Modeling the Growth of Thin SnO_2 Films using Spray Pyrolysis Deposition

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***Abstract*—The deposition of a thin tin oxide film allows for the manufacture of modern gas sensors to replace the bulky sensors of previous generations. Spray pyrolysis deposition is used to grow the required sensing thin films, as it can be seamlessly integrated into a standard CMOS processing sequence. A model for spray pyrolysis deposition is developed and implemented within the Level Set framework. The implementation allows for a seamless integration of multiple processing steps for the manufacture of smart gas sensor devices. From observations it was noted that spray pyrolysis deposition, when performed with a gas pressure nozzle, results in good step coverage, analogous to a CVD process. This is due to the liquid droplets evaporating prior to contact with the heated wafer surface and subsequently depositing on top of the exposed silicon in vapor form.**

I. INTRODUCTION

The spray pyrolysis deposition technique is gaining traction in the scientific community due to its cost effectiveness and ease of integration into a standard CMOS process. The technique is used to grow crystal powders [1], which can then be further annealed for use in gas sensors, solar cells, and other applications. A model for spray pyrolysis deposition which can be incorporated into a standard CMOS process simulator is desired.

A. Tin-Oxide Based Gas Sensors

Different variants of metal oxide based gas sensors, which rely on changes of 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. 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 [2], [3]. The growth of the ultrathin SnO_2 layers on semiconductor structures requires a deposition step which can be integrated after the traditional CMOS process [4]. This eliviates the main concern with today's gas sensor devices and their bulky nature, namely high power consumption and complex manufacturing techniques

A sensor which uses films with thicknesses of 50nm and 100nm has already been reported in [3]. The sensor itself operates on a microsized hot plate which heats the sensor locally to 250–400^{o}C in order to detect humidity and carbon monoxide in the environment, down to a concentration of under 5ppm. The sensing mechanism of SnO_2 is related to the ionosorption of gas species over the surface, leading to charge transfer between the gas and surface molecules and changes in the electrical conductance [3].

B. Level Set Method

Since the introduction of the Level Set Method by Osher and Sethian [5], it has developed into a favorite technique for tracking moving interfaces. The presented simulations and models function fully within the process simulator presented in [6]. 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 $\mathcal{S}\left(t\right)$ as the zero Level Set of a continuous function $\Phi\left(\vec{x},t\right)$ defined on the entire simulation domain,

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

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

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

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

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

In order to find the location of the evolved surface, the velocity field $V\left(\vec{x}\right)$, which is a calculated scalar value, must be found. For the case of spray pyrolysis deposition, this scalar value is derived using Monte Carlo techniques. The droplets formed and accelerated towards the wafer surface are represented by particles whose travel depends on all external forces acting on the particles.

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II. 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 [7]. Thin film coatings may be deposited using physical methods or chemical methods. The chemical methods can be split according to a gas phase deposition or a liquid phase deposition. These processes are summarized in Fig. 1, where chemical vapor deposition (CVD) and Atomic Layer Epitaxy (ALE) are the gas processes.

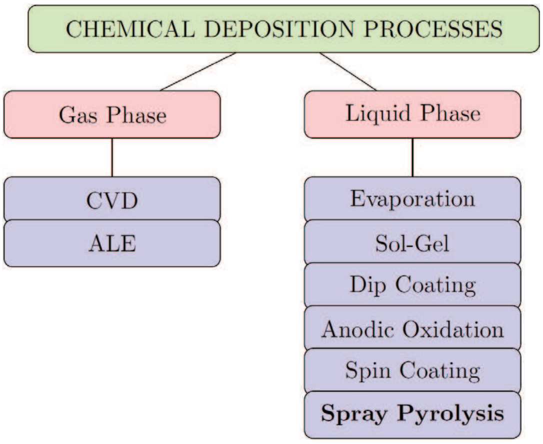


Fig. 1: Summary of chemical thin film deposition technologies.

Spray pyrolysis, as can be seen in Fig. 1, is a technique which uses a liquid source for thin film coating. The first introduction of the spray pyrolysis technique by Chamberlin and Skarman [8] 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 [9], In_2O_3 [10], Indium Tin Oxide (ITO) [11], PbO [12], ZnO [13], ZrO_2 [1], YSZ [14], and others [15]. The main advantages of spray pyrolysis over other similar deposition techniques are:

- Possible integration after a standard CMOS process.
- Cost effectiveness.
- Substrates with complex geometries can be coated.
- Relatively uniform and high quality coatings.
- CMOS-compatible temperatures (¡400°C) are required during processing.

The major interest in spray pyrolysis is due to its low cost and possibility of incorporation after a standard CMOS process flow. It is increasingly being used for various commercial processes, such as the deposition of a transparent layer on glass [16], the deposition of a SnO_2 layer for gas sensor applications [9], the deposition of a YSZ layer for solar cell applications [14], anodes for lithium-ion batteries [17], and optoelectronic devices [18].

The three steps which describe the processes taking place during spray pyrolysis deposition are summarized by:

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

A. Experimental Observations

Spray pyrolysis requires no vacuum and provides high flexibility in terms of material composition. In order to optimize this technology for the heterogeneous integration of gas sensing layers with CMOS fabricated micro-hotplate chips [19], a complete understanding of the spray pyrolysis deposition process by modeling is a challenging issue. It was our goal to develop and incorporate a model for the growth of ultrathin SnO_2 layers into a traditional CMOS process simulator using the Level Set framework [20].

When depositing a thin film using spray pyrolysis, an ultrasonic, electrical, or gas pressure atomizing nozzle can be used [21]. For smart sensor applications, a gas pressure nozzle is ideal due to its ease of use and its ability to create very small droplets which deposit evenly on a desired surface. The retardant forces experienced by droplets during their transport include the Stokes force and the thermophoretic force, while gravity is the only accelerating force, when a gas pressure nozzle is used. An electrical force is included in models which depict ultrasonic or electrical atomizing nozzles. Fig. 2 shows a simplified schematic for spraying a specific precursor solution onto the substrate, which is placed on top of a hotplate.

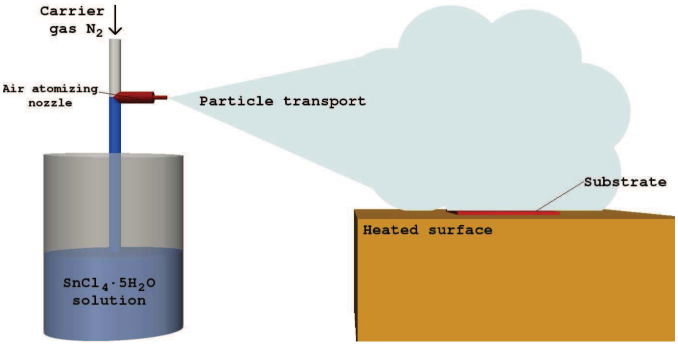


Fig. 2: Schematic of the spray-pyrolysis deposition process.

The substrate is a CMOS chip with four contact electrodes which are coated with SnO_2, as depicted in Fig. 3.

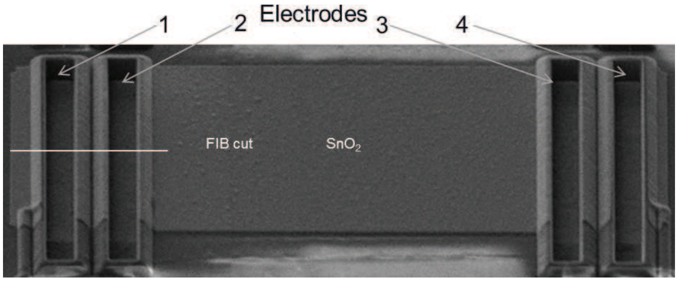


Fig. 3: Electrode locations on the substrate.

Two spray directions have been tested, as shown in Fig. 4, with the spray being directed in parallel or perpendicular to the electrodes. It was noted that regardless of the initial spray direction and the direction of the droplets as they leave the atomizing nozzle, the thickness of the grown thin film and its electrical properties remain unchanged, as shown in Fig. 5.

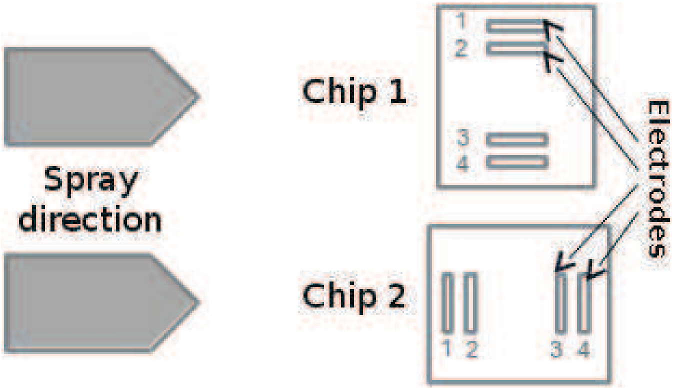


Fig. 4: Spray direction during deposition.

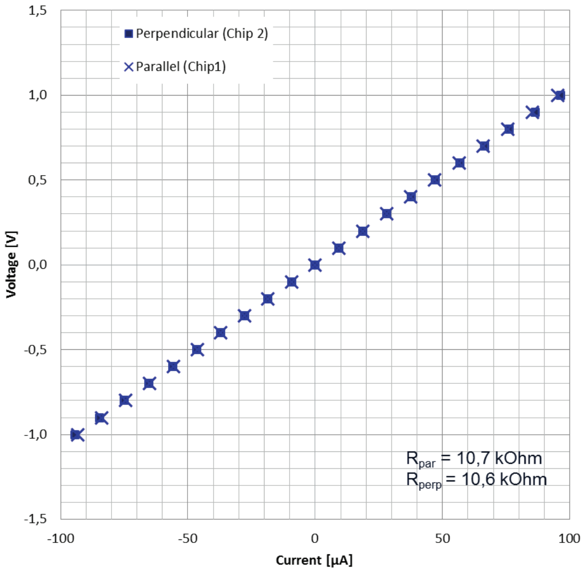


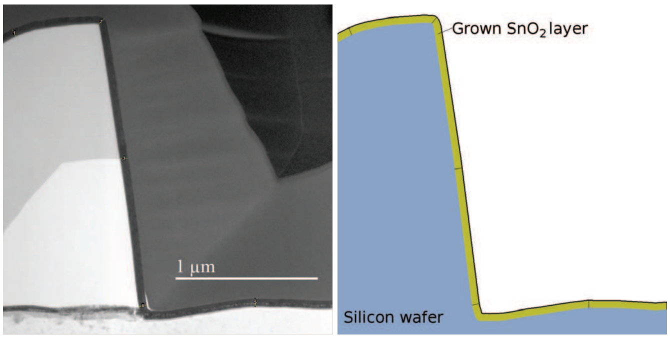
Fig. 5: V-I curves between Electrode 1 and Electrode 4 for the chips depicted in Fig. 3.

This is likely due to the nozzle being placed at a distance of approximately 30cm away from the substrate surface, giving enough time for the Stokes retardant force to effectively remove any influence of the droplets' initial horizontal velocity. Therefore, directionality plays no role in the film deposition process. The lack of directional influence and the good step coverage seen in Fig. 6(a) suggest that the deposition is a result of a CVD-like process. Fig. 6(a) shows a resulting SnO_2 thin film after a spray pyrolysis deposition step lasting 30 seconds with the substrate heated to 400^{o}C. The resulting film thickness is approximately 50nm. We conclude that the droplets, which carry the depositing material, interact with the substrate surface as a vapor and then deposit in a process analogous to CVD.

III. Modeling Spray Pyrolysis

Our experimental data show a linear dependence on spray time and a logarithmic dependence on wafer temperature for the growth rate of the deposited SnO_2 layer. A good agreement is given by the Arrhenius expression

$$d_{SnO_2}\left(t,T\right) = A_1\, t\, e^{(-E/k_B T)}, \tag{4}$$



(a) TEM image of a FIB cut. (b) Simulation of Fig. 5(a).

Fig. 6: Experimental and simulated SnO_2 deposition on a step structure.

where the thickness is given in μm, $A_1 = 3.1\,\mu m/s$, t is the time in seconds, T is the temperature in Kelvin, and E is $0.427 eV$. Given that directionality has no influence on the film growth, a model is implemented which uses a cosine distribution of particles, as is common for CVD simulations. The good coverage of vertical walls also suggests a high reflective coefficient. In fact, a sticking coefficient of 0.01 and a cosine distribution of reflected particles shows the best fit to measured data. With this model we can simulate the coverage of various geometries, required for gas sensor manufacturing. Using the given equation and presented model, a simulation was performed for 30 seconds at 400^{o}C with the result shown in Fig. 6(b). The resulting film has an evenly distributed thickness of approximately 50nm, as expected from measured experiments. When this model is applied to a full geometry of a gas sensing electrode, as shown in Fig. 7(a), the resulting SnO_2 growth, shown in Fig. 7(b), is in agreement with experiments. Using the developed model, we are able to simulate any geometry required in the future. In addition, the model can inherently be used to simulate three-dimensional surface coverage and is integrated fully in a standard CMOS simulator using a combination of Monte Carlo methods within a Level Set framework.

IV. Conclusion

The deposition of tin oxide on a semiconductor using spray pyrolysis techniques is an essential step to the manufacture of smart gas sensors. From observations, it is noted that spray pyrolysis deposition using an air nozzle results in a material deposition analogous to CVD. A model for spray pyrolysis deposition of tin oxide is described and implemented in a standard process simulator within a Level Set environment. The simulator functions fully within a standard CMOS simulator where a sequence of processes can be jointly visualized.

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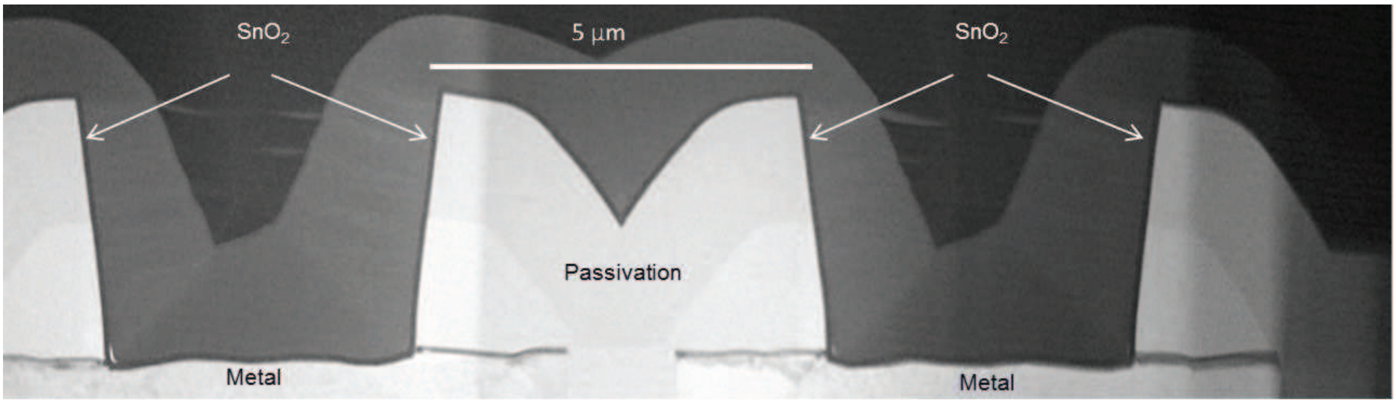
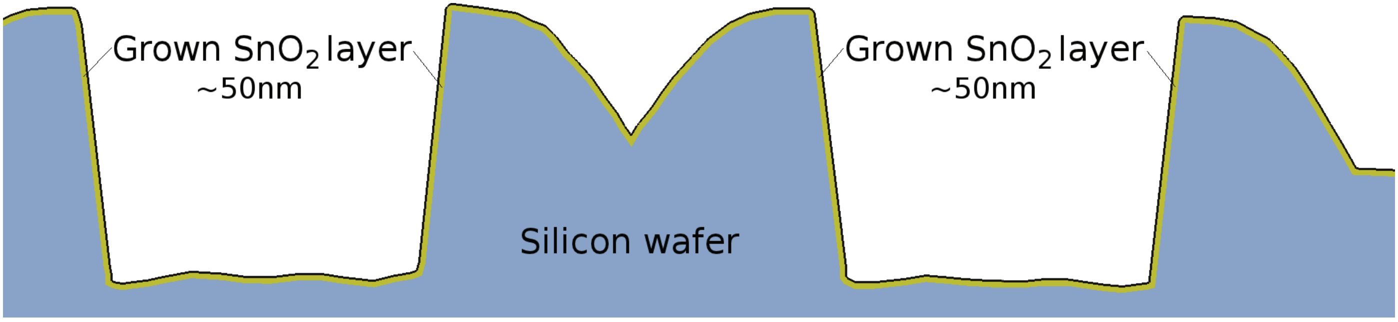


(a) TEM image of a FIB cut with Pt on top, showing the geometry of a typical electrode structure with deposited SnO_2 layer.



(b) Simulated deposition of SnO_2 on a typical electrode geometry.

Fig. 7: Image showing the (a) measured and (b) simulated deposited SnO_2 film as a results of spray pyrolysis deposition. The deposition is performed with the heated substrate at a temperature $T=400^{o}C$ for a time t=30s.

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