Abstract—In order for the gas sensor devices to enjoy the miniaturization trend that has consumed much of the electronic device industry, major research in the field is undertaken. The bulky sensor devices of previous generations can not easily be incorporated into a CMOS processing sequence, because of their bulky nature and potential higher cost of production. More recently, materials such as zinc oxide and tin dioxide have shown powerful gas sensing capabilities. Among many potential deposition methods, spray pyrolysis has become a popular approach because of its ease of use and cost effectiveness. A model for spray pyrolysis deposition is developed and implemented within the level set framework. The implementation allows for a smooth integration of multiple processing steps for the manufacture of smart gas sensor devices. From the 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 mainly due to the atomizing nozzle being placed at a reasonable distance away from the wafer surface and reducing the droplets volume and mass in order to ensure they fully evaporate prior to contact with the substrate surface. A topography simulator for this deposition methodology is presented.

Index Terms—Spray pyrolysis, Level set, Tin dioxide, Gas sensors, Nanosensors.

I. INTRODUCTION

THE ABILITY to detect harmful and toxic gases in the environment is the subject of extensive research. Until recently, available gas sensors relied on a bulky architecture and their manufacture was incompatible with that of the CMOS process sequence. The miniaturization of electronic sensors, Nanosensors, MEMS devices. More recently, it has been shown that several transparent conducting oxides may serve as a gas sensing layer when a thin film of the deposited material is exposed to high temperatures (250–400°C). Two materials, which have been shown to exhibit all the properties required for good gas sensing performance are zinc oxide (ZnO) [1–4] and tin dioxide (SnO2) [5–7], while others such as indium tin oxide (ITO), CdO, ZnSnO4, NiO, etc. have also been widely studied [3]. This work mainly concerns itself with tin dioxide gas sensors and the ability to develop a model which depicts the growth of thin tin dioxide layers to act as a gas sensing surface. The deposition of SnO2 has been performed using various standard techniques such as chemical vapor deposition [8], sputtering [9], pulsed-laser deposition [10], sol-gel process [11], and spray pyrolysis deposition [5].

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 primary development of the technology stems with the growth of the solar cell industry, for which the technique was developed in 1966 by Chamberlin and Skarman [12] where a thin CdS film was initially grown. The technique is used to grow crystal powders [13], which can then be further annealed for use in gas sensors, solar cells, and other applications. The technique is cost-effective as it involves relatively inexpensive equipment and raw materials and is simple to perform. For these reasons, the spray pyrolysis deposition of SnO2 thin films is further explored. A model for spray pyrolysis deposition which can be incorporated into a standard CMOS process simulator is desired [14].

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 [15], 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 SnO2 layers into a traditional CMOS process simulator using the Level Set framework [16].

A. Smart Gas Sensor Devices

Different variants of metal oxide based gas sensors, which rely on changes of electrical conductance due to the interaction devices has proven to be essential, while bulky gas sensors are still lagging behind the overall progress of CMOS and MEMS devices. More recently, available gas sensors relied on a bulky architecture and their manufacture was incompatible with that of the CMOS process sequence. The miniaturization of electronic...
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 fulfill the 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. SnO2 has been one of the most prominent sensing materials and a variety of gas sensor devices based on SnO2 thin films has been realized so far [17], [18].

The growth of the ultrathin SnO2 layers on semiconductor structures requires a deposition step which can be integrated after the traditional CMOS process [6]. This alleviates the main concern with today’s gas sensor devices and their bulky nature, namely high power consumption.

SnO2 is a special material, as it has a low electrical resistance, a wide bandgap, and a high transparency in the visible spectrum [5]. The material has proven itself to be useful in many industries where an electric contact is required without obstructing photons from traveling through the optical active area. Tin dioxide is also highly conductive due to high intrinsic defects.

A gas sensor which uses SnO2 films with thicknesses of 50nm and 100nm has already been reported in [18]. The sensor itself operates on a micro-sized hot plate which heats the gas and surface molecules and changes in the electrical conductance [18].

B. Level Set Method

Since the introduction of the Level Set Method by Osher and Sethian [19], it has developed into a favorite technique for tracking moving interfaces. The presented simulations and models function fully within the process simulator presented in [20]. The current status of the simulator includes models for isotropic and anisotropic deposition and etching (CVD, plasma etching, wet etching, etc.) [16], focused ion beam processing [21], the Bosch process [22], thermal oxidation of silicon [23], local anodic oxidation of silicon [24], etc. The software also allows for shared memory parallelization during execution [25]. 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 \( S(t) \) as the zero Level Set of a continuous function \( \Phi(\vec{x}, t) \) defined on the entire simulation domain,

\[
S(t) = \{ \vec{x} : \Phi(\vec{x}, t) = 0 \}.
\]  

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

\[
\Phi(\vec{x}, t = 0) = \begin{cases} 
-\min_{\vec{x} \in \mathbb{R}^2} \| \vec{x} - \vec{x}_t \| & \text{if } \vec{x} \in M(t = 0) \\
+\min_{\vec{x} \in \mathbb{R}^2} \| \vec{x} - \vec{x}_t \| & \text{else},
\end{cases}
\]  

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

\[
\frac{\partial \Phi}{\partial t} + V(\vec{x}) \| \nabla \Phi \| = 0.
\]  

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. 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. The Level Set equation belongs to the class of Hamilton-Jacobi equations given by

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

where \( H \) denotes the Hamiltonian. The equation can then be solved using finite difference schemes such as the Euler method [26], the Upwind scheme, based on the Engquist-Osher scheme [27], or the Lax-Friedrichs Scheme for non-convex Hamiltonians [28].

II. TIN DIOXIDE BASED GAS SENSOR

A smart gas sensor device has been manufactured using a 50nm SnO2 thin film as the sensing material. The device has four electrodes, shown in Fig. 1 and Fig. 2, which are stationed above a heat source. The substrate is a CMOS chip with four contact electrodes which are coated with SnO2, as depicted in Fig. 1.

The sensor has been tested in a H2 environment at concentrations down to 10ppm and the results are depicted in Fig. 3 and Fig. 4. Additional gas sensing performance of SnO2 thin films in a CO, CH4, H2, CO2, SO2, and H2S environment are explored by Brunet et al. [7].

The gas measurements are performed in an automatic setup to test the functionality of the described SnO2 structure, which is heated up at 350°C. The electrical resistance change is monitored while pulses of H2 at different concentrations (10–90ppm) are injected in the gas chamber. Humid synthetic air (RH=40%) is used as the background gas. In Fig. 3, the normalized resistance of the SnO2 structure is plotted for various H2 gas concentrations. In Fig. 4 the gas response, defined as the relative resistance difference in percentage, is

![Fig. 1. Top view of the electrode locations on the substrate.](image-url)
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 [29]. 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. 5, where chemical vapor deposition (CVD) and Atomic Layer Epitaxy (ALE) are the gas processes.

Spray pyrolysis, as can be seen in Fig. 5, is a technique which uses a liquid source for thin film coating. The first introduction of the spray pyrolysis technique by Chamberlin and Skarman [12] 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$_2$ [30], In$_2$O$_3$ [31], ITO [32], PbO [33], ZnO [34], ZrO$_2$ [13], yttria-stabilized zirconia (YSZ) [35], and others [36]. The main advantages of spray pyrolysis over other similar deposition techniques are:

- Cost effectiveness.
- Possible integration after a standard CMOS process.
- 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 [37], the deposition of a SnO$_2$ layer for gas sensor applications [30], the deposition of a YSZ layer for solar cell applications [35], anodes for lithium-ion batteries [38], and optoelectronic devices [39]. The setup, shown in Fig. 6 is...
Fig. 6. Schematic of the spray-pyrolysis deposition process, as set up for SnO$_2$ deposition.

Fig. 7. Spray direction during deposition.

Fig. 8. V-I curves between Electrode 1 and Electrode 4 for the chips depicted in Fig. 7.

simple and inexpensive when compared to other deposition alternatives.

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 Setup

When depositing a thin film using spray pyrolysis, an ultrasonic, electrical, or gas pressure atomizing nozzle can be used [40]. 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. 6 shows a simplified schematic for spraying a specific precursor solution onto the substrate, which is placed on top of a hotplate.

The atomizer has also been adjusted so that the droplets exiting the nozzle are relatively small in volume with an average diameter of approximately 5–10μm. This ensures that a majority of the droplets reaching the heated wafer surface will evaporate prior to impact, allowing for a uniform deposition of the vapor which results in a uniform film growth. In order to ensure that the initial direction of the solution, as it exits the atomizer, does not affect the deposition process, two spray directions have been tested, as shown in Fig. 7. The initial spray was directed in parallel and perpendicular to the electrodes’ position and afterward the V-I curves for the two chips is compared.

B. Experimental Observations

After performing spray pyrolysis deposition, while directing the spray in parallel and perpendicular to the electrodes, the V-I curves of the two chips are visualized in Fig. 8. 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.

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. This also helps to eliminate the potential of large droplets splashing onto the substrate surface. Large droplets generally do not deposit uniformly on the desired surface, but rather impact the heated wafer while in liquid form, leaving behind a powder residue with weak sticking properties to the silicon. The large droplets experience a higher Stokes retardant force causing them to never reach the 30cm distance between the particle generation and the substrate surface location.

The thickness of the tin dioxide layer is dependent on the spray temperature and the spray time. With the heatpad temperature set to 400°C, the thickness of the SnO$_2$ layer is plotted against the spray time in Fig. 9. A linear relationship is evident.

The thickness of the grown film did not change when the deposition took place on a step structure, as shown in Fig. 10(a), suggesting that the deposition is a result of a CVD-like process and not a process which alludes to a direct interaction between the deposition surface and the liquid droplets. Fig. 10(a) shows a resulting SnO$_2$ thin film after a spray pyrolysis deposition step lasting 30 seconds with the substrate heated to 400°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.
Fig. 9. The influence of spray time on the thickness of the deposited SnO₂ layer, with temperature set to 400°C.

Fig. 10. Experimental and simulated SnO₂ deposition on a step structure, (a) TEM image of a FIB cut, (b) Simulation of Fig. 10(a).

IV. Modeling Spray Pyrolysis

A. Modeling Individual Droplets

Our initial spray pyrolysis deposition models dealt with tracking the movement of each droplet as it exits the atomizer, travels through the ambient, and strikes the wafer surface as a liquid. This model is commonly attributed to a spray pyrolysis setup which involves an atomizer placed directly above the heated surface, as shown in Fig. 11. The droplets are then accelerated towards the wafer at high speeds, impacting with the surface before being able to fully evaporate. The vertical and horizontal acceleration, velocity, and displacement for each droplet are calculated with several variables considered, such as the initial droplet velocity and mass. In addition the external forces acting on the droplet must be taken into account: gravitational and electrical forces accelerate the droplet towards the wafer, while the Stokes and thermophoretic forces retard the droplet movement. The resulting equations are quite complex and must be carried out for each droplet involved in the deposition process [41].

This type of deposition generally results in films which are not very uniform since the droplet sizes influence the deposition at each impact location. For our setup, from Fig. 6, the atomizer is placed such that the droplets do not reach the wafer at a high velocity, resulting in their evaporation and subsequent deposition as a uniform film. The distribution of droplets according to their volume and mass is visualized by Ortel et al. [1], showing clearly that large droplets have a much smaller horizontal displacement in comparison with small droplets.

B. Modeling the Uniform Deposition Process

Our experimental data show a linear dependence on spray time and a logarithmic dependence on wafer temperature for the growth rate of the deposited SnO₂ layer. A good agreement is given by the Arrhenius expression

$$d_{SnO_2}(t, T) = A_1 \exp\left(-\frac{E}{kBT}\right)t,$$

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 0.427eV.

C. Spray Pyrolysis as a Vapor Deposition Process

The growth model given in (5) relates the thickness of the deposited material to the applied time and temperature. However, this representation is only valid when no complex geometries such as deep wells are present. In order to model deposition on a deep well structure, a simulation which considers more than a single deposition rate is required. Since the droplets fully evaporate prior to depositing on the surface, a non-linear simulation model analogous to CVD must be implemented. The implementation requires the combination of the Monte Carlo methods within the Level Set framework. A single particle species is considered during deposition. As the simulation is initiated, multiple particles are generated in the simulation space with an average direction perpendicular to and moving towards the wafer. The particles are represented in terms of individual fluxes, given by

$$\Gamma_{\nu} = \Gamma_{\nu}(\vec{x}, \vec{w}, E),$$

where $P$ is the surface which divides the region above the wafer (reactor-scale) and the region comprising the wafer (feature-scale) and the flux of arriving particles $\Gamma_{\nu}$ is described in terms of particles which are moving in direction $\vec{w}$ arriving with an energy $E$ per unit area. This energy $E$ is dependent on the time and temperature of the simulation space, as it is the deciding factor in the speed of the film growth. The distribution of particles stems from the idea that their transport is characterized by the mean free path of a gas $\lambda$, which, for our process is in the range of 9mm. In this range, the particle...
Fig. 12. Image showing the (a) measured and (b) simulated deposited SnO$_2$ film as a result of spray pyrolysis deposition. The deposition is performed with the heated substrate at a temperature T=400°C for a time t=30s. The image is a side view of the FIB cut shown in Fig. 1, (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.

velocities follow the Maxwell-Boltzmann distribution and the flux has a cosine-like directional dependence

$$\Gamma_{\omega}(E, q, \vec{\omega}, \vec{E}) = F_{\omega c} \frac{1}{\pi} \cos \theta \cos \phi = \vec{\omega} \cdot \vec{n}_P,$$

where $F_{\omega c}$ is uniform, $\vec{n}_P$ is the normal vector to $P$ pointing towards the wafer surface.

In the feature-scale region, particles may also be reflected from the wafer walls, modeled using a sticking coefficient, resulting in their deposition elsewhere on the wafer or them leaving the simulation space entirely. Reflected particles follow the Knudsen cosine law [42]. The total flux is then composed of source particles with flux $\Gamma_{\omega c}$ and re-emitted particles, which stick on recursive impact $\Gamma_{\omega r}$. For the spray pyrolysis deposition process, it was found that a sticking coefficient of 0.01 has the best fit to experimental data and was therefore used for the model. The motion of reflected or re-emitted particles is then tracked with their sticking probability reduced after each surface impact. The tracking of a single particle is deemed concluded when its sticking probability reaches 0.1% of the original sticking coefficient.

Using the given equation and presented model, a simulation was performed for 30 seconds at 400°C with the result shown in Fig. 10(b). The resulting film has an evenly distributed thickness of approximately 50nm, as expected from the measured thickness in Fig. 10(a).

When this model is applied to a full geometry of a gas sensing electrode, as shown in Fig. 12(a), the resulting SnO$_2$ growth, shown in Fig. 12(b), is in agreement with experiments.

D. Sample Trench Simulations

With the presented model we can simulate the resulting coverage of various geometries, required for gas sensor manufacturing. For devices which require a large surface area in order to function adequately, it may be more affordable to deposit a layer on trench and well geometries rather than utilizing expensive chip surface area. Therefore, several simulations are performed to estimate at which trench width to depth ratio and at which sidewall angle is the process no longer appropriate. First, we simulate the trench sidewall angle of 5.7° in Fig. 13 and note that for a trench of height 1000nm, the separation between the walls must be at least 150nm in order for no void to form. However, above 200nm might be desired to allow easy access for the gas which needs detection inside the cavity.

Similarly, a simulation is performed for a structure with the same dimensions, but with the sidewall angles more vertical at 2°, with the results depicted in Fig. 14. It is evident that, even at a trench width of 150nm, a void has formed. Therefore, although vertical walls provide more surface area for the tin dioxide to deposit, one must be careful in ensuring enough separation is provided at the top of the trench, where the deposited material tends to accumulate.

One more simulation is performed to see if shorter trenches, with a smaller height to width ratio reflect different deposition properties. Fig. 15 shows a trench depth of 500nm and varied distances between trench walls. The walls are set to a vertical angle of 2°, as were those in Fig. 14. It is evident that the results emulate those seen for the taller trench. Therefore,
higher trenches with enough separation between walls produce the most surface area on which gas sensing material can be deposited.

In addition, the model can inherently be used to simulate three-dimensional surface coverage, fully integrated in a standard CMOS simulator using Monte Carlo methods within a Level Set framework. Several simulations have been performed in order to evaluate the trench geometries which allow for deposition with no void formation when an increased surface area of the deposited material is required. The models are implemented fully within a standard CMOS simulator where an entire sequence of processes can be jointly visualized.

**V. Conclusion**

Smart gas sensors have grown in popularity and research interest recently due to their ability to detect humidity and harmful gases in the environment. While many CMOS and MEMS electrical devices have experienced extreme miniaturization, gas sensors still generally remain bulky devices whose manufacturing remains difficult to be integrated with CMOS electrical circuits. The deposition of tin dioxide thin films directly on a CMOS chip using spray pyrolysis techniques is an essential step to the manufacture of smart gas sensors. These thin films are able to detect many gases in the environment by being heated locally to temperatures of up to 400°C. From observations, it is noted that spray pyrolysis deposition using an air nozzle at a distance of approximately 30cm and droplets which are relatively small in volume results in a material deposition analogous to CVD. A model for spray pyrolysis deposition of tin dioxide is described and implemented in a standard process simulator using Monte Carlo techniques within a Level Set environment. Several simulations have been performed in order to evaluate the trench geometries which allow for deposition with no void formation when an increased surface area of the deposited material is required. The models are implemented fully within a standard CMOS simulator where an entire sequence of processes can be jointly visualized.

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