Supplemental Document

Energetic ions during plasma ALD and their role in tailoring material properties

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Figure S1. (a) Schematic of a FlexAL system equipped with RF substrate biasing. A gridded retarding field energy analyzer (RFEA) is placed on the substrate table to measure energy distribution of ions (IEDs) impinging on the substrate, (b) IEDs of an O₂ plasma as a function of the time-averaged bias voltage, $\langle V_{bias} \rangle$, applied during plasma exposure. A narrow single peaked feature is developed when no bias is applied and broad multi-peaked features occur when applying $\langle V_{bias} \rangle$. The mean ($\langle E_i \rangle$), maximum ($E_{i,max}$), spread (ΔE) and dose ($E_{i,dose}$) in energy of the impinging ions that can influence material properties are indicated.





Figure S2. Plot showing $\langle E_i \rangle$, $E_{i,max}$ and ΔE expressed as a function of $\langle V_{bias} \rangle$ applied during an O₂, H₂ and N₂ plasma exposure steps. It serves to illustrate how all three parameters increase linearly with $\langle V_{bias} \rangle$ and that $E_{i,max}$ can significantly exceed $\langle E_i \rangle$ at high $\langle V_{bias} \rangle$.

Figure S3. GPC, ref. index and mass density of TiO₂ films at 300°C as a function of $\langle E_i \rangle$ and corresponding $E_{i,max}$. Data is shown for $\langle V_{bias} \rangle$ applied for the entire duration and last half (5s) of the 10s O₂ plasma step. The shaded areas represent the range of ion energies between $\langle E_i \rangle$ and $E_{i,max}$ that a substrate is exposed to when the corresponding $\langle V_{bias} \rangle$ is applied during plasma exposure.