Atmospheric Pressure CVD of TEOS

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Abstract - **The goal of this project is to install an atmospheric pressure chemical vapor deposition of tetraethoxysilane (APCVD TEOS) process at RIT. The advantage of atmospheric TEOS includes, among many reasons, good uniformity, high deposition rate, superior step coverage and conformality, ease of handling, stability, and safety. In developing the process, an experimental design was utilized, using factors: deposition temperature, bubbler temperature, and N_2 carrier gas flow were examined. Responses include: deposition rate on silicon, deposition rate on oxide, thickness uniformity, refractive index, refractive index uniformity, and etch rate in hydrofluoric acid. Etch rate after 30min @ 1050°C anneal, dielectric properties, and composition analysis was also examined with selected samples. The optimum process parameters found were: 640°C deposition temperature, 68°C bubbler temperature, 2.6 L/min N_2 carrier gas flow through bubbler, 3 L/min O_2 flow, and 4.5 L/min pure N_2 flow into tube.**

I. INTRODUCTION

As feature sizes become smaller and properties of interlevel dielectrics need to be more demanding, a relatively new deposition process based on TEOS (tetraethoxysilane) is becoming popular. Some advantages of TEOS include: conformal step coverage and uniformity, smooth surface morphology, void-free oxide, low stress, high moisture resistance, high breakdown voltage, and low leakage current [1]. Handling of TEOS is also safer, easier, and more chemically stable than other silane sources [2].

TEOS can be processed in several ways: LPCVD (Low Pressure CVD), PECVD (Plasma Enhanced CVD), and APCVD (Atmospheric Pressure CVD). The purpose of having APCVD TEOS is its void-free oxide, superior conformality, and have a deposition temperature at ~400°C or lower when processed with ozone. TEOS can also be used with an in-situ doping process [3].

TEOS by itself can decompose into stoichiometric silicon dioxide (SiO_2) by pyrolysis at temperatures above ~600°C. The decomposition can take place with or without oxygen [1]. Here is the chemical reaction that takes place:

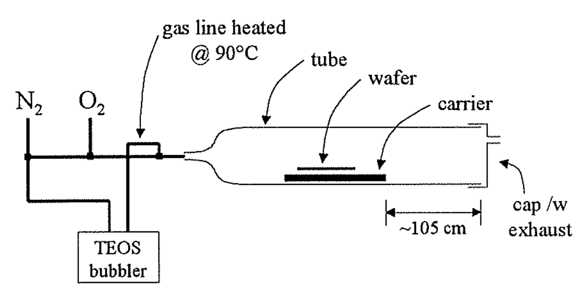
$$Si(C_2H_5O)_4 \rightarrow SiO_2 + 4C_2H_4 + 2H_2O$$

The presence of additional oxygen within the reaction can lower the chance of having carbon within the oxide film [2]. In this experiment, the additional oxygen also buffers and spreads the uniformity of TEOS around the wafer surface.

The TEOS process is also affected by surface properties, mainly if the underlayer is hydrophobic or hydrophilic (having no or strong affinity for water, respectively) [4]. TEOS itself has a hydrophilic nature.

II. EXPERIMENTAL

The schematic of the equipment used is as shown:



A Thermco diffusion tube was used as the reaction chamber. The TEOS source is a Schumacher bubbler with liquid TEOS. Gasses used were nitrogen and oxygen. Nitrogen was pumped straight into the diffusion tube at 4.5 L/min, and into the bubbler at various flows. Oxygen was pumped into the tube at 3

L/min. Since TEOS can liquefy at room temperatures, the piping from the TEOS bubbler to the tube was heated at 90°C to avoid clogging.

Table A - Results of the 15 Deposition Runs

Dep Temp [°C]	Bubbler Temp [°C]	N_2 TEOS [L/min]	Avg Thk [Ang]	% Thk Dev	Avg RI	% RI Dev	Si Dep Rate [A/min]	Oxide Dep Rate [A/min]	Pinholes ?
640	65	3	697.6	7.9%	1.441	0.3%	139.5	141.5	no
640	70	2.5	722.0	5.1%	1.444	0.2%	144.4	144.3	no
640	70	3.5	1016.4	25.6%	1.426	3.8%	203.3	208.6	yes
640	75	3	899.4	25.6%	1.428	5.8%	179.9	181.7	yes
650	65	2.5	730.0	7.8%	1.445	0.2%	146.0	146.9	no
650	65	3.5	914.2	38.8%	1.422	7.0%	182.8	180.2	yes
650	70	3	880.6	12.8%	1.439	1.0%	176.1	177.2	yes
650	70	3	905.6	18.2%	1.431	2.9%	181.1	183.9	yes
650	70	3	840.8	10.6%	1.440	0.4%	168.2	170.8	no
650	75	2.5	925.4	18.4%	1.434	2.7%	185.1	187.8	yes
650	75	3.5	1369.4	54.8%	1.342	11.7%	273.9	276.0	yes
660	65	3	870.8	11.6%	1.446	0.2%	174.2	173.0	no
660	70	2.5	889.2	10.8%	1.440	0.3%	177.8	184.9	no
660	70	3.5	1330.6	29.2%	1.433	4.2%	266.1	269.9	yes
660	75	3	1154.6	26.1%	1.429	2.9%	230.9	232.4	yes

The process parameters examined and its settings were:

- Deposition temperature @ 640, 650, 660°C
- Bubbler temperature @ 65, 70, 75°C
- N_2 carrier gas flow @ 2.5, 3, 3.5 L/min

The experimental design utilized a Box-Behnken set-up with 3 midpoints, for a total of 15 runs.

Thickness and refractive index measurements were done on a Rudolph AutoEL-IV Ellipsometer. Uniformity measurements were obtained by measuring (with flat up) the center, flat, left, off-flat, and right, with a 1 cm edge exclusion. Thickness measurements for etch rate data were taken on a Nanospec 215. Compositional analysis of the films were done by Rutherford Backscattering Spectroscopy technique. Results were entered into RS/1, a data analysis program.

III. RESULTS AND DISCUSSION

The results in tabular format is shown in Table A. To have the film properties to be as close to thermal oxide as possible, results of thickness uniformity, refractive index, and refractive index uniformity were the most critical. Also, the presence of pinholes is a concern. The pinholes were visible through an optical microscope. Note that lower bubbler temperatures and N_2 carrier flows yielded no pinholes, better uniformity, and the closest refractive index to oxide.

Results were entered into RS/1 to validate that the responses were indeed affected by changes in factor settings. The three critical responses (thickness uniformity, refractive index, and refractive index uniformity) were all significantly affected by bubbler temperature and N_2 carrier flow. The R-squared-adjust, a number indicating the accountability of the factors in changing the responses (a 1.0 indicates that all changes in the responses are accounted by changes in factor settings), are:

- Thickness uniformity: 0.8706
- Refractive index: 0.5072

- Refractive index uniformity: 0.7860

Therefore the variability in the refractive index can only be half (50.72%) explained by the three factors.

Interpolating and putting the results into a 3D plot, the expected results of thickness uniformity, refractive index, and the refractive index uniformity are shown in Figures A, B, and C, respectively. For the uniformity results, a lower percentage number yields better uniformity.

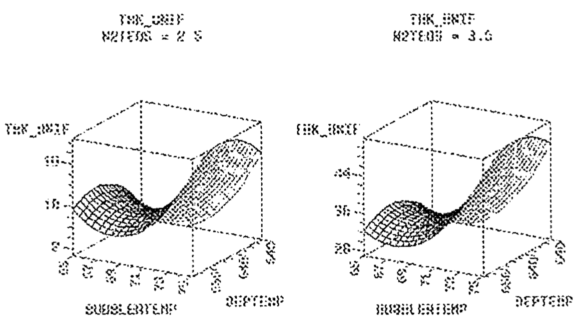


Figure A - 3D Plot of Thickness Deviation

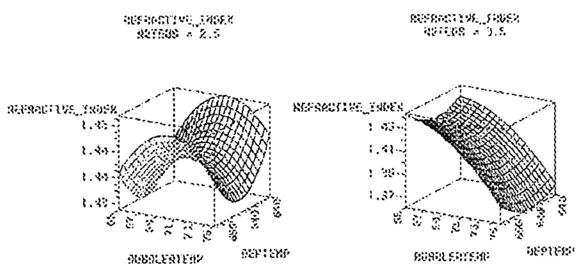


Figure B - 3D Plot of Refractive Index

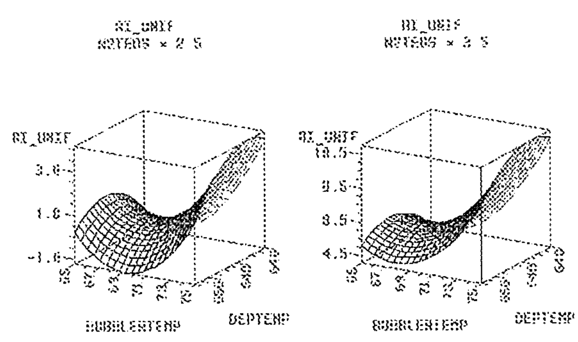


Figure C - 3D Plot of Refractive Index Deviation

In optimizing the process factors to have the highest refractive index and lowest thickness and refractive index deviation, the factor settings are:

- Deposition temperature: 640°C
- Bubbler temperature: 68°C
- N_2 carrier gas flow: 2.6L/min

To validate those parameters, three additional runs were made at those settings. The results are in Table B. Although more deposition runs are needed in order to determine repeatability, the thickness deviation is expected to be less than 15%, a refractive index between 1.44 and 1.45, and a refractive index deviation of less than 1%.

Table B - Results of Repeated Runs

Run #	Avg Thk [Ang]	% Thk Dev	Si Dep Rate [A/min]	Avg RI	% RI Dev	Pinholes ?
1	814.8	9.3%	163.0	1.445	0.2%	no
2	848.0	12.7%	169.6	1.446	0.1%	no
3	888.8	11.7%	177.8	1.445	0.1%	no

The etch rate in buffered hydrofluoric acid (BOE) before anneal is greater than 3kA/min. After a 30 minute, 1050°C anneal, the etch rate drops to 1kA/min, similar to thermal oxide.

Using the Rutherford Backscattering Spectroscopy (RBS) technique, a compositional analysis was obtained. The film is indeed stoichiometric SiO_2 and the presence of carbon is below the detectable limit (less than a few percent). Figure D shows the RBS spectrum plot.

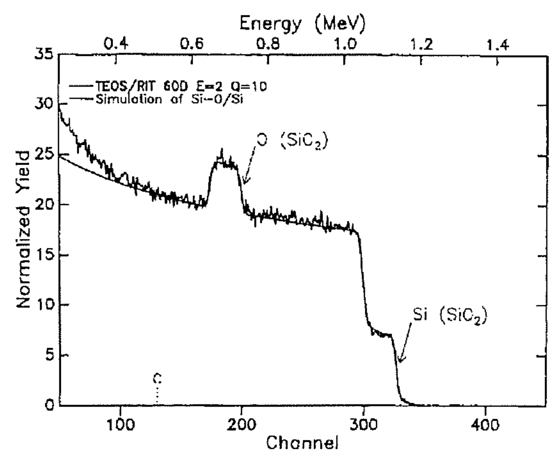


Figure D - RBS Spectrum Plot

IV. CONCLUSION

The optimized process factors to have the highest refractive index and lowest thickness and refractive index deviation are:

- Deposition temperature: 640°C
- Bubbler temperature: 68°C
- N_2 carrier gas flow: 2.6L/min

At that setting the deposition rate on silicon is around 160A/min. The etch rate in BOE is greater than 3kA/min before anneal, and 1kA/min after a 30 minute 1050°C anneal. The film is stoichiometric SiO_2.

Follow-up experiments in this process includes examining the dielectric properties of the film, repeating more deposition runs to determine process control, capability to process more wafers (processing the wafers in an upright position), and adding ozone process to lower the deposition temperature to around 400°C.

ACKNOWLEDGMENTS

Thanks to Dr. Richard Lane and Dr. Santosh Kurinec for their advise and assistance, Dave Yackoff for preparing and installing the equipment, and Dr. G. Braunstein of Eastman Kodak Co. for RBS analysis.

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