Electronic Supplementary Material (ESI) for Nanoscale.

Antireflective Coatings with Enhanced Adhesion strength

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Optical simulation of TAR-H coating

In order to model the reflectance properties of thin film in a trilayer coating stack, TFCalc software is used for simulation. Thin film calculator software helps in selecting the suitable thickness and refractive index of individual layer in a multilayer coating stack system. The TFCalc software for simulating multilayer coating stack comprises of thin and thick films. Thick films are considered as those films in which the phase information (reflected light from top and bottom interface) is lost due to larger thickness of coating which is greater than the incident light radiation. In thin films, the interference as well as phase information is considered. In the present study, the outer three layers deposited on the substrate is considered as thin films and supporting substrate material itself is considered as thick film. Before simulation, the input parameters used for modelling the trilayer stack in a coating comprises of supporting substrate material, number of layers in a coating, effective refractive index of individual layer, layer thickness, and light incident angle. The output parameter comprises of reflectance or transmittance performance of the coating and their corresponding curves in the designed wavelength range.

There are options for best optimization as well as selecting multilayer stack selection, addition or removal of a layer with suitable refractive index which the software calibrate itself and provide the best optimized reflectance results.

After initial analysis, the three layers of HfO_2 selected for studies were dense layer with high refractive index (η=1.87), the middle layer having refractive index of 1.40 and the porous layer with low refractive index (η=1.30). The thicknesses of these three layers in a coating stack should be adjusted appropriately to minimalize reflectance. Thickness optimization of each individual layer in a coating stack was supported by simulated reflectance. Firstly, the simulated reflectance (dS) results of model TAR hafnia coating with suitable thickness on FTO and Sapphire substrates were carried out to lessen reflectance. The outer three layers considered as thin films and supporting substrates considered as thick film. By adopting this method, model design of TAR-H coating were simulated and experiments were carried out according to simulation parameters.

Morphological analysis of TAR-H

Figure S1 represents the SEM image of TAR-H coating at a tilt angle of 45^{o} showing the three layers clearly visualizable within the coating. The top layer is highly porous comprising of slanted nanorods the middle layer is spongy like with medium porosity and the bottom layer is highly dense in nature.

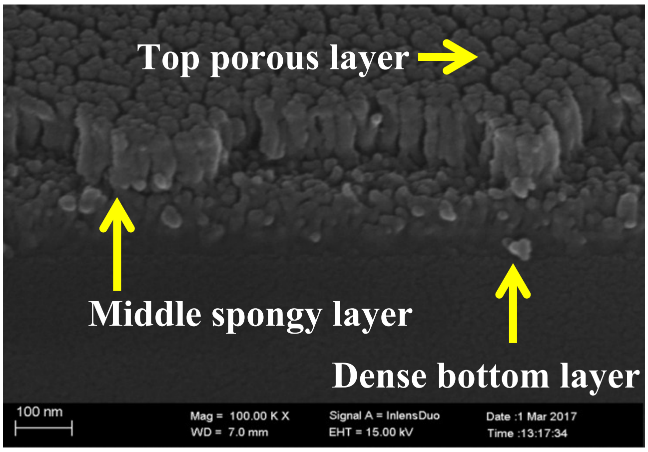

Figure S1: SEM image of TAR-H coating at tilt angle of 45^{o}

Refractive index measurement

Figure S2 represents the refractive index of the HfO_2 nanofilms as a function of the wavelength. The refractive index (η) of single hafnia films deposited at different angles (α = 0°, 80° and 88°) was measured by using WVASE32 spectroscopic ellipsometer at wavelength ranges from 350nm to 900nm at incident angle of 65°. The experimental results shows that refractive index of HfO_2 nanofilms can be easily tuned from 1.87 to nearly 1.29 at 550nm by simply changing the deposition angle (α) by using glancing angle deposition technique. The porosity of films can be tuned and varied from the dense bulk films to nanoporous structures. These three layers are then used to fabricate antireflective coating in a single step using ebeam through vapor deposition by changing the deposition angle only. The three layers are extremely good enough to create a gradual change in refractive index from air media towards the substrate. Inset in Figure S2 represents the top morphology of the single layer HfO_2 films deposited on silicon substrates at different incident angles. SEM images clearly show that the growth morphology of the film is extremely reliant on the oblique angle (α). When (α = 0°) the film morphology is dense and flat. When the film was deposited at higher oblique angles i.e (α = 80°) the film became rough, spongy and self-standing nanostructures. It is noticed that the film became more porous and self-oriented when the film was deposited at higher angle (α = 88°).

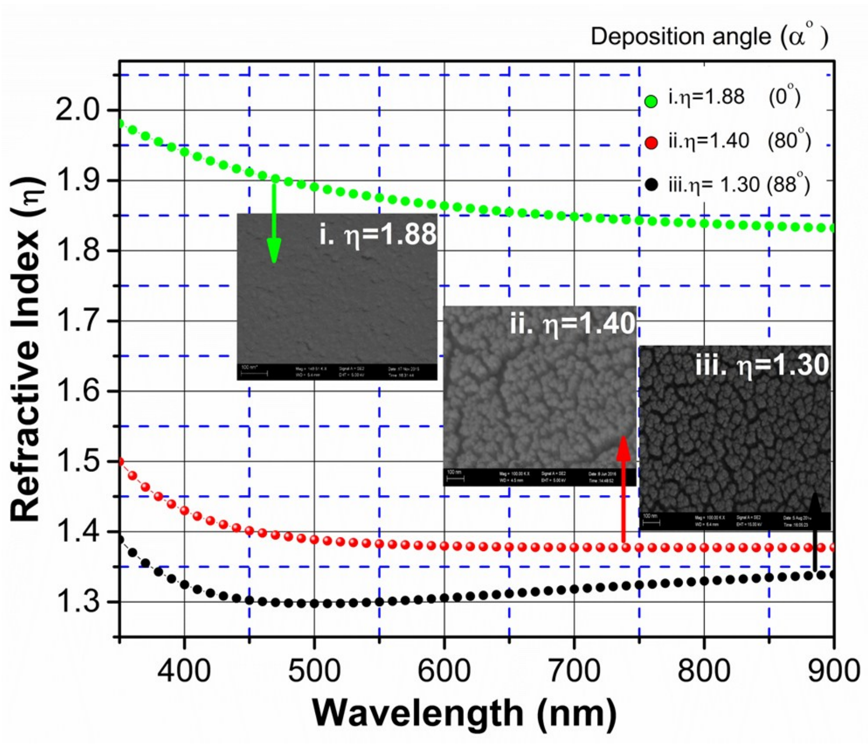

Figure S2. Refractive index (n) of HfO_2 single layers films measured as a function of wavelength at 550nm. Inset showing the top view image of individual hafnia layers deposit at different oblique angles.

XRD Analysis

TAR-H films were annealed for an half an hour at different temperatures from 100°C to 300°C in O_2 atmosphere with 5°C ramp speed per minute. The XRD analysis of trilayer HfO_2 films annealed at different temperatures is shown in Figure S3. The result shows that the annealed films are thermally stable upto 300°C. The asdeposited and film annealed at 100°C TAR-H coating are amorphous in nature while the films annealed at 200°C and 300°C shows very low intensity peak at 2θ =33.68 still showing amorphous as well as partial crystallization nature having same reflectance similar to as deposited film. The appearance of the low intense peak represents the appearance of crystalline phase and slight increment in packing density

[1] . However, this crystallization is not enough to influence the AR efficiency of TAR-H films. The annealed and as deposited TAR-H coating shows nearly same reflectance at normal incidence.

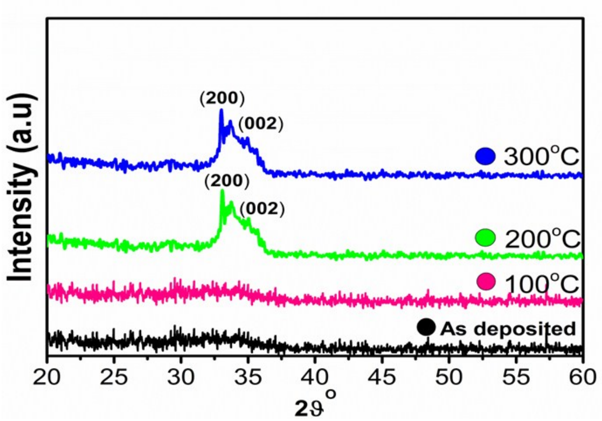

Figure S3. XRD analysis of annealed and asdeposited TAR-H

Young Modulus Calculation

Literature on the mechanical properties with their AR studies is very limited. Researches have been carried out in past on mechanical and AR performance separately but here we try to explain the efficient AR performance of HfO_2 coatings including its mechanical stability. Firstly we measure the young modulus of individul layer deposited at different oblique angles (which comprises the TAR-H coating) as shown in Figure S4.(i) using the laser acoustic surface waves method [2]. It is seen that dense single layer film shows high young modulus as compare to porous single films due to their feeble structure and higher porosity whicy decreases the packing density of nanostructures.

Young Modulus of TAR-H coating shows nearly similar behavior deposited on FTO and sapphire at different annealing temperatures. The modulus reported in the literature differs widely depending on their thermal treatment and fabrication methods. However, the reported young modulus values are between 300GPa to 100GPa [3-4]. Young Modulus directly influences the electrical properties and thermal stability of coatings as it is directly associated to the energy bonds between the atoms, the higher young modulus represents high atomic bonding. Higher young modulus also shows good thermal stability at elevated temperatures which links to negligible changes in volume variation beside the shear strain resistance. The result verify the good quality of TAR-H thin films having young modulus >250Gpa.. The young modulus calculated result shows that tailoring the nanostructure of films not influence the refractive index but also the mechanical properties of coatings. The Young modulus of TAR-H coatings deposited on FTO and sapphire at different annealing temperature , single hafnia layers with varying oblique angle is presented in Table 1 and shown in Figure S4

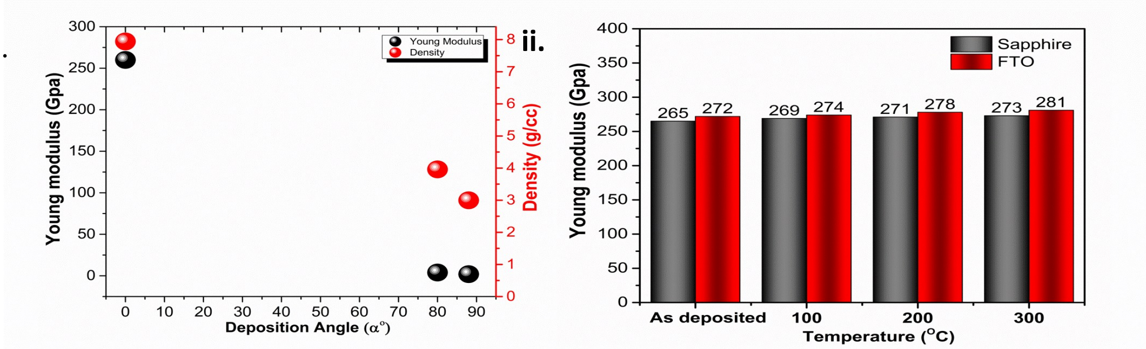

Figure S4. i) Young's Modulus and density variation as a function of deposition angle for asdeposited single layer HfO_2 thin film ii) Graphical representation of calculated young modulus of as deposited and annealed films .

Table S1: Calculated Young modulus of single hafnia layer , annealed TAR-H coatings and as deposited TAR-H coating

HfO_2 single layers		**TAR-HfO_2 Coating**	**FTO**	**Sapphire**
Deposition Angle	Young Modulus	As deposited	272	265
0	260	100°C	274	269
80	3.953	200°C	278	271
88	2.005	300°C	281	273

Refrences

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