Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

Phase stabilization in nitrogen-implanted nanocrystalline cubic zirconia

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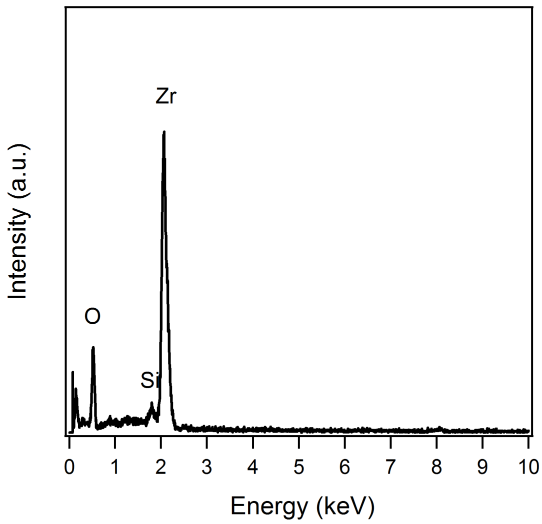

Fig. S1 Energy dispersive spectrum of the as-synthesized nitrogen-implanted ZrO_2 film.

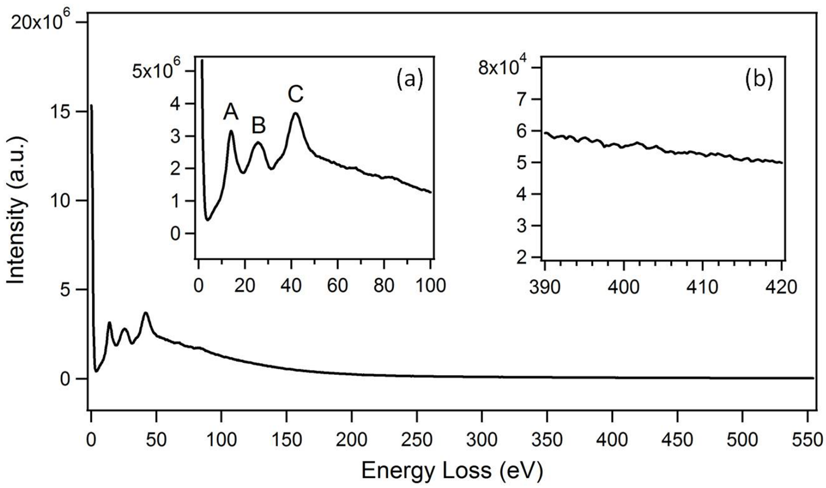

Fig. S2 Electron energy loss spectrum (EELS) of the as-synthesized nitrogen-implanted ZrO_2 film. The insets spectra are (a) the energy loss features corresponding to ZrO_2 and (b) the enlarged energy loss region where the nitrogen EELS signals are expected to appear. Figure (a) shows that the EELS spectrum agrees well with the reported EELS spectrum of zirconium oxide.[1, 2] The energy loss peak at about 14.1 eV (A) is likely associated with a transition between the oxygen 2*p* and 3*s* levels. The loss feature around 25.5 eV (B) corresponds to the excitation of a bulk plasmon. The predominant peak located around 41.7 eV (C) is attributed to an excitation of the Zr 4*p* level to a level 11 eV above E_F. Figure (b) shows no nitrogen signal detected in the EELS spectrum of the nitrogen-implanted ZrO_2 film.

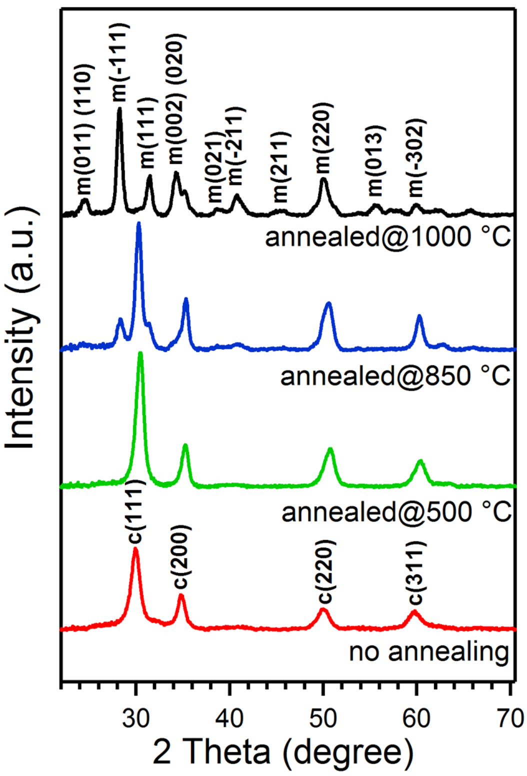

Fig. S3 X-ray diffraction patterns of N-implanted ZrO_2 films without annealing and after annealing at 500 ˚C, 850 ˚C and 1000 ˚C. The XRD experiments were performed only for the purpose of grain size analysis. The grain sizes of these ZrO_2 films were estimated using the Scherrer equation as summarized in Table S1. "c" and "m" denote cubic and monoclinic ZrO_2.

Table S1 Estimated average grain sizes of IBAD ZrO_2 films from XRD data (in Fig. S3). "c" and "m" denote cubic and monoclinic ZrO_2.

XRD Peaks	Grain Size (nm)		
	As-synthesized	Annealed @ 850 ˚C	Annealed@ 1000 ˚C
c-(111)	9.6	12.9	18.1
c-(200)	12.7	16.2	NA
c-(311)	8.0	13.0	NA
m-(-111)	NA	NA	19.3
m-(111)	NA	NA	16.3

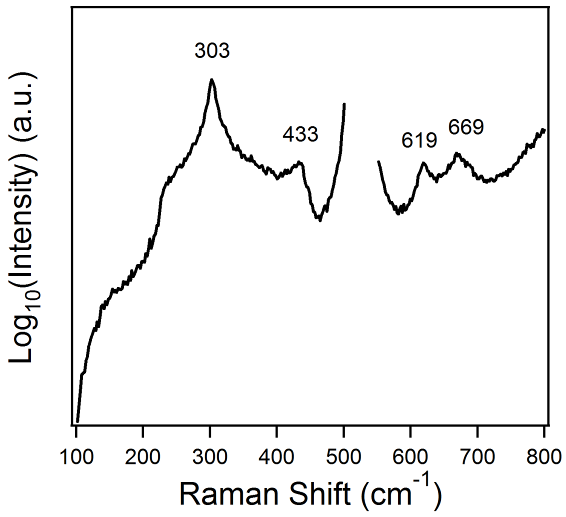

Fig. S4 Raman spectrum of a 200-nm thick silicon nitride film deposited on a (100) silicon wafer substrate.

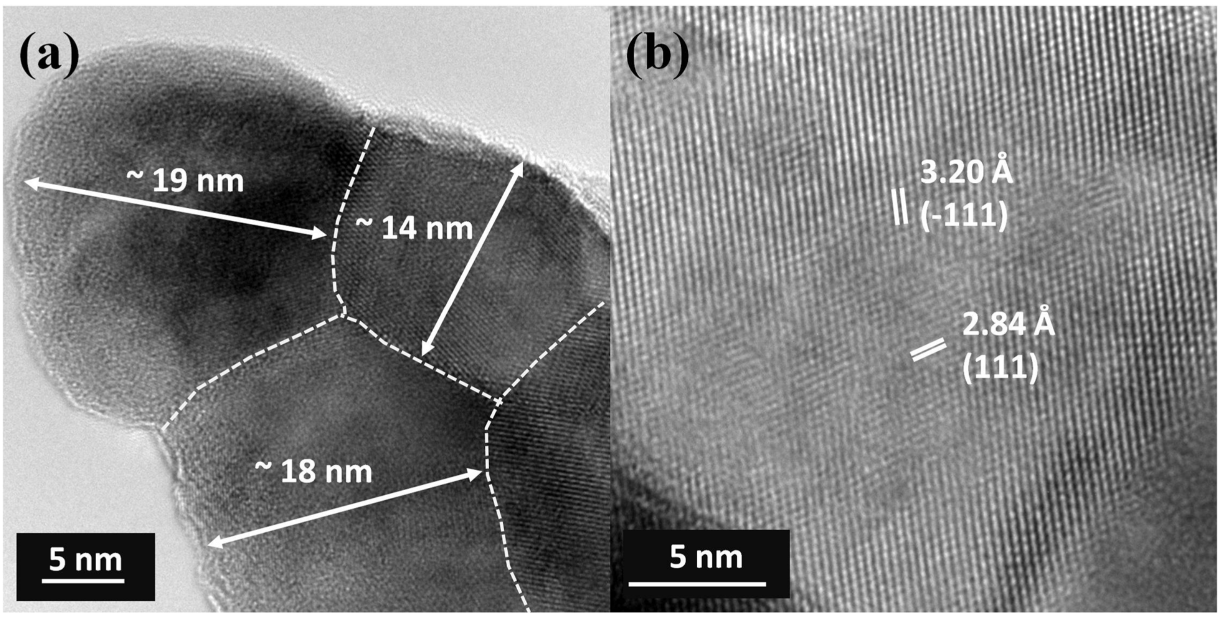

Fig. S5 TEM images of an IBAD ZrO_2 film after an 1-hour annealing at 1000 ˚C in air. (a) Bright field image showing the grain size estimation. (b) a zoom-in image showing the (-111) and (111) planes of a monoclinic phase ZrO_2 crystallite.

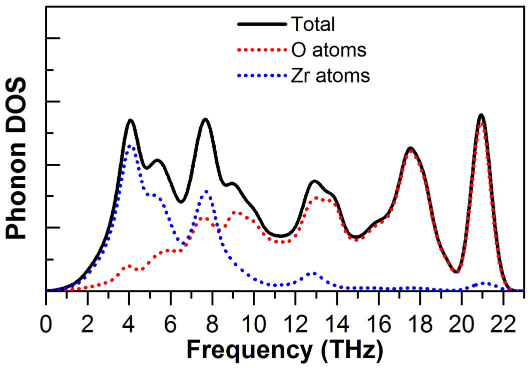

Fig. S6 Total and partial phonon density of states for O and Zr atoms in the tetragonal ZrO_2.

References

1. M. N. Mikheeva, V. G. Nazin, M. Y. Kuznetsov, E. G. Maksimov, S. S. Vasilevskii and M. V. Magnitskaya, *J. Exp. Thero. Phys.*, 2006, **102**, 453-465.
2. G. R. Corallo, D. A. Asbury, R. E. Gilbert and G. B. Hoflund, *Phys. Rev. B*, 1987, **35**, 9451-9459.