Supplemental Document

Ion Energy Characteristics during Plasma-Enhanced Atomic Layer Deposition and their Role in Tailoring Material Properties

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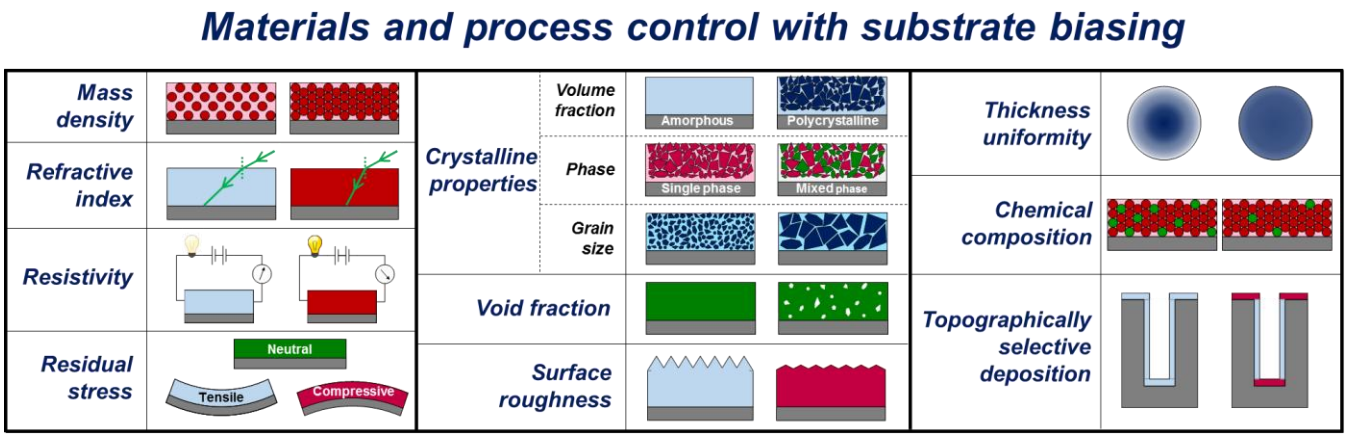

Figure S1. Schematic illustration representative of the material properties and process control enabled by ion energy control with substrate biasing during PEALD on planar and 3D substrate topographies.

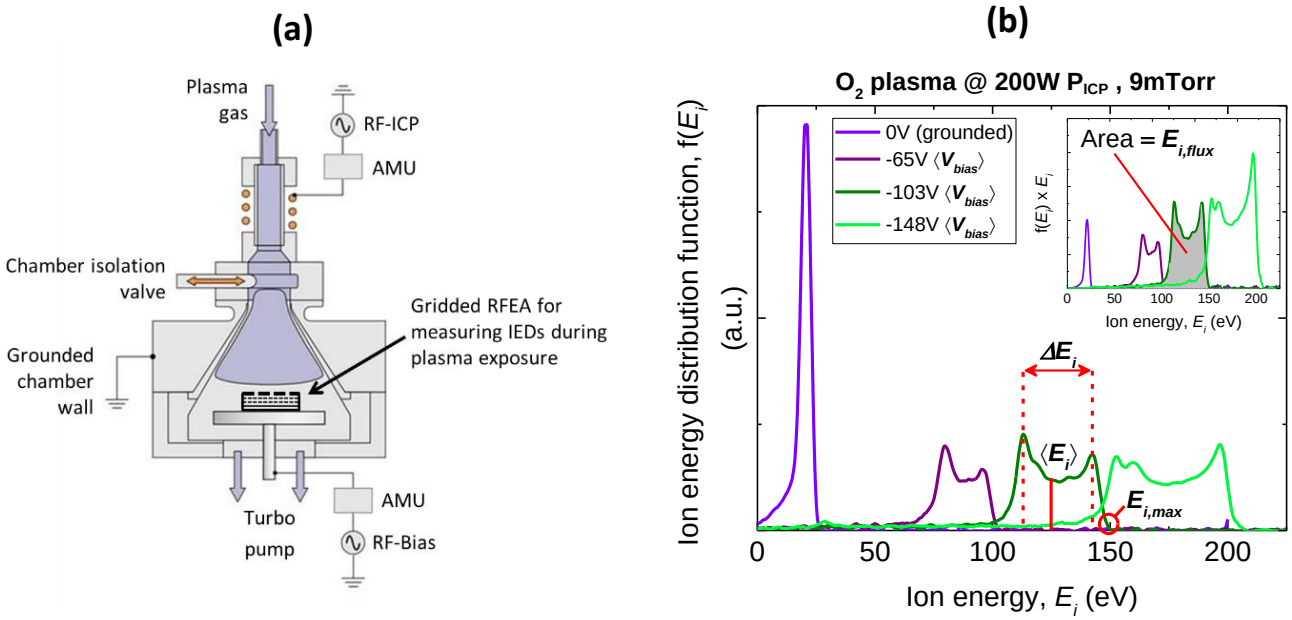

Figure S2. (a) Schematic of a FlexAL system equipped with RF substrate biasing. A gridded retarding field energy analyzer (RFEA) is placed on the substrate table to measure energy distribution functions of ions, f(E_i), impinging on the substrate, (b) f(E_i) of an O_2 plasma as a function of the time-averaged bias voltage, $\langle V_{bias} \rangle$, applied during plasma exposure. The mean ($\langle E_i \rangle$), maximum ($E_{i,max}$) and spread (ΔE_i) in kinetic energy of the impinging ions that can influence material properties are indicated. The product of f(E_i) and E_i is shown in the inset and the area under this distribution function gives the kinetic energy flux imparted to the substrate by the impinging ions ($E_{i,flux}$). The product of $E_{i,flux}$ and plasma duration per ALD cycle allows determination of the kinetic energy dose imparted to the substrate by the impinging ions per cycle ($E_{i,dose}$).

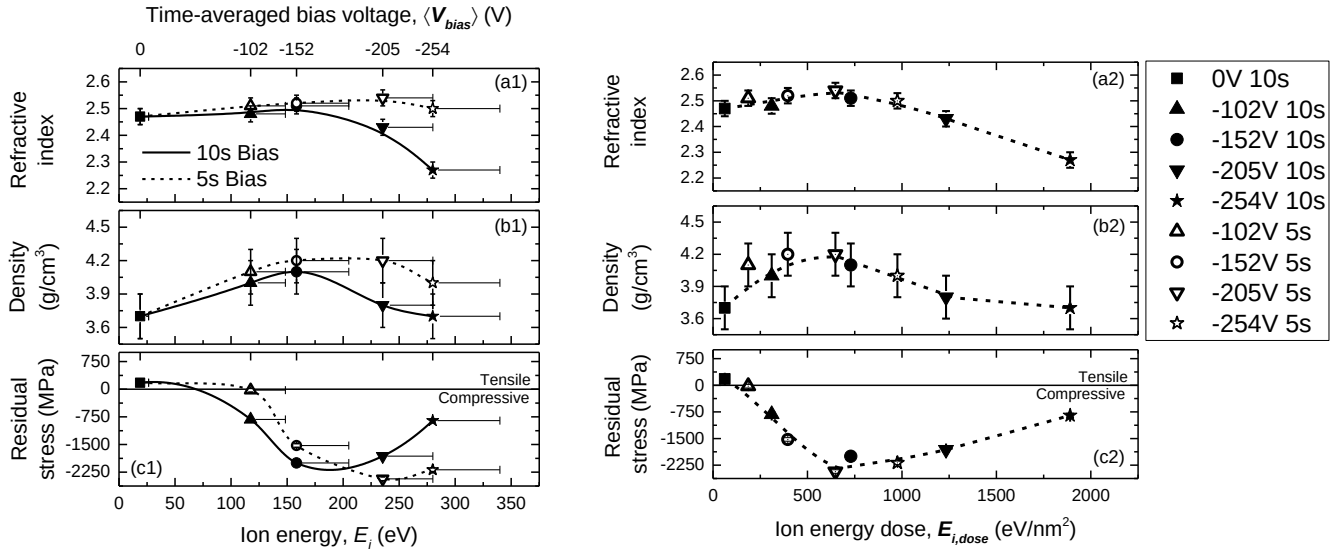

Figure S3. (a1) Refractive index, (b1) mass density and (c1) residual stress of titanium oxide films as a function of the kinetic energy of ions, $\boldsymbol{E_i}$, impinging on the substrate during O_2 plasma exposure. The solid square denotes film growth using an O_2 plasma exposure time, $\boldsymbol{t_{pl}}$, of 10 s without biasing while the rest of the symbols denote film growth with RF substrate biasing spanning the entire duration (10 s, solid symbols) and last half (5 s, hollow symbols), respectively, of the $\boldsymbol{t_{pl}}$. Each non-square symbol denotes a particular mean ion kinetic energy, $\langle \boldsymbol{E_i} \rangle$, for the corresponding negative time-averaged substrate bias voltage, $\langle \boldsymbol{V_{bias}} \rangle$ during the O_2 plasma step. The horizontal bars represent the range of $\boldsymbol{E_i}$ between $\langle \boldsymbol{E_i} \rangle$ and maximum ion energy, $\boldsymbol{E_{i,max}}$, that a substrate is exposed to for the corresponding $\langle \boldsymbol{V_{bias}} \rangle$. (a2) Refractive index, (b2) mass density and (c2) residual stress of the same films expressed as a function of the kinetic energy dose of ions per unit substrate area per ALD cycle, $\boldsymbol{E_{i,dose}}$, during O_2 plasma exposure without and with RF biasing. The symbols represent the same parameters as before (indicated in the legend).

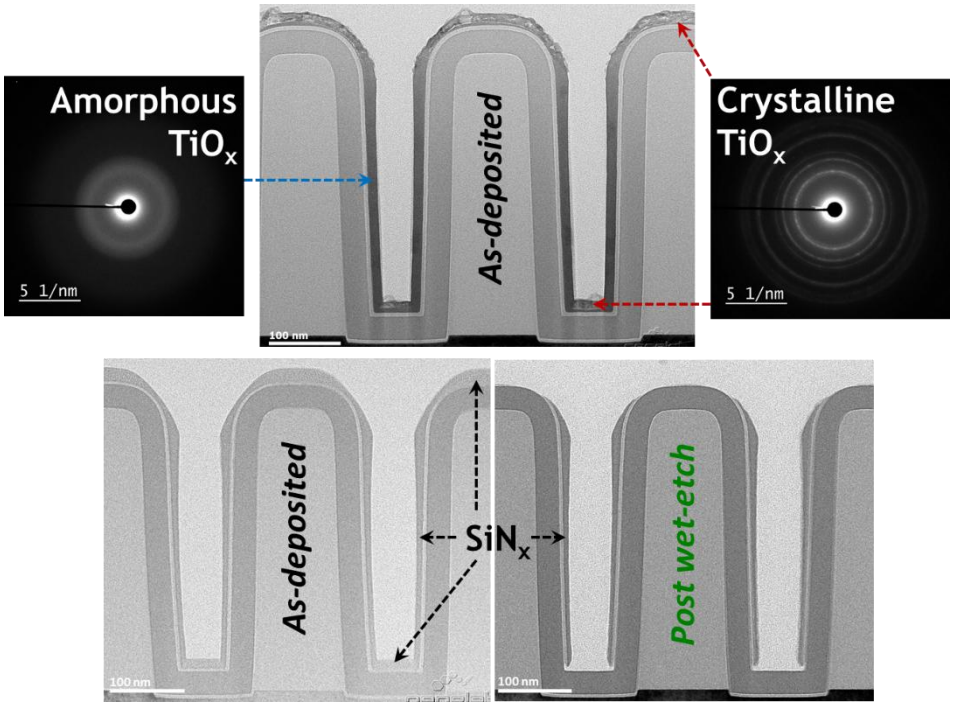

Figure S4. Tuning material properties of TiO_x and SiN_x by ion energy control with substrate biasing during plasma ALD can enable topographically selective processing on 3D trench nanostructures.