

Mixed phase Ti^{3+} -rich TiO_2 thin films by oxide defect engineered crystallization

Supporting information

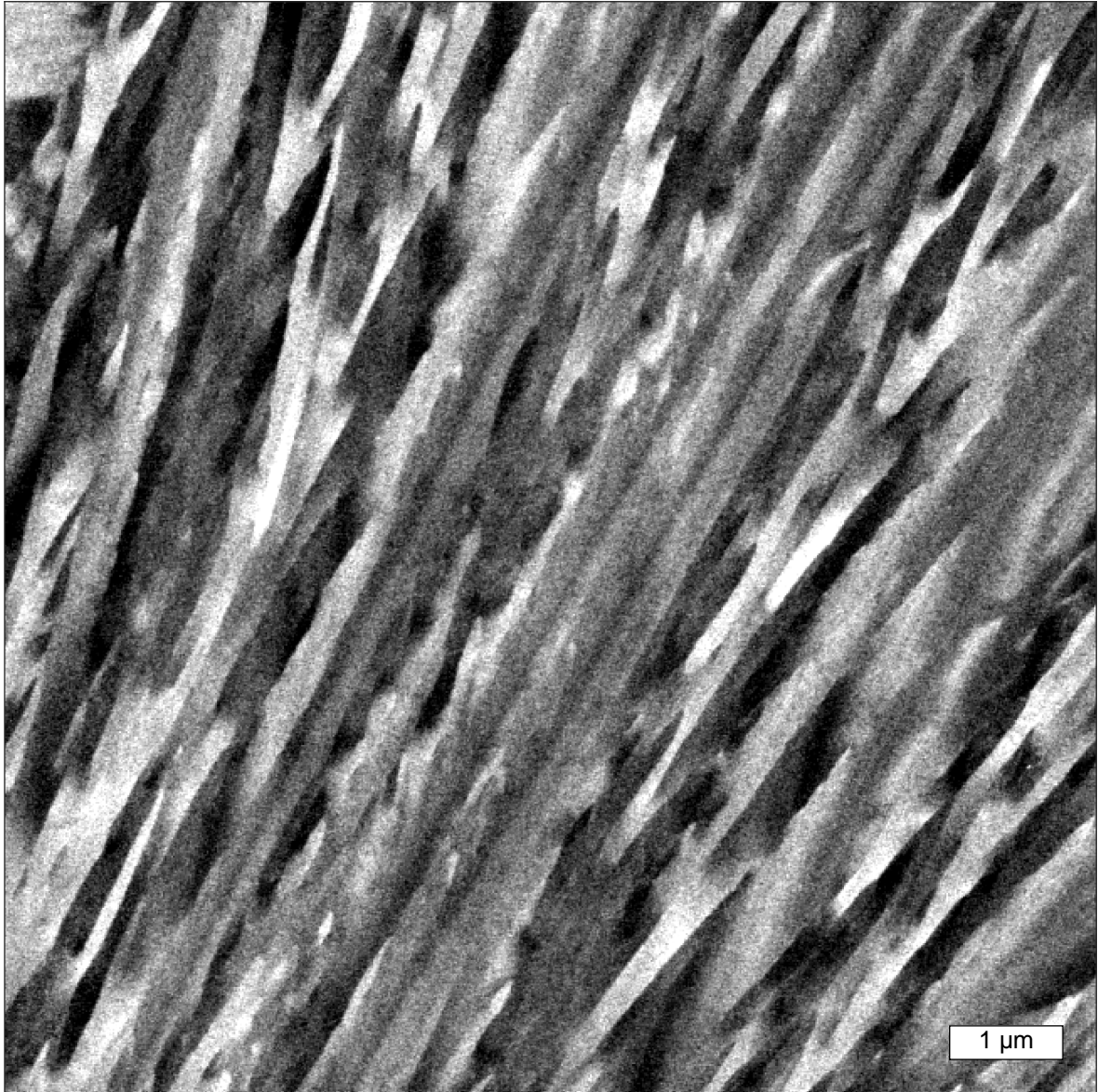
Lauri Palmolahti¹, Harri Ali-Löytty^{1,2*}, Markku Hannula¹, Tuomas Tinus¹, Kalle Lehtola¹,
Antti Tukiainen³, Jarno Reuna³, and Mika Valden^{1*}

¹Surface Science Laboratory, Physics Unit, Faculty of Engineering and Natural Sciences,
Tampere University, Tampere, Finland

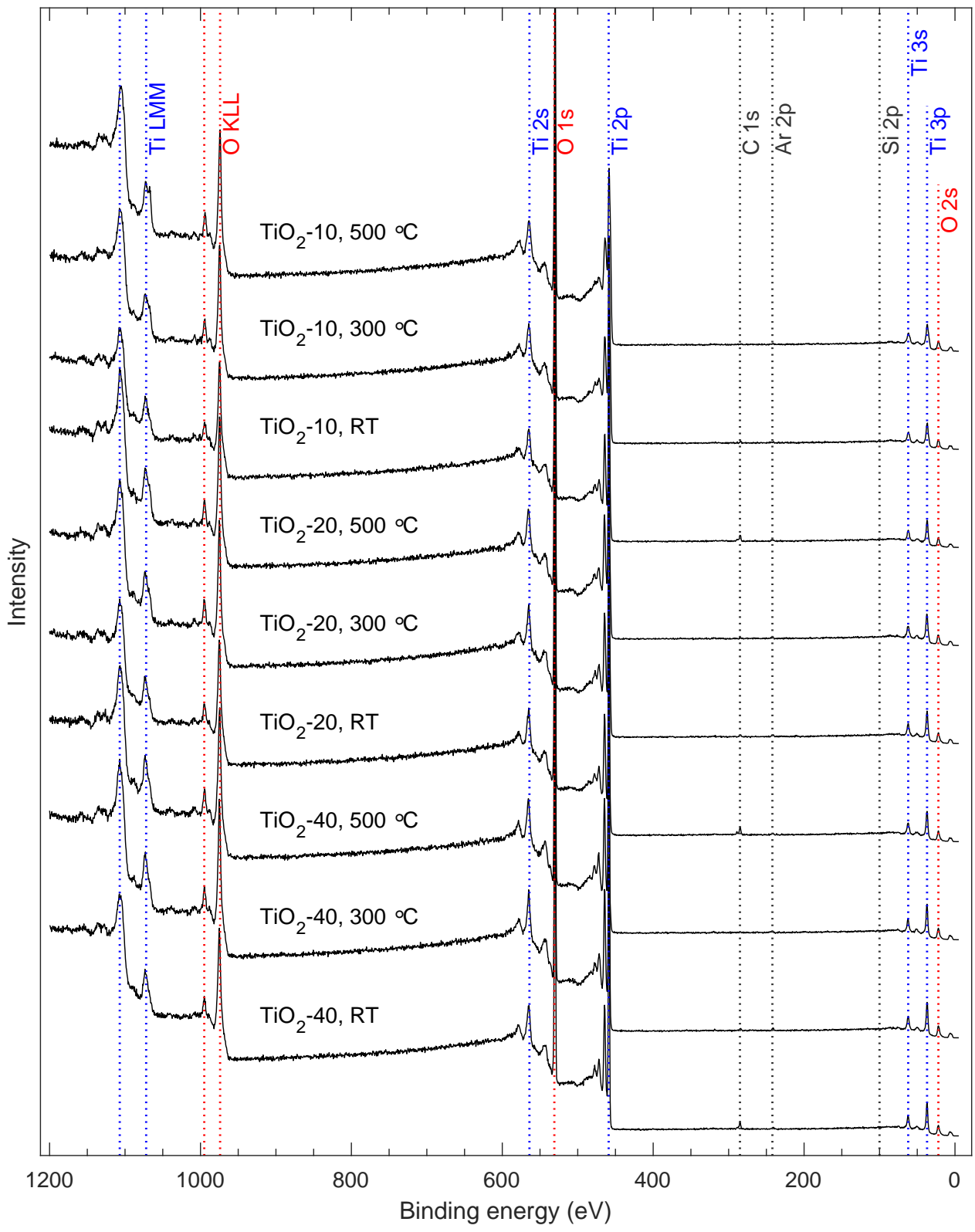
²Liquid Sun Ltd., Tampere, Finland

³Faculty of Engineering and Natural Sciences, Tampere University, Tampere, Finland

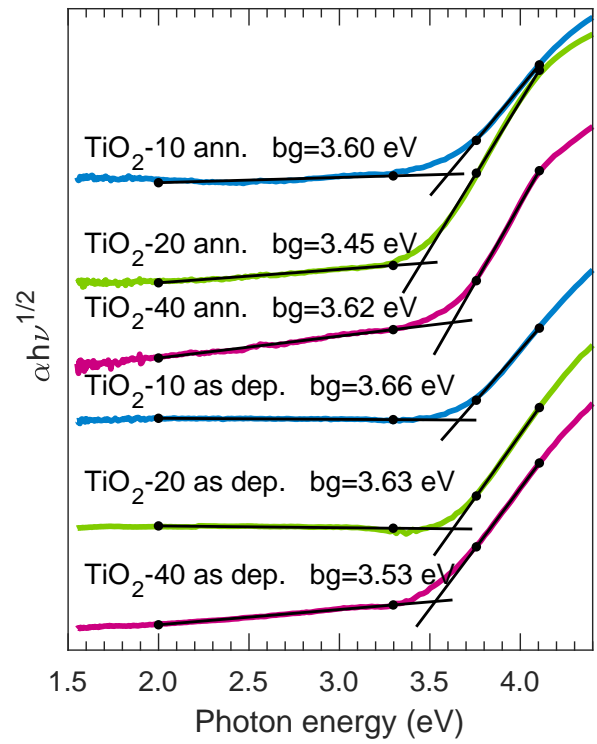
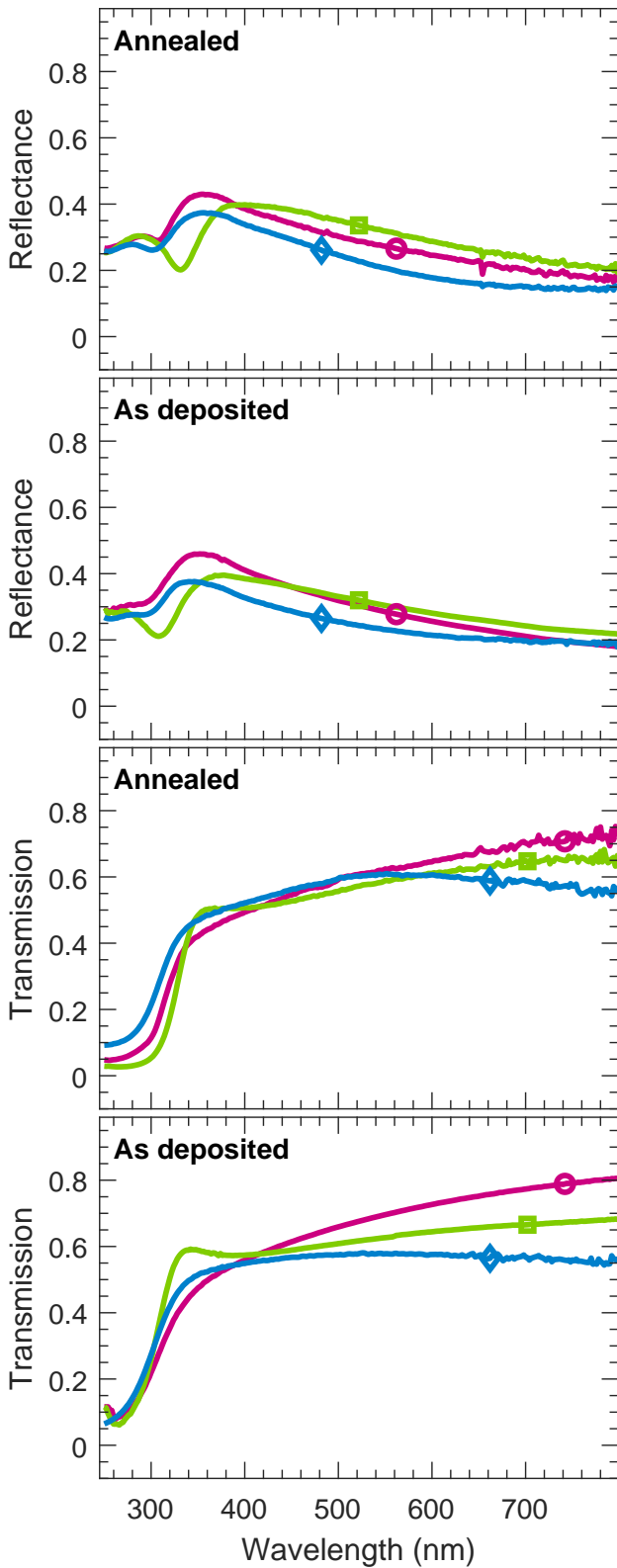
December 15, 2023



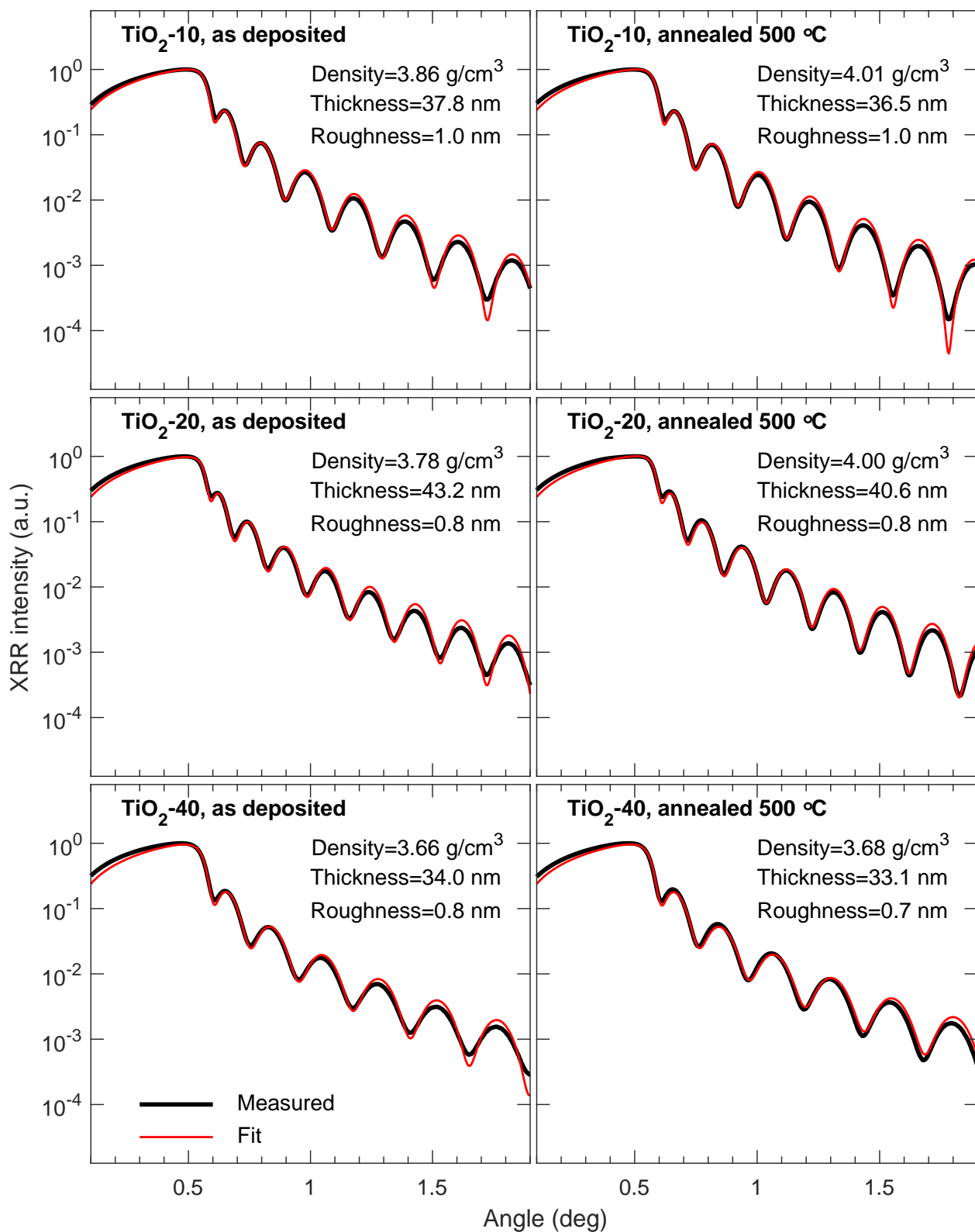
Supplementary Fig.1: SEM image of TiO₂-40 sample after vacuum annealing at 500 °C.



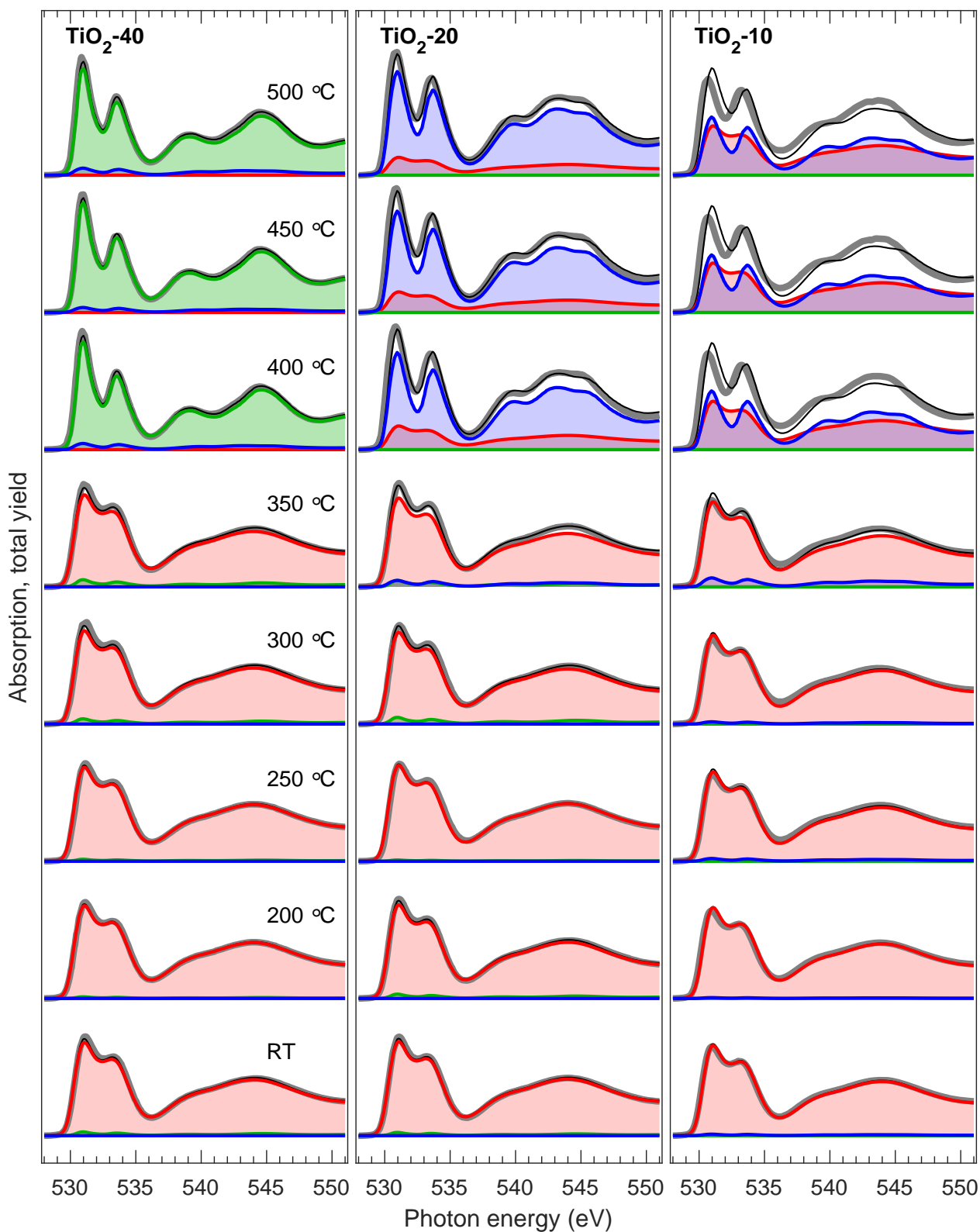
Supplementary Fig.2: XPS survey spectra from the cumulative vacuum annealing series using Al K α radiation ($E_p = 1486.6$ eV).



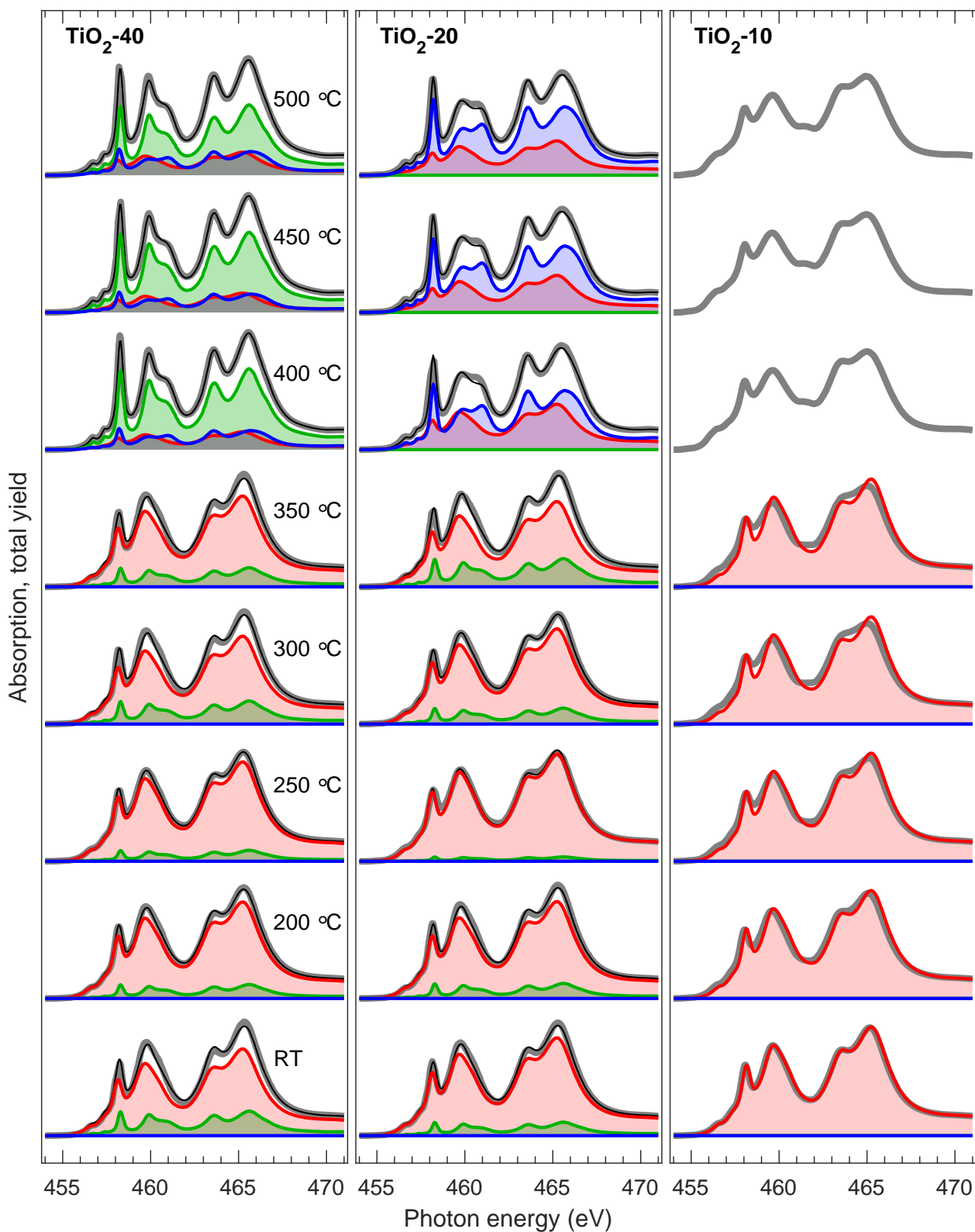
Supplementary Fig.3: Transmission and reflectance spectra of as deposited and 500 °C vacuum annealed samples (left) and Tauc plots calculated from the transmission and reflectance spectra (right).



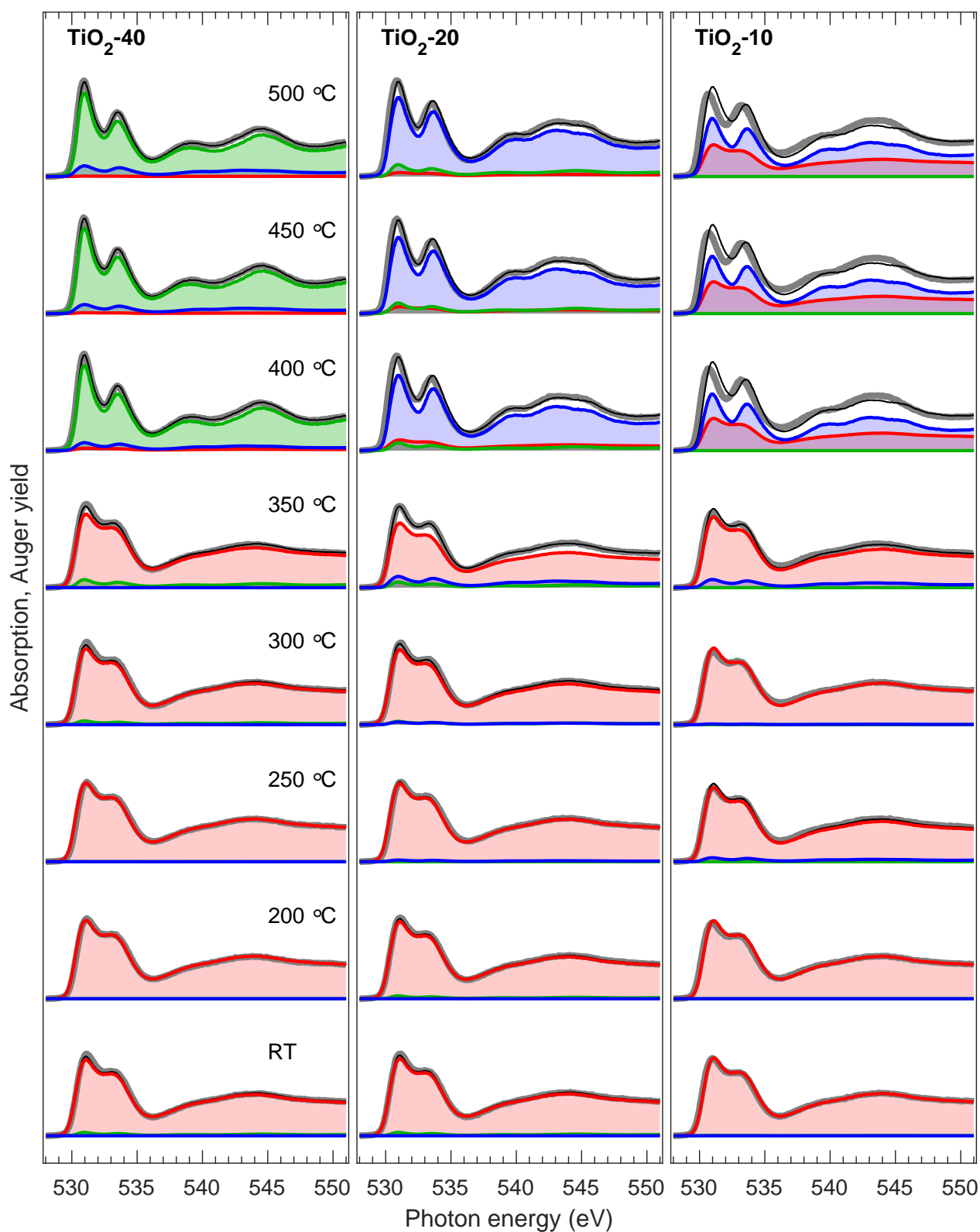
Supplementary Fig.4: X-ray reflection of as deposited samples and samples vacuum annealed at $500 \text{ }^\circ\text{C}$ (black line). The data was fitted with a model of TiO_2 - SiO_2 -Si layer structure (red line).



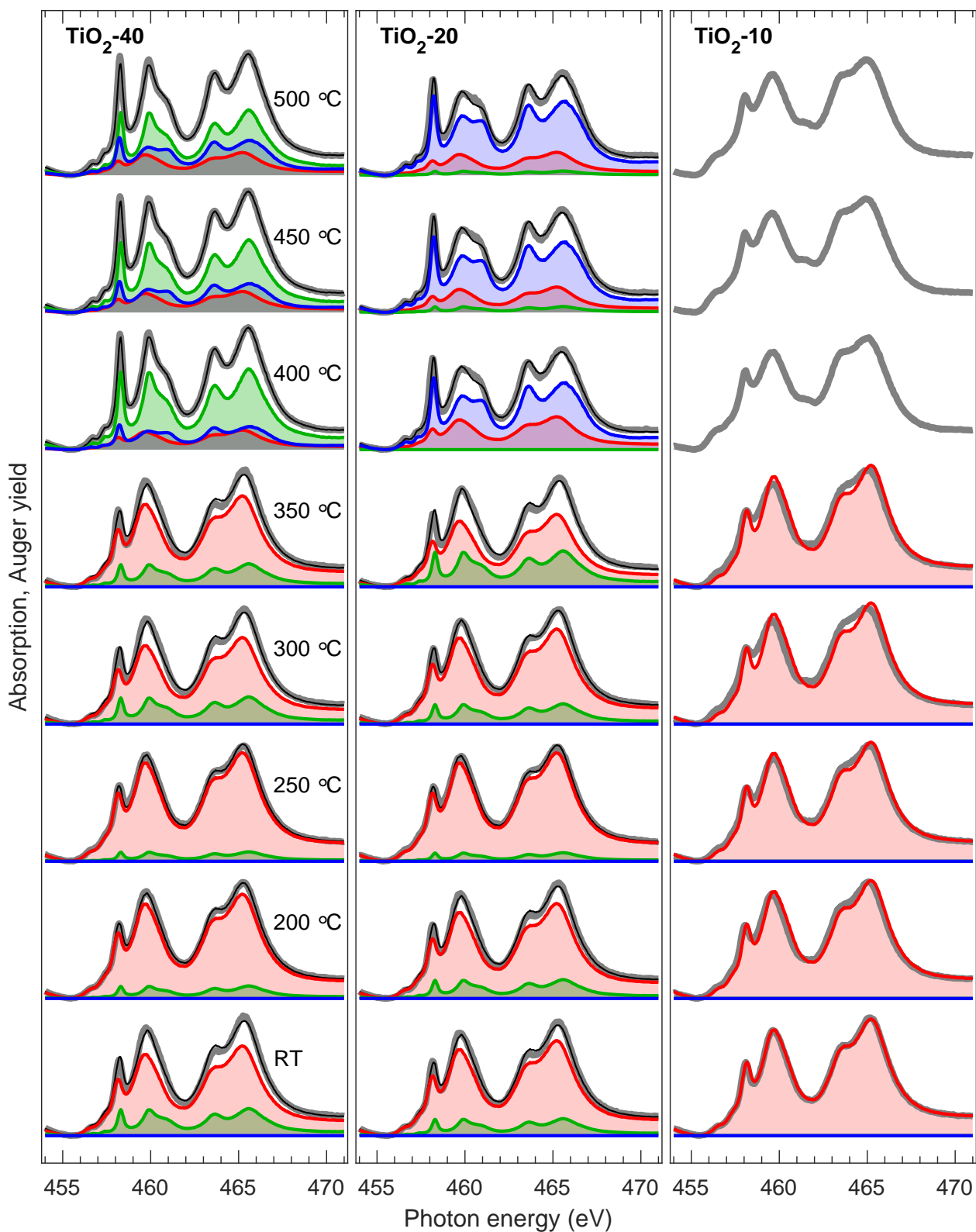
Supplementary Fig.5: X-ray absorption total electron yield spectra of O K-edge from the cumulative vacuum annealing series. The thick gray line represents the measured data. The spectra were fitted with amorphous (red), anatase (green) and rutile (blue) reference spectra and the thin black line is the sum of the fitted components.



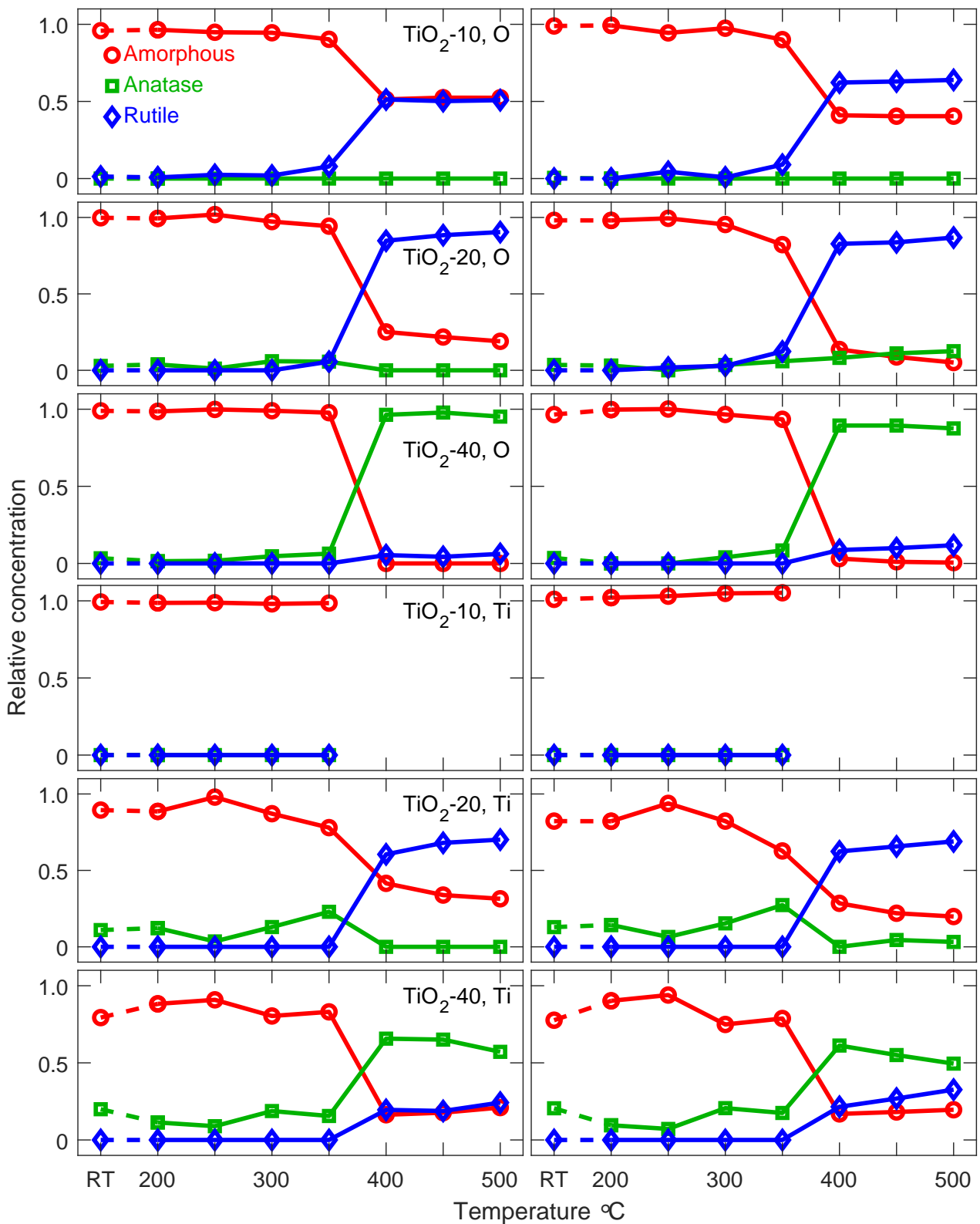
Supplementary Fig.6: X-ray absorption total electron yield spectra of Ti L-edge measured from the cumulative vacuum annealing series. The thick gray line represents the measured data. The spectra were fitted with amorphous (red), anatase (green) and rutile (blue) reference spectra and the thin black line is the sum of the fitted components.



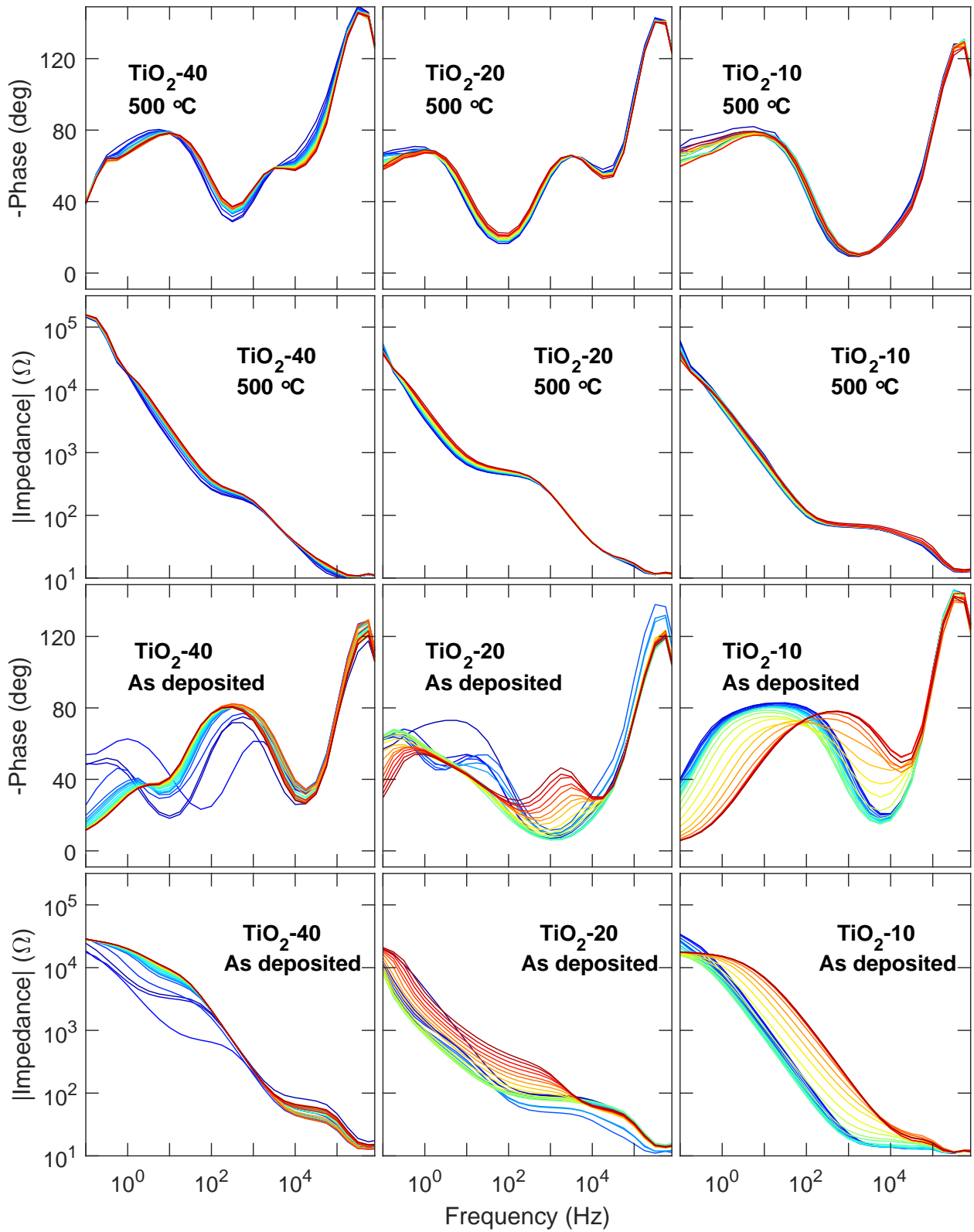
Supplementary Fig.7: X-ray absorption Auger electron yield spectra of O K-edge measured from the cumulative vacuum annealing series. The thick gray line represents the measured data. The spectra were fitted with amorphous (red), anatase (green) and rutile (blue) reference spectra and the thin black line is the sum of the fitted components.



Supplementary Fig.8: X-ray absorption Auger electron yield spectra of Ti L-edge measured from the cumulative vacuum annealing series. The thick gray line represents the measured data. The spectra were fitted with amorphous (red), anatase (green) and rutile (blue) reference spectra and the thin black line is the sum of the fitted components.



Supplementary Fig.9: Relative concentrations of amorphous (red), anatase (green), and rutile (blue) phases for TiO₂-40, TiO₂-20, and TiO₂-10 samples calculated from the Ti L-edge (labeled as Ti) and O K-edge (labeled as O) by fitting reference spectra to the measured spectra (Figure S5–S8) by least squares method. The left column shows the results of the bulk sensitive total yield measurements, and the right column shows the results of the more surface sensitive Auger yield measurements.



Supplementary Fig.10: The magnitude and phase of impedance measured with electrochemical impedance spectroscopy during stability tests in 1.0 M NaOH. For the as deposited samples the spectra are plotted from 1 h (blue) to 25 h (red) with 1 h increments, whereas for the 500 °C vacuum annealed samples the spectra are plotted from 4 h (blue) to 80 h (red) with 4 h increments.