Ion energy control during plasma-enhanced atomic layer deposition: enabling materials control and selective processing in the third dimension

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Enabling materials control and selective processing in the third dimension

As we enter an era of atomic scale devices, there is a strict need for precise control over the thickness and properties of materials employed in device fabrication [1,2]. Furthermore, next-generation devices consist of various material layers across both planar and three-dimensional (3D) layouts which has led to an additional need for processing materials in a selective manner [3,4]. Plasma-enhanced atomic layer deposition (ALD) is a technique that uses the species generated in a plasma (i.e. radicals, ions) for processing materials at the atomic level. In this article, we demonstrate how implementing ion energy control in plasma ALD enhances the versatility of this atomic scale processing technique by enabling control over a wide range of material properties during deposition. Furthermore, we show how controlling ion energies during plasma ALD on 3D trench-shaped nanostructures provide a novel approach for topographically selective materials processing.

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Plasma-enhanced atomic layer deposition

ALD is a cyclic deposition process based on sequential and self-limiting reactant exposure steps for synthesizing thin films in a layer-by-layer manner. Plasma ALD is an energy-enhanced ALD method in which a plasma is used during one of the reactant exposure steps of an ALD cycle (see figure 1) [5]. During the plasma exposure step, the substrate is exposed to a variety of species which consist of radicals and ions among other species. The radicals are highly reactive species that are known to contribute towards film growth during plasma ALD [6]. Furthermore, radicals impinge on a substrate in an isotropic/non-directional manner. In contrast, the plasma ions can impinge on a substrate in an anisotropic/directional manner (see figure 2 and discussion therein). The ions can also deliver additional energy to a growing film surface during plasma ALD. Although the contribution of radicals has been well investigated, very little is known about the role of ions in plasma ALD.

Controlling ion energies during plasma ALD with substrate biasing

A remote inductively coupled plasma reactor, such as the one shown in figure 2, can be used to grow films by plasma ALD. Typically, plasma ALD is carried out using a grounded substrate in the plasma step. This substrate configuration leads to low ion energies (upto 30 eV at sufficiently low pressures ~10 mTorr [5]) causing ions to play a relatively minor role compared to radicals during deposition. An advanced version of plasma ALD can be carried out by implementing RF substrate biasing in the plasma step (see figure 2). This technique can be used to enhance the energy of directional ions during plasma exposure in a controlled manner. In our research, we demonstrated that enhancing the energy of directional ionic species during plasma ALD can have a significant impact on films prepared on both planar and 3D substrates [7-10].

In the following sections, we will highlight the results obtained for three materials, namely titanium oxide (TiO₂), hafnium oxide (HfO₂) and silicon nitride (SiNₓ) deposited without and with substrate biasing during plasma ALD on planar and 3D substrates.

Crystallization of TiO₂ and HfO₂ on planar substrates

TiO₂ and HfO₂ films were both grown by plasma ALD at a low temperature of 150 °C using an oxygen plasma step without and with RF substrate biasing. TDMAT (chemical formula: Ti(NMe₃)₄) and TDMACpH (chemical formula: CpH(NMe₃)₄) were used as the precursors.
ALD process cycle

The ALD process cycle depicted in figure 1 consists of four steps. Step 1 is the ‘adsorption step’ and step 3 is the ‘activation step’ where the surface is exposed to reactants, defined as ‘precurser’ in step 1 and ‘co-reactant’ in step 3. A plasma can be used as the co-reactant in step 3 that leads to the impingement of isotropic radicals and directional/anisotropic ions (indicated by arrows) on the surface. Steps 2 and 4 are ‘purge steps’. Repeating the cycles, and hence the process steps, multiple times leads to film growth where every ALD cycle adds an atomic layer to the film.

Figure 1  Schematic representation of one complete, generalized cycle of atomic layer deposition (ALD) performed using a plasma based activation step.

ALD system

In the commercial remote plasma ALD system shown in figure 2a and b, the plasma is generated from feedstock gas flowing through a dielectric alumina tube. A radio frequency power supply, RF-ICP, connected to a copper coil wrapped around the dielectric tube generates a remote inductively coupled plasma. Precursor gases are delivered to the reaction chamber through a separate gas inlet. The system is evacuated using a turbo pump to create a vacuum environment (10⁻⁴ Torr base pressure). A second RF power supply, RF-Bias, connected to the reactor table enables substrate biasing. Both RF power supplies are connected to the system via automated matching units, AMU, consisting of inductive and capacitive components.

Figure 2  (a) Photo and (b) schematic of an Oxford Instruments FlexAL system equipped with substrate biasing for plasma ALD. (c) Magnified schematic illustrating details of the plasma, sheath and substrate regions during plasma exposure on a biased substrate.

Why are ions directional and energetic species?

The magnified schematic in figure 2c illustrates features of a space change region called the sheath formed between a plasma, consisting of positive ions and negative electrons as the charged species, and the substrate. The sheath forms due to the difference in mobilities of heavy ions and light electrons at the plasma boundaries. The sheath potential, $\Delta V_{\text{sh}}$, is the difference between the plasma potential, $V_{\text{pl}}$, and the substrate potential, $V_{\text{sub}}$. Ions are accelerated across the sheath by $\Delta V_{\text{sh}}$ leading to a flux of positive ions impinging on the substrate with kinetic energy proportional to $\Delta V_{\text{sh}}$. The ion flux is directional provided the ions do not undergo any gas phase collisions while traversing the sheath. This can occur at sufficiently low plasma pressures where the average distance travelled by ions before undergoing collisions (i.e. ion mean free path) significantly exceeds the sheath thickness. On a grounded substrate $\Delta V_{\text{sub}}$ is at zero potential, so $\Delta V_{\text{sh}}$ equals $\Delta V_{\text{pl}}$. RF substrate biasing during plasma exposure causes $\Delta V_{\text{sh}}$ to acquire a negative time-averaged bias voltage, $-\langle \Delta V_{\text{bias}} \rangle$, which increases $\Delta V_{\text{sh}}$ to higher values compared to a grounded substrate. This enhances the kinetic energy of ions impinging on the RF-biased substrate. The ion energy can therefore be controlled (enhanced) during plasma exposure by tuning (increasing) the magnitude of $\langle \Delta V_{\text{bias}} \rangle$ with RF substrate biasing [9].
sors for TiO and HfO, respectively. Both films typically grow in the amorphous phase at this low temperature, evidenced by the diffuse halo patterns in the selected area electron diffraction images of figure 3. However, for films grown with RF substrate biasing during the oxygen plasma step, concentric ring patterns were observed in the electron diffraction images of figure 3 [8]. This indicated the presence of polycrystalline material corresponding to the rutile and monoclinic phases of TiO and HfO, respectively. These are crystalline phases that are normally obtained either by using high temperature deposition environments or by using special substrate materials that have crystal lattice parameters comparable to the deposited film. These results indicate that enhancing ion energies by substrate biasing during plasma ALD of such transition metal oxides can induce crystalline film growth even at low temperatures and also without the need for special substrates.

**Phase-selective deposition on 3D substrates**

Plasma ALD of TiO and HfO was also performed on 3D trench nanostructures with substrate biasing at 150 °C, as shown in figure 4. Films growing at the planar (i.e. horizontal) top and bottom regions of the 3D trenches were polycrystalline (rutile TiO, monoclinic HfO) while those at the vertical sidewalls were amorphous [8]. This phenomenon can be attributed to the directional nature of energetic ions during plasma exposure with substrate biasing. The directional ions impinge on the planar trench surfaces (aligned perpendicular to the ion flux) with much more energy than on the vertical trench sidewalls (aligned parallel to the ion flux) during deposition with substrate biasing. Consequently, films growing at the planar surfaces under the influence of such energetic ions at this low temperature form crystal grains, concurrent with the earlier results of figure 3. The sidewall regions being devoid of energetic ion bombardment provide conditions resembling those on a grounded substrate, thereby yielding amorphous films. These results indicate how enhancing the energy of directional ions during plasma ALD with substrate biasing provides a new approach for conducting selective deposition on 3D substrates, defined in the literature as topographically selective deposition [11]. Therefore, we demonstrated topographically selective deposition of TiO and HfO in terms of simultaneous, phase-selective growth [8,12] of crystalline and amorphous material on the planar and vertical surfaces, respectively, of 3D trench-shaped substrates.

**Tailoring SiN properties on planar substrates**

Plasma ALD of SiN was performed using an aminosilane precursor, DSBAS (chemical formula: SiH2N(Ph)3), and a nitrogen plasma step without and with RF substrate biasing. Dense SiN films with a high refractive index and compressive stress were obtained without any biasing (see figure 5a-c) [8,13]. On implementing substrate biasing during plasma ALD, the refractive index, density and compressive stress of SiN films decreased as a function of \( \langle V_{bias} \rangle \) in the plasma step (see figure 5a-c) [8]. This showed enhancing ion energies during growth on a planar substrate degraded the properties of SiN [8,9]. However, since substrate biasing during plasma ALD influences material properties, it can be used to obtain nanoscale film lay-
ers with tailored properties. For instance, stacked layers with different properties, known as nanolaminates [14], could be obtained from the same material by growing one layer without and the next layer with substrate biasing, as shown in figure 5d. The top SiNₓ layer grown with biasing has a lower contrast, and hence different properties, compared to the bottom SiNₓ layer grown while the same substrate was in a grounded configuration during plasma exposure.

**Microstructure-selective deposition on 3D substrates**

Plasma ALD was also used to grow SiNₓ films on 3D trench-shaped nanostructures without and with substrate biasing during nitrogen plasma exposure. After deposition, the films were subjected to a wet etching treatment of 30 s in dilute hydrofluoric acid. The results for as deposited and post wet etching treatment films are shown in figure 6. For SiNₓ grown without substrate biasing, film thickness at nearly all regions of the 3D trench nanostructures was comparable before and after wet etching [13]. This indicated growth of wet etching resistant SiNₓ without substrate biasing, in line with the earlier results of figure 5 that showed dense SiNₓ films for a grounded substrate. However, for SiNₓ grown with substrate biasing, film regions at the planar top and bottom surfaces of the trenches were completely removed while those at the vertical sidewalls remained behind after wet etching [8]. This is due to the directional nature of energetic ions with substrate biasing where more energy gets delivered to the planar compared to the vertical trench surfaces. It culminates in the selective degradation (i.e., density reduction) of SiNₓ films growing at the planar trench surfaces which are then easily etched, while those growing at the vertical sidewalls are unaffected and therefore, remain intact after wet etching. These results indicate another approach for conducting selective deposition on 3D substrates by controlling the energy of directional ions during plasma ALD.

For the case of SiNₓ, we demonstrated topographically selective deposition in terms of simultaneous, microstructure-selective growth [8,12] of low and high density films at planar and vertical surfaces, respectively, of 3D trench nanostructures.

**Perspective**

The nanoelectronics device industry is currently looking at new ways for topographically selective processing of materials as 3D features become the norm in both device fabrication and final device architectures. The cases above signify how plasma ALD with substrate biasing enables topographically selective deposition on 3D substrates in terms of simultaneous growth of films with different material properties (e.g., phase, microstructure, etc.). These films also have the potential to undergo further processing in a selective context. The additional processing, e.g., wet or dry etching treatment, conducted after deposition could in principle lead to topographically selective etching as shown earlier for SiNₓ. Likewise, the additional processing could also be performed during the deposition itself, e.g., in a cyclic process that sequentially combines selective deposition and selective etch steps. Such methods have the potential to yield films only at desired surfaces of 3D substrates if, for instance, area-selective deposition processes for obtaining films only at particular sur-
Topographically selective processing on 3D substrates

![Area-selective deposition](image1)

![Property-selective deposition & selective etching](image2)

**Figure 7** Schematic illustration of topographically selective processing on 3D trench-shaped substrates in terms of (a) area-selective deposition, (b) material property-selective deposition (e.g. phase, microstructure, etc.) by controlling the energy of directional ions during plasma ALD and (c) material property-selective deposition followed by selective etching.

faces do not exist (see figure 7). For example, the layouts in figure 7a after area-selective deposition resemble those in figure 7c. This could be achieved by conducting additional selective etch treatment after or during material property-selective deposition via ion energy control, depicted in figure 7b. On this accord, controlling the energy of directional ions during plasma ALD extends the portfolio of atomic scale processing techniques by enabling a new approach for materials control and topographically selective processing on 3D substrates.

**References**


**Uitslag NEVAC-prijsvraag 2019**

Ook dit jaar konden studenten en promovendi weer een geldbedrag van € 1.000,- winnen door hun eigen, aan vacuüm gerelateerd, onderzoek te schrijven. Het beste Nederlands- of Engelstalige ingestuurde en gepubliceerde artikel in het NEVAC blad wordt beloond met de NEVAC-prijs. Deze prijs wordt uitgereikt door een jury die de artikelen beoordeelt op onder meer leesbaarheid, wetenschappelijk en technisch niveau en het gebruik van illustraties.

Dit jaar hebben we twee Engelstalige artikelen ontvangen. De kwaliteit van de inzendingen bleek erg dicht bij elkaar te liggen. Aan de beoordelingscommissie, bestaande uit Meike Störh, Jaap Kautz en ondergetekende, de taak om een winnaar aan te wijzen. Na het middelen van de cijfers, gegeven voor de verschillende criteria, is het artikel van Tahsin Faraz van de Technische Universiteit Eindhoven als beste uit de bus gekomen. Het winnende artikel is opgenomen in deze editie. Het beschildert hoe het controleren van de ionenergie tijdens plasma-enhanced Atomic Layer Deposition (ALD) gebruikt kan worden om de eigenschappen van het gedeponeerde materiaal te bevloeden. Het artikel is helder geschreven en begrijpelijk voor een breed publiek met een technische, fisieke of chemische achtergrond. Tijdens de NEVAC-dag op 17 mei in Nijmegen zal de prijs persoonlijk aan Tahsin overhandigd worden, waarna hij een lezing zal geven over het onderwerp.

Vanaf nu kan iedereen weer artikelen inzenden voor de komende prijsvraag. Heeft je een interessant onderwerp dat gerelateerd is aan vacuümtechniek, schroop dan niet en schrijf erover! Wij ontvangen graag en onze lezers zijn benieuwd naar je verhaal. Geplaatste artikelen van studenten/promovendi worden altijd beloond met 250 euro!

Hans van Eck
Voorzitter beoordelingscommissie 2019

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