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Methods of simulating thin film deposition using spray pyrolysis techniques

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ABSTRACT

Integration of thin tin oxide film formation into CMOS technology is a fundamental step to realize sensitive smart gas sensor devices. Spray pyrolysis is a deposition technique which has the potential to fulfil this requirement. A model for spray pyrolysis deposition is developed and implemented within a Level Set framework. Two models for the topography modification due to spray pyrolysis deposition are presented, with an electric and a pressure atomizing nozzle. The resulting film growth is modeled as a layer by layer deposition of the individual droplets which reach the wafer surface or as a CVD-like process, depending on whether the droplets form a vapor near the interface or if they deposit a film only after surface collision.

1. Introduction

Gas sensors are of importance for many applications ranging from air quality monitoring indoors and outdoors to personal safety systems. Different variants of metal oxide based gas sensors, which rely on changes of the electrical conductance due to the interaction with the surrounding gas, have been developed. However, today's gas sensors are bulky devices, which are primarily dedicated to industrial applications. Since they are not integrated in CMOS technology, they cannot fulfil requirements for smart gas sensor applications in consumer electronics.

1.1. Tin oxide based gas sensors

A powerful strategy to improve sensor performance is the implementation of very thin nanocrystalline films, which have a high surface to volume ratio and thus a strong interaction with the surrounding gases. SnO_2 has been the most prominent sensing material and a variety of gas sensor devices based on SnO_2 thin films has been realized so far [1,2]. Spray pyrolysis is a powerful technology for the fabrication of nanocrystalline SnO_2 films for gas sensing applications [3–5]. Spray pyrolysis is a well-known method for the deposition of a wide variety of thin films and has been used for decades in the glass industry [6] and in solar cell production [7]. This technique requires no vacuum, provides high flexibility in terms of material composition, is suitable for fabrication of thin films on full wafer-size, and can be implemented with CMOS technology [8]. Spray pyrolysis is thus a very cost efficient technology, which is a major issue for the development of smart CMOS based gas sensor devices. In order to optimize this technology for the heterogeneous integration of gas sensing layers with CMOS fabricated micro-hotplate chips [9] on a wafer scale, full understanding of the spray pyrolysis deposition process by modeling is an important issue.

1.2. Level Set method

The presented simulations and models function fully within the process simulator presented in [10]. The Level Set method is utilized in order to describe the top surface of a semiconductor wafer as well as the interfaces between different materials. The Level Set method describes a movable surface $\mathcal{S}(t)$ as the zero Level Set of a continuous function $\Phi(\vec{x},t)$ defined on the entire simulation domain,

$$\mathcal{S}t = \{\vec{x} : \Phi(\vec{x},t) = 0\}. \tag{1}$$

The continuous function $\Phi(\vec{x},t)$ is obtained using a signed distance transform

$$\Phi(\vec{x},t=0) := \begin{cases} -\min\limits_{\vec{x}' \in \mathcal{S}(t=0)} \|\vec{x}-\vec{x}'\| & \text{if } \vec{x} \in \mathcal{M}(t=0) \\ +\min\limits_{\vec{x}' \in \mathcal{S}(t=0)} \|\vec{x}-\vec{x}'\| & \text{else,} \end{cases} \tag{2}$$

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where $\mathcal{M}$ is the material described by the Level Set surface $\Phi(\vec{x}, t = 0)$. The implicitly defined surface $\mathcal{S}(t)$ describes a surface evolution, driven by a scalar velocity $V(\vec{x})$, using the Level Set equation

$$\frac{\partial \Phi}{\partial t} + V(\vec{x})\|\nabla\Phi\| = 0. \quad (3)$$

In order to find the location of the evolved surface, the velocity field $V(\vec{x})$, which is a calculated scalar value, must be found. The Level Set equation belongs to the class of Hamilton–Jacobi equations given by

$$\frac{\partial \Phi}{\partial t} + H(\vec{x}, \nabla\Phi, t) = 0 \text{ for } H(\vec{x}, \nabla\Phi, t) = V(\vec{x})\|\nabla\Phi\|, \quad (4)$$

where H denotes the Hamiltonian. The Level Set equation can then be solved using finite difference schemes such as the Euler method [11], the Upwind scheme, based on the Engquist–Osher scheme [12], or the Lax–Friedrichs Scheme for non-convex Hamiltonians [13].

1.3. Spray pyrolysis deposition

During the last several decades, coating technologies have garnered considerable attention, mainly due to their functional advantages over bulk materials, processing flexibility, and cost considerations [14]. Thin film coatings can be deposited using physical methods or chemical methods. Spray pyrolysis is a technique which uses a liquid source for thin film coating as given in Fig. 1, where CVD and Atomic Layer Epitaxy (ALE) are the gas processes.

Although a liquid source is used, many studies suggest that it is the evaporated liquid near the wafer surface that causes the thin film deposition [15]. This work examines the difference between physical and chemical depositions during spray pyrolysis. The first introduction of the spray pyrolysis technique by Chamberlin and Skarman [16] in 1966 was for the growth of CdS thin films for solar cell applications. Since then, the process has been investigated with various materials, such as SnO_x [17], In_2O_3 [18], indium tin oxide (ITO) [19], PbO [20], ZnO [21], ZrO_2 [22], YSZ [15] and others [23]. The main advantages of spray pyrolysis over other similar techniques are:

– No requirement of vacuum.
– Substrates with complex geometries can be coated.
– Uniform and high quality coatings.
– Implementation as post-CMOS backend process.
– Cost effectiveness.

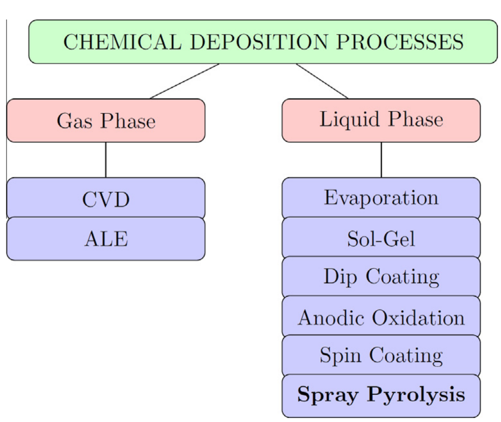

Fig. 1. Summary of chemical thin film deposition technologies.

The spray pyrolysis process is used for the deposition of a transparent layer on glass [24], the deposition of a SnO_2 layer for gas sensor applications [17], the deposition of a YSZ layer for solar cell applications [15], anodes for lithium-ion batteries [25], and optoelectronic devices [26].

The general simplified scheme for spray pyrolysis deposition is shown in Fig. 2, where three processing steps can be viewed and analyzed:

1. Atomization of the precursor solution.
2. Aerosol transport of the droplet.
3. Decomposition of the precursor to initiate film growth

These three steps are individually addressed in the sections to follow.

2. Process sequence during deposition

2.1. Precursor atomization

The atomization procedure is the first step in the spray pyrolysis deposition system. The idea is to generate droplets from a spray solution and send them, with some initial velocity, towards the substrate surface. Spray pyrolysis normally uses air blast, ultrasonic, or electrostatic techniques [27]. The atomizers differ in resulting droplet size, rate of atomization, and the initial velocity of the droplets. It has been shown that the size of the generated droplet is not related to any fluid property of the precursor solution and depends solely on the fluid charge density level ρ_e as shown in [28]

$$r^2 = \left(\frac{-\alpha'}{\beta'}\right)\frac{3\epsilon_0}{q\rho_e}, \quad (5)$$

where ϵ_0 is the permittivity, q is the elementary charge, and $-\alpha'/\beta'$ is a constant value equal to $\sim 1.0 \times 10^{-17}$ J. The mass of a droplet, assuming a spherical shape depends on its density

$$m = \frac{4\pi}{3}\rho_q r^3, \quad (6)$$

where r is the droplet radius and ρ_q is the droplet density. The initial leaving velocity of the droplet is an important parameter as it determines the rate at which the droplets reach the substrate surface, the heating rate of the droplet, and the amount of time the droplet remains in transport

Due to its ease of production, many companies chose to use pressure atomizers instead of the ultrasonic atomizers. Therefore, this work will mainly concern itself with the pressure and electrostatic atomizers, characterized in further detail in [17,27], respectively.

A pressure, or air blast, atomizer uses high speed air in order to generate an aerosol from a precursor solution. Increasing the air pressure causes a direct decrease in the generated mean droplet

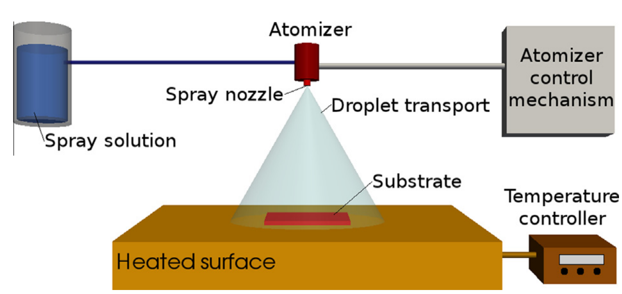

Fig. 2. General schematic of a spray pyrolysis deposition process.