

Phenomenological Model of TEOS-Ozone Atmospheric Pressure SiO₂ Chemical Vapor Deposition Process

A. Lubnin¹, V. Kudriavtsev²
Watkins-Johnson Company
Semiconductor Equipment Group

1. SUMMARY

This paper considers chemical vapor deposition of silicon dioxide (SiO₂ CVD) from a standpoint of polymer science. The relationships of tetraethoxysilane (TEOS)/ozone atmospheric and subatmospheric pressure SiO₂ CVD and traditional polycondensation, and of SiO₂ CVD and combustion are exploited for a description of reactions between TEOS and ozone. Mechanism and kinetic scheme are proposed for TEOS/ozone and TEOS/ozone/dopant SiO₂ CVD. A two-dimensional computer simulation of oligomer transport in the Watkins-Johnson experimental reactor chamber was performed using a CFD-ACE software package. It was shown that TEOS oligomers (up to at least decamers) can be successfully transported to the wafer surface by diffusion, in spite of the convective stagnation in the boundary layer and thermodiffusion effects.

2. REACTION MECHANISM

The simplest way to picture SiO₂ APCVD is to look at it as a combination of a low-temperature combustion and polycondensation processes. The similarity with polycondensation is due to the fact that the silica film is actually a three-dimensional polymer obtained from the TEOS monomer. The association with combustion is invoked by several reactive species which are common for both SiO₂ CVD and combustion of hydrocarbons. These analogies allowed us to use the broad body of knowledge accumulated in both fields. Based on the literature review, we are postulating that for the efficient film growth, oligomers, which are formed in the gas phase, should meet three requirements: optimum length,

sufficient number of functional (silanol or free radical) groups, and they must be transportable to the surface by diffusion or convection. If oligomers are too short and/or do not have enough functional groups, they will bounce off the surface and will be carried away by the gas flow. If the oligomers can not reach the surface, they will become gas phase "powder" and will be lost for the CVD. If oligomers are too long, they will become thermodynamically unstable in the gas phase, and "coagulate" or precipitate out of gas (i.e. nucleate the particles). Either way, deviation from the optimum length and functionality will result in a decrease of the SiO₂ deposition rate. For the equipment designer, it will translate into unique optimum residence time for a given set of process conditions. The importance of the oligomer formation in the gas phase has been already recognized by other authors [1, 2]. In TEOS/ozone SiO₂ CVD, the main chain of events is triggered by the monooxygen produced during thermal decomposition of ozone [3]. TEOS can serve as a source of hydrogen leading to the formation of hydroxyl radical, OH. The latter is known to accelerate ozone decomposition [4] and cannot be neglected in a comprehensive description of the reaction mechanism. Elementary reactions at the initial stages of SiO₂ CVD are shown in Scheme 1 (most of the reactions not involving silicon are not shown). These include abstraction of acetaldehyde, condensation of silanols, and condensation of silanols with ethoxysilanes (heterocondensation). Three types of intermediates are formed during the reaction: free radicals, silanols, and ethoxysiloxanes. Initial reactions lead to the formation of a dimer - hexaethoxydisiloxane (indicated as T₂). The dimer can enter the same cycle of reactions as a substrate and yield trimers, tetramers and longer oligomers (not shown on

¹ BFGoodrich Company, Brecksville, OH 44141; e-mail: lubnin@yahoo.com

² CFD Canada, vvk@@cfdcanda.com

Scheme 1). Reactions can occur at different loci: in the gas phase, at the interface (both at the glass and particulate surfaces), or on the surface and in the bulk. Reaction rates at the glass surface determine the rate of deposition. Reaction rates at the particle surface determine the particle growth.

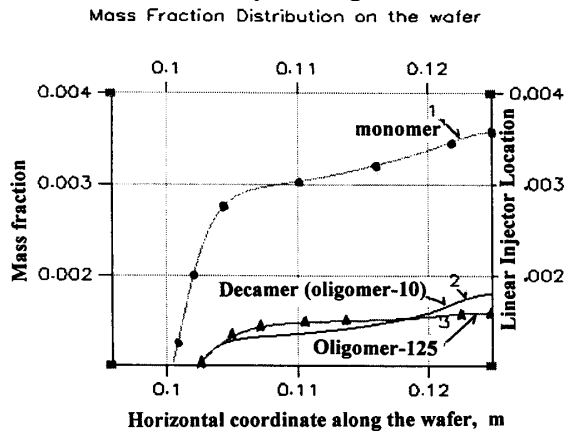


Figure 1. Monomer and Oligomer Mass Fraction Distribution (under static condition) along the wafer surface. Injector is located on the left (see Figure 2)

Reactions on the surface determine the quality of the film [5], because during these reactions functional groups are removed from the surface yielding SiO_2 . If annealing of functional groups on the surface is slower than the deposition rate, unreacted silanol and other unreacted functional groups get buried under the layer of newly deposited oligomers, and create imperfections in the film. Subsequent thermal annealing of the buried functional groups yield volatile product and voids in the film creating another type of imperfection. Both defects (initial and annealed) are loci of the undesirable stress in the film.

3. TRANSPORT

A computational model of Watkins-Johnson atmospheric pressure reactor was generated [6, 7] by the use of CFD-ACE fluid dynamics and generalized transport software package. Effects of oligomer transport in the deposition chamber and near injector were studied (Figures 1 & 2). Diluted TEOS, decamer and oligomer-125 (1.5% mass fraction each) were introduced through the injector

central port with the stream of nitrogen. Effects of convective transport, diffusion transport, thermal diffusion and convective stagnation near the wafer surface were studied for the deposition conditions at 500°C . Diffusion coefficients were calculated on the basis of kinetic theory using oligomer collision diameter and molecular weight as inputs. Corresponding TEOS and oligomer mass fraction distributions within the chamber are shown in Figures 1 and 2(a,b). These results show that TEOS is more diffusive and has much higher concentration at the wafer surface than the decamer (Figure 1). However, the decamer mass fraction at the wafer surface comprises 50% of TEOS. This indicates that oligomer is indeed transported to the surface and can play an important role in the SiO_2 CVD.

4. DOPANTS

The effect of boron and phosphorous dopants is attributed to their Lewis acidity. Lewis acids are known to accelerate condensation reactions including silanol condensation. This results in the formation of a film with much less built-in functional groups and therefore less strain. More detailed discussion of the dopant effects and overall mechanism will be given in the poster.

5. REFERENCES

- [1] T. Satake, T. Sorita, H. Fujioka, M. Adachi, H. Nakajima. *Jpn. J. Appl. Phys.*, **33**, 3339 (1994).
- [2] M. Adachi, K. Okuyama, N. Tohge, et.al., *Jpn. J. Appl. Phys.*, **33**, L447 (1994).
- [3] S. W. Benson and A. E. Axworthy. *J. Chem. Phys.*, **24**, 1718 (1957).
- [4] W. B. DeMore. *J. Chem. Phys.* **45**, 813 (1967).
- [5] D. Dobkin, S. Mokhtari, A. Sherman, et. al. *J. Electrochemical Society*, **142**, 7, 2332 (1995)
- [6] P. Ho, J. Johannes, V. Kudriavtsev, Sandia Report SAND97-2328, UC-401, October, (1997)
- [7] N. Zhou, A. Krishnan, V. Kudriavtsev, Y. Brichko, 5th Int. Conf. on Adv. Thermal Processing of Semiconductors RTP-97, New Orleans, LA, (1997), p. 257-268

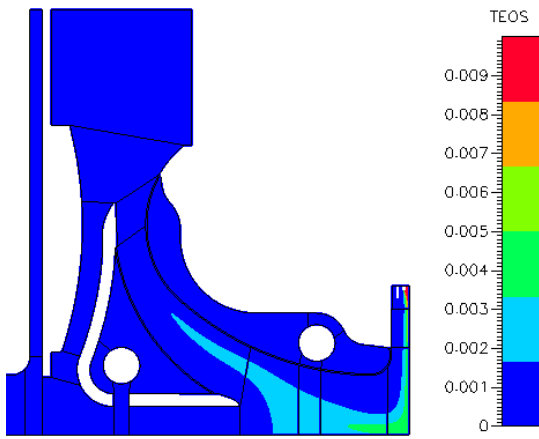


Figure 2(a) TEOS Mass Concentration Distribution in the CVD Chamber

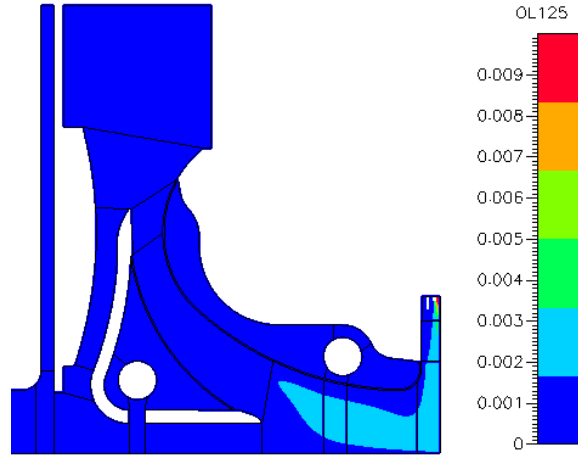


Figure 2(b) Oligomer-125 Mass Concentration Distribution in the CVD Chamber

Scheme R. Elementary Steps in TEOS + O Reaction

