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RAPID DENSIFICATION OF BOROPHOSPHOSILICATE GLASS

by

Lynnette D. Madsen

A thesis submitted to the Faculty
of Graduate Studies and
Research in partial fulfillment
of the requirements for the degree of

Master of Engineering

Ottawa-Carleton Institute for Electrical Engineering
Department of Electronics
Faculty of Engineering
Carleton University

March 1988

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RAPID DENSIFICATION OF BOROPHOSPHOSILICATE GLASS

submitted by Lynnette D. Madsen in partial fulfillment of the requirements for the degree of Master of Engineering.

Prof. A.R. Boothroyd
Thesis Co-Supervisor

Dr. J.S. Mercier
Thesis Co-Supervisor

Prof. M.A. Copeland
Chairman
Department of Electronics

Department of Electronics
Faculty of Engineering
April 1988

(ABSTRACT

The effect of densification, using a rapid thermal annealer, on properties of low pressure chemical vapor deposited borophosphosilicate glass films (4 w/o B, 4 w/o P) is investigated. After densification, the wet etch-rate of the films decreased by a factor of 12, while the infrared Si-O band peak height increased by 10%. An application of these findings to process monitoring is examined and the impact of densification on subsequent processing is discussed. Results show that a single densification cycle at 950°C/20 s induces glass flow behavior. Furthermore, for densification cycles from 500-1000°C for 20 s followed by a fusion cycle of 1100°C/20 s, densification temperature has no effect on the smoothing of glass over step structures. However, for contact sidewalls a densification cycle of at least 700°C/20 s is required for sufficient tapering of the sharp corner. An optimal densification cycle for device processing was determined to be 800°C/20 s.

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1.0 INTRODUCTION

Borophosphosilicate glass (BPSG) is used in the semiconductor industry as a pre-metal passivation thin film for getter of mobile ions and isolation between the device structure and the first metal layer in CMOS devices [1-11], as shown in Figure 1. In addition, it serves the important function of smoothing the topology for continuous metal coverage over sharply-angled steps and contact sidewalls encountered in VLSI structures.

BPSG is a silicon dioxide (SiO_2) glass which has been doped with boron (B) and phosphorus (P). Usually doping is performed in-situ during atmospheric pressure (APCVD) [1,12-18], low pressure (LPCVD) [6-9,19-26] or plasma-enhanced (PECVD) [2-4,27-30] chemical vapor deposition. As deposited, BPSG is not very stable chemically for, typical B and P concentrations used in the industry, namely 4 to 5 weight percent (w/o) each. Specifically, the films become hazy due to some of the boron in the film nucleating into droplets on the surface, possibly in the form of hygroscopic boron oxide. With time, these droplets react with the atmospheric moisture and form boric acid crystals [31]. Analyses showing a decrease in the B concentration in the films after a long period of time suggests that these formations are volatile and continuously sublime [18,32] from the surface. Therefore, the film is usually given a heat treatment after deposition [3-4,6-7,10-11,13-14,19-20,29-31] in either a conventional furnace or a rapid thermal annealer (RTA). This anneal causes a restructuring of the bonds to occur resulting in a film with improved chemical stability

Figure 1. Cross-sectional view of a typical CMOS device structure showing the BPSG layer.

[31]. This phenomenon has been verified with Fourier Transform Infrared Spectroscopy (FTIR) stability studies performed over a two year period on unannealed and annealed films [31]. Furthermore, variations in film properties are easily detected since the etch rates of CVD glass films are sensitive to changes in film density [39].

The terminology commonly used in the industry to refer to the various heat treatments for BPSG is somewhat ambiguous. To clarify the terminology in this document, the first heat treatment following deposition is called the "densification cycle". Furthermore, "rapid densification" refers to heating in an RTA. A subsequent anneal which follows other processing steps, such as contact etch, is called a "fusion cycle". This applies whether the main purpose of the subsequent anneal is to smooth topology over steps (often referred to as "flow") or to taper contact sidewalls (commonly called "reflow").

Traditionally in MOS processes with minimum device features greater than 2.5 μm , PSG (or BSG) has been used as the pre-metal passivation layer [10,12,33-37]. For topology smoothing of these binary glasses, a relatively high temperature anneal is required, causing diffusion of underlying junctions. To minimize this side effect for smaller geometry devices where shallow junctions are required, the anneal temperature has been reduced through the use of a ternary glass having a lower fusion temperature, such as BPSG.

The densification cycle for BPSG is typically performed in a furnace at 700 to 1000°C for 30 to 60 minutes in a nitrogen or steam ambient [2,6,7,19,22,29], although some instances of densification in a RTA have

4

been reported [11,20]. In most cases the criteria for selecting the parameters of the densification are not clear. It appears that the need for a densification anneal is dictated by problems of stability associated with BSG and that the particular specifications of the heat treatment (temperature, duration, ambient) is primarily historical in nature. It is suggested that densification of BPSG has attracted little attention because it has not been linked with device failure, or investigations which have been conducted are proprietary and therefore their results are unpublished. A need existed for a systematic study of BPSG densification, examining both its effects on film properties and on subsequent processing steps.

Although the topic of densification cycles for doped glasses other than BPSG has been discussed briefly in a few papers [1,10,16-17,29], only Levin [38] and Kern's [39-41] work has dealt with this topic in some detail.

In ref. 39 and 40, Kern discusses densification of APCVD BSG films. He examined furnace densification at 450 to 900°C for 2 min to 100 hours in various ambients (air, argon, dry and wet nitrogen, wet oxygen and steam). To study the films, wet etch rate, weight, surface area, film thickness and infrared spectra information was gathered. It was found that the wet etch rate of the films decreased markedly with densification (450 to 500°C), indicating an apparent increase in film density. This was verified for an 800°C densification cycle which led to a density comparable to bulk borosilicate glasses. Infrared spectra indicated thermal densification was essential to produce stable films of

optimum properties. The rate of densification could be accelerated significantly with water vapor, particularly at low temperatures.

The densification of PSG films deposited by APCVD techniques are described by Kern in ref. 41. In this work, he focussed on densification treatments of 450°C and below in dry and wet ambients for periods ranging from 15 minutes to 100 hours. He found that PSG films could be densified to a substantial extent by heating for several hours at 450°C in moist ambients as evidenced by infrared spectroscopy and measurements of wet etch rates, refractive index and absolute film thickness. Infrared spectroscopic measurements further showed that densification treatments (even in steam at 450°C) reduced the water content of the films and the tendency for the films to absorb water. Room-temperature storage of PSG films in dry or humid air led to a wet etch rate decrease due to densification and stress release effects. Experiments exposing PSG films to high-intensity ultraviolet radiation or atomic hydrogen plasma were conducted to explore possible alternatives to thermal densification, but no detectable changes in film density were observed.

Levin [38] examined PSG films which were deposited by LPCVD rather than APCVD techniques. His study of densification included furnace anneals at temperatures ranging from 700 to 950°C for durations of 10 to 20 min in steam, oxygen, argon or nitrogen ambients. As-deposited, the films were porous and prone to water absorption which can adversely affect the electrical characteristics of devices and accelerate corrosion of overlying aluminum metallization. Spectroscopic studies showed an increased inhibition to water absorption, and measurements of

wet etch rates indicated an increase in densification, agreeing with Kern's results. Refractive index values increased with densification, and thickness decreased in nitrogen or argon ambients and increased for oxygen or steam environments.

Since then, the advent of BPSG and newer processing and analytical methods, such as FTIR [42] (to replace dispersive infrared spectroscopy) and RTA (to replace conventional furnace cycles), have suggested the need for a second look at doped glass densification. FTIR spectrometers were introduced in the semiconductor field in the early 1980's. These systems permit more extensive studies to be conducted due to their increased computing speed over the grating spectrophotometers. Rapid thermal annealing offers many advantages over furnace processing which are discussed in the Objectives section.

2.0 OBJECTIVES

A main objective of this work is to investigate the effect that the first thermal cycle (densification) has on LPCVD BPSG film properties using an RTA. There are two motivating factors for this: (i) the topic of BPSG densification has been a relatively unexplored area, and (ii) rapid thermal annealing is more appropriate for wafers 150 mm or greater in diameter [3,37,43-46].

An important advantage of the short duration/high temperature combination of an RTA is that heating cycles can be adjusted to enhance the desired reaction (topology smoothing, junction activation) and reduce side effects (unwanted dopant diffusion in underlying junctions). Because RTA uses single wafer processing, less financial loss is associated with processing errors, improved wafer-to-wafer uniformity and control, and more compact systems are possible. RTA's and their computer-controlled interfaces are very flexible and can therefore accommodate a wider variety of processes than most conventional furnaces. They also operate over a wide range of temperatures, namely 420 to 1150°C for any length of time, specified to the second. Unfortunately, due to the large thermal mass of wafer boats, susceptors and reactor walls, conventional furnaces are difficult to adapt for rapid thermal processing. One major disadvantage of RTA is possible wafer warpage or slip resulting from non-uniform rapid heating or cooling.

Another objective is to propose a production monitoring technique for BPSG thermal treatments for rigorous, fail-safe processing.

The last goal was to determine an optimal densification cycle for device processing by examining the densification cycle effects on the fusion cycle. For example, if the duration of the densification anneal can be decreased, throughput could be improved.

The approach taken to achieve these objectives was to examine the effect of various densification cycles on film properties and on the subsequent fusion cycle. Chemical, optical, mechanical and morphological changes in the films were investigated using wet etch rates, FTIR, thickness, refractive index, cross-sectional scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Smoothing of topology was evaluated using step structures, and tapering of sidewalls was examined using contact line structures. This information was then employed to develop methods for monitoring the thermal treatments and to select an optimal densification cycle.

There are several original aspects to this work. They are:

- 1) examination of densification of BPSG films, 2) study of RTA densification, 3) development of a process monitoring procedure, and 4) extensive use of statistical methods in processing investigation.

3.0 EXPERIMENTAL PROCEDURE

3.1 Film Deposition

The BPSG film was formed by LPCVD in a short (~50 cm hot region) hot wall reactor, using the oxidation of SiH_4 , PH_3 and B_2H_6 gases at a temperature of 400°C and a total pressure of 250 mTorr*. The total reactive flow was approximately 100 sccm, with an oxygen to hydride ratio of about 3:2, giving a typical deposition rate of 10 nm/min. All films which are discussed as a group came from the same deposition run -- unless otherwise stated. The films nominally contained 4 w/o P and 4 w/o B and were $1\text{ }\mu\text{m}$ (10,000 Å) thick. For TEM analysis, $0.7\text{ }\mu\text{m}$ of BPSG was used to facilitate sample preparation.

Blanket deposition of BPSG on 100 mm diameter Si(100) substrates was used to study the film properties. To examine the smoothing of topology over steps, the structure shown in Figure 2 was used. It was fabricated by the thermal oxidation of 100 mm diameter Si(100) substrates to a thickness of ~ $1.2\text{ }\mu\text{m}$. Patterning by reactive ion etching of the oxide was carried out to form $1.0\text{ }\mu\text{m}$ high sharp steps, followed by LPCVD of ~100 nm of polysilicon for interface delineation purposes and LPCVD of a $1.0\text{ }\mu\text{m}$ thick BPSG film. Figure 3 shows a line structure which was used for evaluation of the tapering of contact sidewalls. It was fabricated by LPCVD of $1\text{ }\mu\text{m}$ of BPSG on Si(100) substrates followed by reactive ion etching of the film down to silicon to form $1.0\text{ }\mu\text{m}$ high vertical walls.

*Refer to Appendix A for definition of these and subsequent units or terms.

Figure 2. Step coverage structure used for evaluating smoothing of topology over steps.

Figure 3. Line structure used for examining tapering of contact sidewalls.

3.2 Thermal Treatments

Within an hour of completing the BPSG deposition, wafers were densified in an N_2 ambient by a Heatpulse, Model 210T or 410, tungsten halogen lamp RTA system (A.G. Associates). Any fusion cycles which followed densification were performed in the same RTA at 1100°C for 20 s. The temperature was measured and controlled to within $\pm 5^\circ\text{C}$ using feedback from a chromel-alumel thermocouple attached to a silicon test piece situated at the side of the wafer. Temperature had been previously calibrated with a thermocouple placed directly on test wafers.

For comparison purposes densification was also performed in a conventional furnace in a N_2 ambient for some films. Again, any fusion cycles which followed densification were performed in the RTA at 1100°C for 20 s.

3.3 Film Analysis

The B and P concentrations of the films were measured absolutely to within ± 0.2 w/o by standardized wet chemical colorimetric microanalysis of the dissolved film (Balazs Analytical Laboratory, Mountain View, California). This method based on spectrometric measurements of colored complexes (N-methylthionine for boron, phosphomolybdenum blue for phosphorus), uses pure boric acid and alkali phosphate standards for calibration [16].

Center thickness measurements were made using a Nanospec AFT or a Tylan Tyger reflectometer before and after densification. For selected

studies, a Gaertner ellipsometer was used to obtain both thickness and index of refraction values. Measurements of thickness by the various techniques were found to be closely correlated. Wafers with step coverage or line structures had a center drop-out zone, a 0.5 mm^2 unpatterned region where BPSG was deposited directly on the substrate, which permitted measurements.

The wet etch rate of BPSG was measured using a p-etch solution composed of 3 vol. HF 49% + 2 vol. HNO_3 70% + 60 vol. H_2O [16]. The solution was checked for correctness by verifying that the thermal SiO_2 etch rate (of films grown in dry O_2 at 1000°C) was $0.24 \pm 0.02 \text{ nm/s}$. Similarly, the degradation of the solutions was measured by testing before and after each etch rate measurement session.

Infrared spectral analysis was performed with a Nicolet 20SX-B Fourier transform spectrometer. The Si-O and B-O absorption band frequencies and peak heights were determined automatically with software developed at NT.

A Cambridge 250 SEM instrument was used to obtain cross-sectional micrographs of the test structures which were used to evaluate the smoothing of topology over steps and tapering of contact sidewalls. From these micrographs, the fusion angles θ and α were measured (Figures 2 and 3 respectively), with an accuracy of $\pm 1^\circ$.

The characteristics of densified and undensified films were examined by TEM using a Philips 400 STEM instrument. Cross-sections were prepared by the standard ion milling technique [47].

3.4 Statistical Design of Experiments

The traditional approach to conducting experimental research investigations involves changing one variable at a time. However, statistical experimental design offers many advantages [48-52]. Experimentation becomes more compact when statistical techniques are used since less time or material is required to obtain the same information. The results are more accurate due to the ability to estimate interactions between variables. Studies are more definitive because the statistical significance of results can be stated, and more flexible since alternative hypotheses may be tested.

Summarized below is the method used hereafter, followed by an explanation of the relevant designs, tests and terminology.

A Box-Behnken response surface design [50,52] was used to examine the response changes in etch rate, FTIR spectra, film thickness and refractive index with temperature and duration of the densification anneal. A randomized complete block design and a paired t-test were used to investigate the fluctuations from deposition run-to-run and from wafer-to-wafer. A factorial design was employed to compare fusion angles over step structures for various densification temperatures and times. Thorough investigation of the compound effect of densification and fusion was made using a split-plot design and Student-Newman-Keul's (SNK) test. Details of the analysis involved with the various designs and tests are given in the appendices: Box-Behnken design in Appendix C, paired t-test in Appendix F, and split-plot design (and SNK test) in Appendix G.

A Box-Behnken design is used when a two-dimensional empirical model of a response over a range of input variables is desired. A response or output variable Y is a measured value, such as the yield of a product. An input variable or predictor X is a parameter such as temperature that is adjusted by the experimenter. Input variables are normalized to avoid bias due to the selection of their values, which can lead to misleading results. For example, if a temperature range from 600 to 1000°C is of interest, the normalized variable X_1 would vary from -1 to +1 through the use of the following equation:

$$X_1 = \frac{\text{Temperature} - 800}{200} \quad (1)$$

Figure 4 shows the layout of a two-input-variable design. The center point, $X_1 = 0$ and $X_2 = 0$, would be repeated four times to estimate the experimental or pure error distinctly from the model-to-data fit error. The empirical model generated from this design would take the following form:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_{11}X_1^2 + a_{22}X_2^2 + a_{12}X_1X_2 \quad (2)$$

Through statistical analysis (least squares regression), an analysis of variance (ANOVA) table is developed (see Appendix C for details). From this table, an R^2 value is derived which gives an indication of the quality of the fit between the model and the data where a value of 0 would indicate a poor fit and a value of 1 a perfect fit. Usually an R^2 value of 0.90 or better is considered adequate, although lesser values in the 0.80 to 0.90 range can still provide useful information. The contour map shown in Figure 5 gives a pictorial representation of the

Input variables		Measured response
X_1	X_2	Y
-1	-1	68
0	-1	78
+1	-1	77
-1	0	65
0	0	81
0	0	82
0	0	82
0	0	83
+1	0	95
-1	+1	59
0	+1	72
+1	+1	85

Figure 4. Layout of a 2-input variable Box-Behnken design. o indicates a single sample and ⊙ indicates multiple samples. Corresponding table includes measured response Y.

Figure 5. A contour map for the Box-Behnken design showing the variation of the response Y as a function of the input parameters X_1 and X_2 .

changes in the response Y as a function of the input variables X_1 and X_2 and described by the model of eq. 2

A complete block design [51] is a simple design where the response is measured for a selection of input variable levels administered under two different conditions. An example of this design is given in Figure 6 where the response for temperatures of 600, 800, 850 and 1100°C is measured for two conditions, run one and run two. The t-test (Appendix F), based on the (Student's) t-distribution (Appendix B), tests for significance between pairs of values and, in this case, tests for the impact that a run has on the response.

Factorial designs [49,50] are complete block designs which usually have input variables with levels spaced at equal intervals. For example, consider the layout shown in Figure 7, where the variable X_2 is examined at 100°C intervals over the range of 800 to 1100°C. This particular design, where X_1 is set at 2 levels and X_2 is set at 4 levels, is called a 2x4 factorial.

A split-plot or nested design [49] contains a design within a design, as shown in Figure 8. In this example, the first division into main plots is by furnace manufacturer. A second division of sub-plots is made by type of alloy. Each plot is subjected to a range of temperatures and the response is measured. The results are analyzed using least squares regression and an ANOVA table is generated. The F-values in the table (Appendix G) are used in conjunction with the F-distribution (Appendix B) to evaluate various hypotheses. For

Figure 6. Layout of a complete block design. Each block or deposition run is given the same set of treatments (600°C, 800°C, 850°C and 1100°C).

		800	900	1000	1100		
X_1	60					60	
	20					20	
		X_2					

X_1 at two levels : 20 s and 60 s

X_2 at four levels : 800°C, 900°C, 1000°C
and 1100°C

Figure 7. Layout of a 2x4 factorial design.

Figure 8. Example of a split plot layout design. The division into main plots is by furnaces and the division into sub-plots is by alloy. Each plot is given the same set of temperatures as a treatment.

example, one can test whether all temperatures have the same statistical response (see Appendix G for an example). As a second measure, the SNK test (Appendix G) can be used to test across a range of values, similar to the way the t-test evaluates pairs of numbers.

The analysis of the Box-Behnken designs were performed using a commercial software package, called ENHANSYS; other analyses were done with the aid of a hand calculator.

4.0 RESULTS AND DISCUSSION

4.1 Evaluation of Extent of Densification

Blanket deposition of BPSG was made on Si wafers which were then densified according to the 2-factor (temperature and duration) Box-Behnken matrix shown in Figure 9 and subsequently given a fusion anneal of 1100°C/20 s. Measurements of etch rate, FTIR absorption spectra (peak frequencies and intensities), thickness, and refractive index were made after deposition, densification and fusion.

The densification temperature range studied was 600 to 1000°C and the duration range was 10 to 70 s. These two factors were normalized as follows:

$$X_1 = \frac{\text{Temperature} - 800^\circ\text{C}}{200^\circ\text{C}} \quad (3)$$

and

$$X_2 = \frac{\text{Duration} - 40 \text{ s}}{30 \text{ s}} \quad (4)$$

Four replicates of the center point, 800°C for 40 s (0,0), were made to estimate accuracy.

4.1.1 Etch Rates

The wet etch rate of the BPSG films decreased substantially (by a factor of 12) from after deposition to after densification for the center cycle. However, in order to examine how dense the films had

Figure 9. Layout of RSM Box-Behnken design to study the effect of various densification cycles. x indicates a single sample and * indicates multiple samples.

become, a coefficient comparing the etch rates after densification to a reference taken after fusion was defined as follows:

$$\begin{aligned} \text{Etch Rate Coefficient } (C_{ER}) &= \frac{\text{Etch Rate After Fusion Cycle}}{\text{Etch Rate After Densification Cycle}} \times 100\% \quad (5) \\ &= \text{function } (X_1, X_2). \end{aligned}$$

Using this definition, films were considered to be completely densified if there was no further decrease in etch rate after the fusion cycle and then C_{ER} equals 100%. For the center cycles, 800°C for 40s, it was found that the film was 88.0% densified. This can be compared to the slightly greater densification effect achieved from furnace heating at 700°C for 30 min which yields 93.2%.

After statistical analysis, the resulting relationship expressed in terms of the normalized variables X_1 and X_2 , is given by:

$$C_{ER} = 88.416 + 39.003X_1 + 7.138X_2 - 27.434X_1^2 - 2.539X_2^2 - 4.1325X_1X_2. \quad (6)$$

$(\pm 1.178) \quad (\pm 1.053) \quad (\pm 1.053) \quad (\pm 1.580) \quad (\pm 1.580) \quad (\pm 1.290)$

The high accuracy of the fit of the eq. is indicated by an R^2 value of 0.997 (see Appendix C for the ANOVA table). However, omission of the statistically insignificant X_2^2 term yields a simpler expression; with still a very good value of 0.995 for R^2 :

$$C_{ER} = 87.570 + 39.003 X_1 + 7.1383 X_2 - 28.280 X_1^2 - 4.1325 X_1X_2. \quad (7)$$

$(\pm 1.166) \quad (\pm 1.166) \quad (\pm 1.166) \quad (\pm 1.649) \quad (\pm 1.428)$

A contour map depicting the relationship (7) is given in Figure 10. To assist the user in interpreting the significance of the map, the

Figure 10. Contour map showing variation of etch rate coefficient (percentage of etch rate after fusion to after densification) with densification temperature and duration. All samples received the same fusion cycle of 1100°C for 20 s after densification.

original variables, temperature and duration, have been used instead of the reduced variables. From the slope up to 850°C, it is clear that temperature is the dominant effect over duration. A saturation is also observed above 850°C. However, although the response indicates percentage of densification relative to the fusion cycle, lesser degrees of densification may still be acceptable. The trade-off between processing temperature and duration may also make lower temperatures possible.

4.1.2 FTIR

FTIR is a widely used technique for the characterization and analysis of molecular compounds [53]: Molecules absorb infrared radiation when the frequency of the incident radiation coincides with the normal vibrational frequencies of the molecular bonds within the sample [53]. Typical FTIR spectra of BPSG over Si measured after deposition, densification at 800°C/40 s, and fusion at 1100°C/20 s, are given in Figure 11 where absorbance is plotted against wavenumber. A wavenumber is equal to frequency divided by the speed of light ($3 \times 10^{10} \text{ cm s}^{-1}$) [53]. The broad band in the 1370 to 1400 cm^{-1} range corresponds to B-O ~~bonding~~ [53]. Its unsymmetrical appearance is due to the presence of a shoulder at approximately 1325 cm^{-1} resulting from P=O bonding [53-54]. The major Si-O band in the 1050 to 1100 cm^{-1} range is from Si-O bonding [53-58]. Its peak narrows, sharpens and shifts slightly to a lower frequency with each anneal cycle. Examination of the increase in the height (intensity) of this peak was used in this study to evaluate densification.

Figure 11. FTIR spectra (a) after deposition (b) after densification (800°C/40 s), and (c) after fusion (1100°C/20 s).

Wong has reported similar changes for CVD SiO₂ films using infrared spectroscopy [56]. He notes that a heat treatment of 800°C causes shifts of the Si-O peak to higher frequency and a narrowing of the band. From the spectra shown in ref. 56 and other references [57,58], an increase in the Si-O peak height is also observed. It is suggested that these results are due to structural changes in the silica network.

The FTIR study was conducted in conjunction with the etch rate study, and therefore used the same matrix for densification cycles as shown in Figure 9. The same normalized temperature and duration factors (see eqs. 3 and 4) were used.

The first response studied was the normalized peak height measured after densification, defined as follows:

$$P_{\text{Si-O}} = \frac{\text{Si-O Peak Height [absorbance units]}}{\text{Film Thickness } [\mu\text{m}]} \quad (8)$$

The full model was obtained for $P_{\text{Si-O}}$ and then the insignificant X_2^2 and X_1X_2 terms were eliminated to obtain the following simplified expression shown with an R^2 value of 0.957, indicating a good fit (see Appendix D for details).

$$P_{\text{Si-O}} = 1.0488 + 0.10397 X_1 + 0.02982 X_2 - 0.0501 X_1^2 \quad (9)$$

(±0.009) (±0.009) (±0.009) (±0.012)

The contour map shown in Figure 12 indicates that less change occurs in $P_{\text{Si-O}}$ value for densification cycles higher than 800°C. The $P_{\text{Si-O}}$ value for the center cycle, 800°C/40 s is 1.0622 compared to 1.1197 A.U./μm for 700°C/30 min furnace densification. Again, slightly

Figure 12. Contour map of P_{Si-O} (FTIR Si-O peak height measurements after densification normalized against film thickness).

greater densification of the film is indicated for the furnace anneal, corroborating the results obtained with etch rate measurements.

The second response, the Si-O Coefficient C_{Si-O} , is the ratio of the FTIR measurements taken after densification to those taken after fusion, as follows:

$$C_{Si-O} = \frac{\text{Si-O Peak Height After Densification}}{\text{Si-O Peak Height After Fusion}} \quad (10)$$

The following model, with a somewhat lower R^2 value of 0.835, was found for C_{Si-O} (details given in Appendix E):

$$\begin{aligned} C_{Si-O} = & 0.87095 + 0.10867 X_1 + 0.03127 X_2 - 0.0423 X_1^2 \\ & (\pm 0.023) \quad (\pm 0.023) \quad (\pm 0.023) \quad (\pm 0.030) \\ & + 0.0135 X_1 X_2 + 0.002 X_2^2 \\ & (\pm 0.025) \quad (\pm 0.030) \end{aligned} \quad (11)$$

The contour map of this expression is shown in Figure 13. The form of the model is similar to the contours for the P_{Si-O} (Figure 10) at low temperatures up to 850°C, also with a saturation above this temperature. The Si-O Coefficient for 800°C/40 s densification is 0.8996 compared to 0.9396 for furnace densification at 700°C for 30 min.

An interesting application derived from these results is described in Section 5.1.

4.1.3 Other Measurements

In addition to measuring etch rates and Si-O peak height in the previous study, ellipsometric thickness and refractive index and FTIR

Figure 13. Contour map of Si-O Coefficient (ratio of FTIR Si-O peak height measured after densification to peak height measured after fusion).

peak frequency measurements were made. Statistical analysis was performed on each of the above and no significant trends were found.

TEM analysis was performed on undensified films and on films which received 600°C/60 s, 800°C/60 s and 1000°C/60 s densification anneals. No discernible differences in the film for the various conditions were found. The BPSG film was amorphous and there was a well-defined interface between it and the silicon. Although voids and/or phase separation have been reported [21,36,59] for BPSG films (of slightly different P and B concentrations) deposited and annealed under different conditions, none were apparent in the films used in this study.

4.2 Effect On Fusion Cycles

4.2.1 Smoothing of Topology

A few examples of SEM cross-sections are shown in Figure 14, (refer to Figure 2 for the structure). The undensified sample (a) and the one which had been given an anneal of 800°C/20 s (b) both have nearly vertical steps. The samples which received a high temperature densification at 1100°C/20 s (c), or moderate densification at 800°C/20 and a fusion cycle at 1100°C/20 s (d), both have smooth topologies with angles around 55°. The effect that different densification cycles have on smoothing was examined through a series of experiments explained below.

To obtain enough samples, the BPSG films were deposited across two deposition runs. Identical heating treatments were then duplicated on some wafers from each deposition run to check for the run (or block)

a) No densification or fusion

c) 1100°C/20 s

b) 800°C/20 s

d) 800°C/20 s + 1100°C/20 s

Figure 14. Examples of SEM Cross-sections for: a) no anneal, b) 800°C/20 s densification, c) 1100°C/20 s densification, and d) densification at 800°C/20 s plus fusion at 1100°C/20 s.

effects, (as shown in Table 1(a)). These treatments are organized in a randomized complete block design. A simple paired t-test was performed and in all cases the block (or deposition run) was considered "insignificant and therefore could be ignored in all subsequent analyses (see Appendix F for details). In a similar way, the wafer-to-wafer variations shown in Table 1(b), were examined and found to also be unimportant (see Appendix F for details).

One would like to examine the effect that various densification cycles have on the angle (Figure 2) measured after a subsequent fusion anneal of 1100°C for 20 s. Before doing so, any softening of the glass and hence flow-like behavior due to the densification alone was first examined. A basic 4 x 2 (temperature X duration) factorial design was used, as shown in Table 2, with one extra point at 1050°C/20 s and a control sample (no densification). The results of this study are displayed graphically in Figure 15.

As expected, 60 s anneals result in a larger angle (indicating more flow) than 20 s anneals. This effect is magnified with increasing temperature and at around 950°C considerable flow behavior was observed. The change in angle is nearly exponential as the densification temperature was increased to 1100°C.

Next, the combined effect of densification and fusion was studied, as shown in Table 3. Samples were given a densification anneal for 20 s at a temperature ranging from 500 to 1100°C and then, after cooling to room temperature, were given a fusion cycle of 1100°C for 20 s. The resulting angles ranged from 52 to 60° and are plotted in Figure 16.

Figure 15. Flow behavior for samples which have received only densification anneals.

Figure 16. Compound effect of densification at a range of temperatures for 20 s followed by fusion at 1100°C/20 s. Each $\square$ represents one sample point.

Table 1. Run-to-Run and Wafer-to-Wafer Variations

(a) Effect of Furnace Run on Flow Behavior

RTA Cycles		Angle (°)	
Densification	Flow	Run 1	Run 2
1100°C/20 s	None	57.3	56.3
500°C/20 s	1100°C/20 s	60.0	58.5
600°C/20 s	1100°C/20 s	57.8	56.8
700°C/20 s	1100°C/20 s	53.3	58.2
800°C/20 s	1100°C/20 s	53.4	61.0
900°C/20 s	1100°C/20 s	55.3	58.0
1000°C/20 s	1100°C/20 s	54.8	58.7
1050°C/20 s	1100°C/20 s	60.3	57.7
1100°C/20 s	1100°C/20 s	61.7	66.5

(b) Effect of Wafer on Flow Behavior

RTA Cycle		Angle (°C)*	
Densification	Flow	Wafer 1	Wafer 2
800°C/20 s	1100°C/20 s	54.5	52.3
800°C/60 s	None	9.3	6.2
800°C/60 s	1100°C/20 s	55.5	55.7
900°C/60 s	None	12.8	14.3

* Wafers selected from same deposition run.

All values are the average of 3 readings.

Table 2. Effect of Densification Alone

Temperature (°C)	Duration (s)	Angle (°)
800	20	6.8
900	20	6.2
1000	20	24.0
1100	20	57.3, 56.3
800	60	9.3, 6.2
900	60	12.8, 14.3
1000	60	46.7
1100	60	68.2
1050	20	42.0
control - no densification		3.8

Table 3. Effect of Densification and Fusion Anneals

RTA Cycles		
Densification	Fusion	Fusion Angle (°)
500°C/20 s	1100°C/20 s	60.0
600°C/20 s	1100°C/20 s	57.8
700°C/20 s	1100°C/20 s	53.3
800°C/20 s	1100°C/20 s	52.3, 54.5
900°C/20 s	1100°C/20 s	55.3
1000°C/20 s	1100°C/20 s	54.8
1050°C/20 s	1100°C/20 s	61.7

where there appears to be a minimum at 700-800°C. To discern if this was a valid (reproducible) trend the study was repeated and the amount of data for each set of results was increased.

The test pattern on each of these wafers is composed of a series of 5 lines of 10 μ m steps separated by 10 μ m spaces, as shown in Figure 17. In addition to measuring the angle for the center line (labeled 3), measurements were made for the outer lines (on one side, labeled 1 and 2). Shown in Table 4 is the resulting split-plot design, where the main plots were the deposition runs; the subplots were lines 1, 2 and 3; and the main treatment was the temperature of the densification anneal. A new graph of fusion angle versus densification temperature is given in Figure 18. Now, with the new data, the valley is no longer apparent. Analysis of variance was performed (Appendix G for details), then F-tests were made to test various hypotheses. At a 95 percent confidence level (or probability) the effect of the main plots (deposition runs) was insignificant, agreeing with the earlier conclusion. Similarly, at a 95 percent level, all subplots (lines) and main treatments (densification temperatures) were statistically the same. To obtain a second measure of the significance of the main treatment (densification temperature) and to acquire more detailed information (on whether specific temperatures are significant), the SNK test was also performed.

Figure 17. Test pattern of five 10 μm polysilicon steps each separated by 10 μm .

Figure 18. Effect of densification temperature on fusion angle results. All wafers were densified for 20 s and then annealed at 1100°C/20 s (fusion cycle). Each $\square$ or $\circ$ represents one sample point for each block.

Table 4. Split Plot Design

Densification Cycle: Temperature = Main Treatment ($^{\circ}\text{C}$)
 Deposition Runs = Main Plots
 Lines = Subplots
 Fusion Angle ($^{\circ}$) = Response

Main Treatment	Response						
	Subplot:	Main Plot 1			Main Plot 2		
		1	2	3	1	2	3
500		60.0	60.0	60.0	57.5	59.0	59.0
600		58.0	57.5	58.0	57.0	56.5	57.0
700		53.0	54.0	53.0	59.0	58.5	57.0
800		53.0	52.0	52.0	61.5	60.5	61.0
800		55.0	54.5	54.0	-	-	-
900		56.0	55.0	55.0	58.0	58.0	58.0
1000		55.5	54.0	55.0	59.5	58.5	58.0
1050		60.0	60.0	61.0	57.0	58.0	58.0
1100		61.0	62.0	62.0	67.0	66.5	66.0

* Densification duration was 20 s and fusion cycle was $1100^{\circ}\text{C}/20\text{ s}$.

The SNK test uses percentiles of the t-distribution to test across all ranges of the values. In summary, the test showed that all main treatments (densification temperature), had the same effect on the fusion angle at a 95% confidence level. For details of the analyses, refer to Appendix G.

Combining the results of the F-test and SNK tests, the useful conclusion can be reached that the temperature of the densification cycle has no significant effect on fusion angle.

4.2.2 Tapering of Sidewalls

To study the tapering of contact sidewalls (Figure 3), BPSG was deposited and the wafers were then densified using thermal cycles ranging from 400°C/20 s to 1150°C/20 s (except for the control sample which was given no anneal). This procedure was followed by dry etching of vertical walls and a common fusion cycle of 1100°C/20 s. The cross-sectional profile shape was the same for films which had received 700° to 1150°C densifications. However, a series of pictures displaying a sidewall tapering progression was produced for the control and densification anneals below 700°C, as shown in Figure 19. The first two pictures in the series (the control and the 400°C/20 s densification) are identical and look like freshly etched wafers which have received no fusion cycle. In the next two pictures of the progression (500°C/20 s and 600°C/20 s), some movement of the glass is seen but the upper corner is distinct. In the last picture (700°C/20 s), and for all subsequent higher densification cycles, the corner is rounded completely.

(a) No densification

(b) Densification
400°C/20 s

(c) Densification
500°C/20 s

(d) Densification
600°C/20 s

(e) Densification
700°C/20 s
and above

Figure 19. SEM micrographs showing contact sidewall tapering for: (a) no densification, (b) 400°C/20 s densification, (c) 500°C/20 s densification, (d) 600°C/20 s densification and (e) 700°C/20 s densification cycles. All samples received the same fusion cycle of 1100°C/20 s.

These results indicate that, contrary to glass topography smoothing over sharp step corners, where the profile of the glass itself over the sharp corner has already been rounded by the deposition, adequate contact sidewall tapering involving rounding of a sharp glass corner, cannot be obtained after low densification temperatures. Results similar to these have not been seen in the literature, although lack of tapering of sidewalls has been reported previously for PECVD (5 w/o B, 3 w/o P) BPSG films [4].

5.0 APPLICATIONS

5.1 Monitoring Fusion Cycles in a Production Environment

Checking the completion and correctness of heating cycles is essential in a production facility. Operator errors can occur due to an interruption such as an evacuation, a phone ringing or someone asking a question. Equipment failure or malfunction can be caused by the temperature controlling thermocouple breaking or by the system drifting out of specification. If the densification cycle is incorrectly administered, the film may become unstable or the device characteristics could be modified since this treatment can serve as part of the p^+ anneal. Similarly, monitoring the fusion cycle is important to ensure a smooth (and reproducible) topology for continuous metal coverage and unaltered device characteristics because this cycle can contribute to both the p^+ and n^+ anneals. In this section, two possible methods of achieving such monitoring are presented.

The wet etch rate changes radically from approximately 46 nm/s before densification to less than 4 nm/s, after an 800°C RTA or 700°C furnace densification cycle. More specifically, RTA densification at 800°C for 40 s gives an etch rate of 3.74 nm/s, while furnace densification at 700°C for 30 min gives an etch rate of 2.85 nm/s.

It may be possible to use etch rates to monitor fusion cycles. However, separate test wafers and preparation of the p-etch solution, because it degrades rapidly, would be required with each batch.

For monitoring, the use of a dry, non-destructive technique such as FTIR has many advantages over a wet method like etch rate measurement. Readings can be taken quickly from a region of the wafer approximately 0.5 mm^2 in area which has BPSG deposited directly on the Si substrate. This measurement can be achieved by providing drop-out zones (unpatterned regions) on batch wafers or by including test wafers in each batch. Measurements for monitoring purposes can be combined with others which are commonly made anyway for determining B and/or P content of the glass. Even if the readings are not employed routinely as a follow up to the anneal cycle, they may be used, as necessary, in post-production analysis, if the pertinent information has been stored or recorded.

Figure 20 shows a plot of etch rates versus P_{Si-O} values (the Si-O peak height normalized against film thickness), for samples of various densification durations and temperatures and illustrates the correct region in (etch rate, P_{Si-O}) space. The categorization was made by simply examining the data and dividing it into three distinct groups. These groups were then labelled as excessive, correct or insufficient, with respect to densification. The range of etch rates and average P_{Si-O} values for each group of densification cycles is given in Table 5. By taking approximate midpoints between the sections, the specification limits for correct densification for P_{Si-O} values were set at 1.0000 and 1.1000.

Figure 20. Plot of etch rates versus P_{Si-O} values. Each o represents a data point for a given densification duration and temperature.

Table 5. Categorization of Densification Cycles According to Etch Rate for FTIR Analysis

Densification Condition	Etch Rate [nm/s]	Average P Si-O [A.U./ μ m]
Insufficient	≥ 5.0	0.8983
Correct	3.4-5.0	1.0514
Excessive	< 3.4	1.1476

Specification
for correct densification: $1.0000 < P_{\text{Si-O}} < 1.1000$

In addition, some replicate samples made and measured over a year later were still in agreement suggesting that FTIR measurements of BPSC films are reliable over extended periods of time. However, to firmly establish the specification limits, a larger database would be required in practice. Only the methodology is proposed here.

In Table 6 information from the previous table has been combined with fusion cycle and Si-O Coefficient data. For correct fusion cycles, the Si-O Coefficient (ratio of Si-O heights before and after fusion) has an average value of 0.8699. The Si-O coefficient bounds for both correct densification and fusion cycles can be set at 0.7900 and 0.9300 by selecting intermediate values.

5.2 Effect on Device Processing

The densification cycle used for device processing should have the minimum temperature and duration possible while still ensuring stability, smoothing of topology and tapering of contact sidewalls. The degree of densification, as measured using etch rates and P_{Si-O} values (Figures 10 and 12), changed little as the temperature increased beyond 800°C as well as when the duration changes from 10 to 70 s.

Furthermore, the densification anneal showed no impact on the subsequent fusion-induced smoothing of topology (Section 4.2.1), or tapering of sidewalls, for densification temperatures above 700°C for 20 s (Section 4.2.2). The weight of evidence suggests that 800°C for 10 s would be an optimum densification cycle.

Table 6. Use of FTIR for Monitoring Thermal Cycles

Densification	Fusion	Average	
		P_{Si-O} [A.U./ μm]	C_{Si-O}
Insufficient	Omitted	0.8983	0.9947
Insufficient	Correct	0.8983	0.7350
Correct	Omitted	1.0514	1.0018
Correct	Correct	1.0514	0.8699
Excessive	Omitted	1.1476	1.0089
Excessive	Correct	1.1476	0.9756

Specification for

densification: $1.0000 < P_{Si-O} < 1.1000$ fusion: $0.7900 < C_{Si-O} < 0.9300$

6.0 CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The densification of LPCVD BPSG (4 w/o B, 4 w/o P) using a rapid thermal annealer has been investigated. The effect on film properties of this heat treatment was examined using chemical, optical, mechanical and morphological methods to evaluate the extent of densification. Two good indicators of changes in film characteristics due to densification were identified: wet etch rate and Si-O band peak height (obtained from FTIR readings). After densification, the wet p-etch rate of the films decreased by a factor of approximately 12, while the FTIR Si-O band peak height (normalized against film thickness) increased by approximately 10 percent. Overall, densification was found to depend mainly on temperature and to a much lesser extent, on duration.

The impact of densification on subsequent processing (smoothing of topology over steps and tapering of contact sidewalls) was also examined. Results show that a densification cycle of 950°C for 20 s induces glass flow behavior. Furthermore, for densification cycles ranging from 500 to 1100°C for 20 s, followed by a fusion cycle of 1100°C for 20 s, the densification temperature has no effect on the smoothing of glass over step structures. However, for adequate tapering of contact sidewalls a densification cycle of 700°C for 20 s or greater, before the contact window patterning and fusion cycle, was required.

Two procedures for monitoring the anneal cycles (densification and fusion) in a production environment are suggested and compared. The

first one, using wet etch rates, requires separate test wafers and preparation of a p-etch solution, while the second one, using FTIR peak height measurements is quick and non-destructive and can be performed on either batch or test wafers. The data in this study suggests specification limits for the latter method, which is the preferred one.

The optimum densification cycle, relative to device processing, would have a minimum duration and temperature yet ensure suitable smoothing of glass over steps and at contact sidewalls. From the results of the above studies, conducted for densification cycles ranging from 600 to 1100°C for 10 to 70 s, an optimum densification cycle of 800°C for 10 s was found.

Throughout this work, statistical techniques (Box-Behnken, t-test, split-plot design, factorial design, complete block design and Student-Neuman-Keul test) were extensively used, a practice which is relatively new to the semiconductor processing field.

For the first time, an in-depth, systematic study of the densification of BPSG films was made. Furthermore, rapid densification of glass films had not been studied in any detail. Finally, the procedures proposed for process monitoring are also novel.

6.2 Future Work

Some of the areas of densification warranting further investigation are discussed below.

The prime reason for densifying BPSG is to avoid chemical stability problems resulting from the boron in the film reacting with atmosphere

moisture. To understand how thermal treatments affect glass films further analysis of the material is necessary. Perhaps then, an explanation for the lack of tapering of contact sidewalls experienced for films which had not received adequate densification but were given a high temperature fusion cycle ($1100^{\circ}\text{C}/20\text{ s}$), can be found.

To further extend the work discussed in this thesis, densification in various ambients could also be examined. Possible ambients are air, argon, wet nitrogen, wet oxygen, steam and forming gas. As well, an investigation comparing films deposited by APCVD or PECVD techniques to films deposited with LPCVD might be interesting and could lead to a better understanding of the densification mechanisms. Films deposited using the vapor from liquid sources, namely, tetraorthosilicate instead of O_2 , trimethyl borate instead of B_2H_6 , and/or trimethyl phosphate instead of PH_3 , could be examined.

Furthermore, as mentioned earlier, an extensive database would have to be created to evaluate thoroughly the process monitoring methods proposed in this work.

APPENDIX A: LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

Å	Angstroms
ANOVA	Analysis of Variance
APCVD	Atmospheric Pressure Chemical Vapor Deposition
A _u	Absorbance Units
B ₂ H ₆	Diborane
B	Boron
B-O	Boron-Oxygen
BPSG	Borophosphosilicate Glass
BSG	Borosilicate Glass
°C	Degrees Celsius
CMOS	Complementary Metal Oxide Semiconductor
CVD	Chemical Vapor Deposition
df	Degrees of Freedom
C _{ER}	Etch Rate Coefficient
F*	F Test Value
FTIR	Fourier Transform Infrared Spectroscopy
H ₂ O	Water
HNO ₃	Nitric Acid
HF	Hydrofluoric Acid
LPCVD	Low Pressure Chemical Vapor Deposition
min	Minute
mm	Millimeter
MOS	Metal Oxide Semiconductor
MOSFET	Metal Oxide Semiconductor Field Effect Transistor
MS	Mean Square
MT	Main Treatment
mTorr	Millitorr
N ₂	Nitrogen
nm	Nanometer
NT	Northern Telecom Electronics Limited
PH ₃	Phosphine
P	Phosphorus
P=O	Phosphorus-Oxygen
PECVD	Plasma Enhanced Chemical Vapor Deposition
P-etch	Phosphorus Etch
PSG	Phosphosilicate Glass
R ²	Coefficient of Multiple Determination
RSM	Response Surface Methodology
RTA	Rapid Thermal Annealing
SiH ₄	Silane
SiO ₂	Silicon Dioxide
s	Second
sccm	Standard cubic centimeter per minute of gas at 273°K and 760 Torr
SEM	Scanning Electron Microscopy
Si	Silicon
Si-O	Silicon-Oxygen
SNK	Student-Newman-Keul
SS	Sum of Squares
ST	Subplot Treatment

TEM
um
vol.
w/o

Transmission Electron Microscopy
Micrometer (or micron)
Volume
Weight Percent

APPENDIX B: RANDOM VARIABLES AND THEIR DISTRIBUTIONS

Normal Random Variables

A function Z which assigns one and only one real number to each element in its sample space is called a random variable. A normal random variable Z is distributed according to the normal density function given by eq. B1 [60]:

$$f_Z(Z) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left(-\frac{(Z-\mu)^2}{2\sigma^2} \right), \quad (B1)$$

where the variance of $Z = \sigma^2$ with $\sigma > 0$,
the mean of Z is μ ,

and $-\infty \leq Z \leq \infty$.

t- and F- Distributions

The basis for the t- and F- distributions is the chi-squared distribution expressed by eq. B2 [49]:

$$X^2(v) = Z_1^2 + Z_2^2 + \dots + Z_v^2, \quad (B2)$$

where the Z_i are independent standard ($\mu = 0$, $\sigma = 1$) normal random variables

The form of the t-distribution is shown in equation B3 [49], as follows:

$$t(v) = \frac{Z}{\left[\frac{X^2(v)}{v} \right]^{1/2}} \quad (B3)$$

where v = degrees of freedom (df), see eq. B2 for clarification,

Z is a standard normal random variable,

$X^2(v)$ is a chi-squared distribution with v df,

and Z and $X^2(v)$ are stochastically independent.

The F-distribution is defined by eq. B4 [49] as:

$$F(v_1, v_2) = \frac{X^2(v_1)}{v_1} + \frac{X^2(v_2)}{v_2} \quad (B4)$$

where v_1 = numerator df,
 v_2 = denominator df,

and $X^2(v_1)$ and $X^2(v_2)$ are independent chi-squared distributions.

This distribution is related to the t distribution, described above, through the relationship given by eq. B5 [49]:

$$[t(v)]^2 = F(1, v). \quad (B5)$$

APPENDIX C: ANOVA TABLE FOR ETCH RATE COEFFICIENT (ERC)

Source	SS	df	MS	F*	P-Value†	R ²
Linear	SSL	df _L	SSL/df _L	$\frac{SSL/df_L}{(SSR+SSE)/(df_R+df_E)}$	1 - $\frac{SSR+SSE}{SSTO}$	
Quadratic	SSQ	df _Q	SSQ/df _Q	$\frac{SSQ/df_Q}{(SSR+SSE)/(df_R+df_E)}$		
Regression	SSR	df _R	SSR/df _R	$\frac{SSR/df_R}{SSE/df_E}$		
Error	SSE	df _E	SSE/df _E			
Total	SSTO	df				

† from tabulated values

Source	SS	df	MS	F*	P-Value	R ²
Linear	9433.3	2	4716.6	577.9	0	0.9952
Quadratic	2467.6	2	1233.8	151.2	1.73 x 10 ⁻⁶	
Regression	46.5	4	11.6	3.3	0.179	
Error	10.7	3	3.6			
Total	11958.0	11				

APPENDIX D: ANOVA TABLE FOR P_{SI-0}

Source	SS	df	MS	F*	P-Value	R ²
Linear	701.9×10^{-4}	2	350.9×10^{-4}	79.9	5.13×10^{-6}	0.9969
Quadratic	75.3×10^{-4}	1	75.3×10^{-4}	17.1	3.25×10^{-6}	
Regression	31.9×10^{-4}	5	6.4×10^{-4}	6.0	8.53×10^{-6}	
Error	3.2×10^{-4}	3	1.1×10^{-4}			
Total	812.3×10^{-4}	11				

APPENDIX E: ANOVA TABLE FOR SI-O COEFFICIENT

Source	SS	df	MS	F*	P-Value	R ²
Linear	530.6	2	265.3	13.4	6.13×10^{-3}	0.8355
Quadratic	72.8	3	24.3	1.2	0.379	
Regression	108.2	3	36.1	10.1	4.44×10^{-2}	
Error	10.7	3	3.6			
Total	722.2	11				

APPENDIX F: PAIRED t-TEST

Effect of Furnace Run on Flow Behavior

RTA Cycles		Angle (°)		
Densification	Flow	Run 1	Run 2	$\bar{d} = \frac{y_{11} + y_{21}}{2}$
1100°C/20 s	None	57.3	56.3	+1.0
500°C/20 s	1100°C/20 s	60.0	58.5	+1.5
600°C/20 s	1100°C/20 s	57.8	56.8	+1.0
700°C/20 s	1100°C/20 s	53.3	58.2	-4.9
800°C/20 s	1100°C/20 s	53.4	61.0	-7.6
900°C/20 s	1100°C/20 s	55.3	58.0	-2.7
1000°C/20 s	1100°C/20 s	54.8	58.7	-3.9
1050°C/20 s	1100°C/20 s	60.3	57.7	+2.6
1100°C/20 s	1100°C/20 s	61.7	66.5	-4.8

$$H_0 : \mu_d = 0 : \mu_1 = \mu_2$$

Test statistic

$$t_{n-1 \text{ df}} = \frac{|\bar{d} - \mu_d|}{s_d / \sqrt{n}}$$

where n = sample size
= 9

$$\bar{d} = \frac{\sum_{i=1}^n (y_{1i} - y_{2i})}{n}$$

$$= \frac{-17.8}{9} = -1.98$$

$$s_d = \sqrt{\frac{\sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i \right)^2 / n}{n-1}}$$

$$= \sqrt{\frac{138.32 - 316.84/9}{8}}$$

$$= \sqrt{12.89} = 3.59$$

$$t_8 = \frac{|-1.98 - 0|}{4.15/\sqrt{9}} = +1.65$$

If $t_8 \leq t_{(\alpha, 8)}$ conclude H_0 .

At 95% level: $t_8 = 1.65 \leq t_{(.95, 8)} = 1.860$.

Effect of Wafer on Flow Behavior

RTA Cycle		Angle (°C)*		
Densification	Flow	Wafer 1	Wafer 2	$d_i = y_{1i} - y_{2i}$
800°C/20 s	1100°C/20 s	54.5	52.3	+2.2
800°C/60 s	None	9.3	6.2	+3.1
800°C/60 s	1100°C/20 s	55.5	55.7	-0.2
900°C/60 s	None	12.8	14.3	-1.5

* Wafers selected from same deposition run.

$$H_0 : \mu_d = 0 \quad \mu_1 = \mu_2$$

Test statistic

$$t_{n-1 \text{ df}} = \frac{|\bar{d}_i - \mu_d|}{s_d/\sqrt{n}}$$

where n = sample size
= 4

$$\bar{d}_i = \frac{\sum_{i=1}^n (y_{1i} - y_{2i})}{n}$$

$$= \frac{3.6}{4} = 0.9$$

$$s_d = \sqrt{\frac{\sum_{i=1}^n d_i^2 - \left(\sum_{i=1}^n d_i\right)^2/n}{n-1}}$$

$$= \sqrt{\frac{16.74 - 12.96/4}{3}}$$

$$= \sqrt{4.5} = 2.12^*$$

$$t_3 = \frac{10.9 - 01}{2.12/\sqrt{4}} = 0.848$$

If $t_3 \leq t_{(\%, 3)}$ conclude H_0 .

At 95% level: $t_3 = 0.848 \leq t_{(.95, 3)} = 2.353$.

Conclusions:

Wafer and/or deposition run do not have a significant effect on fusion angle at the 95% level.

APPENDIX G: ANALYSIS OF SPLIT-PLOT DESIGN

$$\text{Model: } y_{ijk} = \mu + \alpha_i + \rho_j + \tau_k + \delta_{jk} + e_{ijk}$$

where y = response, μ = mean, α = block effect,
 ρ = treatment effect, τ = subplot effect,
 δ = interaction between treatment and subplot,
 e = random error

and $i = 1 \dots b$ where b = number of blocks
 $j = 1 \dots t$ where t = treatments per block
 $k = 1 \dots s$ where s = subplots per treatment

ANOVA TABLE

	Source	SS	df	MS	F*
Main Plot:	Blocks	SSB	$b-1$	MSB	$\frac{MSB}{MSEA}$
	Main Treatment (MT)	SSMT	$t-1$	MSMT	$\frac{MSMT}{MSEA}$
	Whole Treatment Error (a)	SSEA	$(b-1)(t-1)$	MSEA	
	Between Whole Plots	SSWP	$bt-1$	MSWP	
Subplot:	Subplot Treatments (ST)	SSST	$s-1$	MSST	$\frac{MSST}{MSEB}$
	MT x ST	SSMS	$(t-1)(s-1)$	MSMS	$\frac{MSMS}{MSEB}$
	Subplot Error (b)	SSEB	$t(b-1)(s-1)$	MSEB	
	Subplot Total	SSSP	$bt(s-1)$	MSSP	
	Grand total	SST	$bts-1$	MST	

where

$$SSB = ts \sum_i (\bar{y}_{i..} - \bar{y}_{...})^2$$

$$SSMT = bs \sum_j (\bar{y}_{.j.} - \bar{y}_{...})^2$$

$$SSEA = SSWP - SSB - SSMT$$

$$SSWP = s \sum_i \sum_j (\bar{y}_{ij.} - \bar{y}_{...})^2$$

$$SSST = bt \sum_k (\bar{y}_{...k} - \bar{y}_{...})^2$$

$$SSMS = \sum_j \sum_k (\bar{y}_{.jk} - \bar{y}_{.j.} - \bar{y}_{..k} + \bar{y}_{...})^2$$

$$SSEB = SSSP - SSST - SSMS$$

$$SSSP = \sum_i \sum_j \sum_k (y_{ijk} - \bar{y}_{...})^2$$

$$SST = SSWP + SSSP = \sum_i \sum_j \sum_k (y_{ijk} - \bar{y}_{...})^2$$

and, in general $MS = SS/df$.

Densification Study

blocks = runs = 2

treatments = densification temperature = 8/run

subplots = lines = 3/temperature

densification duration = 20 s

flow cycle = 1100°C/20 s

ANOVA TABLE

	Source	SS	df	MS	F*
Main Plot:	Runs	64.67	1	64.67	3.9503
	Temperature	316.59	7	45.23	2.7628
	Temperature Error	114.60	7	16.37	
	Between Temperatures	495.73	15		
Subplot:	Lines	4.41	2	2.21	0.1695
	Temperature x Lines	20.52	14	1.47	0.1126
	Line Error	208.29	16	13.02	
	Line Total	233.22	32		
Grand Total		728.95	47		

Testing Of Significance Using F-distribution

Runs:

$$F^* = F_{b-1, (b-1)(t-1)} = F_{1,7}$$

$$H_0: B_i = B$$

If $F^* \leq F(\%; 1,7)$ conclude H_0

At 90% levels: $F^* = 3.9503 \leq F(0.90; 1,7) = 3.59$
is not true

At 95% levels: $F^* = 3.9503 \leq F(0.95; 1,7) = 5.59$
is true

Temperature:

$$F^* = F_{t-1, (b-1)(t-1)} = F_{7,7}$$

$$H_0: \rho_j = \rho$$

If $F^* \leq F(\%; 7,7)$ conclude H_0

At 90% level: $F^* = 2.7628 \leq F(0.90; 1,7) = 2.78$
is true

At 95% level: $F^* = 2.7628 \leq F(0.95; 1,7) = 3.79$
is true

Lines:

$$F^* = F_{s-1, t(b-1)(s-1)} = F_{2,16}$$

$$H_0: \tau_k = t$$

If $F^* \leq F(\%; 2,16)$ conclude H_0

At 90% level: $F^* = 0.1695 \leq F(0.90; 2,16) = 2.68$
is true

At 95% level: $F^* = 0.1695 \leq F(0.95; 2,16) = 3.64$
is true

Temperature x Lines: $F^* = F_{(t-1)(s-1), t(b-1)(s-1)} = F_{14,16}$

$$H_0: \delta_{jk} = \delta$$

If $F^* \leq F(\%; 14,16)$ conclude H_0

At 90% level: $F^* = 0.1126 \leq F(0.90; 14,16) = 1.95$
is true

At 95% level: $F^* = 0.1126 \leq F(0.95; 14,16) = 2.38$
is true

Conclusion

For both 90% and 95% levels temperature differences are insignificant.

SNK

This alternative form of testing was used to obtain more accurate and specific results. It utilizes the t-distribution percentiles, $q(\%; p, f)$, where $p = 2, 3, \dots, 8$ indicating range of comparison and $f = \text{error df} = 7$. The test statistic is defined below:

$$D_p = q(\%; p, f) s_{\bar{y}}$$

$$\text{where } s_{\bar{y}} = \frac{\text{MSEA}}{r} = \frac{16.37}{2 \times 3} = 2.73$$

and $r = \text{number of replications}$
 $= bs$

therefore

P	D_p (90%)	D_p (95%)
2	7.31	9.09
3	9.42	11.32
4	10.70	12.74
5	11.64	13.78
6	12.38	14.59
7	13.00	15.27
8	13.53	15.84

Average Angle (°)	Densification Temperature (°C)	Symbol
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55.75	700	A
55.93	800	B
56.67	900	C
56.75	1000	D
57.33	600	E
59.00	1050	F
59.25	500	G
64.09	1100	H

D₈: H vs A = 64.09 - 55.75 = 8.34 H = A

D₇: H vs B = 64.09 - 55.93 = 8.16 H = B
G vs A = 59.25 - 55.75 = 3.50 G = A

D₆: H vs C = 64.09 - 56.67 = 7.42 H = C
G vs B = 59.25 - 55.93 = 3.32 G = B
F vs A = 59.00 - 55.75 = 3.25 F = A

D₅: H vs D = 64.09 - 56.75 = 7.34 H = D
G vs C = 59.25 - 56.67 = 2.58 G = C
F vs B = 59.00 - 55.93 = 3.07 F = B
E vs A = 57.33 - 55.75 = 1.58 E = A

D₄: H vs E = 64.09 - 57.33 = 6.76 H = E
G vs D = 59.25 - 56.75 = 2.50 G = D
F vs C = 59.00 - 56.67 = 2.33 F = C
E vs B = 57.33 - 55.93 = 1.40 E = B
D vs A = 56.75 - 55.75 = 1.00 D = A

D₃: H vs F = 64.09 - 59.00 = 5.09 H = F
G vs E = 59.25 - 57.33 = 1.92 G = E
F vs D = 59.00 - 56.75 = 2.25 F = D
E vs C = 57.33 - 56.67 = 0.66 E = C
D vs B = 56.75 - 55.93 = 0.82 D = B
C vs A = 56.67 - 55.75 = 0.92 C = A

D ₂ :	H vs G = 64.09 - 59.25 = 4.84	H = G
	G vs F = 59.25 - 59.00 = 0.25	G = F
	F vs E = 59.00 - 57.33 = 1.67	F = E
	E vs D = 57.33 - 56.75 = 0.58	E = D
	D vs C = 56.75 - 56.67 = 0.08	D = C
	C vs B = 56.67 - 55.93 = 0.74	C = B
	B vs A = 55.93 - 55.75 = 0.18	B = A

Conclusion

There are no significant differences due to densification temperature at the 90% or 95% level.

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