**Atomic Layer Deposition Nano-Manufacturing Technology**

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**Introduction**

Miniaturization to the nanometer scale has been one of the most important trends in science and technology over the past ten years (Kim 2007). Atomic Layer Deposition (ALD), with its superior ability in obtaining atomic layer control of film growth and depositing highly uniform and conformal thin films on extremely complex surfaces, plays a key role in the miniaturization of nano-scale devices and structures in a broad array of industrial sectors [[1](#_ENREF_1), [2](#_ENREF_2)]. For example, the *International Technology Roadmap for Semiconductors* (ITRS) has recognized ALD as a key technology for the semiconductor industry to break beyond the 45nm device node in the quest for continuous miniaturization towards ever smaller nanotechnology nodes [[3](#_ENREF_3)]. In recent years, ALD has found a broad array of applications on such industrial sectors as semiconductors [[4](#_ENREF_4)], solar cells [[5](#_ENREF_5)], fuel cells [[6](#_ENREF_6)], lithium-ion batteries [[7](#_ENREF_7)], medical devices [[8](#_ENREF_8)], sensors [[9](#_ENREF_9)], polymers [[10](#_ENREF_10)], and even nano-particle coating [[11](#_ENREF_11), [12](#_ENREF_12)].

ALD is able to meet the needs for atomic layer control and conformal deposition using sequential, self-limiting surface reactions. By alternatively pulsing two or more chemical precursors, ALD processes are based on binary reaction sequences where two surface reactions occur and deposit films. Between pulsing steps, purging step is needed by using inert gas to remove the by-product during the reaction and the unreacted precursor. As a result, one ALD cycle contains four steps: pulsing the first precursor; purging; pulsing the second precursor; purging. By repeating ALD cycles, desired thickness of films can be obtained.

The advantages of ALD are precise thickness control at the Angstrom or monolayer level. The self-limiting aspect of ALD leads to excellent step coverage and conformal deposition on high aspect ratio structures. As a result, ALD films remain extremely smooth and conformal to the original substrate [[13](#_ENREF_13)]. The self-limiting characteristic of ALD is extremely important for the deposition of excellent dielectric films.

ALD processing is also extendible to very large substrates and to parallel processing of multiple substrates since ALD precursors are gas phase molecules, and they fill all space independent of substrate geometry and do not require line-of-sight to the substrate. ALD is only limited by the size of the reaction chamber. Because the surface reactions are performed sequentially, the two gas phase reactants are not in contact in the gas phase. This separation of the two reactions limits possible gas phase reactions which can form particles that could deposit on the surface, thus guaranteeing the uniformity of films.

While ALD is a key thin film deposition technique for a wide range of industrial applications, its sustainability issues are significant due to the heavy wastes of toxic chemicals, nano-particle emissions, and high energy use. The low sustainability performance of ALD technology draws concerns in its wide applications and needs to be improved.

**Rationale: Energy Storage for ensuring Sustainable Manufacturing**

After years of rapid development, ALD has already been adopted in industrial-scale production of  
semiconductors, introduced itself properly in electronics and solar, and finds its way into many other  
fields and industries. While ALD is such a key nanotechnology for a wide range of industrial applications, its sustainability performance is quite low due to the use of toxic chemicals and the binary reaction nature of ALD processes. According to our preliminary results, large-scale applications of ALD technology based on current processes and operations have significant environmental and societal impacts which needs to be systematically improved [[14-16](#_ENREF_14)]. While ALD just starts its journey in industrial-scale applications, a thorough investigation of the ALD’s sustainability performance and development of a suite of scientific methods for sustainability improvement of ALD technology would provide valuable “Design for Sustainability” feedback during the development and large-scale applications of ALD technology in various industrial sectors in the future. In this module, both experiments and theoretical simulation of ALD process are included in order to analyze the parameters that influence the sustainability performance of ALD technology.

**Course Content: ALD theory, Manufacturing Steps, Model Formulation**

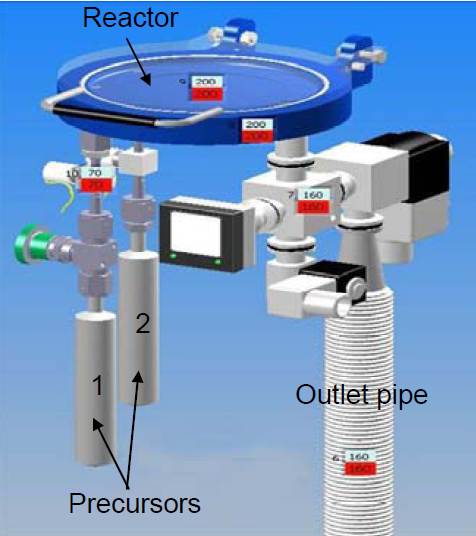
Though ALD instruments vary, their mechanisms of deposition are similar with each other, which can be described as gaseous precursors depositing on substrates layer by layer. A schematic of a typical ALD instrument (Savannah 100) is shown in figure 1. As shown in the figure, ALD is operated by alternately pulsing two or more chemical precursors into a vacuum chamber to form thin layer deposition on substrates through surface reactions. For example, Al2O3 nano-film, a representative of ALD reactions, is generated by trimethylaluminum (TMA) as the metal source and water vapor as the oxidant. The overall reaction of TMA and H2O is described as:

Fig.1 Savannah ALD system

(1)

H2O can be replaced by O3 to achieve a more uniform deposition [[17](#_ENREF_17)]. The reaction of TMA and O3 is:

(2)

ALD is able to deposit different films through corresponding precursors. For example, by using H2O as oxidant, TiCl4, Zn(CH2CH3)2 and SiCl4 generate TiO2, ZnO and SiO2 films, respectively [[2](#_ENREF_2)]. The reactions are:

(3)

(4)

(5)

Heating and vacuum are provided along the system continuously. Pressure of the system is kept at around 0.1 torr. Temperature is set at 150°C in the exhaust area and in the range of 80 and 300°C in the reaction chamber depending on the requirements. To prevent oxidation and to carry precursors, N2 is purged through the entire ALD system continuously. Interval time between two pulsed are set between 4 and 30 s. Because deposition is applied sequentially, the amount of films deposited on substrates is consistent and mixing of different precursors is prevented. Therefore, ALD shows its advantage on thickness control, quality of films and reduction of side-reactions.

Due to the limitation of resources, sustainability has become an essential project for the entire world. There are five major categories concerned in the concept of sustainability: societal needs, preservation of biodiversity, regenerative capacity, reuse and recycle, and constraints of nonrenewable resources and waste Generation. ALD has many advantages, however, it is an energy-consuming process with significant amounts of waste due to continuous heating, high vacuum and low precursor efficiency. This research studies the sustainability of ALD using Savannah 100 as a model. It has three main projects: study energy usage and exergy efficiency, simulate reactions inside ALD system and analyze ALD deposition and emissions.

The degree of energy intensiveness of ALD system and exergy flow are calculated based on the first and second law of thermodynamics, respectively. The total energy supplied to the system is the sum of total enthalpy change of ALD reactions, energy consumption and work flow. The energy consumption is the sum of internal energy gain and dissipated energy. The workflow can be consumed by multiplying pump power with the operation time. Exergy is defined as the maximum reversible useful work that can be obtained from a system at a given state in a given environment. Exergy analyze the efficiency of chemical and thermal process and therefore is used to improve efficiency of energy [[18](#_ENREF_18)]. The exergy balance equation of a steady flow open system can be obtained from the second law of thermodynamics. Degree of energy intensiveness is depicted in Gutowski’s diagram as 1.54 × 1012 J/Kg, and exergy efficiency is estimated at around 3.68 × 10–4 and 3.26 × 10–11 by using two estimation methods, indicating that ALD is a high-energy usage process with low exergy efficiency. Study also shows the exergy distribution in ALD system, where reactor heating consumes about 85% of energy usage.

Gas flow and reactions are simulated by several mathematical models. The gas flow in reaction chamber is modeled numerically by Lattice Boltzmann Method (LBM) which is rooted on the classical kinetic theory of gases to study flow properties. Reaction processes can also be simulated through partial differential equations using the finite volume methods. ALD thermal-fluid dynamics with surface reactions in various process conditions are simulated to better understand ALD deposition process and to optimize deposition parameters. Simulations are well correlated with experimental results.

The effect of parameters (pressure, temperature, and purging time, etc.) on ALD process, including deposition quality and emissions are studies experimentally by series of instruments. Thickness of ALD deposition is analyzed by ellipsometry, an optical technique measuring the dielectric properties of thin films which is then transferred to thickness of film. Each cycle of TMA Al2O3 reaction deposit about 1 Å of film on substrate. Compared with the volume of chamber, surface area of substrate is limited, so most precursors are not able to contact with surface. By estimating deposition is uniform along the system, only 7% of precursors can deposit on the surface, while rest of them are exhausted as waste.

There are mainly two types of ALD emissions: gases and particles. As described in equation (1) to (5), CH4, C2H6 and HCl are common gaseous resultants. Gas analysis of Savannah 100 using Residual Gas Analyzer (RGA) indicates that CH4 emitted from one cycle of TMA/H2O reactions takes up to 45-51% of C contained in TMA. CH4 has global warming potential of 25 (100 years), so its greenhouse warming effect is 25 times larger than CO2 [[19](#_ENREF_19)]. Both CH4 and C2H6 are flammable when concentration is around 5 - 12% in air [[20](#_ENREF_20)]. HCl is not as flammable as CH4 and C2H6, but it is a corrosive gas and causes damage to body issue when contact with it.

Besides gases, particles are another major type of ALD emissions. To investigate nanoparticles, Scanning Mobility Particle Sizer (SMPS, TSI 3936) and Nanometer Aerosol Sampler (TSI 3089) are applied to measure concentration, size distribution, and compositions, etc. SMPS is made up by combining Electrostatic Classifiers (TSI 3080) and Ultrafine Condensation Particle Counter (UCPC, TSI 3776) together. Electrostatic Classifier divides particles according to their sizes and UCPC measures concentration of particles. So combination of these two instruments gives size distribution of particles. SMPS results show that about 2 × 108 of ultrafine nano-particles within the range of 100 nm are generate during each cycle of reaction. Effects of nanoparticles are strongly related to their sizes. Those nanoparticles which are smaller than 100 nm can penetrate membranes of respiratory system, enter blood and finally arrive in brain through circulatory system [[21](#_ENREF_21)].Nanoparticles are collected on TEM grid using nanometer aerosol sampler sample. The collect nanoparticles are then sent to Energy-dispersive X-ray Spectroscopy and Scanning Electron Microscope to obtain their elemental components and morphologies.

This is a systematic research on ALD reactions. Energy usage and efficiency is calculated. ALD reactions are simulated to study internal reactions and to optimize deposition parameters. Meanwhile, experimental measures have found out the most abundant emissions and their chemical and physical properties. These studies will benefit ALD industry to give useful guides on improving energy efficiency, optimizing deposition, reducing emissions and process of waste treatment.

**Case Study Description**

ALD of Al2O3 high-k dielectric nano-film is chosen as the case study. ALD of Al2O3 nano-film is widely recognized as the representative of ALD process in which trimethylaluminum (TMA) is used as the metal source, and water vapor as the oxidant. Inert gas nitrogen is used as the carrier and purging gas. The ALD experimental system is shown in figure 1. TMA and water are injected into chamber sequentially and pulsing (in milliseconds) is controlled by ALD stop valves. Nitrogen gas flows through the system continuously during all the operations. A vacuum pump is connected with outlet pipe to maintain the low vacuum pressure in the chamber. The deposition process can be expressed by the following chemical reaction:

 (6)

This reaction can be split into two half reactions:

 (7)

 (8)

However, there are sustainability issues associated with ALD of Al2O3 process. The precursor TMA is a flammable and toxic. In addition, the principle byproduct of the process is methane, which is a major greenhouse gas and has a global warming potential 25 times that of carbon dioxide [IPCC, 2007]. As ALD is a self-limiting process, the unreacted precursors are pumped out and ended as environmental emissions.

**Design of ALD process for sustainability**

Based on ALD principles and instrumental setup, the most important parameters in ALD include temperature, purge time, flow rate of carrier gas and dosage of precursors. The dosage is controlled by changing the pulse time of precursors. The growth rate of ALD films in different dosage is non-linear, which means that the deposition rate will reach the highest value and cannot be improved when concentrations of precursors reach certain values. In this Savannah 100 system, pulse time of 0.015 s and flow rate of 20 sccm are chosen for both TMA and H2O because concentration of TMA and H2O will reach the highest point and cannot be improved significantly at higher dosage. Therefore, in this design of ALD process for sustainability, temperature and purging time are considered as factors, while the goal this design is to minimize the gaseous emission and the nano-wastes and nano-particles.

To be specific, Factorial design is a statistic design to study the effects of factors on the response variable and interactions among the factors. The objectives of design of experiments (DOE) include: determine the most and least influential variables and minimize effects of uncontrolled parameters. Four levels are tested for each factor: 100, 150, 200 and 250 °C for deposition temperature, and 8, 12, 16 and 20 s for purge time. The factors and levels are summarized as Table 1.

Table 1. Factors and levels

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Factors | Levels | | | |
| Reactor Temperature (°C) | 100 | 150 | 200 | 250 |
| Purge time (s) | 8 | 12 | 16 | 20 |

Two-factor four-level factorial design of experiments is carrier by Minitab as following:

Multilevel Factorial Design:

Factors: 2 Replicates: 1

Base runs: 16 Total runs: 16

Base blocks: 1 Total blocks: 1

Number of levels: 4, 4 Responses: 2

The experimental design table is as Table 2.

Table 2. Factorial design table

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| StdOrder | RunOrder | PtType | Blocks | Purge Time (s) | Temperature (C) |
| 13 | 1 | 1 | 1 | 20 | 100 |
| 15 | 2 | 1 | 1 | 20 | 200 |
| 4 | 3 | 1 | 1 | 8 | 250 |
| 7 | 4 | 1 | 1 | 12 | 200 |
| 2 | 5 | 1 | 1 | 8 | 150 |
| 6 | 6 | 1 | 1 | 12 | 150 |
| 16 | 7 | 1 | 1 | 20 | 250 |
| 8 | 8 | 1 | 1 | 12 | 250 |
| 3 | 9 | 1 | 1 | 8 | 200 |
| 12 | 10 | 1 | 1 | 16 | 250 |
| 14 | 11 | 1 | 1 | 20 | 150 |
| 10 | 12 | 1 | 1 | 16 | 150 |
| 5 | 13 | 1 | 1 | 12 | 100 |
| 1 | 14 | 1 | 1 | 8 | 100 |
| 11 | 15 | 1 | 1 | 16 | 200 |
| 9 | 16 | 1 | 1 | 16 | 100 |

The experimental results of emissions of nano-particles and CH4 are presented in Table 3 and 4, respectively.

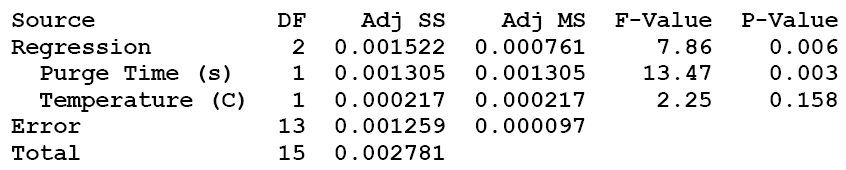
Table 3. Number concentration of nano-particles emitted during each cycle of ALD reactions

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Purge Time  (s) | No. Conc. of Nano-particles emitted per cycle (×108 #) | | | |
| 100 °C | 150 °C | 200 °C | 250 °C |
| 8 | 1.96 ± 0.80 | 2.79 ± 0.98 | 2.92 ± 1.18 | 2.28 ± 0.95 |
| 12 | 1.44 ± 0.82 | 1.63 ± 1.11 | 1.54 ± 1.02 | 2.01 ± 1.29 |
| 16 | 1.31 ± 1.23 | 1.90 ± 1.50 | 1.18 ± 0.99 | 1.64 ± 1.18 |
| 20 | 1.11 ± 1.07 | 1.43 ± 1.38 | 1.28 ± 1.21 | 2.07 ± 1.85 |

Table 4. Average volume of CH4 emitted during each cycle of reactions

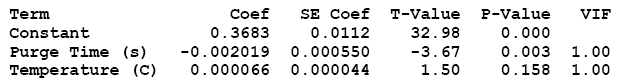
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Purge Time (s) | Average Volume of CH4 emitted per cycle (cm3) | | | |
| 100 °C | 150 °C | 200 °C | 250 °C |
| 8 | 0.3636 ± 0.0028 | 0.3696 ± 0.0029 | 0.3665 ± 0.0028 | 0.3716 ± 0.0026 |
| 12 | 0.3422 ± 0.0043 | 0.3551 ± 0.0029 | 0.3539 ± 0.0046 | 0.3524 ± 0.0031 |
| 16 | 0.3361 ± 0.0026 | 0.3611 ± 0.0027 | 0.3562 ± 0.0050 | 0.3496 ± 0.0032 |
| 20 | 0.3444 ± 0.0016 | 0.3320 ± 0.0015 | 0.3255 ± 0.0016 | 0.3576 ± 0.0027 |

The two factors are analyzed by the general regression analysis which is conducted in Minitab. For the CH4 emission, ANOVA (Analysis of Variance) is performed by Minitab to test the effects of the two factors and the analysis result is as following,



The regression equation is Volume of CH4 per cycle (cm3) = 0.3683 - 0.002019 Purge Time (s) + 0.000066 Temperature (C).

The regression coefficients is achieved as following,



From both ANOVA and regression analysis, the temperature effect has p-value large than purge time. It is concluded that temperature has a weaker effect on the gaseous emissions. Additionally, purge time has a negative effect, while temperature has positive effect. Furthermore, the contour plot of CH4 emission is shown as Fig.2, and it is found the least emission (Dark green area) is found at longest purge time, and at moderate temperature.

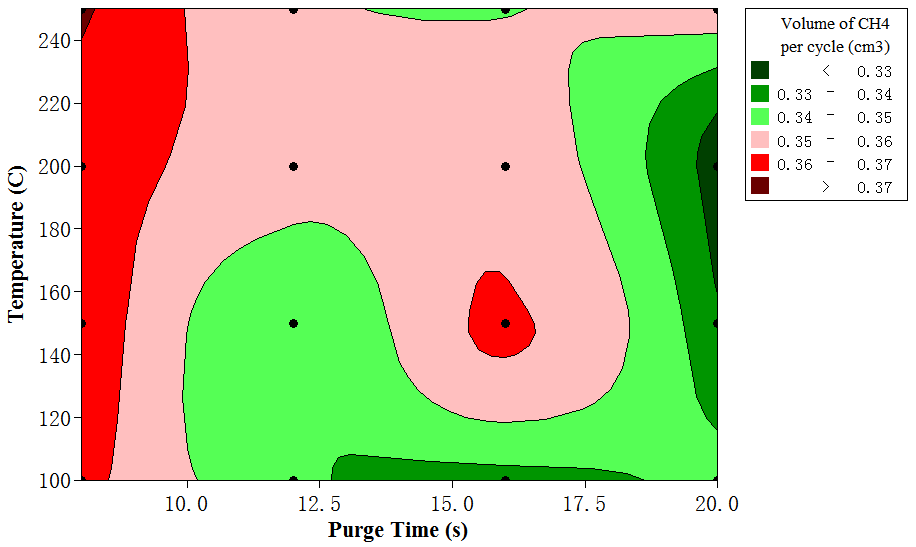
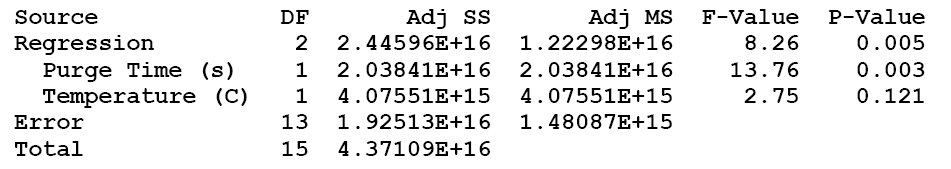


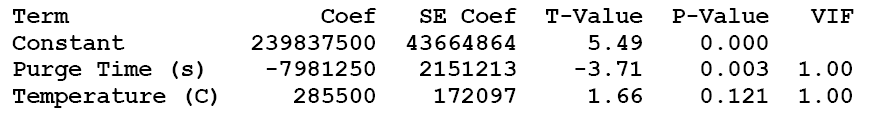
Fig.2. Contour Plot of Volume of CH4 per cycle vs. Temperature (C), Purge Time (s)

Similarly, for nano-particle emission, ANOVA result is as following,



The regression equation is No. of Nanoparticle per cycle = 239837500 - 7981250 Purge Time (s) + 285500 Temperature (C).

The regression coefficients is achieved as following,



By both ANOVA and regression analysis, it is concluded that temperature has a weaker effect on the nano-particle emissions. Additionally, purge time has a negative effect, while temperature has positive effect. Furthermore, from the contour plot of nano-particle emission as shown by Fig.3, compared to gas emission, it is found the least emission of nano-particle (Dark green area) is found at shorter purge time, and at a comparable level of temperature.

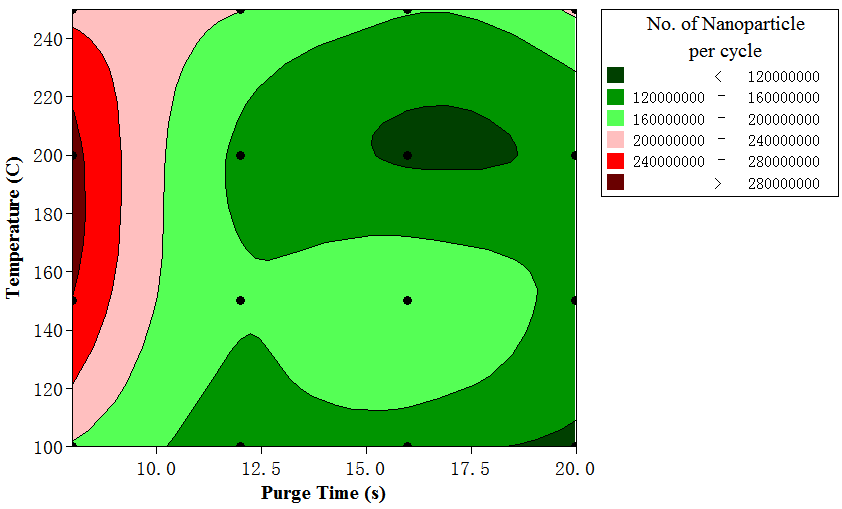


Fig.3. Contour Plot of No. of Nanoparticle per cycle vs. Temperature (C), Purge Time (s)

**Connections to Existing Core Curriculum**

This is a project concerning about new technology, simulation, optimization of reactions and measurements of different type of emissions. Therefore, this educational module can be introduced in various courses, such as sustainability of industry process, sustainable development, green chemistry, nanotechnology, environmental analysis and so on. It will help students to learn about a useful technology, analysis method, simulation models and sustainability development.

**References and Relevant Literature**

[1] R.L. Puurunen, Surface chemistry of atomic layer deposition: A case study for the trimethylaluminum/water process, Journal of applied physics, 97(12) (2005) 121301.

[2] S.M. George, Atomic layer deposition: an overview, Chemical Reviews, 110(1) (2009) 111-131.

[3] ITRS, International technology roadmap for semiconductors, 2009 edn, Executive Summary. Semiconductor Industry Association, (2009).

[4] O. Sneh, R.B. Clark-Phelps, A.R. Londergan, J. Winkler, T.E. Seidel, Thin film atomic layer deposition equipment for semiconductor processing, Thin solid films, 402(1) (2002) 248-261.

[5] M. Nanu, L. Reijnen, B. Meester, A. Goossens, J. Schoonman, CuInS 2–TiO 2 heterojunctions solar cells obtained by atomic layer deposition, Thin solid films, 431 (2003) 492-496.

[6] X. Jiang, H. Huang, F.B. Prinz, S.F. Bent, Application of atomic layer deposition of platinum to solid oxide fuel cells, Chemistry of materials, 20(12) (2008) 3897-3905.

[7] Y.S. Jung, A.S. Cavanagh, A.C. Dillon, M.D. Groner, S.M. George, S.-H. Lee, Enhanced stability of LiCoO2 cathodes in lithium-ion batteries using surface modification by atomic layer deposition, Journal of The Electrochemical Society, 157(1) (2010) A75-A81.

[8] X. Zhang, J. Zhao, A.V. Whitney, J.W. Elam, R.P. Van Duyne, Ultrastable substrates for surface-enhanced Raman spectroscopy: Al2O3 overlayers fabricated by atomic layer deposition yield improved anthrax biomarker detection, Journal of the American Chemical Society, 128(31) (2006) 10304-10309.

[9] X. Du, S. George, Thickness dependence of sensor response for CO gas sensing by tin oxide films grown using atomic layer deposition, Sensors and Actuators B: Chemical, 135(1) (2008) 152-160.

[10] C. Wilson, R. Grubbs, S. George, Nucleation and growth during Al2O3 atomic layer deposition on polymers, Chemistry of Materials, 17(23) (2005) 5625-5634.

[11] J. Ferguson, A. Weimer, S. George, Atomic layer deposition of ultrathin and conformal Al 2 O 3 films on BN particles, Thin Solid Films, 371(1) (2000) 95-104.

[12] D.M. King, X. Liang, Y. Zhou, C.S. Carney, L.F. Hakim, P. Li, A.W. Weimer, Atomic layer deposition of TiO 2 films on particles in a fluidized bed reactor, Powder Technology, 183(3) (2008) 356-363.

[13] F.H. Fabreguette, R.A. Wind, S.M. George, Ultrahigh x-ray reflectivity from W∕ Al2O3 multilayers fabricated using atomic layer deposition, Applied physics letters, 88(1) (2006) 013116.

[14] C.Y. Yuan, D. Dornfeld, Environmental performance characterization of atomic layer deposition, in: Electronics and the Environment, 2008. ISEE 2008. IEEE International Symposium on, IEEE, 2008, pp. 1-6.

[15] Y. Yuan, A System Approach for Reducing the Environmental Impact of Manufacturing and Sustainability Improvement of Nano-scale Manufacturing, UMI Dissertations Publishing, University of California, Berkeley, 2009.

[16] C.Y. Yuan, D.A. Dornfeld, Integrated Sustainability Analysis of Atomic Layer Deposition for Microelectronics Manufacturing, Journal of Manufacturing Science and Engineering, 132 (2010) 030918-030911.

[17] Y. Shen, Y. Li, J. Zhang, X. Zhu, Z. Hu, J. Chu, Excellent insulating behavior Al2O3 thin films grown by atomic layer deposition efficiently at room temperature, (2012).

[18] H. Torio, A. Angelotti, D. Schmidt, Exergy analysis of renewable energy-based climatisation systems for buildings: A critical view, Energy and Buildings, 41(3) (2009) 248-271.

[19] P. Forster, V. Ramaswamy, P. Artaxo, T. Berntsen, R. Betts, D.W. Fahey, J. Haywood, J. Lean, D.C. Lowe, G. Myhre, Changes in atmospheric constituents and in radiative forcing. Chapter 2, in: Climate Change 2007. The Physical Science Basis, 2007.

[20] R.A. Ogle, Explosion hazard analysis for an enclosure partially filled with a flammable gas, Process Safety Progress, 18(3) (1999) 170-177.

[21] D. Krewski, R.A. Yokel, E. Nieboer, D. Borchelt, J. Cohen, J. Harry, S. Kacew, J. Lindsay, A.M. Mahfouz, V. Rondeau, Human health risk assessment for aluminium, aluminium oxide, and aluminium hydroxide, Journal of Toxicology and Environmental Health, Part B, 10(S1) (2007) 1-269.