Materials Horizons

Supplementary Materials for

Growth of 2 cm metallic porous TiN single crystals

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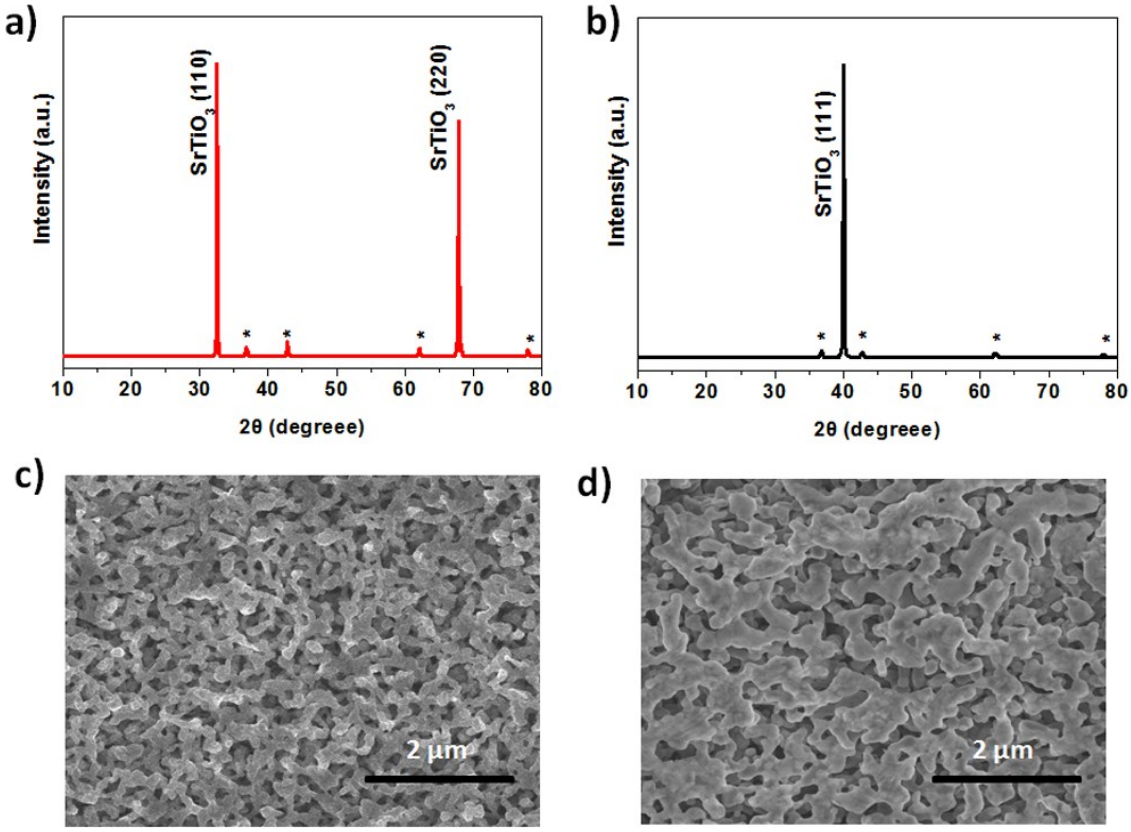

Fig. S1 XRD patterns and SEM image of porous TiN crystals grown on $SrTiO_3$. With 110 orientation (a, c and 111 orientation (b, d), at 333 mbar and a flow rate of 600 sccm of NH_3 for 20 hours at the growth temperature of 1300 ^oC. * stands for the diffraction peak of TiN crystals.

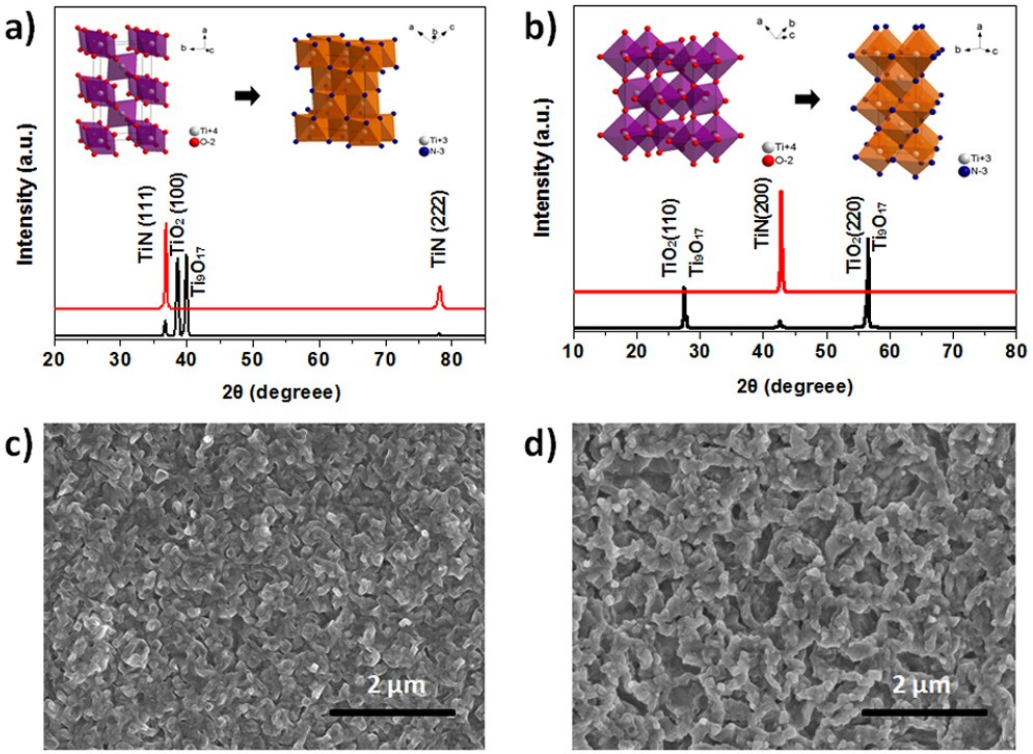

Fig. S2 XRD patterns and SEM image of porous TiN crystals grown on TiO_2. With 100 orientation (a, c) and 110 orientation (b, d), at 67 mbar and a flow rate of 1000 sccm of NH_3 for 20 hours at the growth temperature of 950 ^{o}C.

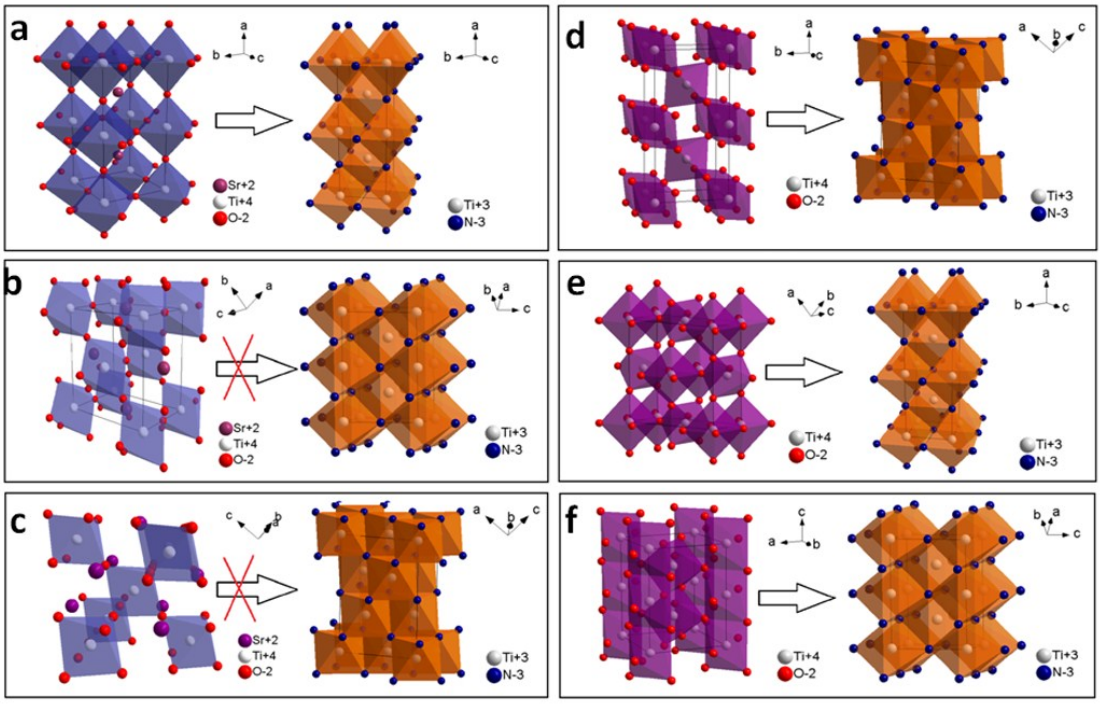

Fig. S3 Transformation characteristic TiN single crystals in relation to parent $SrTiO_3$ and TiO_2 crystals under nitridation conditions. The $SrTiO_3$ parent crystals (a) with [100] planes have been successfully converted into TiN crystals with [100] planes. The $SrTiO_3$ parent crystals (c and c) with [110] and [111] planes only harvested polycrystalline TiN. The TiO_2 parent crystals (d, e and f) with [100], [110] and [001] planes have been successfully converted into TiN crystals with [111], [100] and [110] planes, respectively

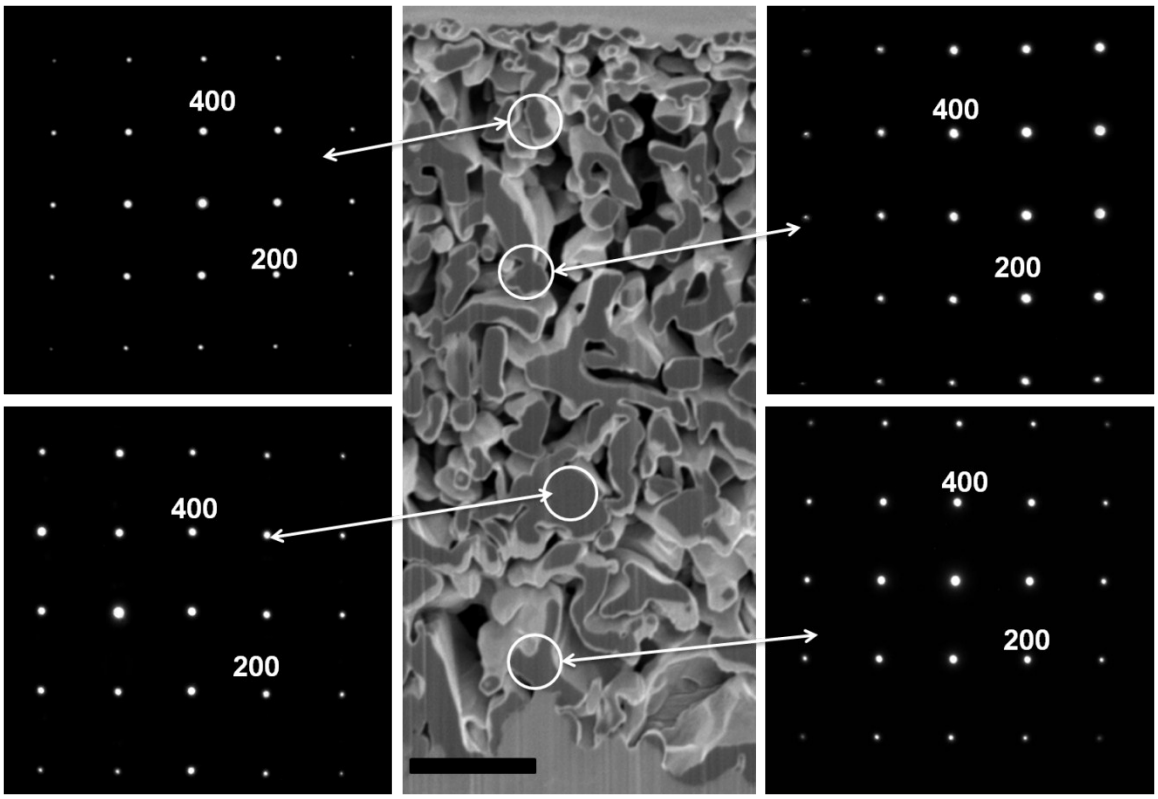

Fig. S4: Cross-sectional TEM characterization and corresponding four SEAD patterns at different locations of porous TiN film grown on a SrTiO3 (100) substrate. The scale bar is 1 μm.

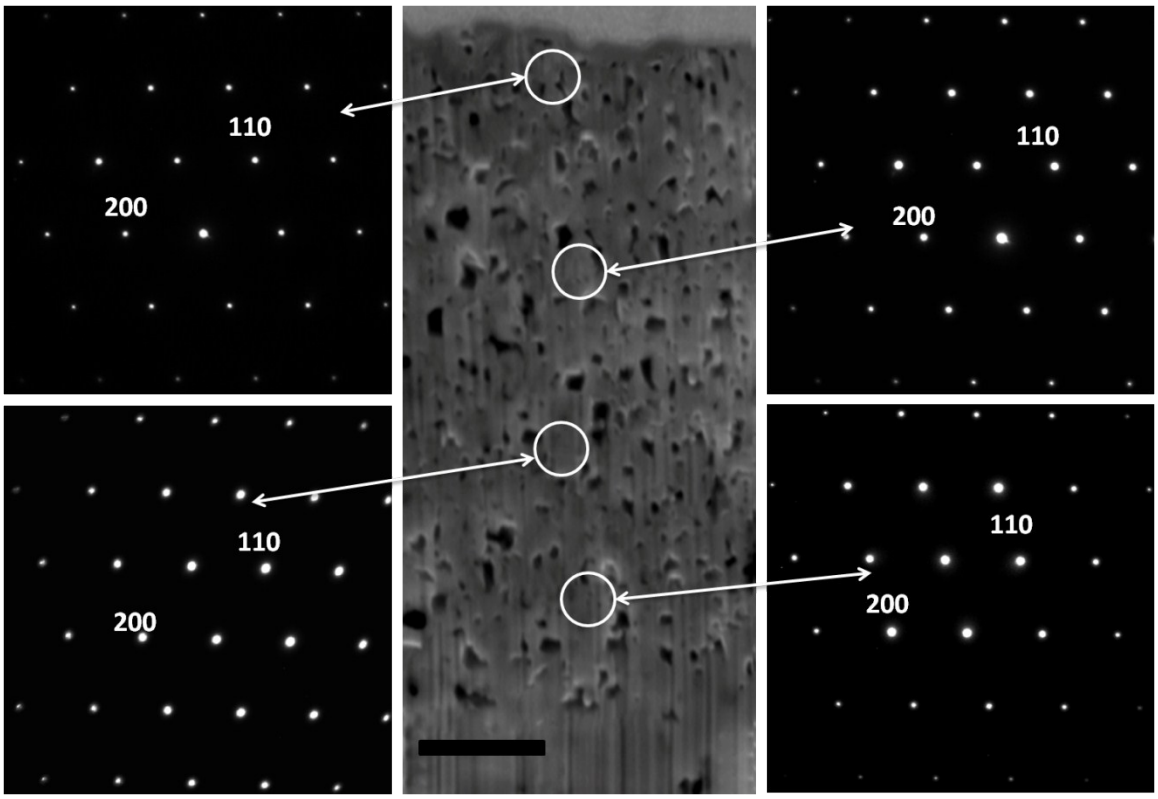

Fig. S5: Cross-sectional TEM characterization and corresponding four SEAD patterns at different locations of porous TiN film grown on a TiO_2 (001) substrate. The scale bar is 1 μm.

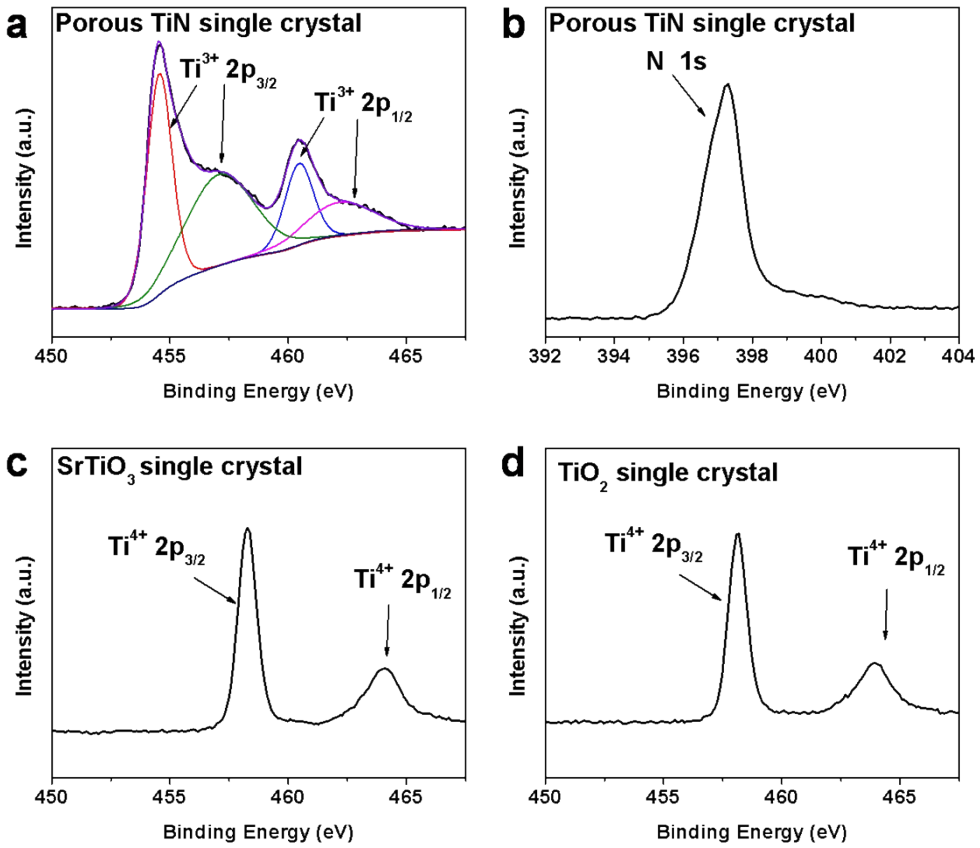

Fig. S6 XPS spectra of porous TiN, $SrTiO_3$ and TiO_2 single crystal. (a) Ti 2p peaks of porous TiN single crystal. (b) N 1s peak of porous TiN single crystal. (c) Ti 2p peaks of $SrTiO_3$ single crystal. (d) Ti 2p peaks of TiO_2 single crystal.

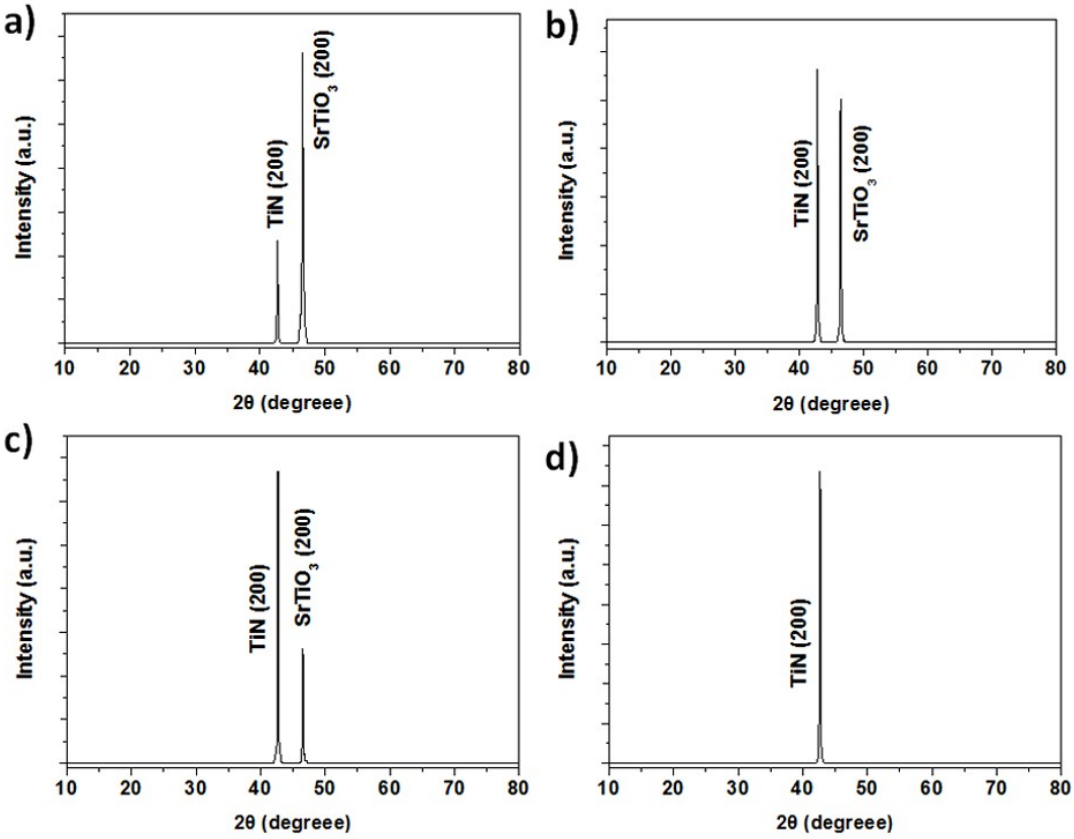

Fig. S7 XRD patterns of porous TiN crystals grown on (100) $SrTiO_3$ at 333 mbar and NH_3 flow rate of 600 sccm for 20 h at different temperature. (a) 1200 ^oC. (b) 1250 ^oC. (c) 1300 ^oC. (d) 1350 ^oC.

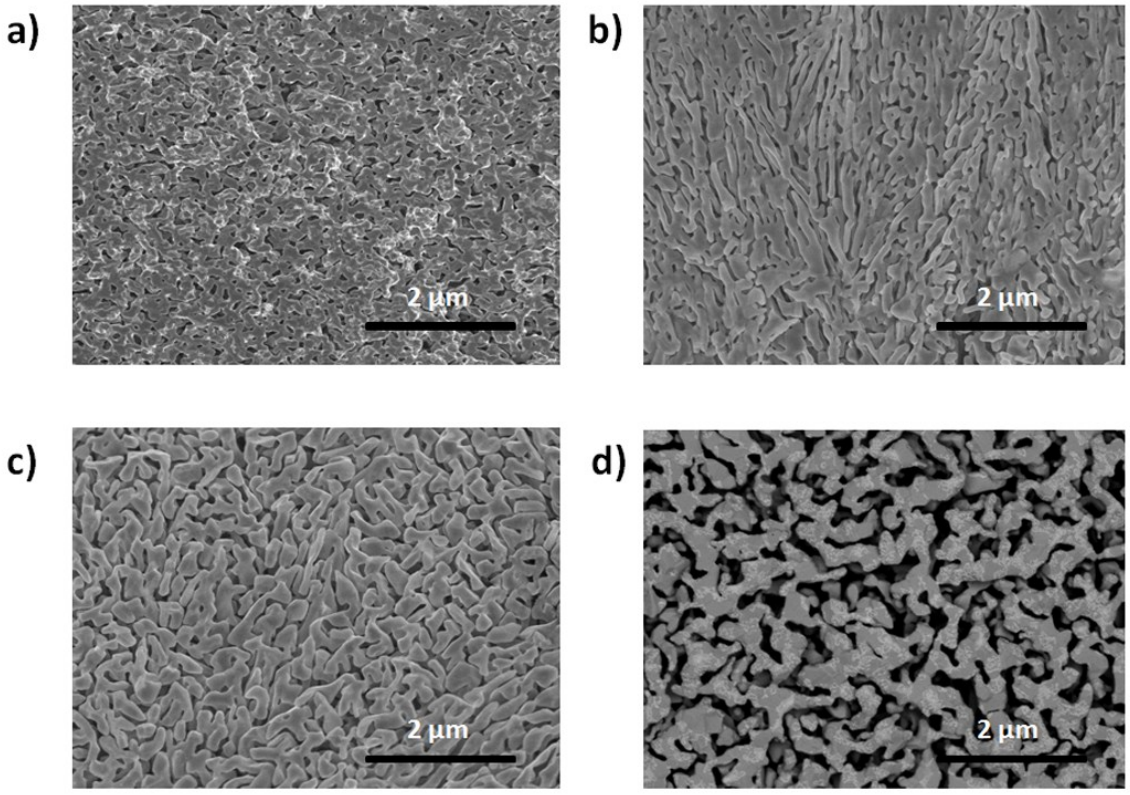

Fig. S8 SEM images of porous TiN crystals grown on (100) $SrTiO_3$ at 333 mbar and a flow rate of 600 sccm of NH_3 for 20 hours at different growth temperatures. (a) 1200 ^oC. (b) 1250 ^oC. (c) 1300 ^oC. (d) 1350 ^oC.

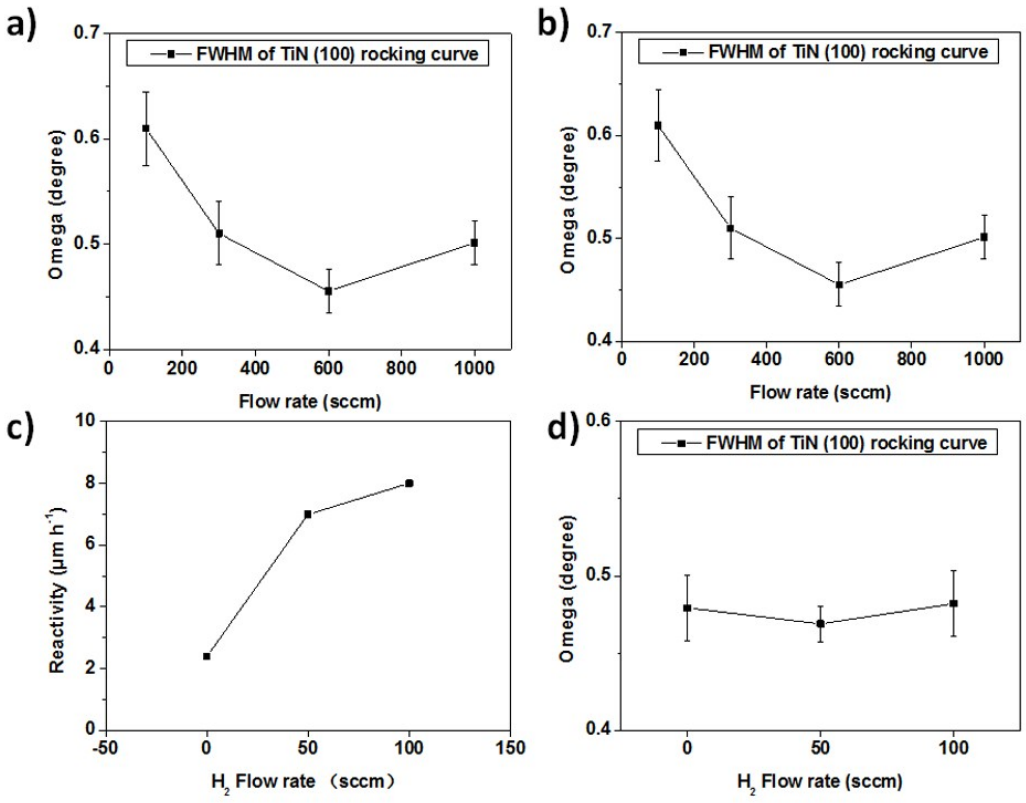

Fig. S9 (a) The crystal quality of TiN with increasing NH_3 flow rate from 100 sccm to 950 sccm at 1300 ^oC; (b) the crystal quality of TiN with increasing system pressure from 67 mbar to 1050 mbar at NH_3 flow rate of 950 sccm and 1300 ^oC; Adding appropriate ratio of H_2 gas to the ammonia flow was found to improve decomposition of $SrTiO_3$ and accelerate the conversion of TiN (c) without affecting the crystal quality (d).

Table S1. Transformation characteristic TiN single crystals in relation to parent $SrTiO_3$ and TiO_2 crystals under nitridation conditions.

Substrate	Orientation	Detected Phase	Orientation	Single Crystal	Porosity
$SrTiO_3$	100	TiN	100	Y	Y
$SrTiO_3$	110	TiN	Polycrystalline	N	Y
$SrTiO_3$	111	TiN	Polycrystalline	N	Y
TiO_2	100	TiN	111	Y	Y
TiO_2	110	TiN	100	Y	Y
TiO_2	001	TiN	110	Y	Y