CVD Trap 시스템 내부 Titanium Nitride 부산물의 CFD 모델링

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CFD Modeling of Reaction on Titanium Nitride Byproducts in CVD Trap System

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INTRODUCTION

Currently, as CVD surface reaction applied in semiconductor industry requires complicated chemistry, it is concerned on critical issue that the byproducts resulted from the residue gases damages the exhaust line and pumping system of CVD equipment. The Surface reaction in the exhaust line and pumping system is generally occurring in low temperature. The research on the surface reaction of high temperature has already many outcomes in terms of material science of product, but that of low temperature has rare interest and results. In terms of equipments to productivity improvement, The research on the surface reaction of low temperature is critical and meaningful works in this states of semiconductor industry.

In current industrial steam line, TiN is essential process to make a diffusion barrier of semiconductor. Trap system located behind TiN CVD chamber has a significant rule to reduce damaging the exhaust line and pumping system because TiN byproducts (TiCl4.4NH3(s)) formed below 200℃ in Trap system.

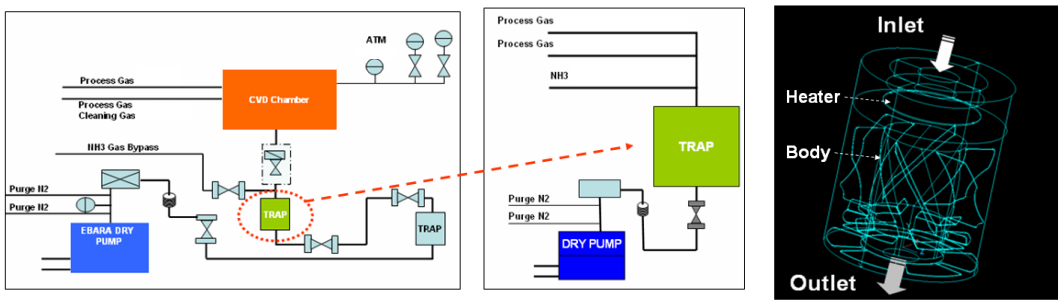
In this work, to understand the character of the condition and reaction product (TiCl4.4NH3(s)) in trap system, the study of computation fluid dynamics(CFD) coupled with experimental studies is used to analyze the Trap system. At low-pressure and temperature below 200℃, CVD of TiN byproducts has been achieved by experiment data[1] and modeling the chemical formation of TiN byproducts by Gaussian 98 program and Chemkin program[2]. Of these, TiCl4.4NH3(s) is recommended to one of the main byproduct of TiN byproducts because of its thermal stability of chemical reaction.

$$TiCl_4\ (g) + 4NH_3\ (g) \rightarrow TiCl_4.4NH_3(s)$$

EXPERIMENTAL AND CALCULATIONAL DETAILS

The trap system used in actual stream line is equipped just behind CVD chamber, shown schematically in Figure 1. After The TiN reaction products were synthesized at below 200℃ and deposited at 530℃ in CVD Chamber, the residue process gases of NH_3(60sccm) with carrier gas of N_2(500sccm), $TiCl_4$(60sccm) with carrier gas of N_2(500sccm) and NH_3(100sccm) gas injected from bypass line make $TiCl_4.4NH_3$(s) as TiN byproduct at below 200℃. Inlet

mixture gases sum up as $TiCl_4$ (60sccm), NH_3 (100sccm), N_2 (1000sccm), shown in Figure 1. The processing pressure of Inlet was maintained at 4.4 Torr using the throttle valve under the Trap.



(a) Schematic diagram of CVD (b) Trap system

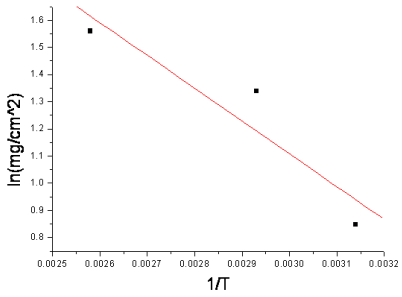
Figure 1. Schematic diagram ; (a) and (b)

The temperature and the amount of $TiCl_4.4NH_3(s)$ depositions measured in experiment to compare with calculated values. The core part of Trap is Trap body because $TiCl_4.4NH_3(s)$ deposition mainly takes place in. So, the Trap body is determinant of Trap efficiency. The temperature of Trap body (Figure.1(b)) is measured with a thermocouple, changing the heating temperature of heater to three cases of 530℃/ 450℃/ 350℃.

Model Description and Development The surface reaction is modeled using the Arrhenius model. The following reaction mechanism proposed by Brager[5] :

$$TiCl_4\ (g) + 4NH_3\ (g) \rightarrow TiCl_4.4NH_3(s)$$

The activation energy and reaction coefficient for this reaction are obtained from the experiment, plotting Arrhenius plots (figure. 2).



Y = 4.73044 - 1207.434 X

Figure 2. The Arrhenius plot of $TiCl_4.4NH_3(s)$ deposition reaction

The experiment of The $TiCl_4 \cdot 4NH_3(s)$ deposition rate [mg/㎠ · sec] of Trap body surface is measured by processing for 4hr. To accurately measure the obtained compound of $TiCl_4 \cdot 4NH_3(s)$, electrical scale is used according to 6㎠ of the Trap Surface, depending on the identified temperature of heater (530℃/ 450℃/ 350℃). The $TiCl_4 \cdot 4NH_3(s)$ deposition rate per unit area of Trap surface is calculated through the following equation,

$$\omega_s = AT^n \exp(-E_a / RT)[TiCl_4]^{\alpha}$$

The simulation condition of this reaction is sum up to table 1.

Table 1. The simulation condition of the $TiCl_4 \cdot 4NH_3$(s)deposition reaction

preexponential constant, A (m/sec)	1.333 m/sec
temperature exponent n	1
activation temperature , E_a / R (K)	1207.430 K
the order of reaction (α)	1

RESULTS AND DISCUSSION

Chemical Vapor deposition of Trap system depends on a complex interaction between the diffusive and convective heat and mass transport and chemical reaction occurring in the system. The temperature at the body of Trap is shown in Figure 3 as comparing the real experimental estimation. It can be seen that the trap body at three different temperatures of heating (530℃/ 450℃/ 350℃) has certain trend of increasing the temperature of the trap body by heat transfer phenomena.

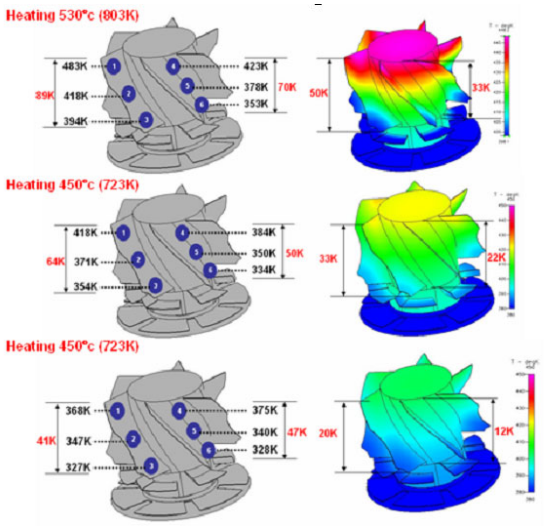
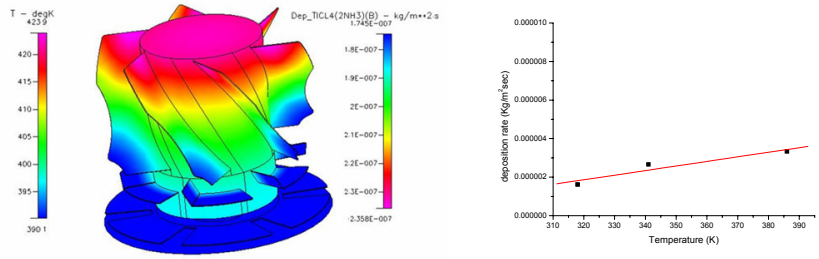


Figure 3. Temperature profile of Trap body depending on heating temperature

The $TiCl_4 \cdot 4NH_3$(s) deposition rates predicted by the model at different temperature and deposition pressures are further compared with the corresponding ones obtained from experiments in the CVD TRAP system used. Figure 4 (a) shows $TiCl_4 \cdot 4NH_3$(s) deposition rate at body temperate of 390 - 420℃. Although the $TiCl_4 \cdot 4NH_3$(s) deposition rate of simulation result differ from the experimental results by 1st order, it reveals that $TiCl_4 \cdot 4NH_3$(s) deposition is critically depending on the temperature on the Trap body as meaningful results.



(a) deposition rate of simulation result (b) deposition rate of experimental result

Figure 4. $TiCl_4 \cdot 4NH_3(s)$ deposition rates of
(a) simulation result and (b) experimental result

CONCLUSION

Computational fluid dynamics is an effective method for studying CVD TRAP systems, because it enables three-dimensional representation of the system and good visualization of the physical phenomena that occur in this work on $TiCl_4 \cdot 4NH_3(s)$ deposition from gases. CFD studies are shown to predict the velocity, temperature, and concentration profiles as well as deposition rate in the TRAP system. Simulation results indicate somewhat good agreement with experimental data obtained in the MOCVD Trap system. The effect of Trap body temperature on the $TiCl_4 \cdot 4NH_3(s)$ deposition are predicted satisfactorily to meaning aspect. The deposition rate is found to increase significantly with increasing Trap body temperature; this suggests the $TiCl_4 \cdot 4NH_3(s)$ deposition is surface-reaction-controlled. In addition, the deposition kinetics model used to in the simulation is found to describe the overall Trap surface phenomena well.

REFERENCE

1. An Improved Single-Source Precursor to Titanium Nitride Films, Charles H. Winter T. Suren Lewkebandara, James W. Proscia,lb and Arnold L. Rheingoldlc , Delaware 197 16 Received July 28, 1993
2. Thermodynamics and Kinetics of Initial Gas Phase Reactions in Chemical Vapor Deposition of Titanium Nitride. Nakhimovskii prosp., Kosigina, Fachbereich Chemie, Philipps-UniversitätMarburg, Hans-Meerwein-Strasse, D-35032Marburg, Germany 4Advanced Systems Research Lab, SPS Motorola Inc., Mesa, Arizona 85202 Received 9 January 2001; accepted 26 February 2001 Dedicated to Professor Paul von R. Schleyer
3. Modeling of the Metalorganic Chemical Vapor Deposition of Tantalum Oxide from Tantalum Ethoxide and Oxygen Sukanya Murali,† Anand Deshpande, and Christos G. Takoudis* Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607 S. Iijima, *Nature (London)*. 354, 56 (**1991**)
4. CFD-ACE+ V2006 Modules Manual, ESI CFD Inc. 6767 Old Madison Pike, Ste. 600 Huntsville, AL 35806
5. Direct Obeservation of the Formation Process of TiN particles by CVD Method, Junichi HOJO and Akio KATO, Department of Applied Chemistry, Faculty of Engineering, Kyushy University 6-10-1, Hakozaki, Fukuoka-shi 812, Received August 15, 1980. H. Abe, "Seramikkusu Zairyogijutsu Shusei", ed. H. Tagai et al., Sangyo Gijutsu Center (1979) p.1044-48
6. Designing low pressure systems with continuum models Vikram Singh and Butch Berney Lam Research Corporation, 4650 Cushing Parkway, Fremont, California 94538 Anantha Krishnan CFD Research Corporation, 3325 Triana Boulevard, Huntsville, Alabama 35805, Received 4 October 1995; accepted 4 March 1996. J. Vac. Sci. Technol. A 14(3), May/Jun 1996 0734-2101/96/14(3)/p. 1252-6