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A hybrid life cycle assessment of atomic layer deposition process

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ABSTRACT

Atomic layer deposition (ALD), as a key enabling nano-manufacturing technology, has found a wide range of potential applications in a number of industrial sectors. However, due to the binary reaction and self-limiting nature of the ALD process, its life cycle environmental impact is significant but has never been investigated before. This study is conducted using a hybrid life cycle assessment (LCA) approach for evaluating the comprehensive environmental impacts of the ALD process based on the typical ALD of Al_2O_3 high-k dielectric gate on semiconductors. The hybrid life cycle inventory analysis is conducted using process-based LCA data, economic input–output LCA data, and stoichiometric simulation data for a robust LCA study. The impact assessments are conducted using the TRACI method, with both original and U.S. normalized impact results analyzed. Normalized impact results show that, among the twelve selected impact categories, ALD produces the highest impact in the category of fossil fuels use which is 10^8 times that of the least impact in air acidification potential. Significant differences are also observed among the environmental impacts of the ALD life cycle stages. The environmental impacts associated with the auxiliary infrastructure, equipment, and tools for ALD operation are intensive mainly due to the slow ALD cycling process. This hybrid LCA study provides a comprehensive data support for understanding the potential environmental impacts of ALD nanotechnology and is useful for sustainable scale-up of the ALD technology in future.

1. Introduction

Atomic Layer Deposition (ALD), with its superior ability to obtain atomic layer control of film growth and to deposit a highly conformal thin film on complex surfaces, plays a key role in the miniaturization of nano-scale devices and structures in a broad array of industrial sectors (Puurunen, 2005; George, 2010). ALD can avoid discontinuities in interfaces and has the potential to manipulate the physical and electronic properties of thin films by manipulating their compositions (Sneh et al., 2002). In recent years, ALD has found a broad array of industrial applications such as semiconductors (Sneh et al., 2002), fuel cells (Jiang et al., 2008), lithium-ion batteries (Jung et al., 2010), solar cells (Gao et al., 2013a,b), medical devices (Zhang et al., 2006), sensors (Du and George, 2008), polymers (Wilson et al., 2005), and even nanoparticle coating (King et al., 2008). In particular, the *International Technology Roadmap for Semiconductors* (ITRS) has recognized ALD as a key enabling technology to break beyond the 45 nm device node for continuous miniaturization toward even smaller nanotechnology nodes (ITRS, 2009; Baumgart, 2009). According to Infiniti Research (2013), from 2012 to 2016 the global annual growth rate of ALD nanotechnology market can be as high as 35.4%.

ALD operates by alternatively pulsing two or more chemical precursors into a vacuum reactor to enable surface reactions to form a thin layer deposition on the substrate. To limit the reactions only on the exposed surface, ALD requires complete purging between two precursors' pulsing. In nature, ALD is a cycling process and can produce self-limited atomic layer-by-layer growth. ALD coating is highly uniform and can be controlled in an extremely precise way at the atomic level. The growth rate of deposited film can be controlled to be as accurate as 0.1 ± 0.01 nm per cycle (Gao et al., 2003), while the root mean square (RMS) surface roughness can be controlled as low as 0.3 nm (Henkel et al., 2009).

ALD can be used to deposit a number of materials (George, 2010; Ponraj et al., 2013). However, the precursors typically used in ALD operations are toxic, volatile, and highly reactive. For example, the deposition of aluminum oxide high-k dielectric gate on semiconductors is widely recognized as the representative process for ALD technology in which trimethylaluminum (TMA) is commonly used as the metal source, and water as the oxidant (George, 2010; Ponraj et al., 2013). $2Al(CH_3)_3 + 3H_2O{=}Al_2O_3 + 6CH_4$. In this process, the primary metal-organic precursor, TMA, is a toxic

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chemical with an EC50 (algae, 96 h) value of 38.054 mg/l (DNF CO., 2012). It is super flammable with high reactivity. In addition, the byproduct, methane, is a major greenhouse gas with 25 times global warming effect of carbon dioxide.

The primary limitation of ALD technology lies in its slow deposition rate. For example, often only a small fragment of a monolayer is able to be deposited within one single cycle (Ponraj et al., 2013; Houssa, 2003; Werner et al., 2011; Satpati et al., 2013). But ALD also has such issues as low material unitization efficiency (defined as the amount ratio of the materials deposited on wafer over the total material input, as low as 12%) and significant energy consumption (1.2 MJ for depositing a 20 nm Al_2O_3 film) (Yuan and Dornfeld, 2010; Yuan and Zhang, 2013; Wang et al., 2013). In ALD operations, an excessive supply of precursors is often required to create a high precursor concentration in the chamber to improve the efficiency of chemical surface reaction. Since ALD is a self-limiting process in which the amount of deposited materials during each individual cycle is fixed, the excessive supply will result in extra resource and energy waste and environmental pollutions. Also, ALD process has to be operated under vacuum conditions and typically at a temperature between 200 and 400 °C, which requires a significant amount of energy input into the process.

In industrial-scale production, the environmental impact associated with ALD technology can be potentially significant (Şengül et al., 2008; Yuan and Zhang, 2013). A comprehensive assessment of the environmental impact of ALD has to be conducted through life cycle assessment (LCA). Depending on the defined system boundaries, LCA can measure the environment burden from cradle to gate or grave which allows the investigations to be conducted within different domains. On the basis of methods for compiling life cycle inventory (LCI), an LCA can be classified into two methods: a process-based LCA and an economic input–output (EIO) LCA (Pérez Gil et al., 2013; Williams, 2004; Hendrickson et al., 1998).

The process-based LCA collects data based on the process operations and parameters (Pérez Gil et al., 2013; Williams, 2004) which is accurate and reliable, but often subject to such difficulties as data scarcity, boundary selection uncertainties, data allocation issues, etc. (Finnveden et al., 2009). EIO-LCA uses the monetary flows to correlate the environmental emissions and impacts from economic sectors, which is comprehensive without boundary issues, but is non-specific and less accurate when compared to the process-based LCA method (Hendrickson et al., 1998).

Overall, these two LCA methods have their advantages and disadvantages. A hybrid integration of these two LCA methods can take both their advantages and supplement each other to provide a better and more reliable life cycle environmental impact assessment (Williams, 2004; Treloar et al., 2000).

This study reports development of a hybrid life cycle assessment method for the ALD process, to address the research gap in quantifying and understanding the life cycle environmental impacts of ALD technology. The typical ALD application of depositing aluminum oxide high-k dielectric film on a 4-inch silicon wafer is used as the ALD model process and systematically investigated. This study is expected to provide valuable environmental information to assist in reducing the overall environmental impacts of ALD technology from a life cycle perspective.

2. Methods and materials

2.1. ALD of Al_2O_3 process

The ALD of aluminum oxide is investigated on the lab-scale experimental process using the Cambridge NanoTech Savannah ALD system for standard 4″ wafer processing. A schematic illustration of the process flows is shown in Fig. 1. Fig. 1 contains the boundary of the ALD production module, the disposal module of the ALD components, and the detailed ALD process flows.

The major devices and tools used in the ALD of the Al_2O_3 process, including a carrier gas supplying system, a precursors reacting system, and a waste pumping system, are heated to facilitate the process flows and surface reactions. In the deposition, the ALD reactor is heated to and maintained at a constant temperature of 200 °C, the inlet pipelines at 150 °C and the outlet pipelines at 160 °C. Nitrogen (99.9999% purity) is used as the carrier gas for transporting the precursors into the chamber and purging the unreacted precursors out of the chamber. The nitrogen is supplied at a source pressure of 25 psi prior to entering the mass flow controller and the flow rate is controlled at 3.38×10^{-2} Pa m^3/s.

The two precursors, TMA, and water are sequentially pulsed into the ALD reactor to react on the substrate surface, with the duration of 1 s pulsing time for each precursor and 5 s for purging in between. The waste materials, containing the unreacted precursors and the generated byproducts, are purged out of the chamber using a vaccum pump attached to the outlet pipe of the ALD system. A total number of 300 cycles are performed with an average layer growth rate at 0.1 nm per cycle in this deposition process.

2.2. Hybrid LCA model for ALD process assessment

For such an emerging technology, ALD involves complicated unit processes with the components in the production system including equipment, chemicals, infrastructure, wastes, etc. In particular, the ALD process parameters are not fully determined for future large-scale industrial productions. Lack of process-based LCI data for chemicals, e.g., TMA, is a significant obstacle for the environmental impact assessment (Hischier et al., 2005; Wernet et al., 2009).

Given these challenges, a hybrid LCA model is developed here for the application on the ALD process to quantify its potential environmental impacts based on the lab-scale data and operations. The hybrid LCA model is constructed by integrating the strengths of componential process-based LCA, EIO-LCA and the stoichiometric method (Appendix A for more details). Following the standard procedure, the hybrid LCA has four steps: goal and scope definition, hybrid life cycle inventory analysis, life cycle impact analysis, and interpretation, as shown in Fig. 2.

2.2.1. Step 1: goal and scope

This research is intended to investigate the life cycle environmental impacts of the ALD deposition process, with functional unit selected as deposition of 1 g Al_2O_3 on 4″ silicon wafers. A typical

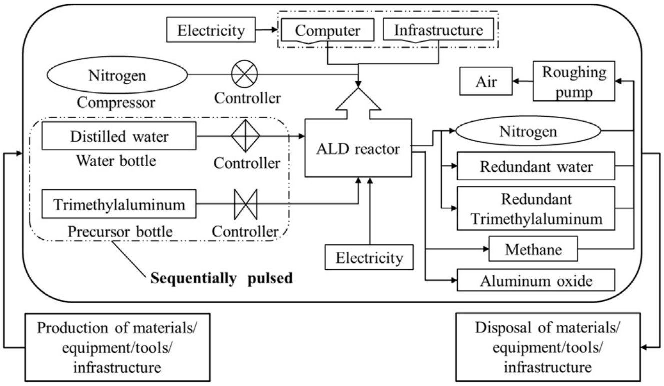

Fig. 1. Deposition of aluminum oxide high-k dielectric film on a 4-inch silicon wafer.

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