of the $B_2O_3:SiO_2$ glassy thin films will not be discussed in this report.

2.2.2 Sample Etching

The data reported here for the phosphosilicate films were obtained before a clean bench became available. With a relatively short etch time, environmental contamination was less severe than in the case of the Si:Al films, and the provision for a class 100 environment (though an excellent precaution later adopted) was not absolutely necessary.

The etchant (3 ml of 0.5% hydrofluoric acid) was applied to the glassy surface of the approximately 5 cm diameter sample wafers. The etching times for removal of the phosphosilicate films varied from 5 minutes to 40 minutes, depending on the thickness of the glass and its phosphorus content. When the etchant had

completed removal of the glassy layer, it tended to bead on the silicon substrate, and this provided an easily recognizable signal to terminate the etch. Analysis of etchant contacted directly with a silicon substrate for 30 minutes showed that less than 20 micrograms of silicon were removed from the substrate. During a sample etch, direct contact of the etchant with the silicon substrate was never longer than 10 minutes. The borosilicate films were solubilized by the same procedure.

2.2.3 Phosphorus, Boron and Silicon Measurements

The etchant solutions from the phosphosilicate and borosilicate films were rinsed off the substrates with deionized water and diluted in plastic volumetric flasks. It is necessary to complex the fluoride ion prior to aspiration into the inductively coupled plasma so as to minimize attack by fluoride ion on the quartz portions of the plasma nebulizer and torch assemblies. Attack by fluoride ion not only reduces the efficiency of the plasma nebulizer by eroding small orifices, but also introduces silicon from the quartz into the plasma torch, which interferes with the silicon determination. Fluoride ion was complexed by adding boric acid solution to the phosphosilicate etchant and a solution of aluminum to the borosilicate etchant prior to the dilution. Phosphorus, boron and silicon concentrations in the etchant solutions were measured by their atomic emission at 213.6 nm (phosphorus), 249.5 nm (boron) and 288.1 nm (silicon) from the microwave plasma. Solution detection limits of 0.5 microgram/mL for phosphorus, 0.2 microgram/mL for silicon and 0.03 microgram/mL for boron are achievable by this technique.

2.2.3 Infrared Absorption Measurements

Infrared data acquisition and data reduction were intentionally kept simple so that personnel not extensively trained in infrared spectroscopy could perform the analysis with a minimum of difficulty. No electronic signal enhancement, infrared beam expansion, or peak deconvolution techniques were used. All spectra were obtained on a Perkin-Elmer Model 21 Double Beam IR Spectrophotometer with no special attachments except a comb attenuator. The infrared beam sampled a 7 mm by 25 mm rectangle approximately in the center of the 5 cm diameter wafers. Spectra of vapor-deposited phosphosilicate layers were obtained with a silicon wafer "blank" in the spectrophotometer reference beam in order to compensate for weak lattice absorption bands in the silicon substrate [15]. A comb attenuator was inserted in either the sample or reference beam in order to set the "baseline" as close as possible to zero absorbance. Figure 1 displays the infrared spectrum of a sample (number 6) containing about 15 mole percent P_2O_5 in the silicon dioxide layer. The Si-O peak near 1100 cm^{-1} and the P=O peak near 1320 cm^{-1} are indicated in the figure. The optical densities of the P=O and Si-O bands are the maximum differences in absorbance between the hand-drawn baseline and the peak absorbance for each band. Thus, from Figure 1, an absorbance ratio, $(R=(P_1-B_1)/(P_2-B_2))$, is calculated from the ratio of optical densities of the P=O band to the Si-O band. This R is the same as the linear absorbance ratio described by Tenney and Ghezzi [14]. No attempt was made to calculate band area ratios,

Fig. 1. Infrared absorption spectrum of a submicron layer of vapor-deposited phosphosilicate glass (~15 mole % P_2O_5) on a silicon substrate.

as was done by Tenney and Ghezzi [14]. It was felt that band area ratio calculations offered no advantage in accuracy over linear absorbance ratios for weak bands (due to difficulties in determining band widths) and unnecessarily complicated data reduction.

2.3 Results and Discussion

2.3.1 Phosphosilicate Films

Table V summarizes the data obtained by both wet analysis and infrared analysis for 22 silicon wafers with vapor-deposited phosphosilicate films and one wafer with undoped vapor-deposited SiO_2 . The table lists the sample number; analyzed weights of phosphorus and silicon (as P_2O_5 , SiO_2 and the total of P_2O_5 + SiO_2); the difference in weight of the sample before and after the etch; the mole ratio P_2O_5 (moles P_2O_5 divided by moles SiO_2);

Table V
Analysis of Phosphosilicate Glass Films

Sample Number	WET ANALYSIS						IR ANALYSIS		
	P ₂ O ₅ μg	SiO ₂ μg	SiO ₂ +P ₂ O ₅ μg	Weight Loss ⁽²⁾ μg	Mole Ratio P ₂ O ₅ :SiO ₂	Mole% P ₂ O ₅ ⁽³⁾	Optical Density P=O ⁽⁴⁾	Optical Density Si-O ⁽⁵⁾	R ⁽⁶⁾
1	141	2037	2178 (-16%) ⁽¹⁾	2605	.029	2.8	.004	.661	.006
2	141	2118	2259 (-17%)	2738	.028	2.8	.007	.675	.010
3	615	2428	3043 (-12%)	3447	.107	9.7	.051	.745	.068
4	574	2203	2777 (-12%)	3160	.110	9.9	.045	.705	.064
5	658	2460	3118 (-11%)	3518	.113	10.2	.058	.788	.074
6	1104	2706	3810 (-10%)	4212	.173	14.7	.123	.890	.138
7	1031	2449	3480 (-11%)	3922	.178	15.1	.116	.812	.143
8	522	1144	1666 (-5%)	1748	.194	16.2	.041	.315	.130
9	353	1700	2053 (-13%)	2362	.088	8.1	.021	.516	.041
10	353	1861	2214 (-14%)	2570	.080	7.4	.0145	.540	.027
11	446	1840	2286 (-11%)	2559	.103	9.3	.039	.564	.069
12	415	1326	1741 (-7%)	1865	.132	11.7	.035	.406	.086
13	710	2417	3127 (-14%)	3637	.124	11.1	.066	.799	.083
14	790	3048	3838 (-13%)	4405	.110	9.9	.072	1.001	.072
15	195	2139	2334 (-10%)	2595	.039	3.8	.008	.716	.011
16	378	2449	2827 (-11%)	3184	.066	6.2	.016	.726	.022
17	538	2503	3041 (-6%)	3246	.091	8.4	.049	.737	.066
18	641	2096	2737 (-16%)	3258	.129	11.4	.050	.718	.070
19	470	3155	3625 (-9%)	3970	.063	5.9	.022	.912	.024
20	235	1583	1818 (-11%)	2037	.061	5.7	.006	.444	.014
21	195	1091	1286 (-9%)	1416	.077	7.1	.004	.308	.013
22	166	877	1043 (-6%)	1104	.082	7.6	≤.002	.242	≤.008
23	--	--	-----	--	negligible ⁽⁷⁾		≤.001	.572	≤.002

(1) Number in parentheses is % difference between the sum of SiO₂+P₂O₅ and the measured weight loss.

(2) Measured weight loss caused by etching the phosphosilicate film off the wafer.

(3) Mole% P₂O₅ = Moles P₂O₅ / (Moles P₂O₅ + Moles SiO₂) times 100%.

(4) Near 1320 cm⁻¹.

(5) Near 1100 cm⁻¹.

(6) R = O.D. of P=O/O.D. of SiO₂.

(7) Undoped SiO₂, not wet analyzed.

mole percent P_2O_5 (moles P_2O_5 divided by the total moles P_2O_5 + moles SiO_2 times 100 percent); and the IR analysis data, including the optical densities of the $P=O$ ($\sim 1320\text{ cm}^{-1}$) and $Si-O$ ($\sim 1100\text{ cm}^{-1}$) bands and their ratio, $R = O.D. (P=O)/O.D. (Si-O)$.

Included in parentheses in the " $SiO_2 + P_2O_5$ " column is the percent difference between the measured weight loss in the sample due to etching and the calculated weight of the phosphosilicate layer (total of $SiO_2 + P_2O_5$). The calculated weights vary from 5% to 17% less than the measured weight loss, with 9%-12% differences occurring most frequently. The estimated accuracies in the silicon and phosphorus analyses are $\pm 5\%$ and $\pm 10\%$, respectively; there appears to be a regular difference between the calculated weights and the measured weight losses that is not due to a statistical or experimental artifact. The difference is probably due to one or both of two causes. First, there may be impurities (atoms other than Si, O and P) in the phosphosilicate layer or adsorbed on its surface. A complete qualitative analysis for trace constituents might reveal their identity. Second, silicon and phosphorus may be present, in part, as silicates ($Si_2O_5^{2-}$) and phosphates (PO_4^{3-}), or other forms, which in addition to having larger gravimetric factors than SiO_2 and P_2O_5 , require cations as charge compensators.

The percent difference between the measured weight loss of the sample and the calculated weight of the phosphosilicate layer as shown in Table V is believed to be indicative of the accuracy of the analytical method. It was decided for subsequent

analyses to analyze the etchant solution only for phosphorus and assume that the difference between the calculated weight of P_2O_5 and the measured weight loss of the sample is the weight of SiO_2 present. This modification of the analytical technique simplified the analysis and was considered sufficiently accurate for quality control purposes.

The infrared absorption data in Table V were obtained at room temperature. Cooling samples to liquid nitrogen temperature in a Dewar did not result in any observable narrowing of the silicon or phosphorus absorption bands, which implies that the line shapes observed in Figure 1 are heterogeneously broadened by the lack of long-range crystalline order in the glassy phosphosilicate layer.

Figure 2 graphs the absorbance ratios, R , versus the mole percent P_2O_5 for 20 of the samples listed in Table V. Two samples (21 and 22) deviated significantly (low absorbance ratio, R) from the trends of the other samples and were not included in the calibration graph. These two samples contained significantly less of the phosphosilicate layer ($SiO_2 + P_2O_5$) than the other samples. This resulted in very small optical densities for their $P=O$ absorption bands and consequently questionable infrared data. Also, any variation in phosphosilicate composition across the wafer (resulting from inhomogeneities in the vapor deposition process) would be less likely to be "averaged out" in thinner, as compared to thicker films. Such variation in phosphosilicate composition becomes serious if, as is the case for these data, the infrared beam sampled only a small portion

Fig. 2. Calibration graph plotting absorbance ratios (optical density of the P=O vibration near 1320 cm^{-1} divided by the optical density of the S-O vibration near 1100 cm^{-1}) versus mole % P_2O_5 for vapor-deposited phosphosilicate films on silicon substrates. The data are from Table V.

of a wafer's surface area (9% in these experiments). The data in Figure 2 differ from comparable graphs published by Tenney and Ghezzi [14] in that it contains two regions of linearity with different slopes. The significance of this will be discussed later. The solid line in Figure 2 was drawn by eye and is biased towards those samples containing the greatest total film weight ($SiO_2 + P_2O_5$). These thicker samples should yield the most accurate absorbance ratios and are suspected to be the most homogeneous.

The graph of the absorbance ratio, R , versus mole percent P_2O_5 (Figure 2) is significantly different from that previously published by Tenney and Ghezze [14]. Whereas the graph of Figure 2 shows two regions with distinctly different slopes, the points on the previously published graph lie on a gentle curve that is nearly linear and whose slope approximates that of the 10-15 mole % P_2O_5 region in Figure 2. Although the reasons for this discrepancy are not readily apparent, some contributing factors can be proposed. Differences in the vapor deposition temperature (450°C here, 300°C-700°C in the previously published work) could result in variations in sample morphology and therefore in variation in the infrared absorption profiles. In the work reported here and presumably in the previously published work [14], the infrared data result from sampling a relatively small area of the wafer surfaces. Both sets of infrared data are representative of the composition of the entire phosphosilicate layer only if the composition does not vary significantly across its surface. In the previously published work the film compositions were analyzed by electron microprobe. This method samples small areas of the wafer surface, and the results may not be representative of the entire sample. In addition, the electron probe beam must be operated at relatively low energy in order not to penetrate through the phosphosilicate layer and sample the silicon substrate. Thus, the microprobe could only sample a fraction of the depth of the phosphosilicate layer. For the microprobe results to be representative, one must assume that the phosphosilicate composition is uniform throughout the depth of the layer. However, depth profiling experiments [16]

have shown significant variation with depth in the composition of phosphosilicate films vapor-deposited on silicon wafers. In the analysis reported here, the entire phosphosilicate layer was dissolved and analyzed, and the results should be representative of the average composition of the film.

Assuming that the results reported here accurately reflect the variation in infrared absorption with phosphosilicate film composition, the shape of the graph in Figure 2 may be interpreted as establishing the existence of two different phosphorus species in the silicate matrix. The data in Figure 2 show a linear increase in relative phosphorus absorption up to 5 mole percent P_2O_5 , a nonlinear transition region from 5 to 7 mole percent P_2O_5 , and a linear region of greater slope at concentrations greater than 7 mole percent P_2O_5 . The different slopes must arise from a variation in the P=O vibrational transition intensity since the Si-O vibrational intensity appears constant with varying phosphorus content (see Figure 3 subsequently discussed). This implies the existence of different phosphorus species, one predominant below 5 mole percent P_2O_5 and the other predominant above 7 mole percent P_2O_5 . It may be that species containing single phosphorus atoms (isolated from other phosphorus atoms by the silicon dioxide matrix) are in the majority when the phosphorus concentration is low, but that there is a strong tendency for phosphorus atoms to aggregate into dimeric and higher order phosphorus species as the overall phosphorus concentration is increased. Aggregation of aliovalent dopant ions in crystalline matrices has been described by several authors [17-19].

In Figure 3 the optical density of the Si-O absorption band is graphed versus the analyzed weight of SiO₂ for each sample listed in Table V. The abscissa also shows the equivalent thickness of the film based on the analyzed weight of SiO₂ (ignoring phosphorus content) and assuming a film density of 2.2 gm/cm³ on a 5 cm diameter disk. The line plotted in Figure 3 represents a linear least squares fit of the data, and follows the equation $x = 2896y + 202$ (4% relative standard deviation), where y = optical density of the SiO₂ absorption band (in absorbance units) and x = weight of SiO₂ (in micrograms). From the slope of the least squares fit of these data, one may calculate an apparent absorption coefficient [20], $\alpha_{app} = 2.303 \left(\frac{dA}{dt} \right) = 3.4 \times 10^4 \text{ cm}^{-1}$; where A is the band maximum absorbance and t is the equivalent thickness of the SiO₂ film (cm), here calculated from the analyzed weight of SiO₂. This value is close to the $\alpha_{app} = 3.3 \times 10^4 \text{ cm}^{-1}$ calculated from the data of Dial et al. [21] for "dry" SiO₂ (film thickness measured interferometrically) produced by oxidation of silicon wafers with dry oxygen and to the $\alpha_{app} = 3.4 \times 10^4 \text{ cm}^{-1}$ obtained by Wong [20] for heat-treated (800°C) vapor-deposited SiO₂ film thickness measured ellipsometrically; but is significantly greater than the $\alpha_{app} = 2.5 \times 10^4 \text{ cm}^{-1}$ obtained by Wong for as-deposited (450°C) SiO₂. The SiO₂ thin films examined by Wong and Dial et al. were relatively pure, with no intentionally introduced dopants. Some uncertainty is introduced into the value reported here by the need to calculate film thickness from the analyzed weight of SiO₂, which involves estimation of the wafer area from its diameter (some wafers were slightly irregular) and the use of a bulk SiO₂ density for the thin films. The fact that the data

Fig. 3. Calibration graph plotting the optical density of the Si-O vibration near 1100 cm^{-1} versus the weight of SiO₂ (from wet analysis) for vapor-deposited phosphosilicate films on silicon substrates. Equivalent thickness was calculated from the weight of SiO₂ assuming a 5 cm diameter wafer with a film density of 2.2 gm/cm^3 and ignoring the presence of P₂O₅. The data are from Table V.

of Figure 3 do not extrapolate to (0,0) may result from the method of establishing a baseline [20] from which absorbance was measured or from distortion of the SiO_2 band by the phosphorus dopant.

The variation in the optical density of the Si-O absorption transition with the analyzed weight of silicon dioxide (Figure 3) is surprisingly linear, considering the variation in phosphorus content of the samples and the relatively small area sampled in the infrared measurements. This implies that the silicon is reproducibly, if not homogeneously, distributed across the surface of the wafer, and that phosphorus has no effect or a constant effect on the silicon absorption transition at 3 to 15 mole percent dopant levels.

2.3.2 Borosilicate Films

Borosilicate films have been analyzed less extensively than the phosphosilicate films. Those borosilicate films that have been analyzed were analyzed by the modified technique, i.e., only the boron in the etchant solution was measured (by inductively coupled plasma atomic emission spectrometry) and the SiO_2 content of the film was taken as the difference between the calculated weight of B_2O_3 and the weight loss of the sample before and after the etch. The accuracy of the borosilicate film analysis appears to be as good as that of the phosphosilicate film analysis. The sensitivity is better for the borosilicate film analysis since the sensitivity of inductively coupled plasma atomic emission spectrometry for boron in solution is an order of magnitude lower than that for

phosphorus in solution (see Section 2.2.3). As little as 0.1 mole % B_2O_3 in a 2 mg borosilicate film has been measured. This corresponds to less than a microgram of total boron in the film. Samples ranging up to 15 mole % B_2O_3 in a 2 mg borosilicate film have been analyzed. An infrared analysis of borosilicate films similar to that described for phosphosilicate films appears feasible using the B-O vibrational band at about 1300 cm^{-1} and the Si-O vibrational band at about 1050 cm^{-1} . Published curves [22] of absorbance ratios versus B_2O_3 content for borosilicate films are similar in shape to that of Figure 2.

2.4 Conclusion

The wet chemical analysis of submicrometer thick phosphosilicate and borosilicate films by inductively coupled plasma atomic emission spectrometry is accurate and reliable. As little as 15 micrograms of phosphorus (about 0.7 mole % P_2O_5 in a 2 milligram phosphosilicate film) or less than 1 microgram of boron (about 0.1 mole % B_2O_3 in a 2 milligram borosilicate film) can be detected by this technique. Samples up to about 15 mole % P_2O_5 or B_2O_3 have been analyzed.

Estimation of the relative phosphorus content (Figure 2) and the total silicon content (Figure 3) of phosphosilicate films appears feasible by infrared absorption spectrometry. A similar technique may be applicable to borosilicate films. This technique is nondestructive, requires no sample preparation and may be applicable for quality control at the point of sample production. However, its accuracy is less than that of the wet chemical analysis. The infrared technique is probably not

sensitive enough for the reliable analyses of samples containing less than 5 mole % P_2O_5 and/or less than 2 milligrams of total film. The effect of deposition temperature on the morphology and infrared absorption behavior of these films is a subject that has not been adequately addressed.

3. Analysis of Metal Boride Films

3.1 Introduction

Titanium boride and tantalum boride are refractory compounds which, as coatings, form protective layers that are wear- and corrosion-resistant under extreme conditions. The technology involved in applying metal borides as coatings by chemical vapor deposition is fairly new and is still undergoing development. Titanium boride is under study (Dept. 5830) as part of the Tokamak Improvement Program for applications as a wall coating for H/D/T plasma fusion reactors. It is expected to be applied to limiters, neutral beam injector tubes, beam dumps and armor wall in these reactors. One goal of the program is to establish the conditions for depositing stoichiometric (TiB_x , $X=2$) titanium boride, which is more refractory and more resistant to plasma etching than compositions containing free, amorphous boron (TiB_x , $X>2$). The work on tantalum boride (Dept. 5830) is basic research into the stoichiometry of TaB_x as produced by chemical vapor deposition and is funded by the Basic Energy Sciences Division of the U. S. Department of Energy. The tantalum boride system is more complex than the titanium boride system since free tantalum as well as free boron can codeposit

in TaB_x , whereas only free boron can occur in TiB_x . The possible applications of chemical vapor deposited tantalum boride are in the area of corrosion-resistant and wear-resistant coatings, e.g., on drill bits used in oil drilling. Completion of gas/solid phase diagrams for both the titanium boride and tantalum boride chemical vapor deposition systems is also a goal of the Basic Energy Sciences research.

The goal of the analytical work on both of these coatings was to provide B:Ti and B:Ta ratios, i.e., x in TiB_x and TaB_x . The graphite substrates on which the metal borides were deposited did not provide any interference in the dissolution and subsequent analysis of the metal boride films. However, more strongly corrosive etch solutions were required to dissolve the metal boride films than were required for the Al:Si films and the glassy films. Standard analytical methods for the analysis of bulk metal boride samples [23] (utilizing titrimetric and gravimetric techniques) were not sensitive enough to measure the amount of material in these thin films. Inductively coupled plasma atomic emission spectrometry was found to provide more than sufficient sensitivity for accurate and reliable analyses.

3.2 Experimental

3.2.1 Sample Preparation

The metal borides were chemical vapor deposited on 25 mm diameter by 4 mm thick graphite disks. TiB_x films were deposited at temperatures ranging from 500°C to 900°C from the mixture of gases: $TiCl_4$, BCl_3 , H_2 and Cl_2 . The films were from 25 to 90 micrometers thick. TaB_x films were deposited at temperatures ranging from 550°C to 750°C from the mixture of gases: $TaCl_5$, B_2H_6 (or BCl_3), H_2 , and Cl_2 . The TaB_x films were presumed to be of approximately the same thickness as the TiB_x films. Approximately one-fourth of the disk was available for analysis. The available portion of the disk was divided into segments of 25 mm² to 75 mm² area, each containing 5 to 50 milligrams of TiB_x or TaB_x film, to provide replicates for analysis.

3.2.2 Sample Etching

Because of the corrosive and volatile nature of the etchant solutions, dissolution of the samples was carried out in a normal chemical fume hood. Class 100 facilities with an exhaust capability were not available and do not appear absolutely necessary, under normal laboratory conditions, for the dissolution of these samples. The etchant solutions were prepared from "Ultrex" [8] or Electronic Grade reagents. Segments of disks coated with TiB_x were immersed in 5-10 mL of 6M HNO_3 . The TiB_x coatings were dissolved in approximately one hour with mild heating (no boiling). Segments of disks coated with TaB_x were placed in small plastic beakers to which was added 2.5 mL of concentrated nitric acid and 0.5 mL of 48%

hydrofluoric acid. Most of the TaB_x coatings appeared to be completely dissolved in less than 30 minutes, but one sample was etched for about an hour longer because the substrate-coating interface flaked extensively and it was difficult to determine when all the TaB_x had dissolved. Flaky particulates from the coating-substrate interface and/or particles of the graphite substrate were noted in some of the etchant solutions from the TiB_x and the TaB_x coatings. The observed flaking may be related to reaction of the coatings with the graphite substrates at higher deposition temperatures. These etchant solutions were filtered prior to dilution of all the etchant solutions in plastic volumetric flasks. Prior to dilution, dissolved aluminum was added to the TaB_x etchant solutions to complex the fluoride ion, which otherwise would attack the quartz portions of the nebulizer of the inductively-coupled plasma. Both uncoated graphite "blanks" and solutions made up of known quantities of boron, tantalum and titanium were subjected to these etching procedures and subsequently analyzed. These tests showed that the etching procedures neither contaminate the sample significantly nor result in the loss of significant amounts of boron, tantalum, or titanium.

3.2.3 Boron, Tantalum and Titanium Measurements

Diluted etchant solutions were aspirated into an inductively-coupled plasma, and the resulting emission was measured at 249.5 nm (boron), 334.9 nm (titanium), and 268.2 nm (tantalum). The only interference found using a monochromator that provided .03 nm spectral resolution was an overlap of a weak tantalum

emission line with the boron emission line used for measurement. The tantalum emission intensity at the boron line was less than five percent of the typical boron emission intensity. A correction for the tantalum/boron emission line overlap was easily made. Boron was typically measured at the 5 to 20 $\mu\text{g/mL}$ level, while titanium and tantalum were typically present at 20 to 100 $\mu\text{g/mL}$. The detection limit for tantalum by inductively coupled plasma atomic emission spectrometry is a few tenths of a microgram/mL, and those for titanium and boron are an order of magnitude lower [24]. The ratio of the boron to titanium (or tantalum) concentrations multiplied by the ratio of the titanium (or tantalum) to boron atomic weights, yields x in TiB_x (or TaB_x).

3.3 Results and Discussion

Because standard materials with accurately known metal: boride ratios are not available, it is not possible to assess directly the accuracy of the results from these analyses. Since the dissolution techniques result neither in significant loss nor in contamination of the analyte species, since chemical manipulation is not extensive, and since there is good instrumental sensitivity with only minor and easily compensated interferences, one can reasonably expect the analysis to be accurate within the precision of the results.

The precision achieved for replicates of a number of titanium boride samples is presented in Table VI. The estimated standard deviation of the results is less than five percent relative for all the samples and is typically less than four

Table VI

Analysis of TiB_x

<u>Deposition Temperature</u>	<u>x =</u>	<u>Average x $\pm$ est. std. dev.</u>
500 C	6.15, 6.21, 6.27, 6.66	6.32 $\pm$ 0.23 ($\pm$ 3.7%)
500 C	8.63, 9.09, 9.52	9.08 $\pm$ 0.45 ($\pm$ 5.0%)
600 C	2.49, 2.54, 2.56	2.53 $\pm$ 0.04 ($\pm$ 1.6%)
700 C	1.97, 1.97, 2.03	1.99 $\pm$ 0.03 ($\pm$ 1.5%)
800 C	1.92, 2.04, 2.07	2.01 $\pm$ 0.08 ($\pm$ 4.0%)
850 C	2.07, 2.16, 2.18	2.14 $\pm$ 0.06 ($\pm$ 2.8%)
900 C	2.00, 2.05, 2.10	2.05 $\pm$ 0.05 ($\pm$ 2.4%)

Table VII

Analysis of TaB_x

<u>Deposition Temperature</u>	<u>x =</u>	<u>Average x $\pm$ est. std. dev.</u>
550 C	2.66, 2.76, 2.83, 3.15	2.85 $\pm$ 0.21 ($\pm$ 7.4%)
600 C	2.24, 2.27, 2.30	2.27 $\pm$ 0.03 ($\pm$ 1.3%)
650 C	1.84, 1.87	1.86 (Range = 0.03, or 1.6%)
700 C	1.57, 1.60, 1.61	1.59 $\pm$ 0.02 ($\pm$ 1.3%)
750 C	1.82, 1.86, 1.86, 1.88	1.86 $\pm$ 0.03 ($\pm$ 1.4%)
800 C	1.37, 1.42, 1.47	1.42 $\pm$ 0.05 ($\pm$ 3.5%)

percent relative. The samples prepared at deposition temperatures of 500 and 600°C have significantly greater boron:titanium ratios than those prepared at higher deposition temperatures, as has been noted in other series of titanium boride samples. The two samples prepared at 500°C have different boron:titanium ratios because of a variation in deposition conditions other than temperature as is discussed elsewhere [25].

Table VII lists analysis results for samples of tantalum boride. For these analyses the estimated standard deviation (the range for one sample available only in duplicate) is again typically less than four percent relative. As in the titanium boride samples there is a general decrease in the boron content of the samples (except for the sample deposited at 750°C) as the deposition temperature is increased. This decrease in boron content with deposition temperature semiquantitatively correlates with an increase in the carbon content (by electron microprobe analysis) of the tantalum boride film. Carbon as Ta_2C , is substitutional for boron in tantalum boride. Carbon in the graphite substrate is believed to react with the tantalum boride in a reaction that proceeds more quickly as the deposition temperature is increased [26].

The accuracy implied in these results could be maintained even if a considerably smaller mass of titanium or tantalum boride film were available for analysis. One milligram of film, dissolved and diluted to 25 mL, would provide a few micrograms/mL of boron and tens of micrograms/mL of titanium or tantalum. These concentrations are approximately two orders

of magnitude larger than the detection limits for these elements by inductively coupled plasma atomic emission spectrometry. However, as the total mass of sample decreases, environmental contamination of the samples could become significant, and use of a class 100 environment, at least for sample dissolution and subsequent chemical manipulation, could become mandatory. One milligram of a titanium or tantalum boride film with at least ten micrometers thickness would cover a few square millimeters of surface area. Therefore the amount of sample destroyed in the analysis could be minimized, variations in B:Ti or B:Ta ratios across small areas of the sample surface could be detected, or many replicates could be analyzed to improve the reliability of the statistics. Alternatively, films of a few micrometers thickness could be analyzed if larger areas of sample, say a 45° sector of a 25 mm diameter disk, could be consumed. In either case the results on these smaller samples should be precise (and, presumably accurate) to five percent relative or less.

4. Summary

The analyses described in this report are now considered "routine." That is not to imply that the results always are within the precision and accuracy standards set forth in previous chapters. Environmental contamination, or contamination from reagents, interferences from solubilized substrates, and reaction of the deposited film with the substrate can all complicate the interpretation of the analytical results and/or

degrade their precision and accuracy. Rather, the "routine" designation indicates that most of the conditions that affect the analyses have been recognized, if not understood, that standard procedures have been established, and that these procedures in general provide results with acceptable precision and accuracy.

It is the combination of the small total amount of material in these films, their refractory nature, and the possibility of interferences from solubilized substrates that has required the application of special techniques to their analysis. By careful selection of the etchant solutions and, in one case, protection of the substrate with a passive coating, the films were dissolved without introducing intolerable contamination or interferences. Amplification techniques and inductively coupled plasma atomic emission spectrometry were found to provide the sensitivity necessary to measure the small concentrations of solubilized elements.

In the future these techniques are expected to be applied to other types of thin films. A microelectronics fabrication group, for example, has a requirement for the measurement of tungsten/silicon ratios in submicrometer films sputtered onto silicon substrates. Samples to be chemically analyzed will be sputtered onto substitute graphite substrates. Substitution of graphite substrates for silicon substrates is permissible in this case since the substrate is not expected to react with the sputtered materials or to affect the sputtering process. The

tungsten silicide films should be solubilized by a mixture of hot nitric and phosphoric acids [27], and the solubilized tungsten and silicon will be measured by their atomic emission from an inductively coupled plasma.

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