

Structural, optical, and magnetic properties of Ar⁺, Mn⁺ and Ag⁺ ions implanted ZnO thin films: effect of implantation dose and stopping energy

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Supplementary Information

Section S1: Calculation of crystallite size “D” and lattice parameter “c”

The crystallite size “D” is estimated as follows

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

Where, λ is wavelength of radiation used. β is full width at half maximum for most intense peak, θ is Bragg angle.

The lattice parameters, c , of these films were calculated using the relation,

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

where (h,k,l) are the miller indices of a plane, d the interplanar spacing, and a and c are the lattice constants of unit cells. The lattice parameter, c , was derived from the (002) peak of the XRD patterns.

Table S1: Parameters used for simulation of RBS spectra of implanted films.

Ions	Dose (ions/cm ²)	Thickness (Å)	Composition ratio		M ⁺ (Ar/Mn/Ag)	Areal density of Zn (×10 ¹⁵ /cm ²)
			Zn	O		
No	Pristine	1380	1	1		
Ar ⁺	1×10 ¹³	1205	1	1	low	4550
	1×10 ¹⁴	1164	1	1	low	4389
	1×10 ¹⁵	1156	1	1	0.01	4360
	2×10 ¹⁶	1101	1	1	0.04	4144
Mn ⁺	1×10 ¹³	1114	1	1	overlap	4215
	1×10 ¹⁴	1151	1	1	overlap	4361
	1×10 ¹⁵	1159	1	1	overlap	4392
	2×10 ¹⁶	1106	1	1	overlap	4185
Ag ⁺	1×10 ¹³	1161	1	1	low	4399
	1×10 ¹⁴	1172	1	1	low	4444
	1×10 ¹⁵	1159	1	1	0.001	4389
	2×10 ¹⁶	1000	1	1	0.002	3776

Table S2: Main edge energy and spectral features in Zn *K*-edge NEXAFS spectra.

Ions	Dose (ions/cm²)	Main Edge Energy (eV)	a₁	b₁	c₁
Ar⁺	Pristine	9659.8	9667.8	9679.0	9713.8
	1×10 ¹³	9659.9	9668.2	9679.7	9712.9
	1×10 ¹⁴	9659.8	9667.8	9679.4	9713.0
	1×10 ¹⁵	9659.9	9667.8	9679.4	9713.8
	2×10 ¹⁶	9659.8	9668.2	9679.4	9713.8
Mn⁺	1×10 ¹³	9660.0	9667.8	9679.8	9713.8
	1×10 ¹⁴	9659.9	9667.8	9679.8	9713.0
	1×10 ¹⁵	9659.9	9667.8	9679.4	9713.0
	2×10 ¹⁶	9659.9	9667.8	9679.8	9713.8
Ag⁺	1×10 ¹³	9659.8	9667.8	9679.4	9713.0
	1×10 ¹⁴	9659.8	9667.8	9679.4	9713.0
	1×10 ¹⁵	9660.0	9668.1	9679.8	9713.8
	2×10 ¹⁶	9659.8	9667.8	9679.4	9713.8

Table S3: Simulated parameters from EXAFS spectra for Ar⁺ implanted ZnO films. N is coordination number, R is bonding length, and σ^2 is Debye-Waller factor.

Path	Parameters	Pristine	1×10^{13} (ions/cm ²)	1×10^{14} (ions/cm ²)	1×10^{15} (ions/cm ²)	2×10^{16} (ions/cm ²)
Zn-O (I)	N	4.2±0.9	3.9±0.4	4.0±0.5	3.9±0.4	3.8±0.4
	R (Å)	1.97±0.01	1.98±0.03	1.98±0.04	1.97±0.03	1.97±0.03
	σ^2 (Å ²)	0.006±0.004	0.004	0.005	0.004	0.004
Zn-Zn (I)	N	4.9±1.5	5.4±1.1	5.6±1.3	5.2±1.1	4.9±1.1
	R (Å)	3.14±0.02	3.30±0.001	3.3±0.11	3.29±0.10	3.31±0.12
	σ^2 (Å ²)	0.001	0.001	0.001	0.001	0.001
Zn-Zn (II)	N	6.0±1.5	4.9±1.2	5.2±1.4	4.7±1.2	5.5±1.2
	R (Å)	3.29±0.02	3.15±0.005	3.15±0.004	3.15±0.003	3.16±0.01
	σ^2 (Å ²)	0.001	0.001	0.001	0.001	0.002
Zn-O (II)	N	8.2±2.4	8.9±2.5	8.4±2.9	8.6±2.6	7.8±2.3
	R (Å)	3.78±0.03	3.79±0.05	3.79±0.05	3.78±0.04	3.79±0.05
	σ^2 (Å ²)	0.001	0.003	0.002	0.003	0.003
	ϵ_0 (eV)	5.2	6.0	6.0	6.0	6.0
	R-factor	0.05	0.04	0.05	0.04	0.03

Table S4: Simulated parameters from EXAFS spectra for Mn⁺ implanted ZnO films.

Path	Parameters	Pristine	1×10^{13} (ions/cm ²)	1×10^{14} (ions/cm ²)	1×10^{15} (ions/cm ²)	2×10^{16} (ions/cm ²)
Zn-O (I)	N	4.2±0.9	4.1±0.5	3.9±0.5	3.9±0.5	3.7±0.5
	R (Å)	1.97±0.01	1.98±0.04	1.98±0.04	1.98±0.04	1.99±0.04
	σ^2 (Å ²)	0.006±0.004	0.005	0.004	0.004	0.004
Zn-Zn (I)	N	4.9±1.5	5.7±1.2	5.8±1.3	5.8±1.3	5.8±1.3
	R (Å)	3.14±0.02	3.31±0.011	3.3±0.11	3.31±0.12	3.2±0.12
	σ^2 (Å ²)	0.001	0.001	0.001	0.001	0.001
Zn-Zn (II)	N	6.0±1.5	5.7±1.4	5.7±1.4	5.6±1.3	5.4±1.3
	R (Å)	3.29±0.02	3.16±0.01	3.15±0.004	3.16±0.01	3.16±0.01
	σ^2 (Å ²)	0.001	0.002	0.002	0.001	0.002
Zn-O (II)	N	8.2±2.4	8.5±2.5	7.7±2.5	8.4±2.7	8.4±2.9
	R (Å)	3.78±0.03	3.80±0.06	3.80±0.06	3.80±0.06	3.82±0.08
	σ^2 (Å ²)	0.001	0.002	0.001	0.003	0.003
ϵ_0 (eV)		5.2	6.0	6.0	6.0	6.0
R-factor		0.05	0.04	0.05	0.05	0.05

Table S5: Simulated parameters from EXAFS spectra for Ag⁺ implanted ZnO films.

Path	Parameters	Pristine	1×10¹³ (ions/cm²)	1×10¹⁴ (ions/cm²)	1×10¹⁵ (ions/cm²)	2×10¹⁶ (ions/cm²)
Zn-O (I)	N	4.2±0.9	4.0±0.9	3.9±0.5	3.7±0.5	3.5±0.4
	R (Å)	1.97±0.01	1.98±0.04	1.98±0.04	2.00±0.06	1.98±0.04
	σ ² (Å ²)	0.006±0.004	0.004	0.004	0.004	0.003
Zn-Zn (I)	N	4.9±1.5	6.0±1.3	6.1±1.3	6.2±1.2	6.0±1.2
	R (Å)	3.14±0.02	3.31±0.12	3.3±0.11	3.34±0.15	3.32±0.13
	σ ² (Å ²)	0.001	0.001	0.001	0.001	0.001
Zn-Zn (II)	N	6.0±1.5	6.0±1.4	5.8±1.4	6.1±1.2	6.1±1.3
	R (Å)	3.29±0.02	3.16±0.01	3.16±0.008	3.19±0.04	3.17±0.02
	σ ² (Å ²)	0.001	0.002	0.002	0.001	0.002
Zn-O (II)	N	8.2±2.4	7.5±2.4	7.7±2.4	9.2±2.7	6.6±2.3
	R (Å)	3.78±0.03	3.81±0.07	3.80±0.06	3.86±0.12	3.82±0.08
	σ ² (Å ²)	0.001	0.001	0.001	0.003	0.001
ε₀ (eV)		5.2	6.0	5.6	6.1	7.1
R-factor		0.05	0.03	0.05	0.05	0.04

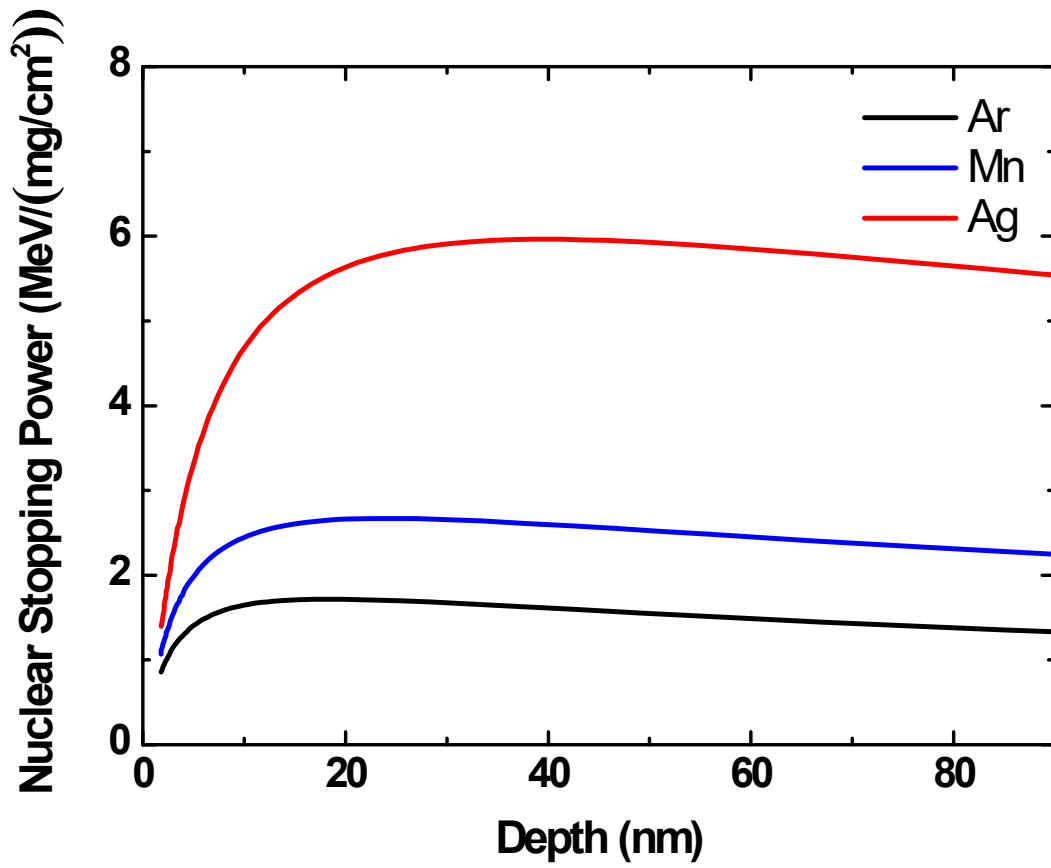


Figure S1: Energy transferred to the ZnO lattice during the implantation using Ar⁺, Mn⁺ and Ag⁺ ions.

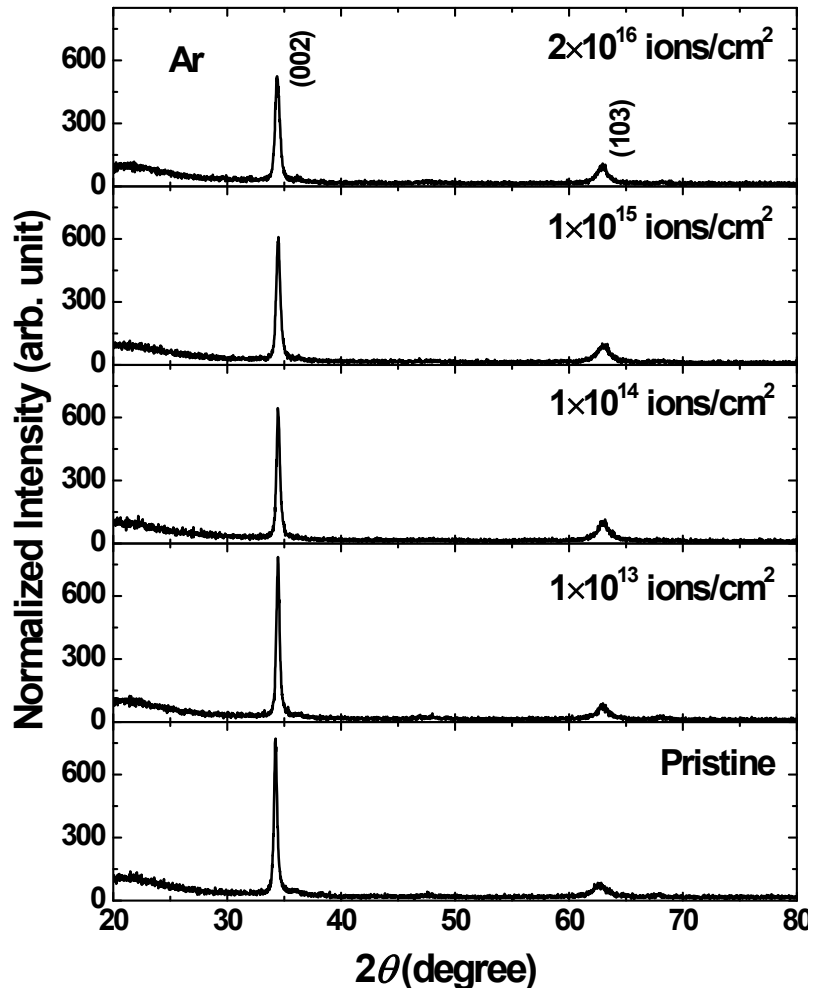


Figure S2: XRD patterns of the Ar⁺ implanted ZnO at different doses.

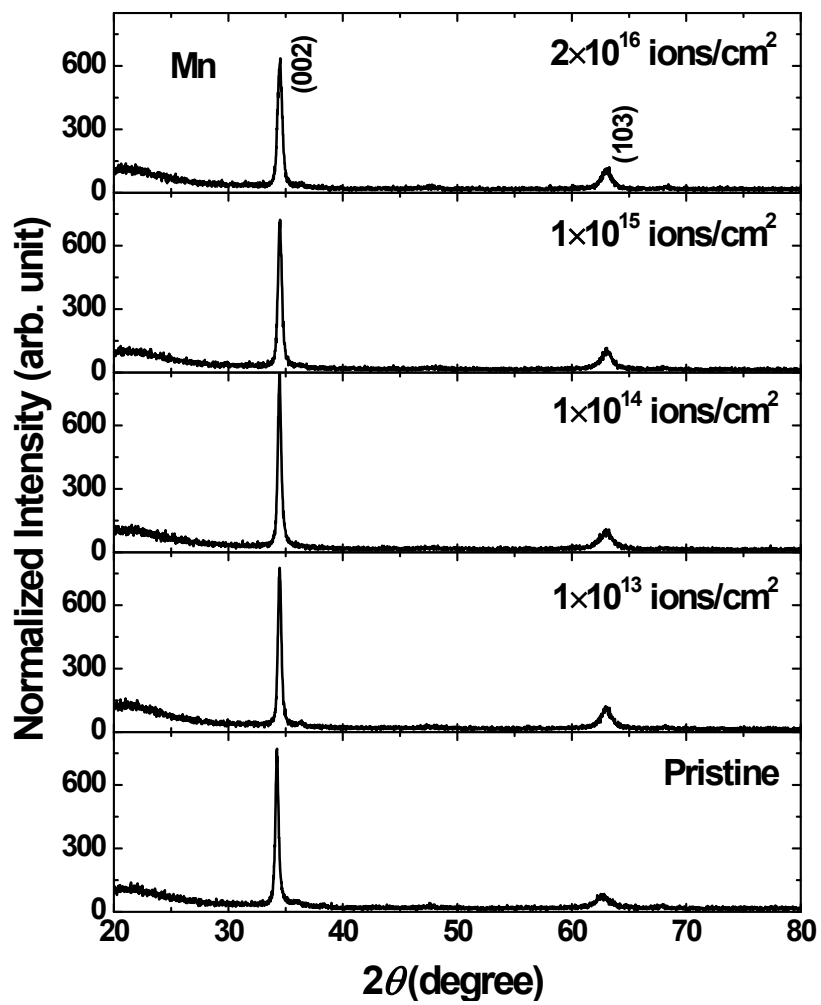


Figure S3: XRD patterns of the Mn⁺ implanted ZnO at different doses.

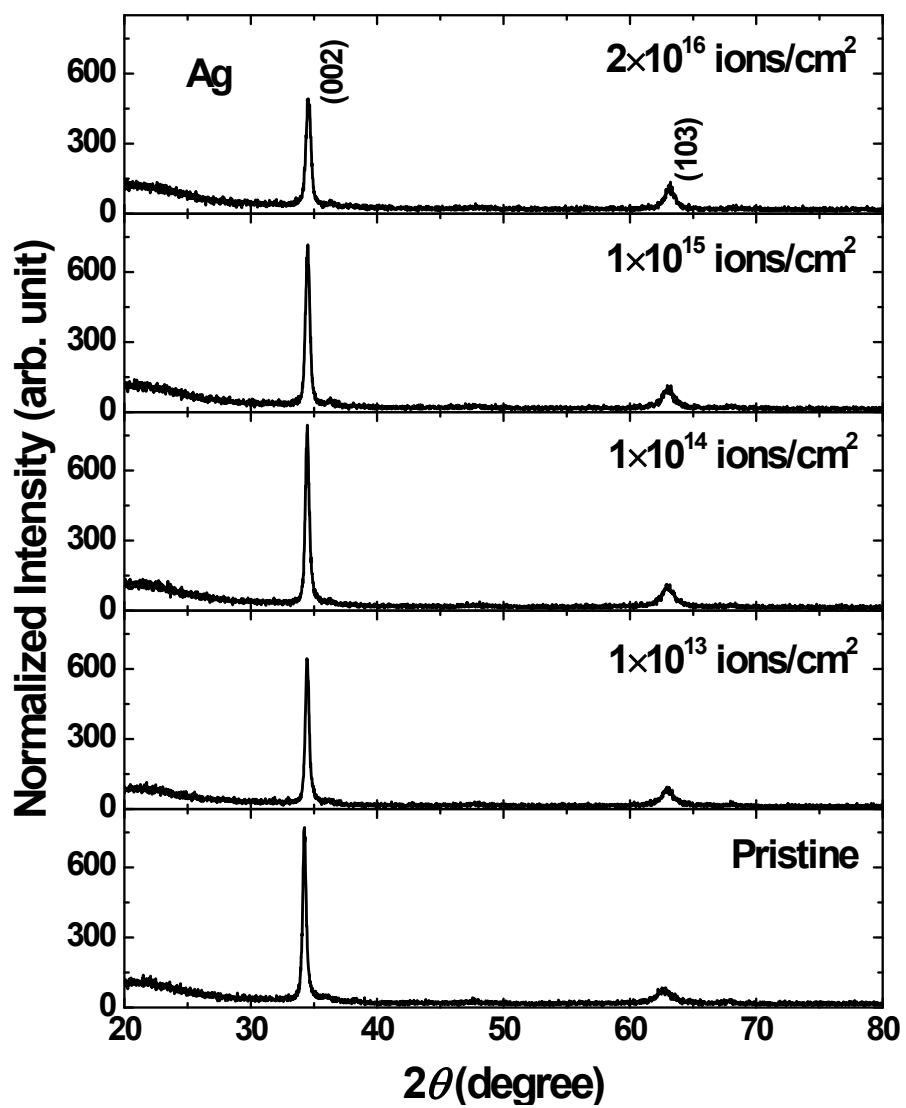


Figure S4: XRD patterns of the Ag⁺ implanted ZnO at different doses.

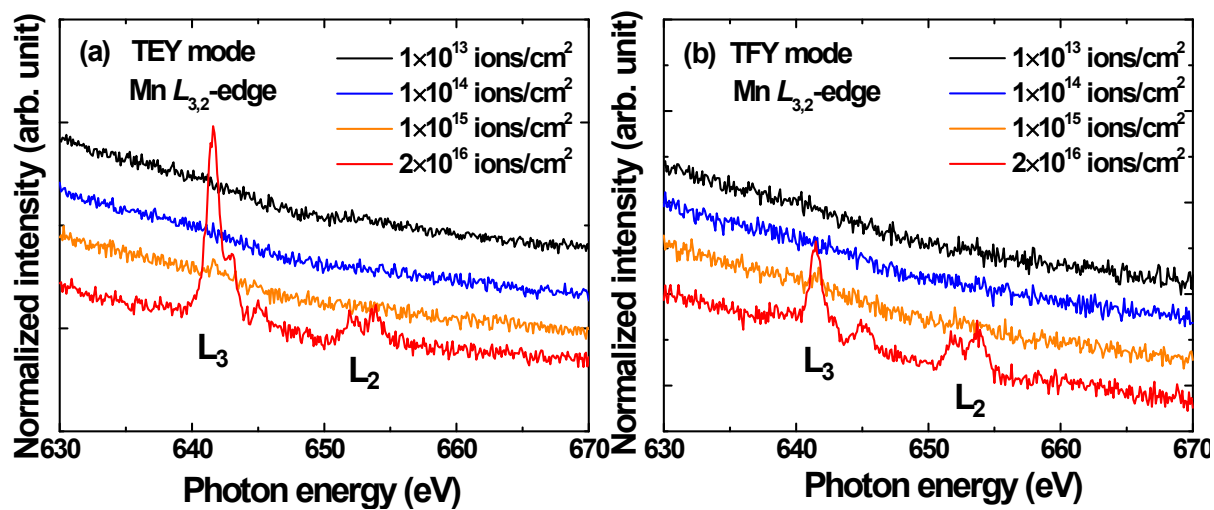


Figure S5: NEXAFS spectra at the Mn $L_{3,2}$ -edge of Mn doped ZnO thin films. (a) TEY mode (b) TFY mode.

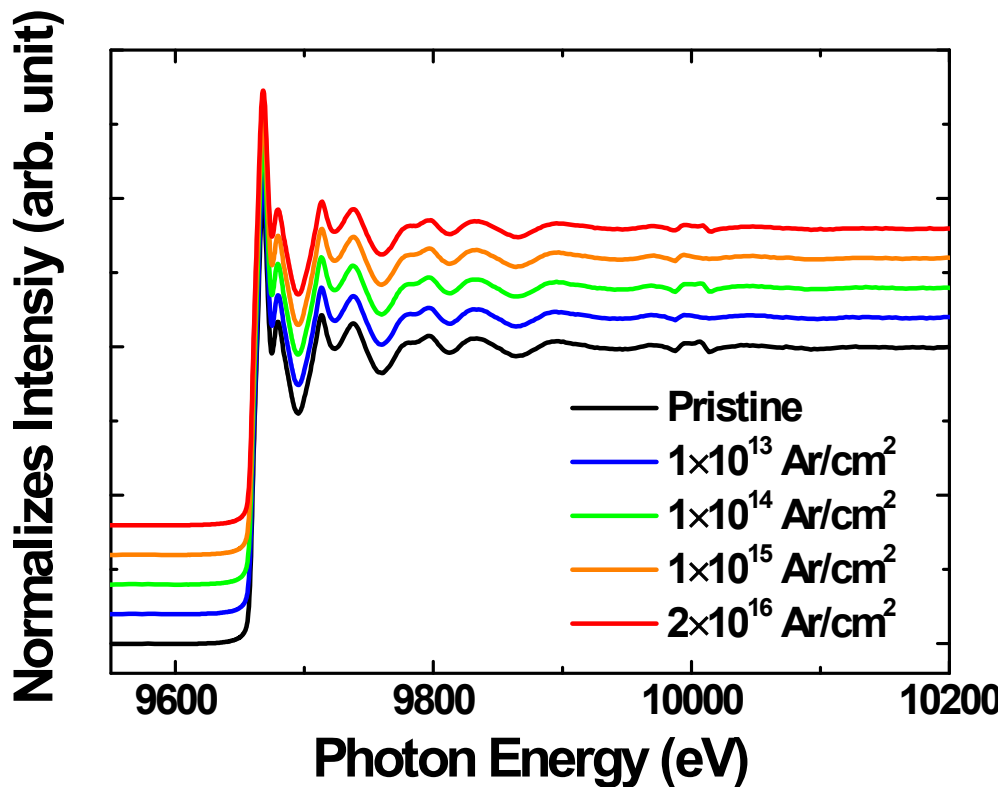


Figure S6: *k*-weight EXAFS spectra for Ar-implanted ZnO films at various doses.

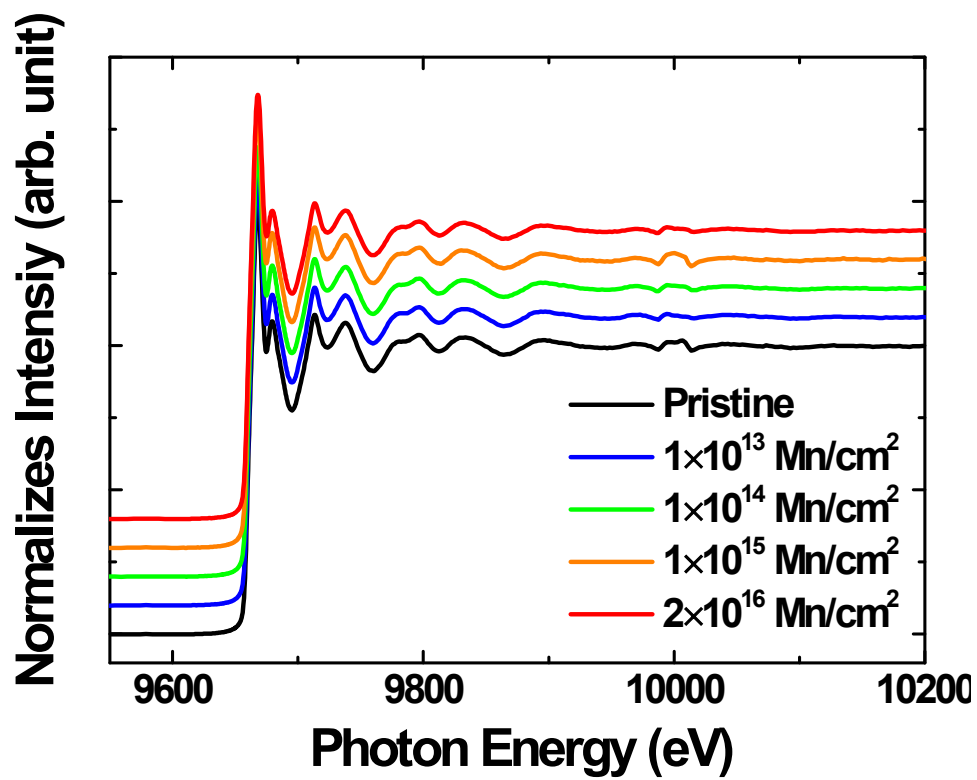


Figure S7: *k*-weight EXAFS spectra for Mn-implanted ZnO films at various doses.

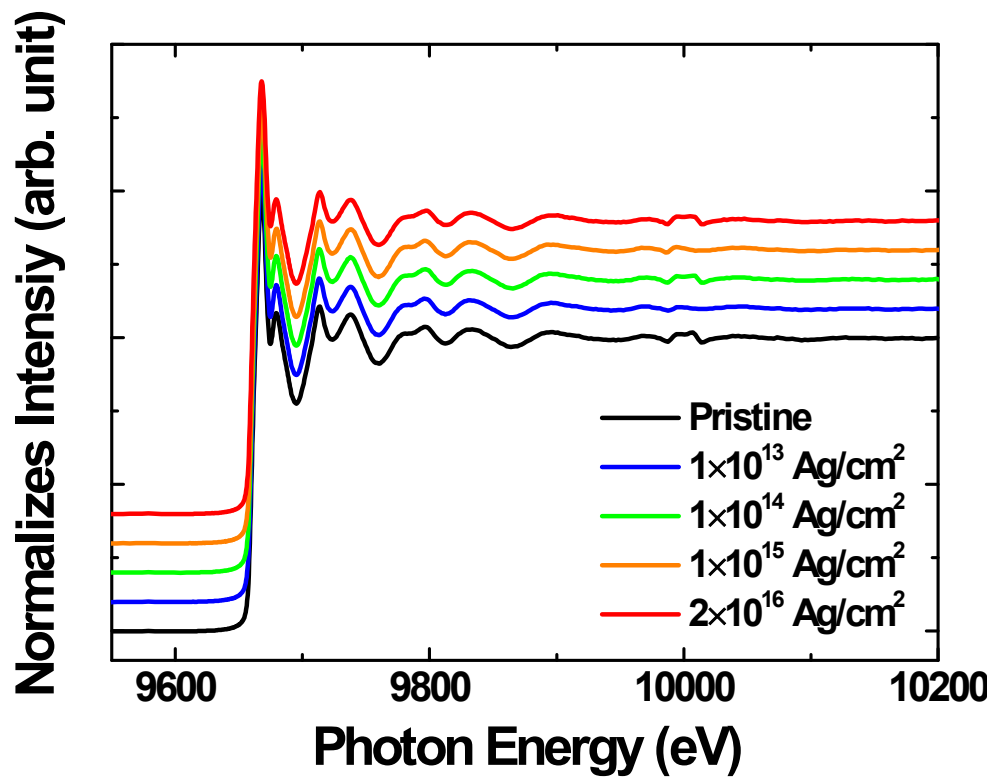


Figure S8: *k*-weight EXAFS spectra for Ag-implanted ZnO films at various doses.

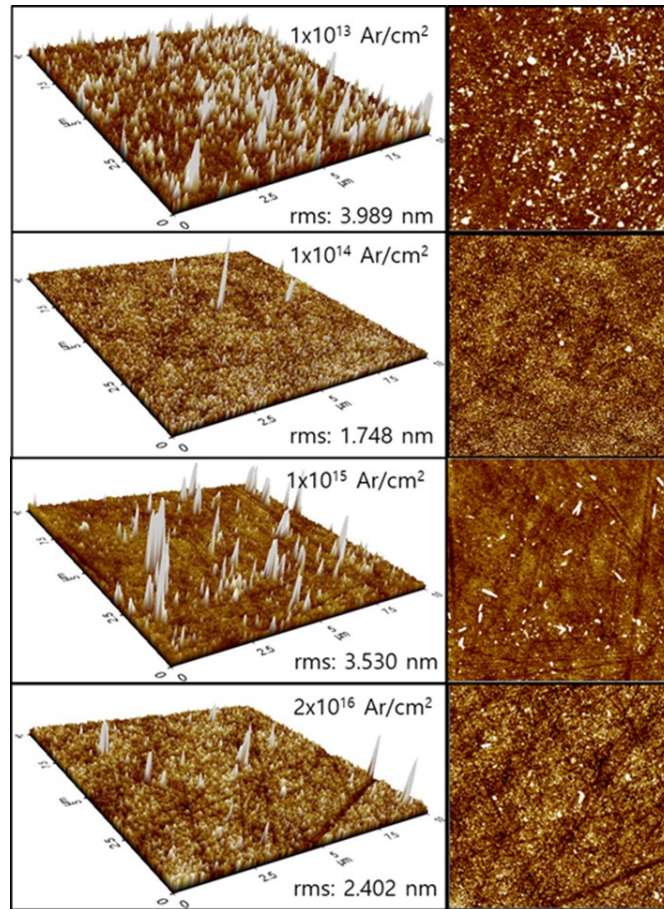


Figure S9: AFM images of the Ar-implanted ZnO at different doses.

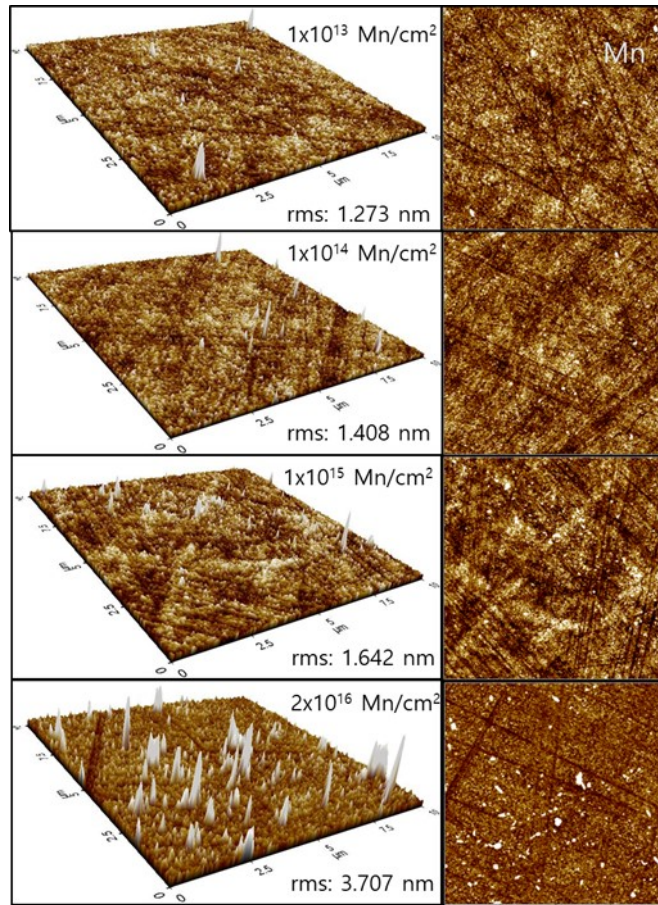


Figure S10: AFM images of the Mn-implanted ZnO at different doses.

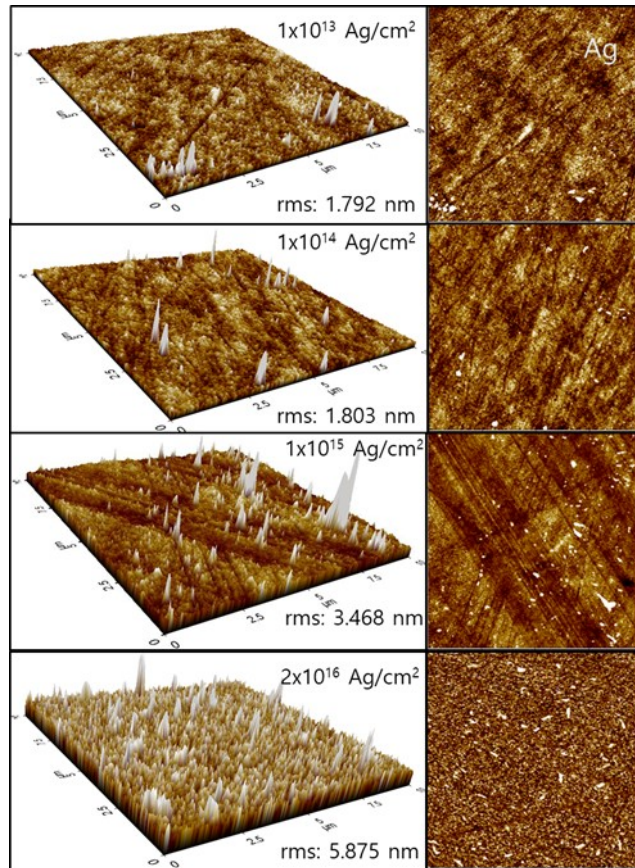


Figure S11: AFM images of the Ag-implanted ZnO at different doses.

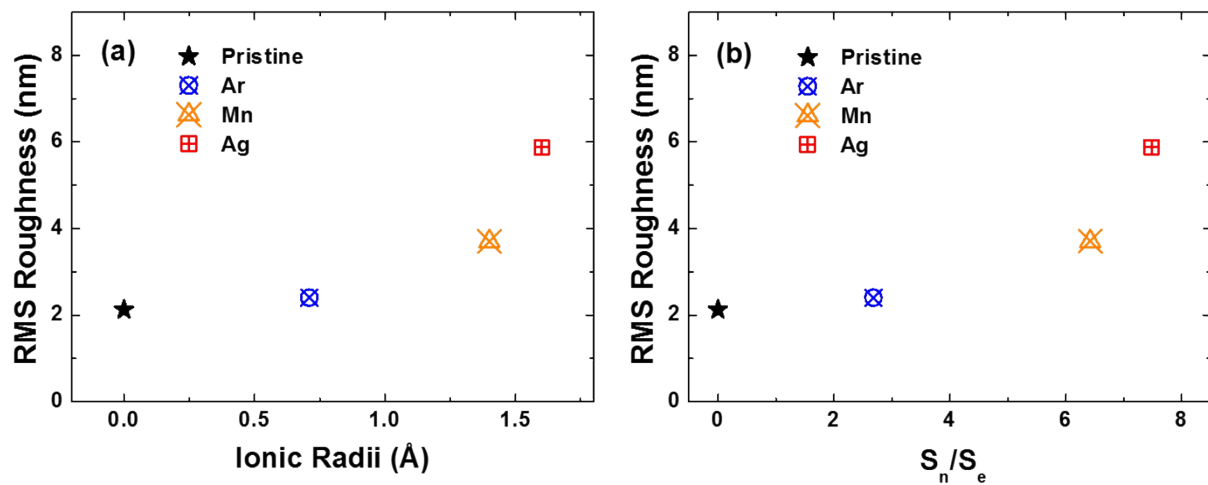


Figure S12: RMS roughness as a function of (a) ionic radii and (b) S_n/S_e .

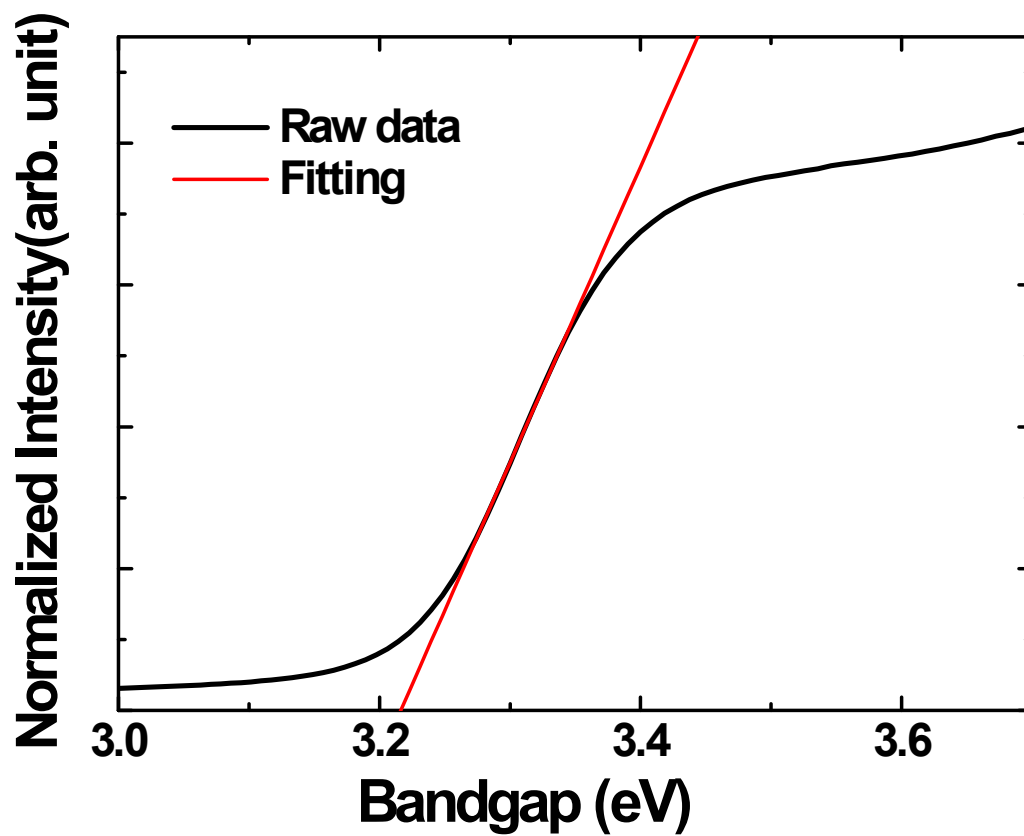


Figure S13: Estimation of optical bandgap from Tauc's plot for a representative film.

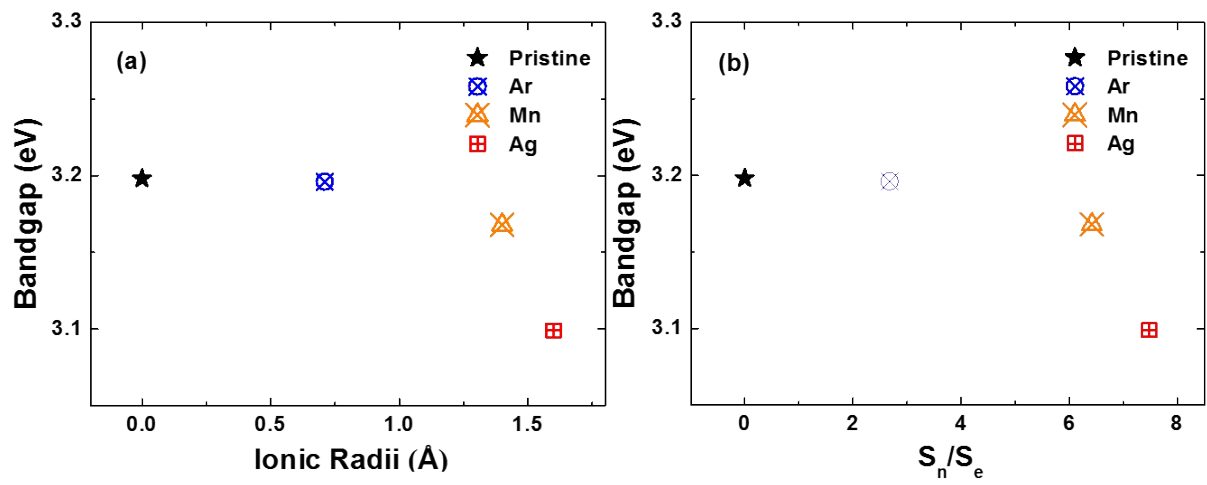


Figure S14: Optical band-gap as a function of (a) ionic radii and (b) S_n/S_e corresponding to various implanted ions.

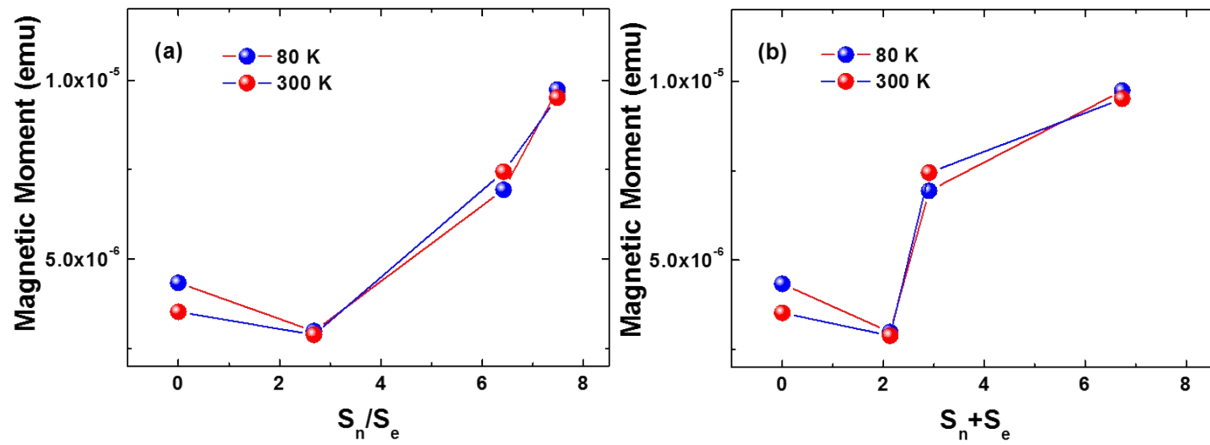


Figure S15: Magnetic moment as a function of (a) ionic radii and (b) S_n/S_e corresponding to various implanted ions.

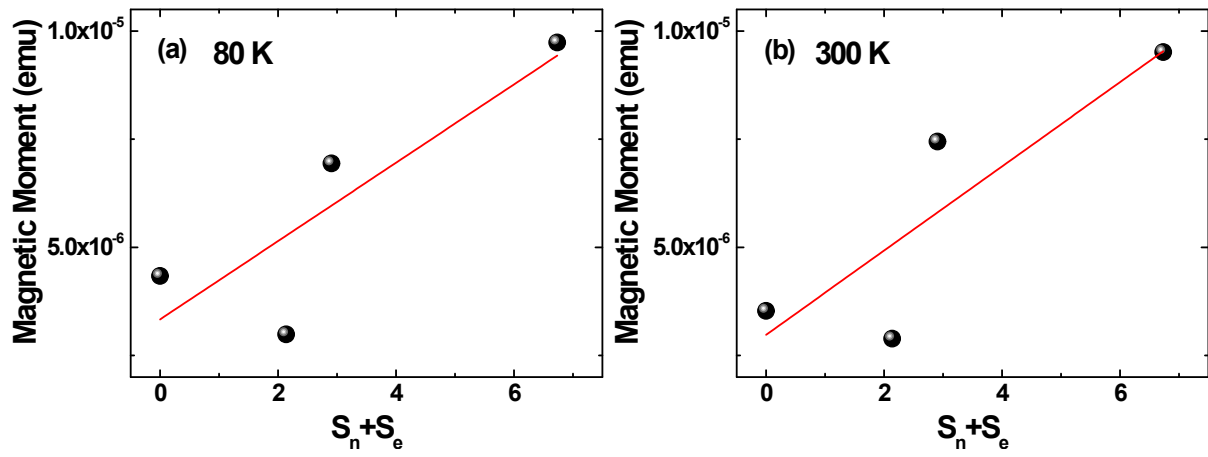


Figure S16: Magnetic moment as a function of $S_n + S_e$ corresponding to various implanted ions at (a) 80 K and (b) 300 K.

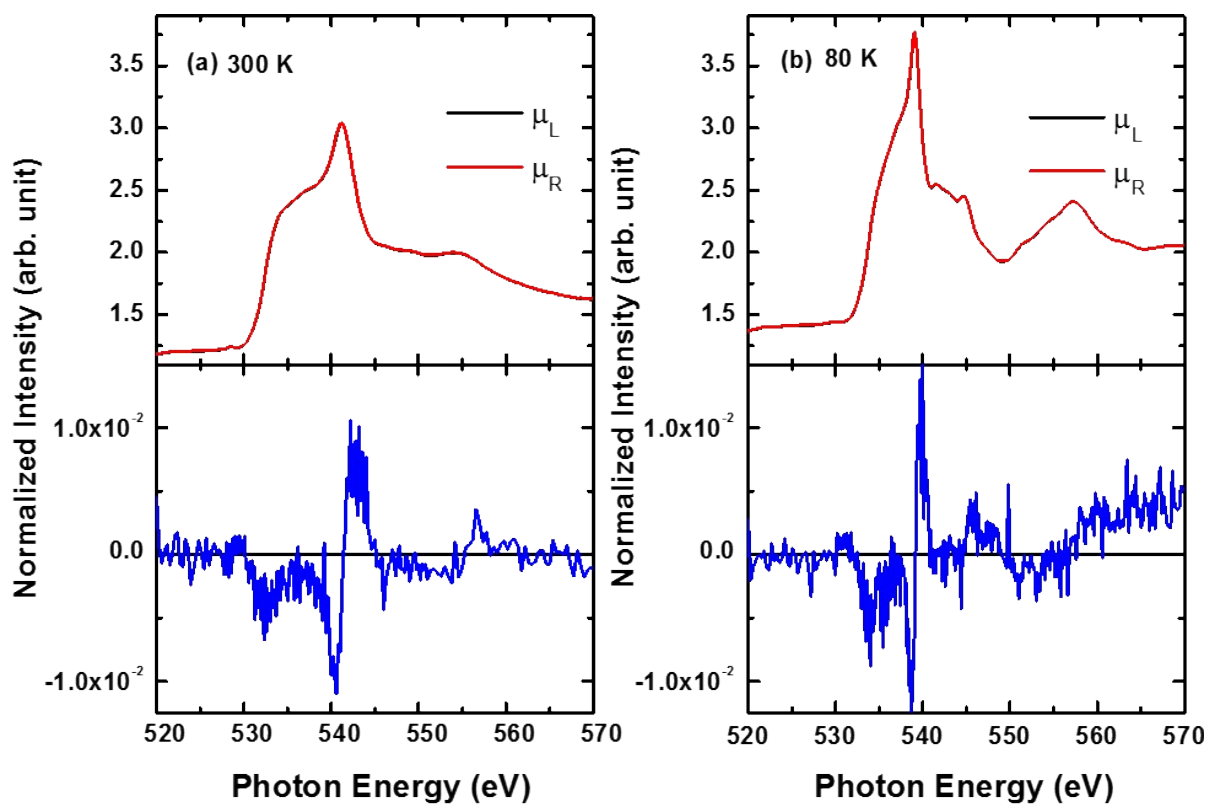


Figure S17: O K-edge NEXAFS spectra under different helicity of light (upper panel) and XMCD signal (lower panel) measured at (a) 300 K and (b) 80 K for non-implanted ZnO film.

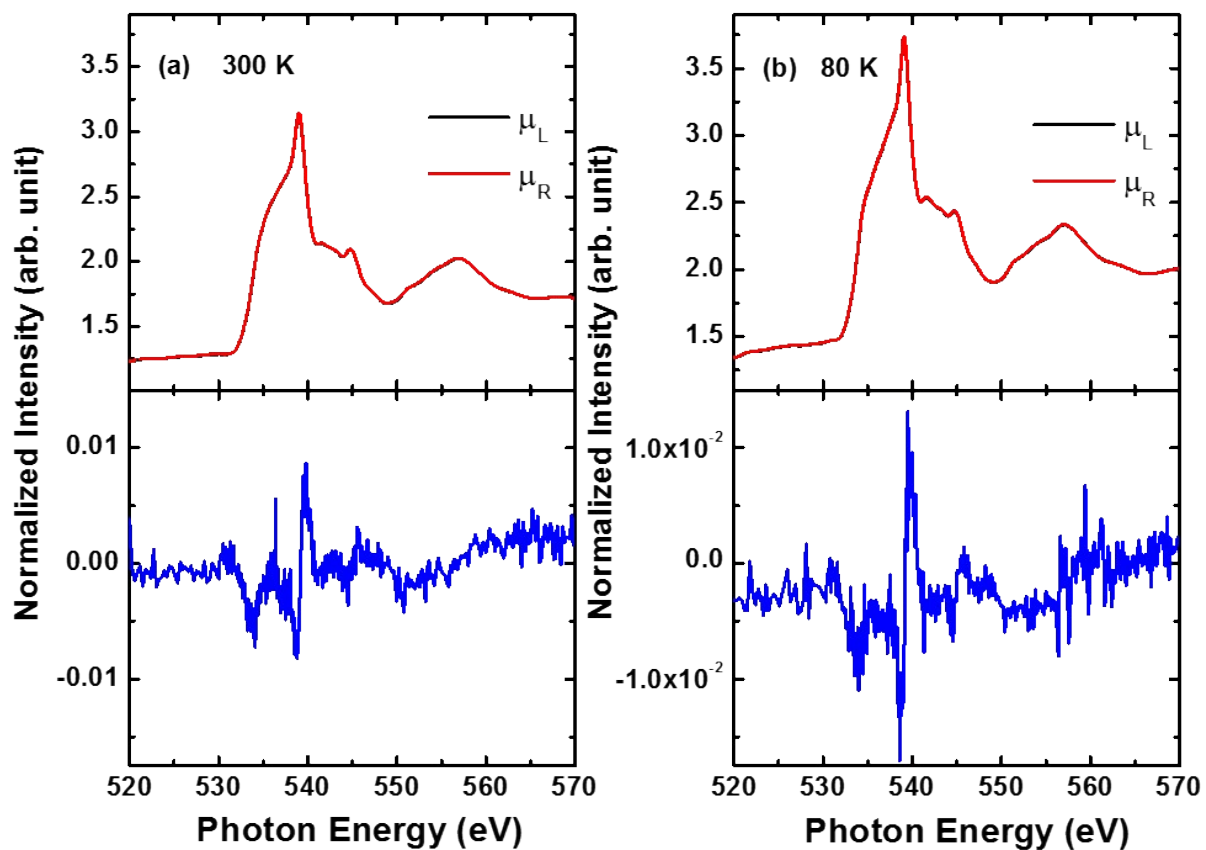


Figure S18: O K-edge NEXAFS spectra under different helicity of light (upper panel) and XMCD signal (lower panel) measured at (a) 300 K and (b) 80 K for Ar-implanted ZnO film.

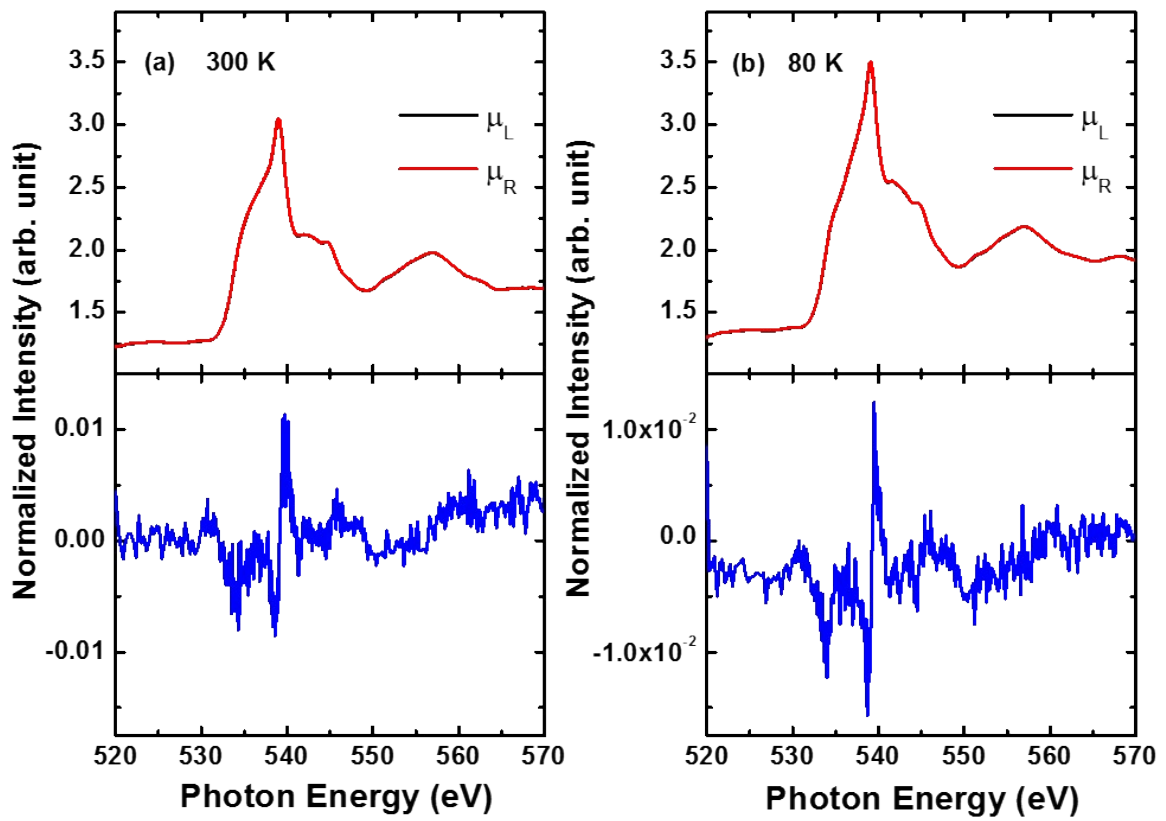


Figure S19: O K-edge NEXAFS spectra under different helicity of light (upper panel) and XMCD signal (lower panel) measured at (a) 300 K and (b) 80 K for Mn-implanted ZnO film.

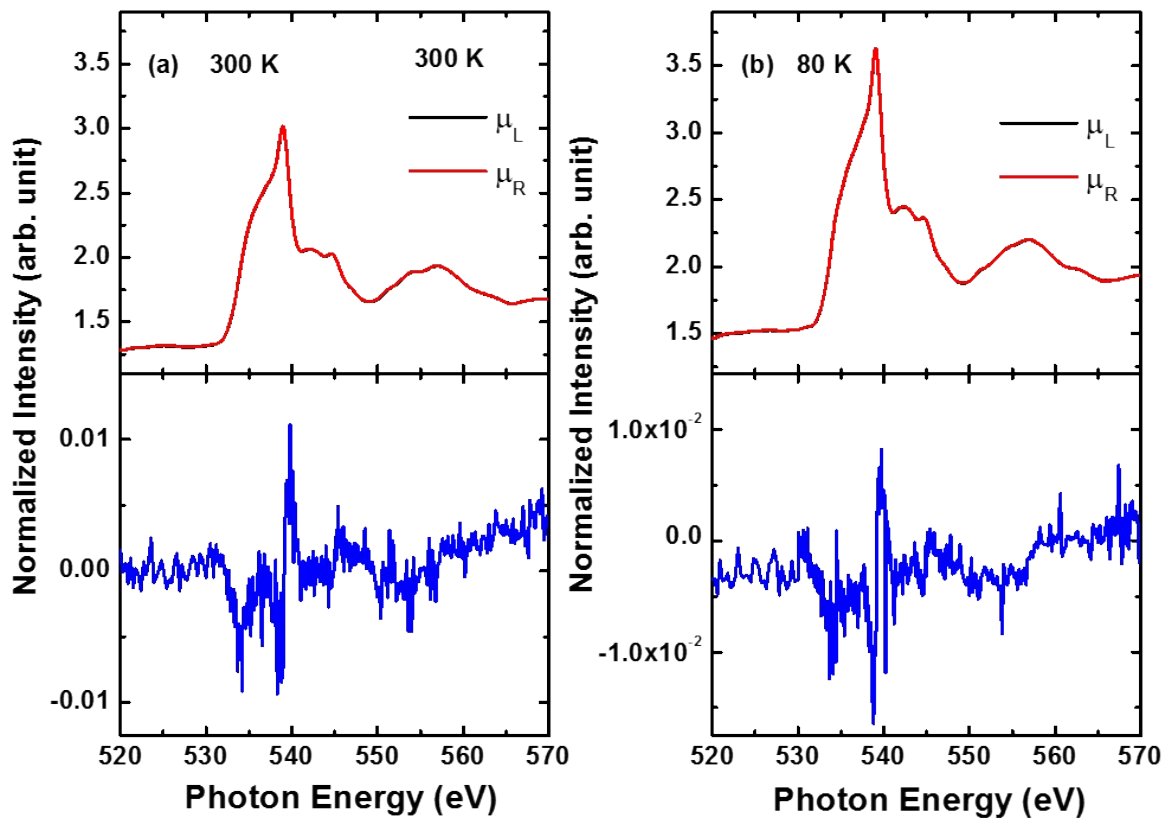


Figure S20: O K-edge NEXAFS spectra under different helicity of light (upper panel) and XMCD signal (lower panel) measured at (a) 300 K and (b) 80 K for Ag-implanted ZnO film.

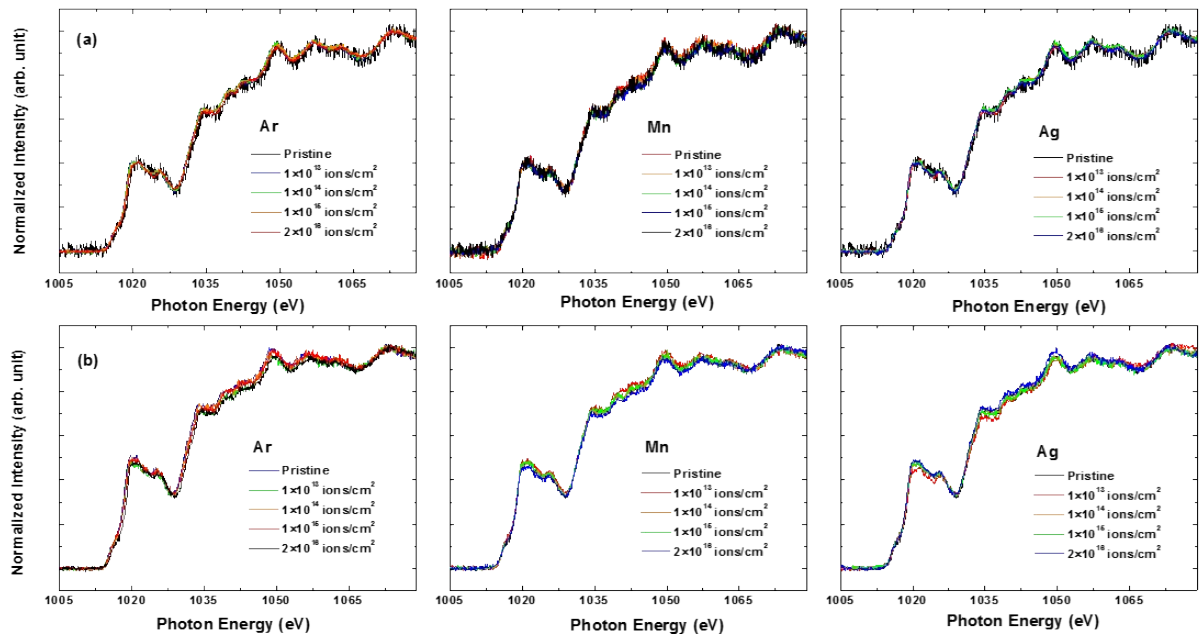


Figure S21: Zn L-edge (a) TEY mode and (b) TFY mode NEXAFS spectra for the implanted ZnO films at various doses.

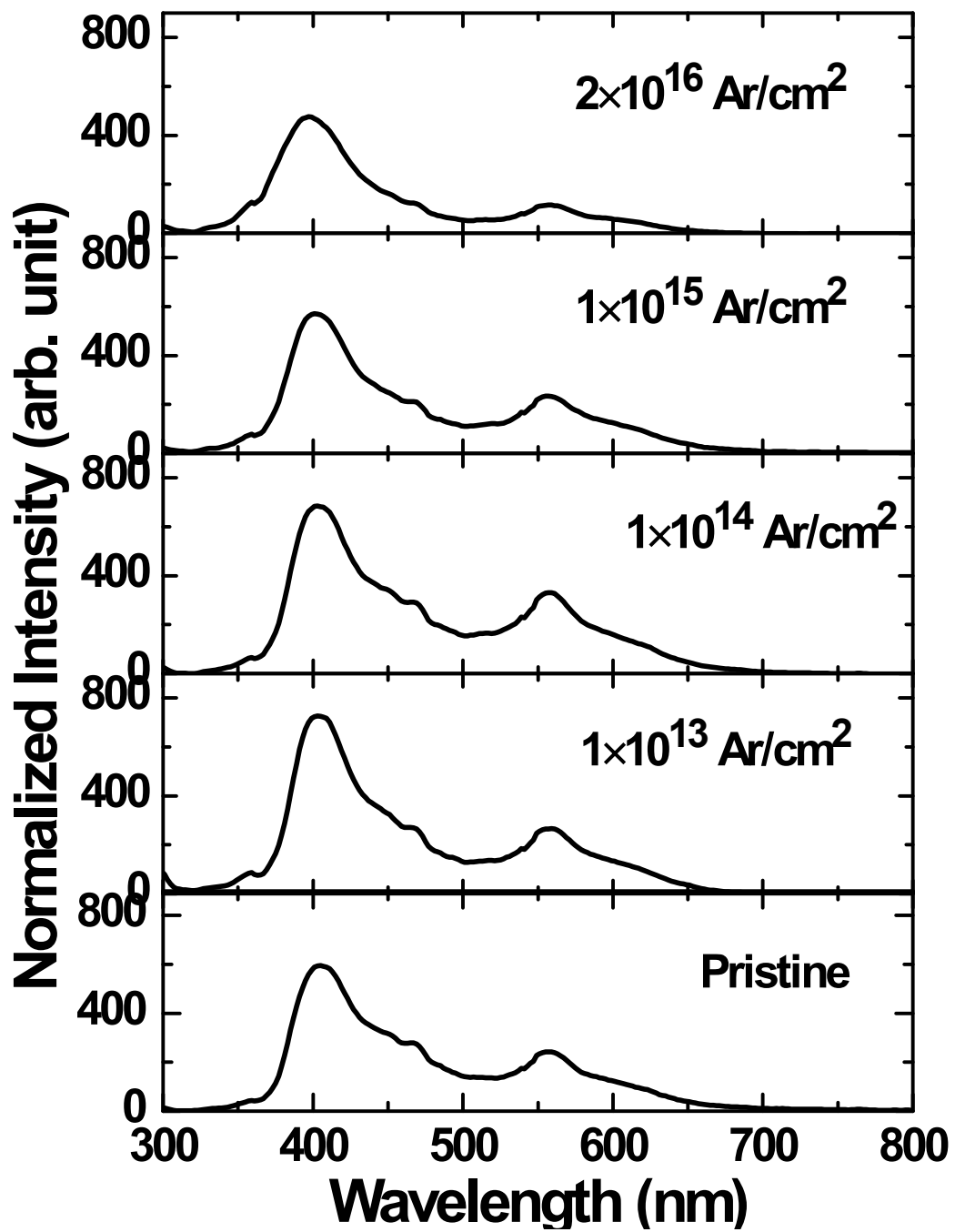


Figure S22: PL spectra of the Ar-implanted at various doses.

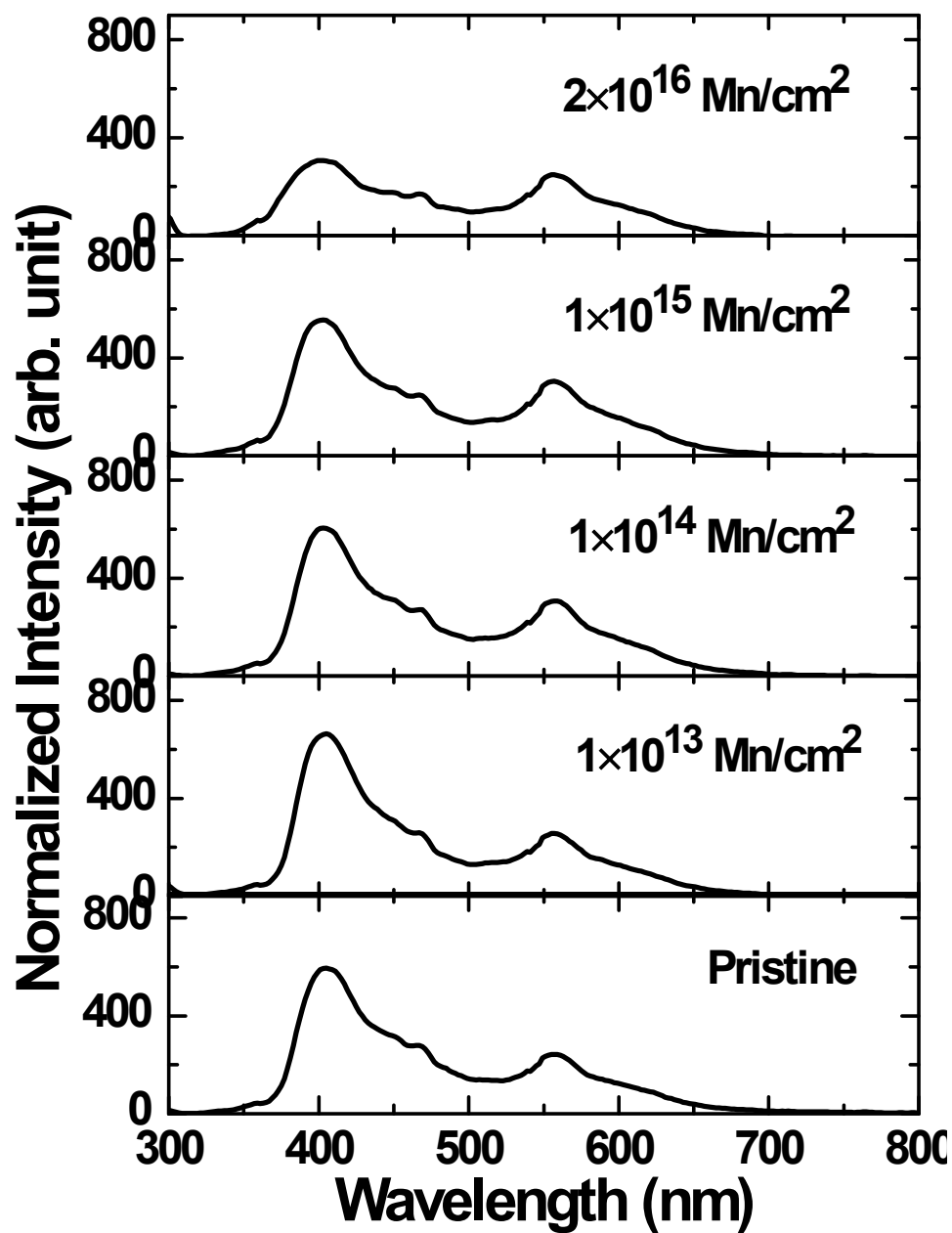


Figure S23: PL spectra of the Mn-implanted at various doses.

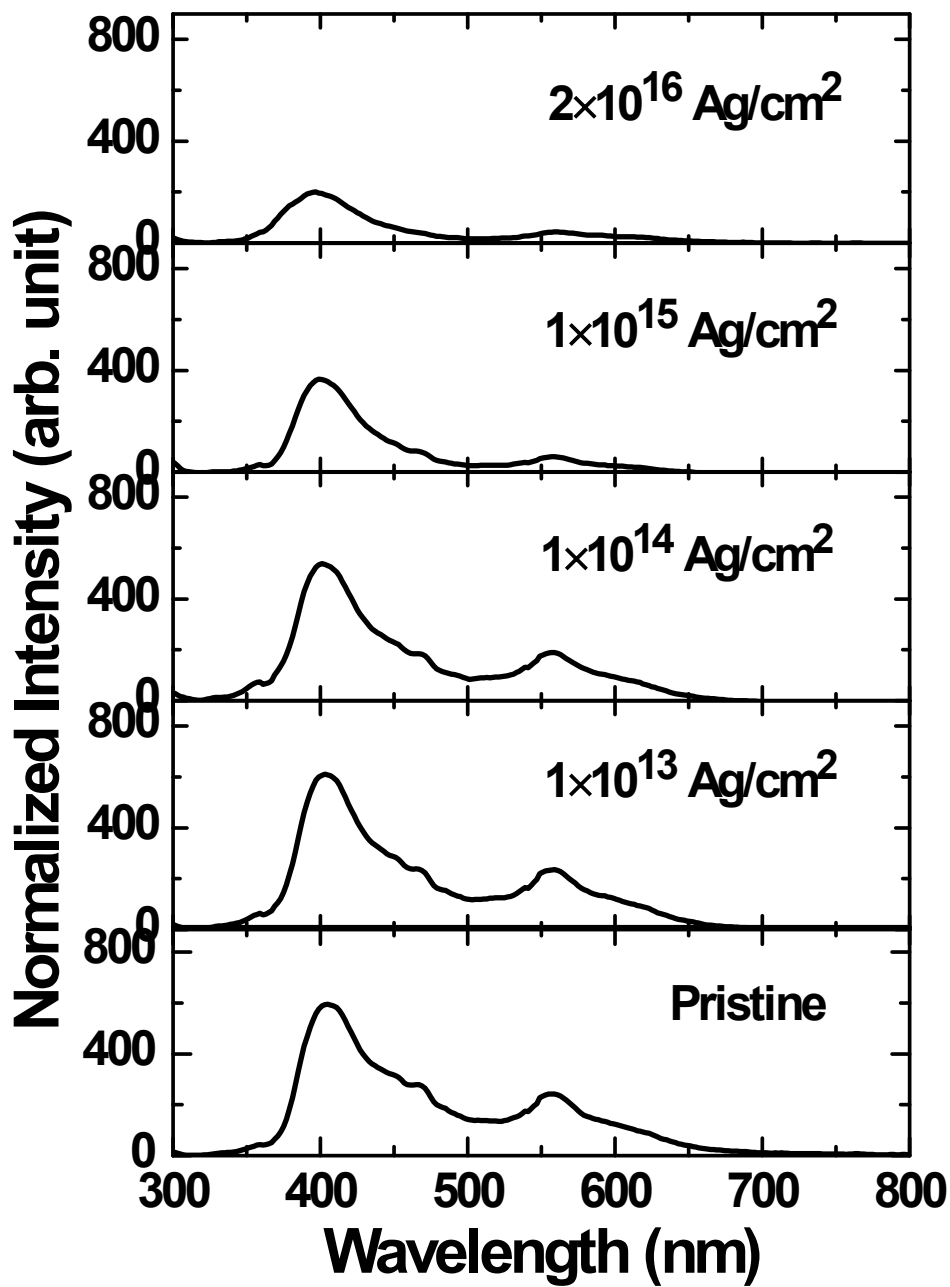


Figure S24: PL spectra of the Ag-implanted at various doses.

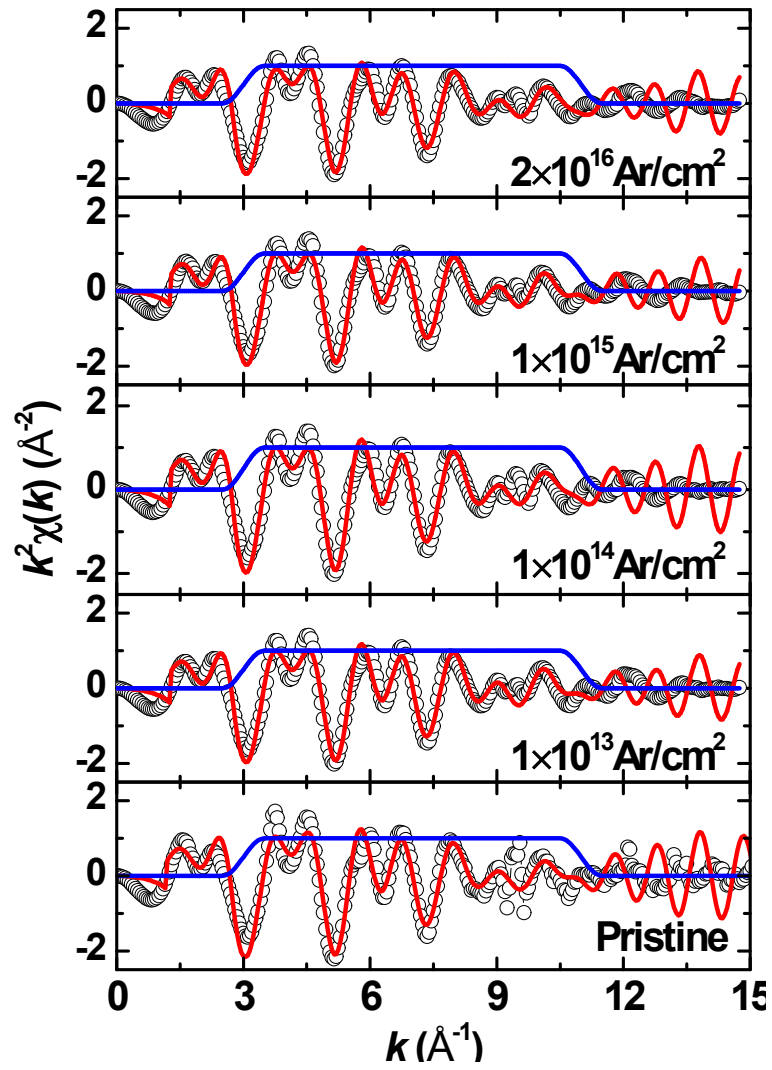


Figure 25: Simulated k -weight EXAFS spectra of Ar-implanted films at various doses.

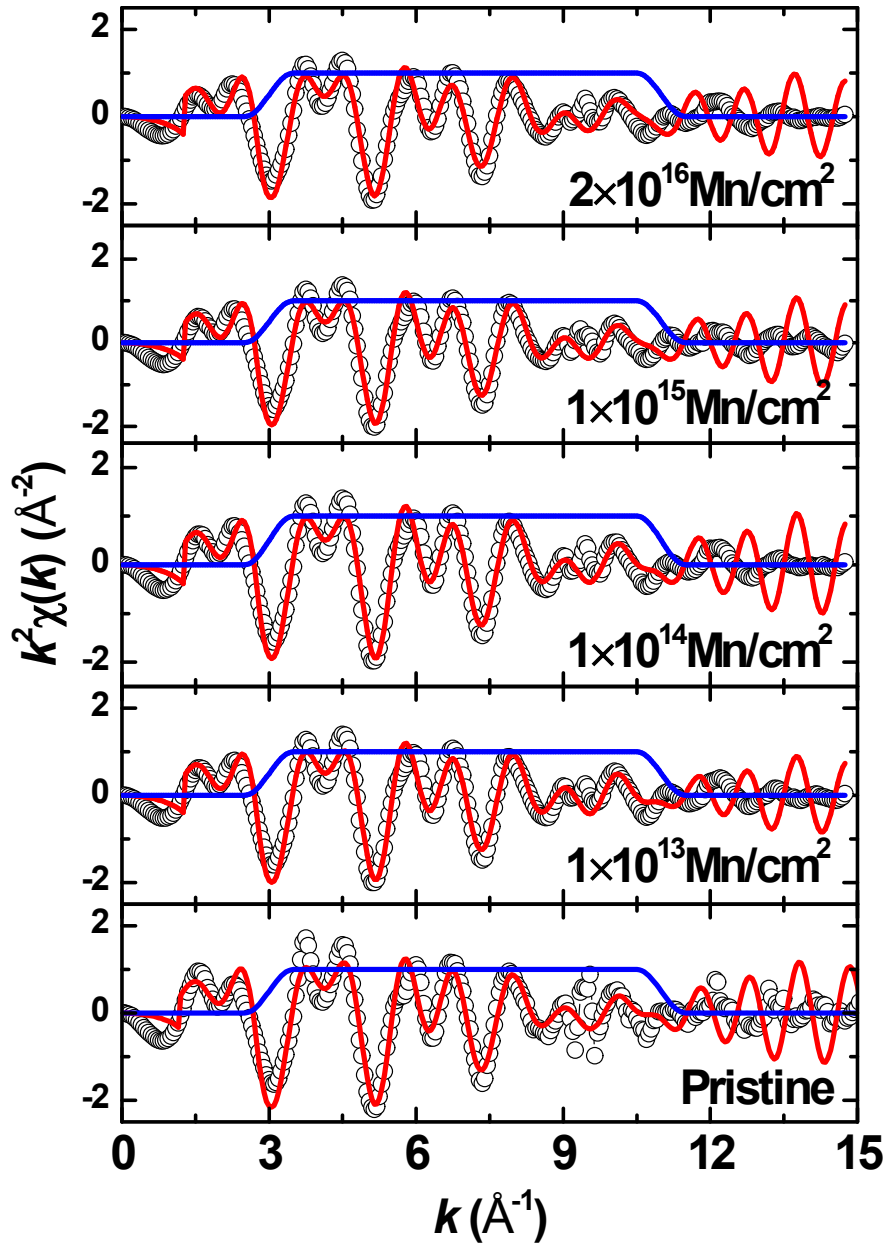


Figure 26: Simulated k -weight EXAFS spectra of Mn-implanted films at various doses.

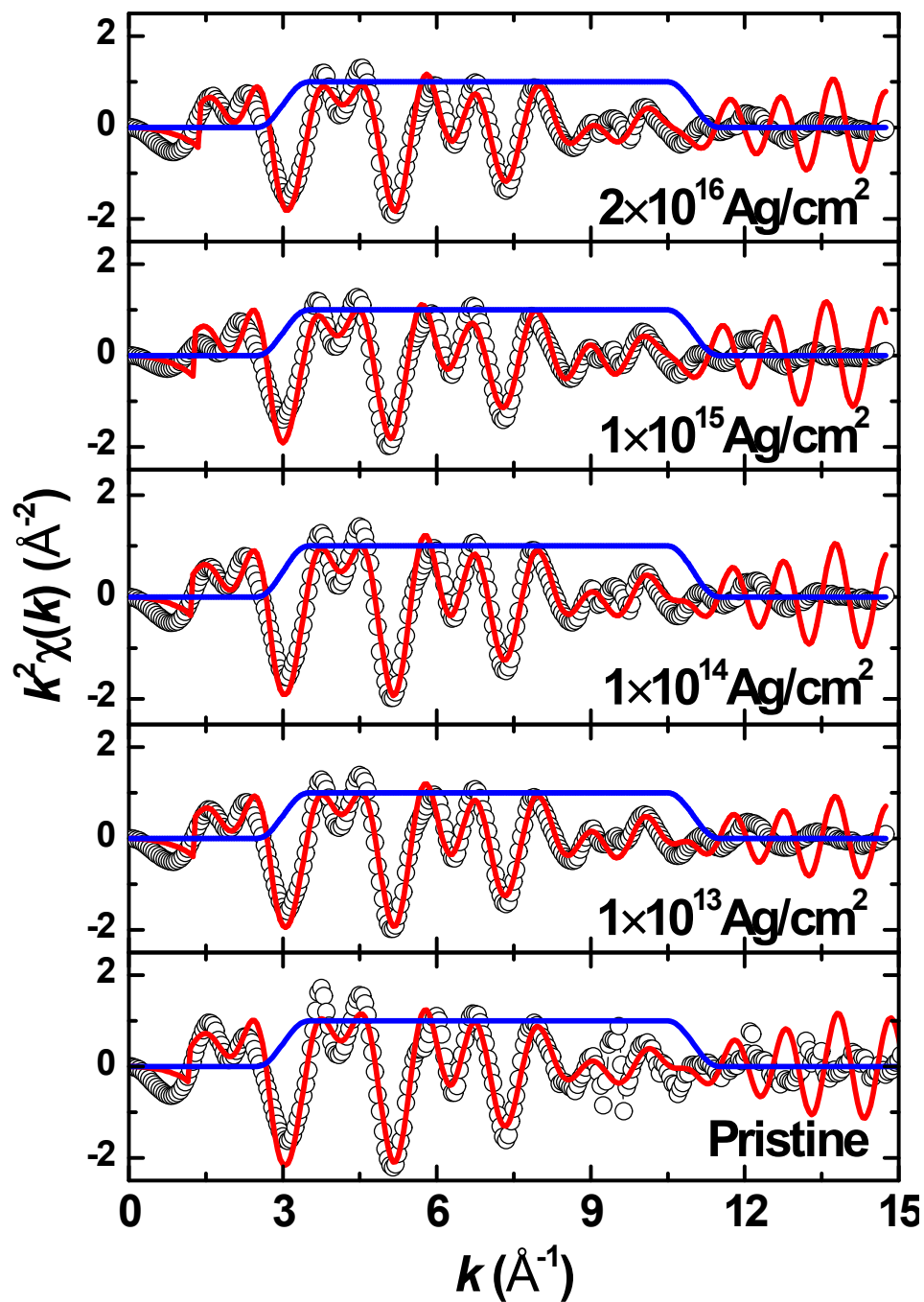


Figure 27: Simulated k -weight EXAFS spectra of Ag-implanted films at various doses.