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Evaluating Stresses in the SiO_2 Thin Films Using Molecular Dynamics Simulations

Sachin Shendokar, Nikhil Ingle, Ram Mohan and Shyam Aravamudhan

*Joint School of Nanoscience and Nanoengineering, NCA&TSU, USA; smshendo@aggies.ncat.edu (S.S) .
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Abstract: Semiconductor electronics is transform computing, communication, energy harvesting, automobiles, biotechnology, and other electronic devices' landscape. This transformation is brought about by the ability to sense, receive, manipulate, and transmit data from the diverse systems of vertical stacks of semiconductor layers and microdevices. Though the discrete design details of each semiconductor may be extremely complex, the fundamental processing steps of each semiconductor device align well with the photolithography procedure. When these semiconductor layers are stacked using photolithography, the signal noise between the device features and layers is restricted by passivation or dielectric insulation provided by SiO_2 layers. Depending on the type of functionality and data sensing mechanism of semiconductors, SiO_2 layers have an intended fitness for their purpose. The purpose of SiO_2 layers can be segregated as an encapsulation of the semiconductor device, making part of the semiconductor layer inert, i.e., passivated, creating a hard mask to prevent an impact of the subsequent process like ion implantation or diffusion, insulating a part of the layer as in intermetallic dielectric or gate dielectric or to improve adhesion of the subsequent deposition.

The functionality of adhesion of SiO_2 is by far been a less studied area. The adhesive characteristics of SiO_2 for subsequent deposition and the thickness of SiO_2 affect the stress distribution. Stresses due to SiO_2 thin film, which could be a few nanometers to a few microns thick depending on the functionality, are modeled in this research. The stresses in SiO_2 films may cause delamination or discontinuity, affecting the performance and reliability of the optical or semiconductor devices they are built into. The classical molecular dynamics (MD) simulation technique is employed to investigate the stress characteristics of deposited films by leveraging the outcomes of atomistic modeling. A cluster made of fused silica is employed as the substrate. For the SiO_2 deposition process simulation, silicon atoms with high energies and low-energy oxygen atoms are injected. This model is carefully controlled to ensure the stoichiometry conditions. This analysis uses open-source code LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) and Ovito (Open Visualization) tool. The research in this paper is focused on the SiO_2 thin-film simulation to validate the analytical and experimental stress.

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Synthesis of SiO_2 for pre-defined

The chemical vapor deposition is a process involving the chemical reaction between the precursors involved. The substrate is heated to an extent to receive the reactant precursors in vapor form. Thus, for CVD, very high temperature is required, which could be a deterrent factor for the complex stacks of functional layers deposited at different stages of semiconductor development. PECVD is a variant of CVD where precursors have high vapor pressure, and the reaction is enhanced with plasma generation; thus, the PECVD process can be carried out at lower temperatures and reasonably low pressures. PECVD provides high uniformity in thickness and stoichiometry, conformality, and deposition rate, making it ideal for mass manufacturing.

The simplified chamber components of PECVD are shown in Figure 1.

$$SiH_4 + 2N_2O \rightarrow SiO_2 + 2\,(H_2 + N_2)$$

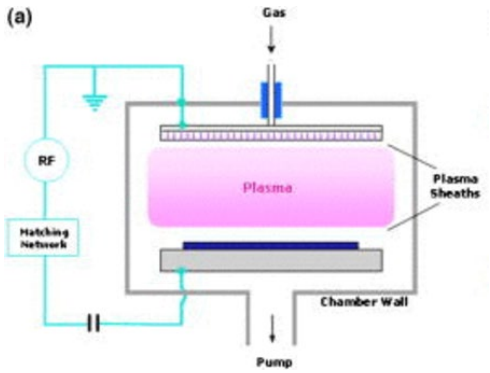

Figure 1. Schematic of PECVD.

Material System and PECVD Recipe:

There are several ways by which SiO_2 can be deposited. The material system to deposit SiO_2 is dependent on the capabilities of PECVD systems available. From mass production perspective, once the instrument is procured, installed, and commissioned, making changes to the material system is difficult. The difficulties are from the perspective of cost, space, time, and disruption in the routine production cycles. The most frequently used PECVD systems has following capabilities from the perspective of material systems for SiO_2 deposition.

i. Temperature Control with maximum rating up to 350 ^{0}C, for PECVD is intended to accomplish uniform deposition at low temperatures.

ii. Vacuum systems with capability of chamber vacuum of 5000 mT

iii. Shower head chamber with Mass flow controllers (MFC) for Silane (usually SiH_4), MFC for N_2O (1K, 5K), N_2 (1K, 5K), Ar (1K, 5K), NH_3 and SF_6. The 1K and 5K are mass flow capabilities in square cubic centimeter (sccm). The SF6 MFC is useful for intermittent chamber cleaning.

iv. High frequency RF (13.56 MHz)

v. Low frequency RF

The precursors silane (SiH_4) is pumped into a shower head vacuum chamber with N_2 or Ar as carrier gas. The specification maintained for SiH_4 supply is usually 2%, 5% or 10% of SiH_4 mixed with carrier gas dilution. Thus, for a flow of 2% of SiH_4 with N_2 at 200 sccm would mean 4 sccm of SiH_4 and 196 sccm of N_2. If the independent flow of silane and N_2 or Ar is provided, the proportion of the MFC is programmed to achieve the targeted proportion in the recipe [1]. For the ready reference, the typical recipe for Plasma therm CVD is shared herewith in Table 1. It is apt to note, the rows for NH_3 and RF_2 are left blank. These rows are kept for noting their requirement for developing recipes suitable for specific applications. While NH_3 is used if the same equipment is used to deposit SiN_x and modulate density, deposition rate of deposition or other characteristics, low-power RF_2 is employed. The recipe may include temperature, pressure, and gas stabilization steps for pre-conditioning of the vacuum chamber. The pre-processing step helps condition the Silicon substrate to remove dangling bonds or passivation. The recipe may also include a post-processing step to maintain and improve the properties of SiO_2 films deposited by stress reliving. The PECVD chamber also needs periodic dry or wet cleaning depending upon the frequency of usage and level of impact of impurities.

	Recipe Parameters
Time	02:00.0
Pressure	1500
SiH_4 1k	500
SiH_4 5K	--
NH_3 50	--
SF_6 1K	--
AR 5K	2000
N_2O 5K	2000
N_2 5K	--
RF1	200
RF2	--

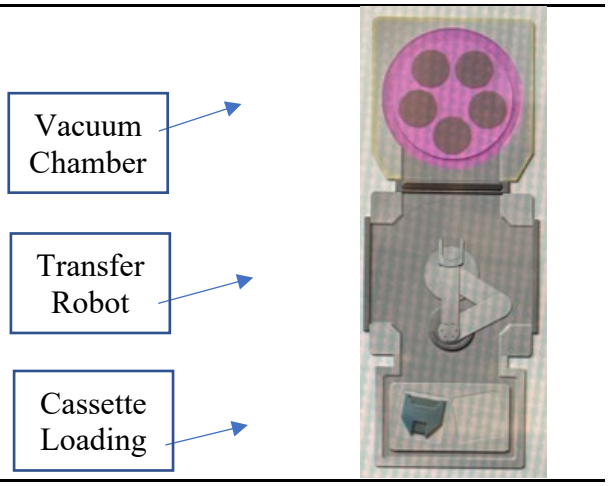

Table 1. PECVD Recipe for SiO_2 deposition.

Functional properties:

Once the recipe for SiO_2 deposition is finalized, the PECVD process can be carried out to optimize the SiO_2 layer properties. Depending on the process capabilities, each PECVD equipment may have different deposition rates for SiO_2 growth. The PECVD process is preferred for high-quality, uniform SiO_2 growth at low temperatures of less than 400 ^{0}C. The composition and geometry of the earlier and subsequent deposition layer and, the functional requirement of the SiO_2 layer determine the acceptable range of the deposition rate (based on thickness evaluation), density, IR, % non-uniformity, dry-wet etch rate, and stress. The stress of the deposited SiO_2 layer may cause Si wafer to bow out of bounds, disrupting the integrity of the deposition. Delamination of the deposited layers affects the electrical or optical performance of the device being developed [2]. The density of the deposited SiO_2 affects the etch rate.

Table 2. SiO_2 thin film parameter and response characteristics.

SiH_4	N_2O	RF Power	Thickness	Density	RF Index	Stress
150	770	300	1488	2.1878	1.4532	-218.752
165	840	330	1806	2.1892	1.4583	-279.463
135	700	270	1457	2.1973	1.4563	-319.317

Stoney's Equation

$$\sigma = \frac{1}{6}\frac{E}{(1-\upsilon)}\frac{t_s^2}{t_f}\left[\frac{1}{Rf} - \frac{1}{Rs}\right]$$

R = radius of curvature

R_s = radius of curvature of the bare substrate

R_f = radius of curvature of substrate with film

E = Young's modulus for the wafer (substrate)

υ = Poisson's ratio

The deposition rate affects the overall time for the production cycle to complete. % non-uniformity determines the level of acceptance of the process. For this research, the SiO_2 deposition characteristics measured to determine intrinsic stress as per Gerald Stoney's equation 1 are listed in Table 2. The pressure was kept constant 900 mT and the temperature was constant at 150 °C.

Experimental Stress Determination:

The following procedure explains the sample values of Experimental Stresses obtained as listed in Table 2. The experimental procedure to determine these stresses involved the following steps.

1. First the production-quality Silicon Wafer lot was weighed on a weighing scale before deposition. Typically the weight for each wafer of diameter 150 mm single flat wafer was 25 to 28 gms measured till 5th decimal e.g. 25.97812 or 28.43109.
2. The surface area for a standard 150 mm single notch wafer was computed.
3. Once the virgin wafers were weighed, their initial stress without deposition of SiO_2 was determined on the KLA Stress measuring machine. This initial stress state was to be used as reference surface stress after deposition.
4. Deposition of SiO_2 on Si substrate by changing the PECVD input parameters was carried out. The input parameters of SiH_4, N2O, RF Power SiO_2 deposition was carried out for the decided time of 120 to 240 sec.
5. The thickness of SiO_2 deposited was measured using KLA Tencor spectroscopic ellipsometer. For example, some sample thickness of SiO2 deposition was about 1500 Å, equal to 0.15 µm or 0.000015 cm.
6. Based on the above data density was computed in Kg/cm^3 which should have been nearly equal to the standard value for SiO_2 of 2.65 Kg/cm^3.
7. The density of the above-observed values will be,

Wafer Dia	Area (mm2)	Thk (Ang)	Thk (cm)	Area(cm2)	Vol (cm3)	wt (kg)	**Density**
150	70672.5	1500	0.000015	706.725	0.010601	0.028	**2.641291**

8. Final stress after deposition was measured for the thickness of deposition using KLA laser scanner. The laser scans the SiO_2 surface for curvature to assess thickness per Stoney's above equation. Negative sign of stress in Table 2 is for convex curvature of SiO2 that causes compressive stresses. Ideally the SiO2 deposition should have a value of -350 MPa to -50 MPa.
9. The refractive index was also computed along with thickness on KLA Tencor SE instrument.

Computational Setup:

Predicting stresses in silica thin films is a crucial aspect of materials science and engineering, especially in microelectronics, optics, and nanotechnology applications. Silica thin films can experience various types of stress due to factors like film deposition, temperature changes, and film-substrate interactions. To predict stress, various approaches can be employed such as analytical, Experimental, or Molecular dynamics.

The study of silica, using molecular dynamics (MD) simulations is of great importance in various scientific and industrial fields. Molecular dynamics is a computational technique that allows researchers to simulate the behavior of atoms and molecules over time, providing insights into the structural, dynamical, and thermodynamic properties of materials. Silica molecular dynamics simulations are a viable and powerful approach for studying the behavior of silica at the atomic and molecular levels. However, successful simulations require careful consideration of force fields, computational resources, initial conditions, equilibration, and data analysis. Additionally, validation against experimental data is crucial to ensure the accuracy and reliability of your simulations. Previous studies employing molecular dynamics (MD) simulations have delved into the characteristics and attributes of silica, encompassing both crystalline and amorphous varieties, and have employed various potentials while operating within different strain rate regimes.

For this simulation, the deposition of SiO_2 films was simulated using the MD-based approach. Initially, crystalline Silica is modeled using Material Studio [3]. A cubic unit cell of Silica is generated using a Materials Project database [4]. A SiO_2 model, representing alpha quartz, was generated in accordance with the trigonal P3_221 space group. Si^{4+} ions formed corner-sharing SiO_4 tetrahedra, each bonding with four equivalent O^{2-} ions. Two Si–O bonds exhibited shorter lengths (1.61 Å), while the other two were longer (1.62 Å).

O^{2-} ions were arranged in a bent 150-degree geometry, connecting with two equivalent Si^{4+} ions. The initial box size is 5.06 nm × 5.06 nm × 5.06 nm and contains 1125 atoms as in Figure 2. For this simulation, ReaxFF (Reactive Force Field) [5] is used to better capture the effect of the chemical reaction of a complex system.

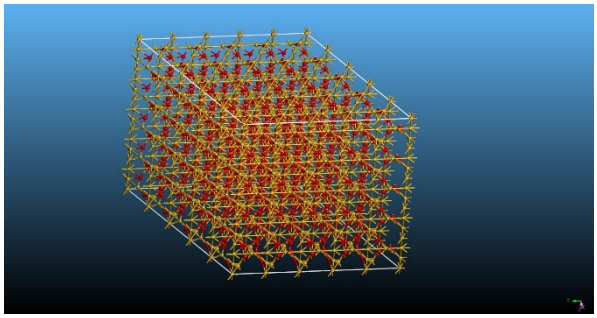

Figure 2. Silica Crystal Structure modeled in Material Studio.

It accurately models bond breaking and forming, making it suitable for diverse applications, from materials science to catalysis, and enables efficient, large-scale simulations, aiding in the understanding and design of materials and chemical processes. The MD timestep used is 0.5 fs and periodic boundary conditions are used. The density of the system is maintained at 2.61 g/cm^{-3}. Amorphous silica is created in LAMMPS [6], through an annealing procedure applied to crystalline silica. The development of the amorphous silica model involves a sequence of three steps: first, a heating phase in the NVT (canonical ensemble), followed by cooling in the NVT ensemble, and finally, a relaxation phase in the NPT (isothermal–isobaric ensemble).

The crystalline silica model is then subjected to a heating process at an elevated temperature of 6000 K for a duration of 250 picoseconds (ps), employing the NVT ensemble. It is worth noting that the real-world melting temperature of silica is approximately 1,986 K [7] and using significantly higher temperatures expedites computational procedures. This was followed by cooling of the system using an NVT ensemble with a cooling rate of 5K/ps to 300K.

To apply axial tensile force, we uniformly stretch the model in the X-direction, using FIX Deform in LAMMPS with a constant axial strain rate. This involves scaling the coordinates of all atoms along the X-direction at each time step, which is followed by MD time integration. To mimic plane-stress conditions, we allow movement in the Y- and Z- Directions. These uniform expansion loading conditions are ideal for studying high-strain rate stress-strain responses, with stress calculated using the virial stress definition. The stress tensor is calculated in LAMMPS using the Virial Theorem.

$$P_{ij} = \frac{\sum_{k=1}^{N} m^{(k)} v_i^{(k)} v_j^{(k)}}{V} + \frac{\sum_{k=1}^{N} r_i^{(k)} f_j^{(k)}}{V} \quad \text{-- Eq (1)}$$

where V is the model volume, N is the number of atoms in the model, m is the mass of an atom, v is the velocity of an atom, r is the interatomic distance, and f is the interatomic force. The subscripts i and j stand for X, Y, and Z direction values. The above virial stress corresponds to true stress. Engineering stress is determined by scaling the virial true stress with the initial cross-section area of the model. The strain is calculated using the current and initial lengths of the model.

Within the physical chamber, silicon atoms and oxygen molecules coexisted. In our modeling framework, we used the representation of oxygen to its molecule state. During this phase, silicon and oxygen atoms from the gas phase engage in interactions with each other and the surface atoms of the film, culminating in the formation of covalent bonds that facilitate film growth. The film growth simulation was conducted for low-energy

deposition methods such as physical vapor deposition, involving sputtered Si atoms with an energy of 0.1 eV. This Silica film deposition simulation was modeled through a well-followed approach [8], involving a few injection steps. In each step, silicon and oxygen atoms, in a 1:2 stoichiometric ratio, were randomly and alternately introduced at the uppermost portion of the simulation box. This involved 750 total atoms deposited in each deposition cycle. After each step film growth is observed.

Results and Discussion

The REAXFF potential is evaluated first by running the tension test on a modeled Silica crystal in LAMMPS. The results obtained (Figure 3 & Table 3) agree with previous MD studies [9], though these studies were performed using different forcefields. This enhances the confidence in using REAXFF for our simulation.

Table 3. Output response from LAMMPS.

Sr No.	Temperature (K)	Strain Rate (s^{-1})	Young's Modulus (GPA)
1	300	10^5	61.38
2	300	10^7	65.55
3	300	10^9	75.49
4	300	10^{11}	78.21

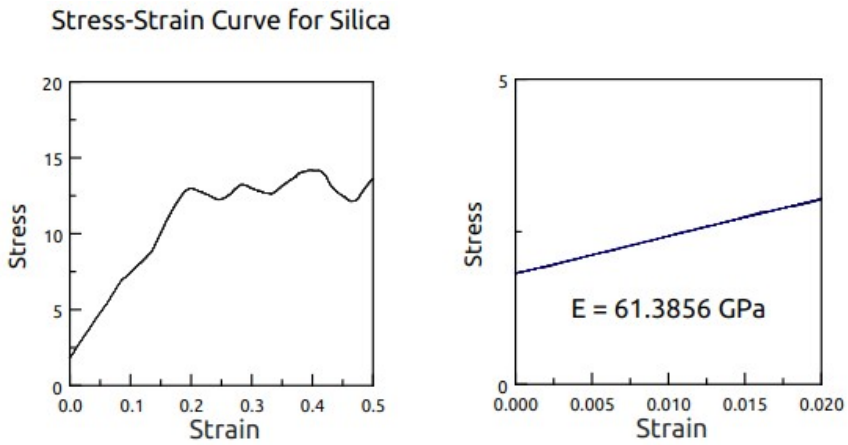

Figure 3. Extrinsic Stress Characteristics by LAMMPS.

From Figure 4a, it is evident that the deposition is happening as expected. The radial distribution function peak at about 0.16 nm, shows that the Silica is forming at the surface level. Figure 4b shows the Oxygen molecules moving towards the silicon surface and interacting with Silicon to form SiO_2. Blue color molecules are Oxygen molecules and Red and yellow are Silicon atoms. four

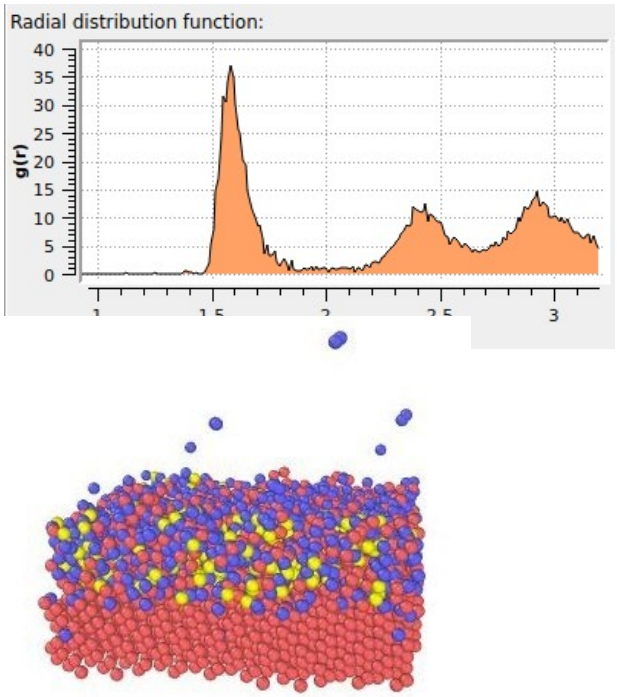

Figure 4. a: Radial Distribution Function of Layer 1. 4b: Random O_2 molecules being deposited on Si Substrate.

In Figure 5, we present stress distributions over one complete deposition cycle. The solid yellow line represents normal stress in the x-direction (Px), solid green in y direction, and the solid blue line depicts normal stress in the z-direction (Pz). Stress values were computed as ensemble averages of atomic stresses at each cycle. All the stresses Px, Py, and Pz are compressive within the layer surface and substrate.

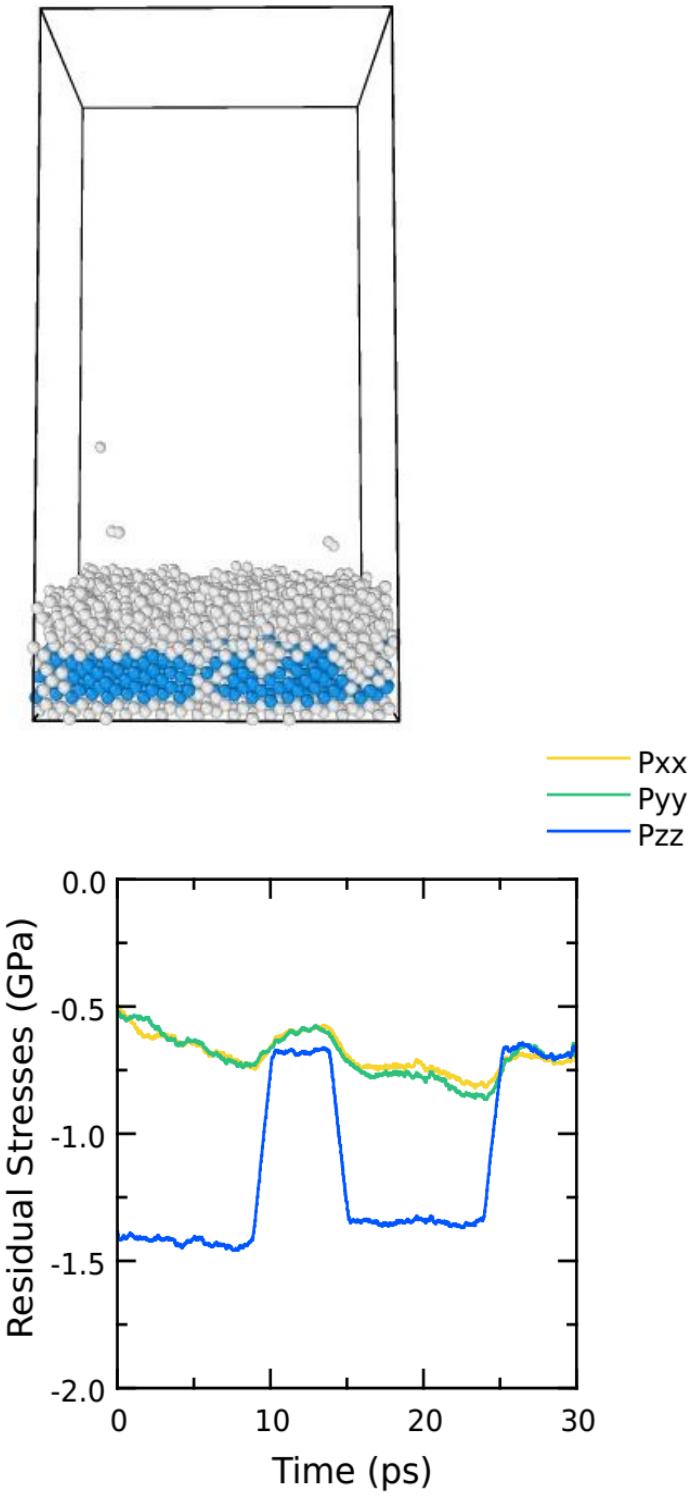

Figure 5. a: Deposition process visualization using OVITO. 5b: Residual stresses generated over one cycle of deposition.

Conclusion:

This study outlines a standard process for the Silica deposition process. Utilizing the ReaxFF force field, superior predictions of amorphous silica's structure and mechanical properties are achieved compared to other force fields. Variations in Young's modulus and strength are attributed to strain rate, cooling rate, and temperature, with strain rate exerting the most pronounced influence as in Table 3. The obtained stress-strain behavior is in

good agreement with simulation-derived results published previously. However, the validation of experimental results for amorphous silica glass was not conclusive, requiring improvements in the parameter in the reactive force field. However, residual stresses during the deposition process evaluated confirmed compressive stress formation as depth increases, the stresses also increase.

This research investigated the stresses that emerge during the initial silicon dioxide film growth phase. Experimental stress analysis typically covers films with thicknesses of about 150 nm for which simulations could not complemented. Failure to validate experimental results opens up future scope of the study.

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