Plasma-assisted Atomic Layer Deposition

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High-volume manufacturing and new opportunities in research

The usage of plasma as a reactant in atomic layer deposition processes started out as a niche process but in the meantime had its breakthrough in high-volume manufacturing in nano-electronics. Understanding the processes in plasma ALD is challenging but the knowledge in the Netherlands on plasma science, surface science and the ALD end-applications are a perfect foundation for a globally leading position in this field.

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Atomic layer deposition (ALD) is a processing technique that has been widely adopted for the growth of nanometer-scale films of a variety of materials. Besides the control at small length scales, there are also increasingly stringent requirements on material properties and limits on processing temperature. Therefore, a strong research effort into ALD has been present for the past few decades to improve and extend ALD processes. New chemistries are being sought continuously and the use of a plasma as one of the steps in ALD has been a common method to extend the processing capabilities of ALD [1,2]. Plasma ALD differs from thermal ALD by the use of a plasma as the reactant (e.g., an O_2 plasma instead of H_2O exposure to grow oxides). Interestingly, plasma ALD – which originally started as a niche method to expand the capabilities of ALD – has become an enabling technology in high-volume manufacturing and a large field of study [3]. Currently, its use in high-volume manufacturing is dominantly for patterning, but it is now also considered for masking and barrier layers, gate spacers, and low temperature encapsulation layers. Furthermore, plasma ALD and related methods are expected to be a prominent part of atomic-scale processing techniques envisaged for emerging developments.

Breakthrough into high-volume manufacturing

Around 2009 there were initial indications in the open literature for plasma ALD of SiO_2 to become a vital method for self-aligned patterning [4]. Besides the patterning techniques using multiple lithography steps, which can suffer from image placement limitations, there was a lot of interest in self-aligned techniques. For these techniques, the alignment of the individual patterns to each other is inherent to the technique and not affected by image placement. In Self-Aligned Double Patterning (SADP) a spacer is deposited conformally over a patterned mandrel. After anisotropic etching of the top and bottom parts of the spacer, and subsequent mandrel removal, the resulting pitch is half of the original pitch. Nowadays, SADP is indispensable among producers of logic and memory devices due to the repetitive patterns used which are relatively easy to produce by SADP. A key requirement for SADP has been the conformal deposition of the spacer material (typically SiO_2) to have accurate sidewall thicknesses which are needed for accurate reproduction of the desired pattern [4]. The spacer deposition typically has to occur at low temperature [5]. Thermal ALD of SiO_2 is challenging and generally requires high temperatures, while plasma ALD of SiO_2 is a facile process [6,7]. Interestingly, the use of ALD for self-aligned patterning has become the biggest of all the individual ALD markets and here the main process used is plasma ALD of SiO_2. EUV has become available as a possible alternative, but costs and throughputs are still prohibitive to replace most process steps [8]. To this end, plasma ALD is also used for self-aligned quadruple patterning (SAQP) as shown in figure 1 [5,9,10]. For SAQP, the doubling of the pattern resolution is carried out similarly as in SADP, by basically performing SADP twice. Since aligned deposition occurs twice and the resulting features are smaller, the requirements on the ALD processes are even stricter for SAQP compared to SADP and the drive for usage of plasma ALD is even bigger.

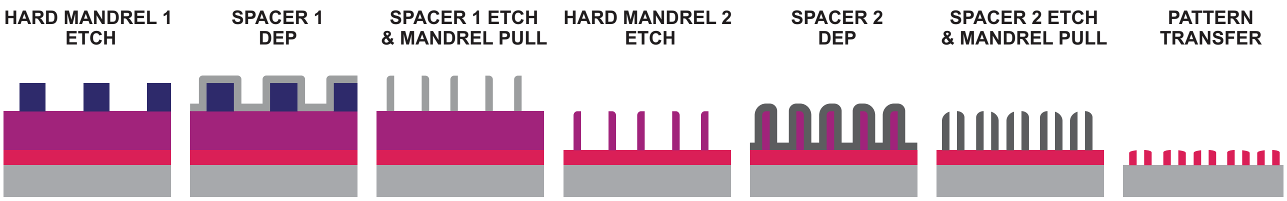

Figure 1 Schematics of a self-aligned quadruple patterning (SAQP) process. The mandrels are the patterns that define where the sidewall spacers are subsequently situated. In this example two hard mandrels are used [9]. Both spacers can be SiO_2 prepared by plasma ALD. High conformality and high film quality are needed to enable correct target pattern reproduction. Reproduced under CC-BY-NCND Attribution License [3].

New opportunities in research

Plasma ALD is typically performed with a wide range of different plasma species present near the surface. But the variety of species present makes it very complex to predict what happens in the ALD process and what needs to be done to optimize or improve the process. Figure 2 illustrates some of the effects and mechanisms considered important in plasma ALD [3]. Radicals are generally considered as one of the key growth species as they are numerous and highly reactive. Radicals can be lost through recombination (e.g., O radicals recombining back into O_2) which predominantly occurs at surfaces at typical pressures. Ions, although less numerous than radicals, are considered as a contributor to the plasma ALD process due to their possible high kinetic energy. The flux and energy of radicals, ions, electrons, and photons depend on plasma input power and pressure and are typically not easily measured or predicted which makes it difficult to understand their exact roles.

Nevertheless, more insight into the relevant processes has been obtained. Studies from Eindhoven University of Technology have shown that photons can play a crucial role in the formation of device defects [11]. For ions in plasma ALD the typical energies and fluxes have been determined, and a first insight into the role of ions has been obtained by studies in which the ion energy was enhanced by RF substrate biasing [12-14] i.e., substrate-tuned biasing and RF biasing, have been implemented in a remote plasma configuration, enabling control of the ion energy during plasma-assisted atomic layer deposition (ALD). Figure 3 shows some of the effects on material properties identified that occur due to increased ion energies by applying substrate biasing. These effects indicate that ions can have a strong role in ALD surface reactions and can be used to tailor film properties or eventually cause damage. It is known from sputter and etch literature that ions can cause damage, although the energies and fluxes present during plasma ALD are typically lower [11,14,15]. Due to the limited lifetime of plasma species, the ease of conformal deposition has been a concern in plasma ALD. Figure 2 highlights key parameters on which con-

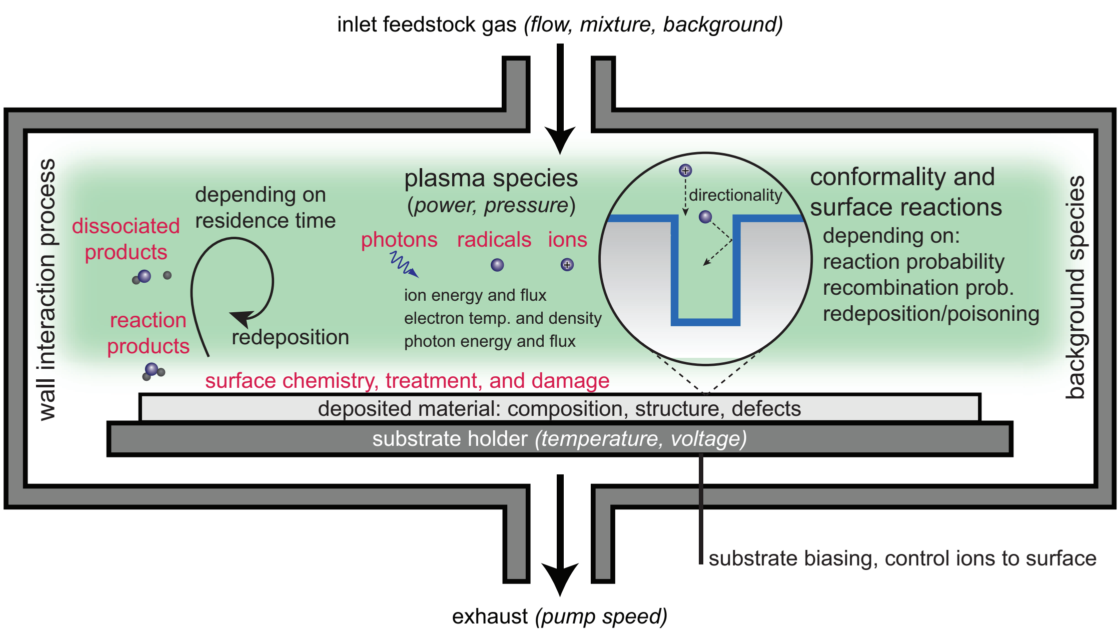

Figure 2 Schematic to illustrate species and processes important in plasma ALD. Plasma species generated from the feedstock gas interact with the surface, lead to film deposition, and affect film conformality and properties. Reaction products formed on substrate and wall surfaces can dissociate in the plasma, redeposit and get incorporated in the film being prepared. Reactor aspects such as the gases used, background species, and pumping speed all have to be considered in possible processes during plasma ALD. Reproduced under CC-BY-NCND Attribution License [3].

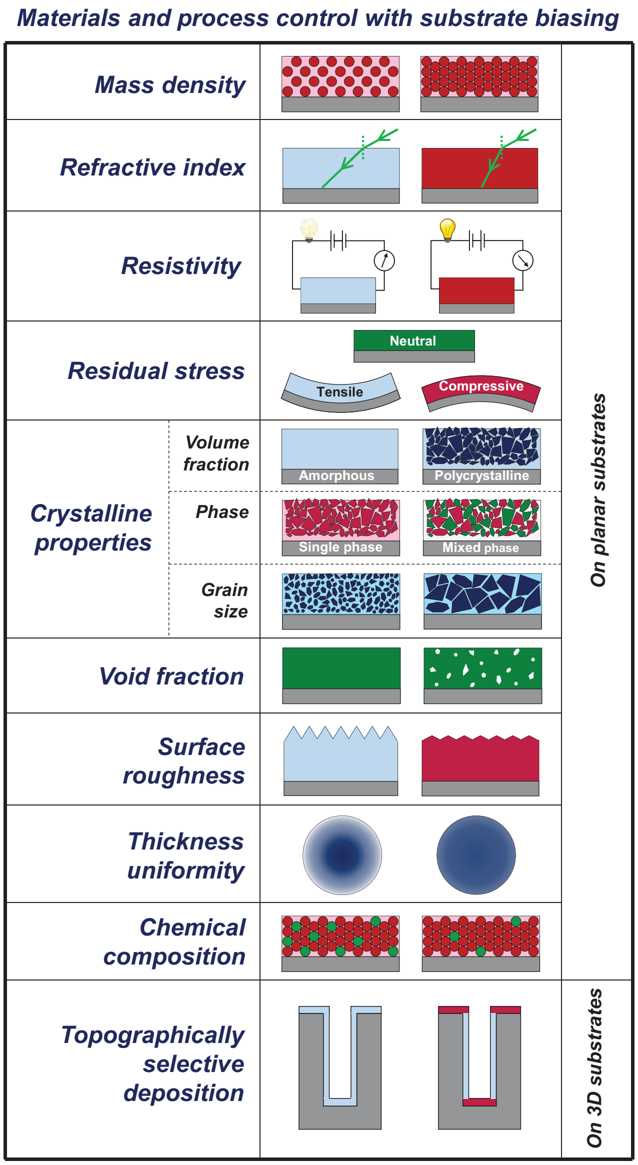

Figure 3 Schematic illustration representative of the material properties and process control enabled by ion energy control through substrate biasing during plasma ALD on planar and 3D substrate topographies. Note that also in plasma ALD without substrate biasing such effects could occur even though the effects would typically be small due to lower ion energies. Reproduced under CC-BY-NC-ND Attribution License, ACS AuthorChoice [13].

formality in plasma ALD depends and illustrates the directionality of ions and the isotropic nature of radicals going into 3D structures. Conformality for plasma ALD is much better understood than in the past, on the basis of both experimental results and theoretical models. For radical-driven processes, conformal deposition can be achieved as long as enough radicals are provided to compensate for radical recombination [16,17]. Recent studies at Eindhoven University of Technology have revealed that for plasma ALD of SiO_2 and TiO_2, even aspect ratios up to ~900 can be coated due to the low recombination probabilities involved [18]. Such studies are good examples of how fundamental understanding can lead to new and even unexpected capabilities for plasma ALD.

Many technical and fundamental questions remain regarding the effect of plasma species on ALD surface reactions. For example, how do the fluxes and energies of plasma species affect the ALD chemistry and what are their exact roles? Are there any synergistic effects such as known from plasma etching, and how do they work? In devices, the ALD layers are often close to sensitive interfaces, where the challenge is to deposit a high quality ALD film without negatively affecting the interface. Although there is a concern of damage even from remote plasmas, there are many cases where plasma ALD has been used to the benefit of such sensitive devices. Understanding all these processes should allow for better design of plasma ALD systems and in general, the understanding of radical and ion processes and surface interaction is expected to benefit a whole range of atomic scale processing techniques required to allow upcoming applications.

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