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Orientation-dependent chemistry and band-bending of Ti on polar ZnO surfaces

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1 Zn LMM/Ti *2p* ratio by XPS

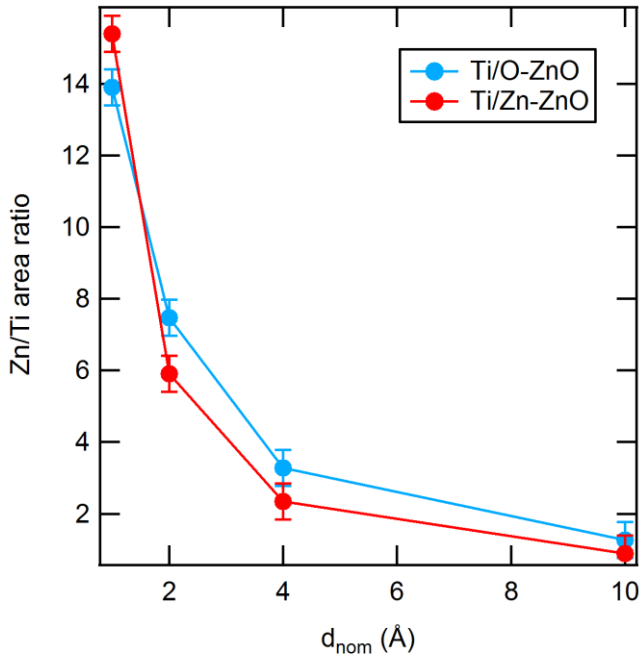

Figure S1 *Zn $L_2M_{45}M_{45}$/Ti* 2p *area ratio as a function of nominal Ti thickness dnom as measured on a quartz microbalance. The blue and red curves correspond to Ti/O-ZnO and Ti/Zn-ZnO, respectively.*

2 Fit procedure of Ti *2p* spectra

Due to their proximity in energy, the fit of the Ti *2p* spectra is performed together with that of the Zn $L_2M_{45}M_{45}$ spectra using CasaXPS software (Figure S2-S4).[1] Ti *2p*-Zn $L_2M_{45}M_{45}$ spectra are normalized to the same background in the low binding energy range (BE ~445 eV). The Ti *2p* and Zn

$L_2M_{45}M_{45}$ spectra are fitted using a Shirley background, a set of pseudo-Voigt functions for the Ti^{4+}, Ti^{3+}, Ti^{2+} and Auger components and a Doniach-Sunjic line profile for the metallic Ti^{0} component. In the following, the GL parameter indicates the Gaussian/Lorentian mixing (0 is a pure Gaussian, 100 is a pure Lorentian), while *a* indicates the asymmetry parameter of the Doniach-Sunjinc function.[1]

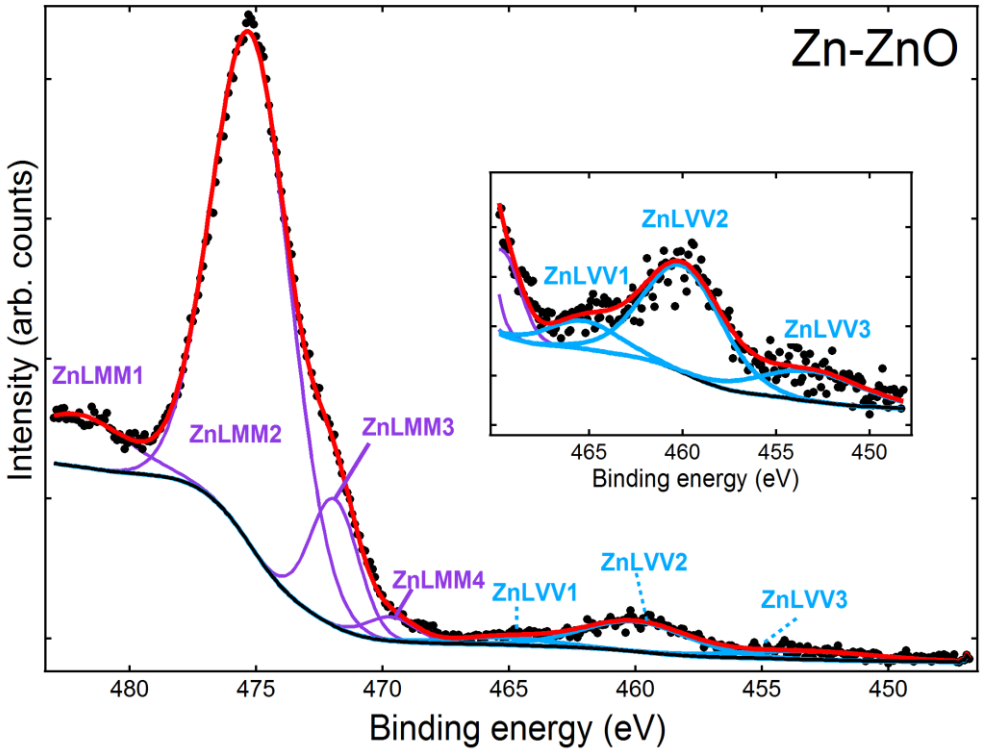

Figure S2 *Fit of the Zn L2M45M45 spectrum of clean Zn-ZnO. In the inset, the region corresponding to Zn LVV components is magnified.*

	BE(eV)	**FWHM**	**Area Ratio***
ZnLMM1	481.99	4.5	0.14
ZnLMM2	474.99	3.6	1.00
ZnLMM3	471.88	2.2	0.34
ZnLMM4	469.78	3.0	0.12
ZnLVV1	465.27	4.5	0.03
ZnLVV2	459.98	4.9	0.10
ZnLVV3	453.11	6.5	0.03

Table S1 *Fitting parameters of the Zn L2M45M45 spectrum of clean Zn-ZnO shown in Figure S2.* **Area Ratio between the selected component and Zn LMM2.*

Regarding the Zn $L_2M_{45}M_{45}$ spectra, the spectra of clean ZnO are well reproduced by four components. Their energy distance and intensity ratio reproduce in a satisfactory way the multiplet structure of the Auger transitions Zn $L_2M_{45}M_{45}$ calculated for Zn.[2–4] As an example, the decomposition of the spectrum of clean Zn-ZnO is shown in Figure S2. Since the Zn $L_2M_{45}M_{45}$ spectra of Ti/ZnO contain the Auger components of both metallic Zn and ZnO, each one with its proper BE and FWHM, some simplifications in the fitting procedure are needed:

- The total number of components is fixed to four, covering all the BE range expected from the metallic and oxidized Zn.
- The overall FWHM of each peak is inferred from the analysis of the clean surface spectrum and kept constant across the spectra series (Table S1).
- To simplify the deconvolution, the GL is maintained fixed to the same value for all the peaks. The best value given by the fit is 50.

In the spectrum of clean Zn-ZnO, three less intense components (named Zn LVV1, Zn LVV2, Zn LVV3 in Figure S2) are also observed in the low binding energy side, which are shifted 12 eV from the main component Zn LMM2. These components are also found in the low binding energy side of Zn $L_3M_{45}M_{45}$ spectra with similar BE shifts and intensity ratios relative to the main component Zn LMM2. They do not depend on the sample orientation or quality, as we have observed them on several ZnO crystals of different orientations. Because of their relative intensity and energy with respect to the Zn LMM spectra and in the absence of literature, they are tentatively assigned to the Zn LVV transitions, *i.e.* the Auger transition involving the Zn states close to the *Fermi* level. Since in the spectra of Ti/ZnO they overlap with Ti 2p components, the analysis is simplified by assuming that the intensity ratios between the LVV components and the Zn LMM2 component are constant and correspond to the values found for the spectra of the clean surfaces (Table S1).

Zn-ZnO	d = 1 Å		d = 2 Å		d = 4 Å		d = 10 Å	
	BE (eV)	Area	BE (eV)	Area	BE (eV)	Area	BE (eV)	Area
Ti^{4+}	458.83	955	458.76	837	458.44	831	458.44	816
Ti^{3+}	457.26	267	457.26	582	457.84	864	456.74	952
Ti^{2+}	455.65	123	455.65	336	455.23	1095	455.13	2108
Ti^{0}	--	--	454.35	200	454.11	790	453.86	4760

O-ZnO	d = 1 Å		d = 2 Å		d = 4 Å		d = 10 Å	
	BE (eV)	Area	BE (eV)	Area	BE (eV)	Area	BE (eV)	Area
Ti^{4+}	458.62	505	458.60	568	458.60	531	458.10	441
Ti^{3+}	457.09	297	457.07	690	457.07	738	456.60	663
Ti^{2+}	455.46	242	455.49	850	455.42	1541	454.89	2062
Ti^{0}	--	--	454.21	596	454.13	2183	453.66	6322

Table S2 *BE and peak area of the Ti $2p_{3/2}$ components as induced by the fit of Ti 2p spectra shown in Figure S3 and S4.*

Regarding the Ti *2p* components, the FWHM, GL, *a* values of the Ti $2p_{1/2}$ and Ti $2p_{3/2}$ components are kept constant across the spectra series [FWHM(Ti^0 $2p_{1/2}$)=2.1 eV, FWHM(Ti^0 $2p_{3/2}$)=1.4 eV, FWHM($Ti^{2+,3+,4+}$ $2p_{1/2}$)=2.8 eV, FWHM($Ti^{2+,3+,4+}$ $2p_{3/2}$)=1.7 eV, GL=85, α(Ti^0 $2p_{1/2}$)=0.08, α(Ti^0 $2p_{2/2}$)=0.04)]. The chemical shift between the Ti components (Table S2) and the spin orbit splitting for Ti^{4+}, Ti^{3+},Ti^{2+} and Ti0 (which is set to 5.6, 5.7, 5.7 and 6.1 eV, respectively) are in accordance with literature.[5] The branching ratio between Ti $2p_{1/2}$ and Ti $2p_{3/2}$ components is set to 0.55. The BE and the peak area of the Ti $2p_{3/2}$ components are left as free parameters of the fit (see Table S2). The error on the BE and on the peak area corresponds to ± 0.05 eV and ± 10%, respectively. Finally, in

the low binding energy side of Ti *2p* spectra a component is added to take into the account the photoemission of Ti *2p* level from the Al K$\alpha_{3,4}$ line.[6]

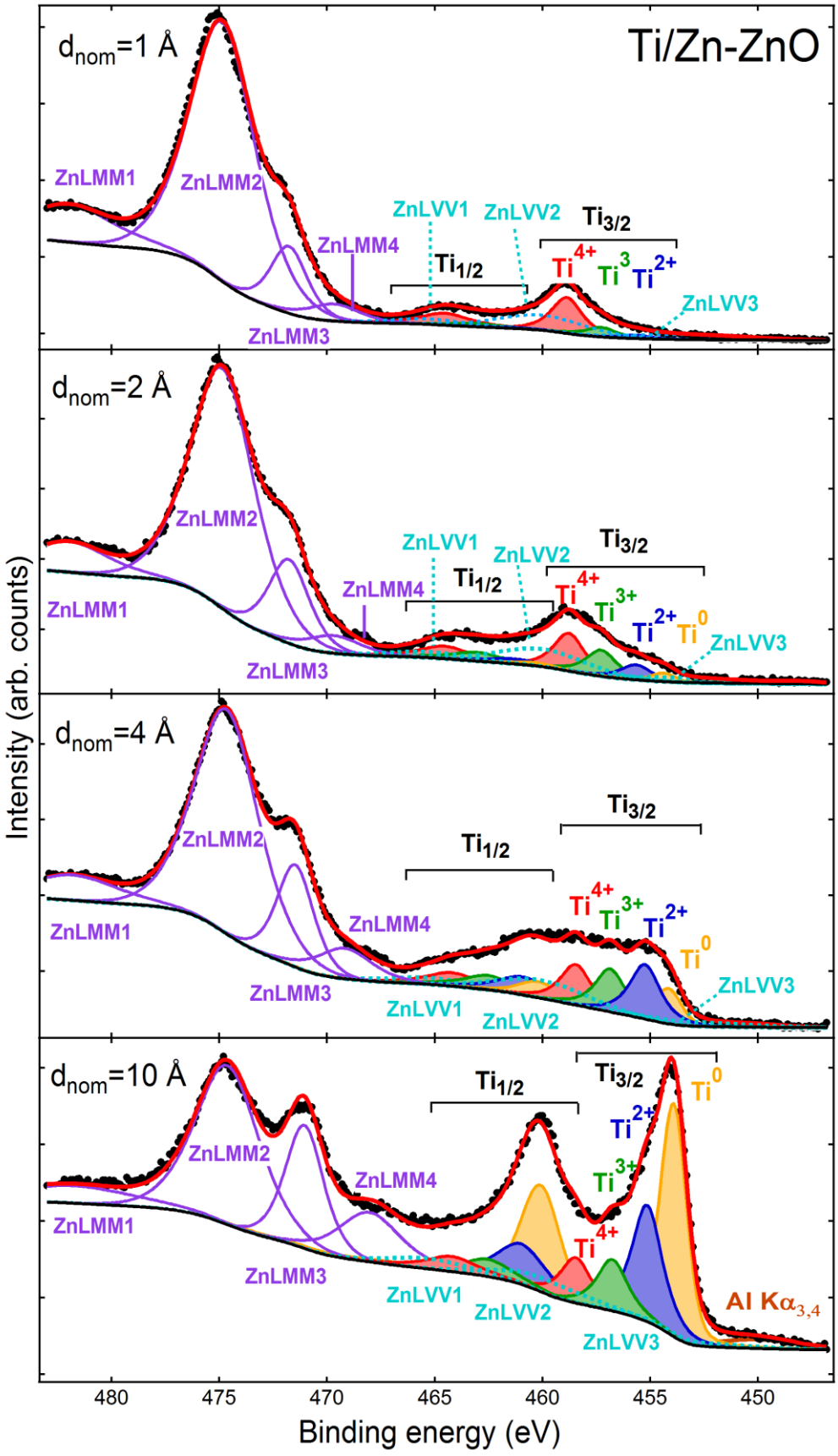

Figure S3 *Fit of the Zn $L_2M_{45}M_{45}$-Ti* 2p *spectra of Ti/Zn-ZnO.*

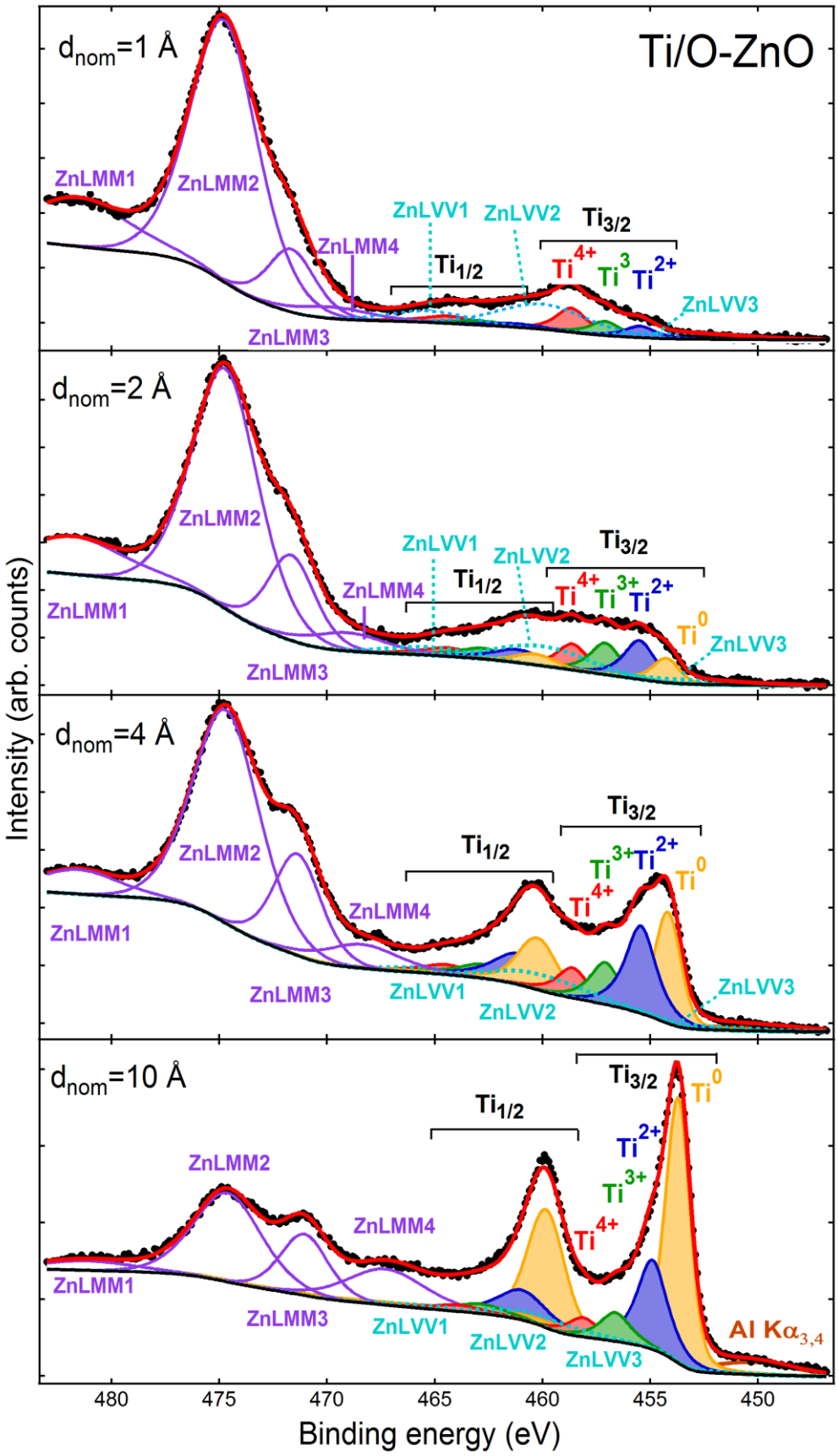

Figure S4 *Fit of the Zn* $L_2M_{45}M_{45}$*-Ti* 2p *spectra of Ti/O-ZnO.*

References

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