Supplementary Information (SI) for Journal of Materials Chemistry A.

SUPPLEMENTARY INFORMATION

Enhanced Thermoelectric Performance in $Fe_2V_{0.8}W_{0.2}Al$ Thin Films: Synergistic Effects of Chemical Ordering and Tungsten Substitution

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The theta-two theta measurements for all the deposited films of $Fe_2V_{0.8}W_{0.2}Al$ can be seen in SI 1-SI 6. Here, instead of the usual 1D plot, 2D maps are portrayed for a more complete information. SI 1-SI 3 are the 2D maps correspondent to (1 1 0) oriented films grown on Al_2O_3 substrate, and measured at ψ=0°, 45°, and 35.26°, respectively. On the other hand, SI 4-SI 6 show the 2D maps of (1 0 0) oriented films grown on MgO substrate, and measured at ψ=0°, 45°, and 54.7°, respectively. Identification of B2 and $L2_1$ phases comes from the presence of (2 0 0) and (1 1 1) diffraction spots, respectively. In these 2D maps, it is evident that from a certain threshold, the diffused diffraction intensity of Fe_2VAl peaks progressively concentrates into a spot, indicating an evolution form polycrystalline to single-oriented phase.

Other important structural characteristic is the in-plane order of the crystallites of $Fe_2V_{0.8}W_{0.2}Al$. In SI 7 and SI 8 are portrayed the ϕ-scans of the (2 2 0) and (4 0 0) peak respectively, the first for films deposited on MgO and the latter for films deposited on Al_2O_3. Ideally (1 0 0) oriented films show a four-fold rotation symmetry in the ϕ-scan of the (2 2 0) peak, this behavior is observed for most of the films. However, for (1 1 0)-oriented films, a two-fold rotation is expected on ϕ-scans of the (4 0 0) peak, this behavior is only seen clearly for the film deposited at T_{dep}=950 °C, for the rest of the cases (excluding films deposited below 650°C, which do not show any feature in the ϕ-scans) a four-fold rotation is observed. This implies an in-plane disorder of the crystallites having two preferential orientations with respect to the substrate lattice.

SI 9 shows the plot of the lattice parameter of all the deposited films as a function of the deposition temperature (T_{dep}) along with the lattice parameter of undoped Fe_2VAl[1]. Here, it is apparent that the lattice parameter decreases with increasing deposition temperature, from 5.90 Å at 350 °C to 5.78 Å at 950 °C for both (110) and (100) oriented films. However, at each Tdep, the values are similar for both orientations.

To complete the crystallographic information of the films in SI 10, we show the out-of-plane crystallite size obtained at different T_{dep} for (1 1 0) and (1 0 0) oriented films. This crystallite size was calculated by the Scherrer's formula[2] on symmetrical $\theta/2\theta$ measurements. In this figure, minor differences can be observed between (1 1 0) and (1 0 0) oriented films. For both orientations, an increase in crystallite size with T_{dep} is observed, as it is the usual behavior in thin film growth.

Regarding the morphological characterization of the films, SI 11 and SI 12 show SEM micrographs with x100000 magnification for all the deposited films. SI 11 show SEM micrographs for (1 1 0) films deposited on Al_2O_3, while SI 12 show the micrographs of (1 0 0) oriented films grown on MgO substrates. In these two figures its visible the effect over morphology that T_{dep} has, and also the different morphological aspect caused by the different substrate choice.

A summary table of differences of Seebeck coefficient, electrical conductivity and overall PF values between representative samples in the $L2_1$ regime and a B2 sample is shown in table 1.

T_{dep} (°C)	S (μV/K)	σ (Ω·cm)$^{-1}$	S^2	PF (μW/m·K^2)	ΔS^2 vs 650°C	Δσ vs 650°C	ΔPF observed
550	-15	2550	225	55	-	-	0
750	-50	2370	2500	580	+1011%	-7%	+954%
800	-57	2130	3249	700	+1344%	-16.5%	+ 1172%

Table 1: Seebeck coefficient, electrical conductivity, and overall PF differences between samples in the $L2_1$ *regime and a B2 sample.*

References

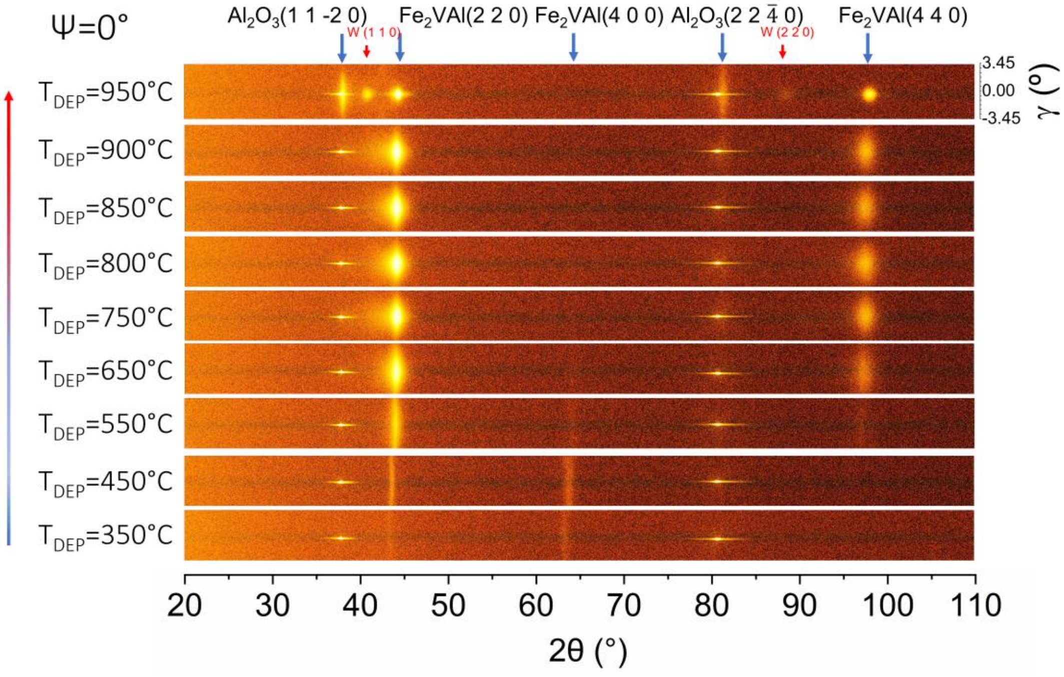
[1] Y. Kawaharada, K. Kurosaki, and S. Yamanaka, ‘Thermophysical properties of Fe2VAl’, *J Alloys Compd*, vol. 352, no. 1–2, pp. 48–51, Mar. 2003, doi: 10.1016/S0925-8388(02)01132-5.

[2] P. Scherrer, ‘Nachr Ges wiss goettingen.’, *Math. Phys.*, vol. 2, pp. 98–100, 1918.

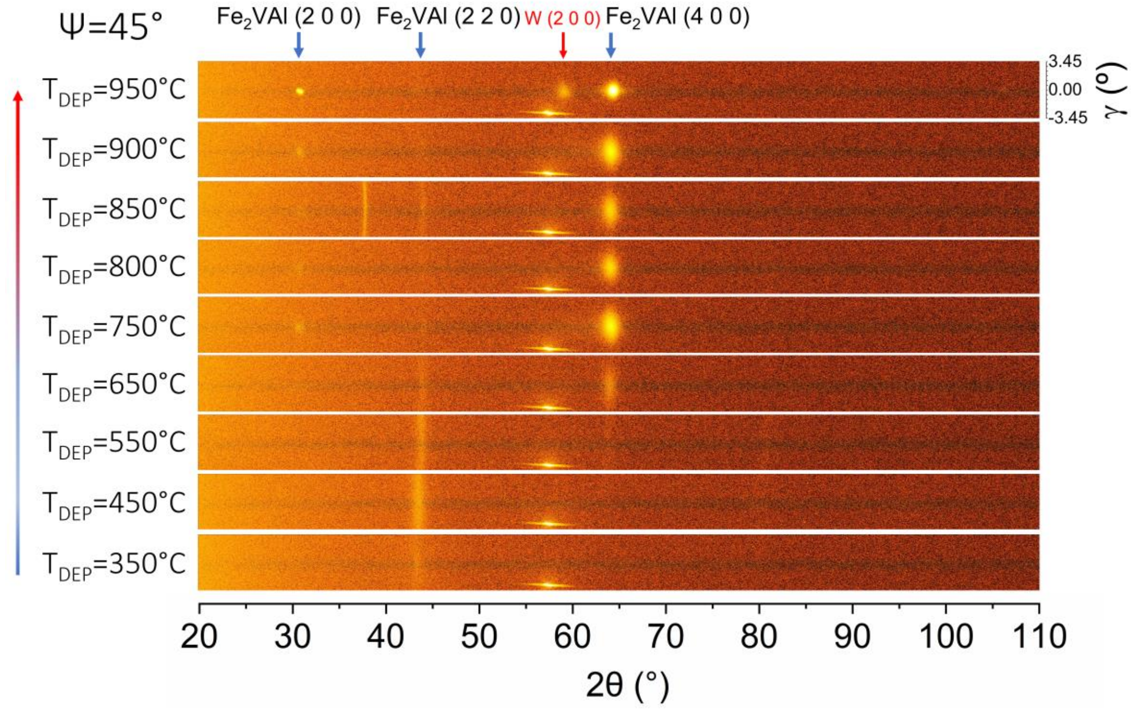
[3] J. M. Domínguez-Vázquez *et al.*, ‘Thermoelectric performance boost by chemical order in epitaxial L21 (100) and (110) oriented undoped Fe2VAl thin films: an experimental and theoretical study’, *J Mater Chem A Mater*, vol. 13, no. 30, pp. 24716–24726, 2025, doi: 10.1039/D5TA02619A.

XRD

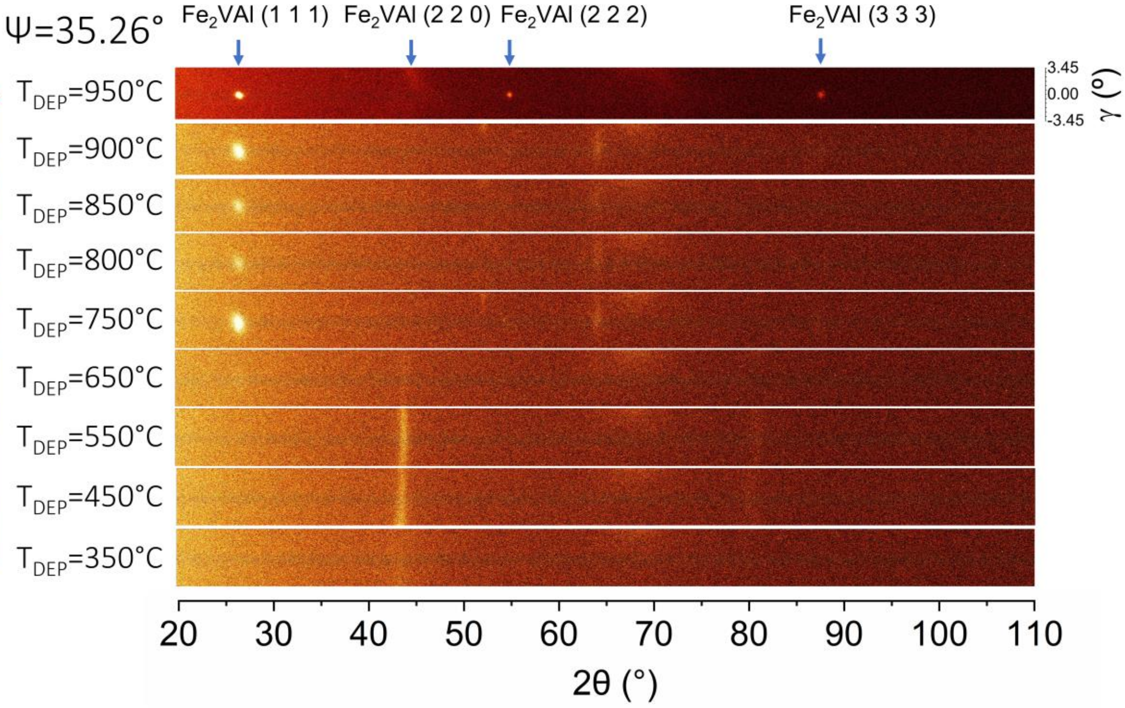
Al_2O_3 substrate:



SI 1: Specular (ψ=0º) X-Ray $\theta/2\theta$ vs γ 2D maps for $Fe_2V_{0.8}W_{0.2}Al$ films at all deposition temperatures (T_{dep}) deposited on Al_2O_3 substrate.

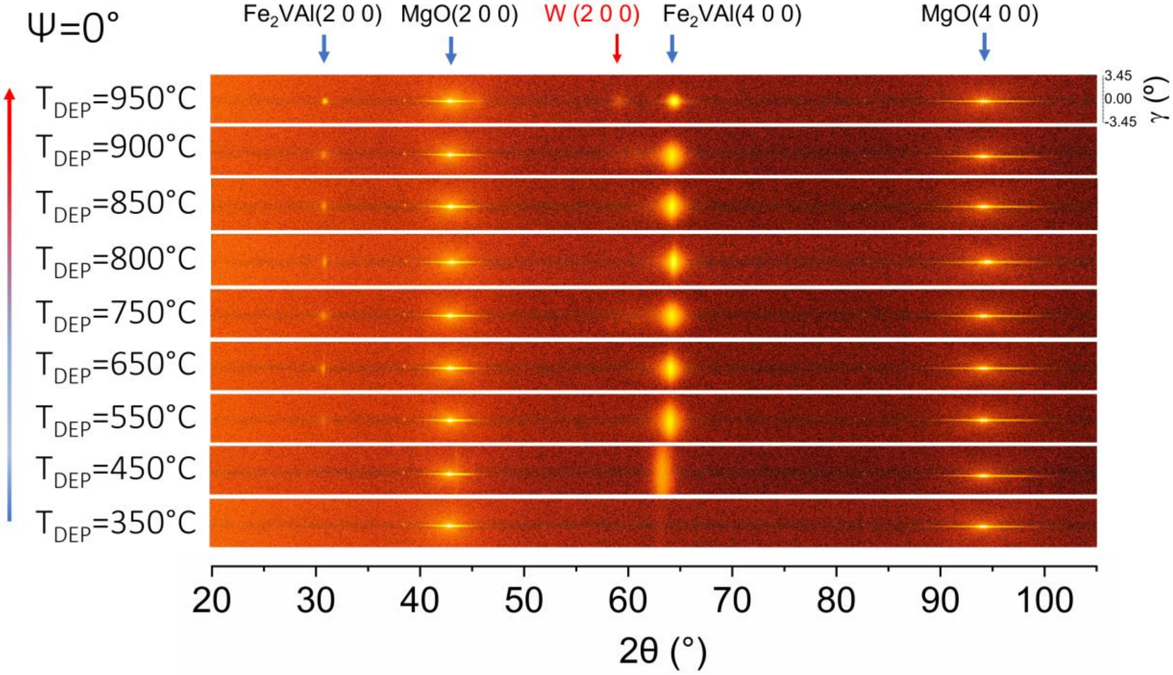


SI 2: Off-specular (ψ=45º) X-Ray $\theta/2\theta$ vs γ 2D maps for $Fe_2V_{0.8}W_{0.2}Al$ films at all deposition temperatures (T_{dep}) deposited on Al_2O_3 substrate.

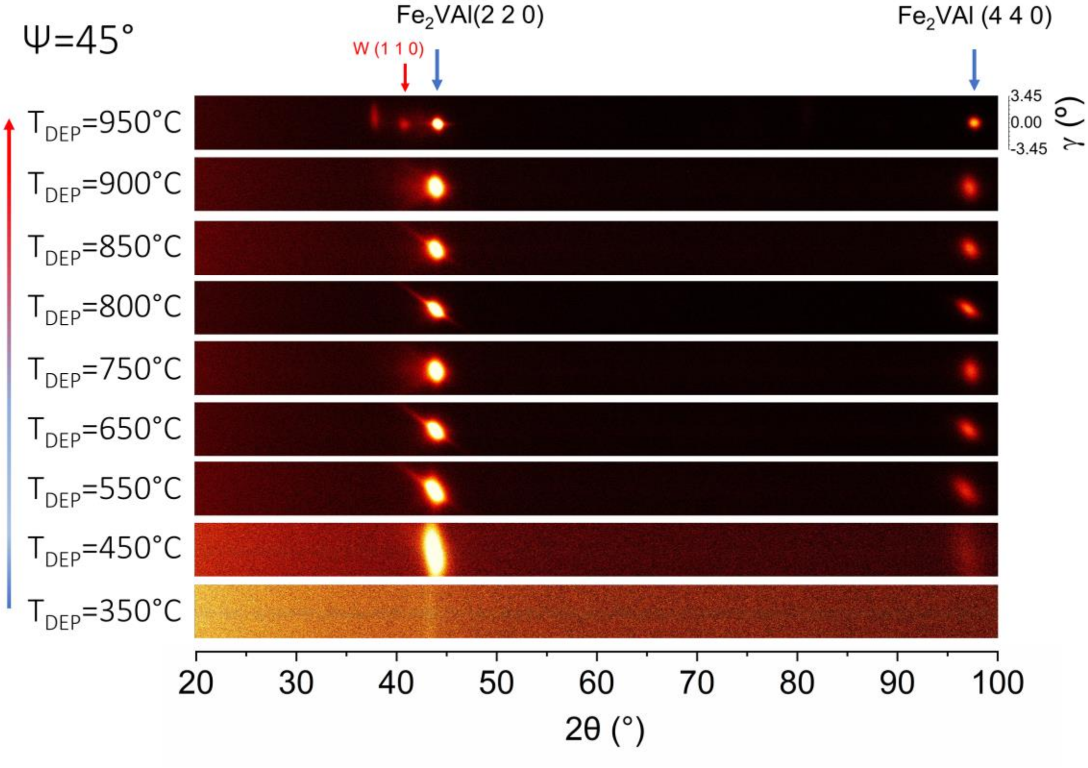


SI 3: Off-specular (ψ=35.26°) X-Ray $\theta/2\theta$ vs γ 2D maps for $Fe_2V_{0.8}W_{0.2}Al$ films at all deposition temperatures (T_{dep}) deposited on Al_2O_3 substrate.

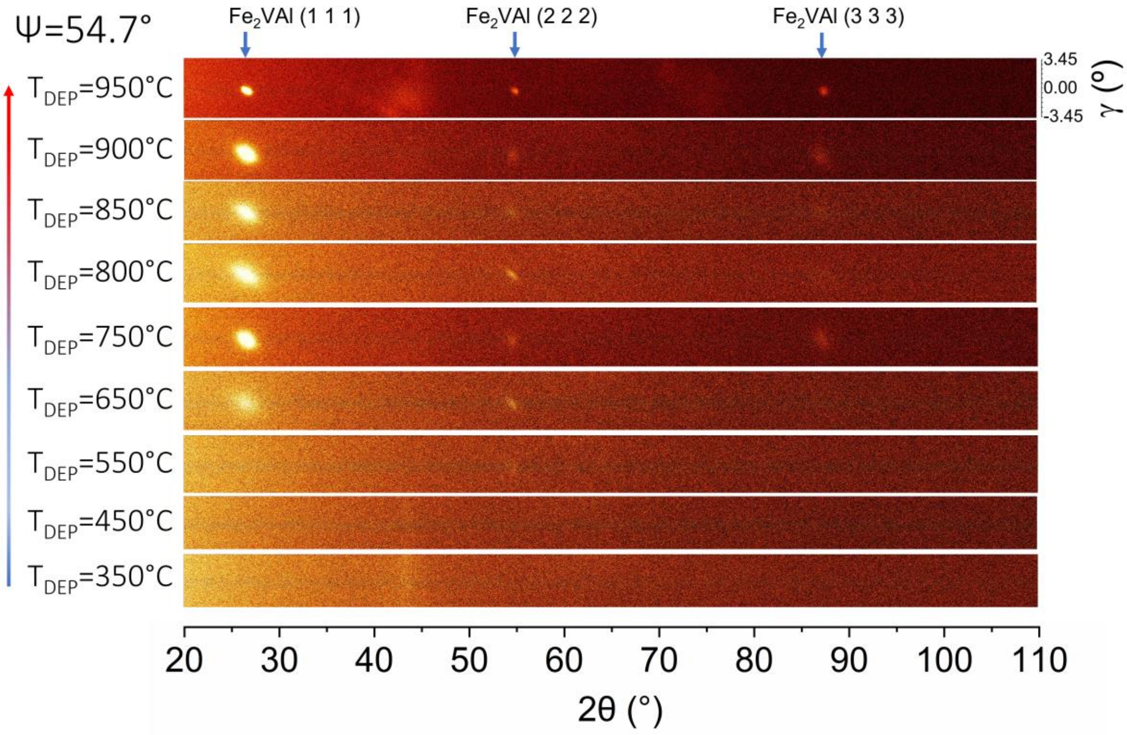
MgO substrate:



SI 4: Specular (ψ=0°) X-Ray θ/2θ vs γ 2D maps for $Fe_2V_{0.8}W_{0.2}Al$ films at all deposition temperatures (T_{dep}) deposited on MgO substrate.

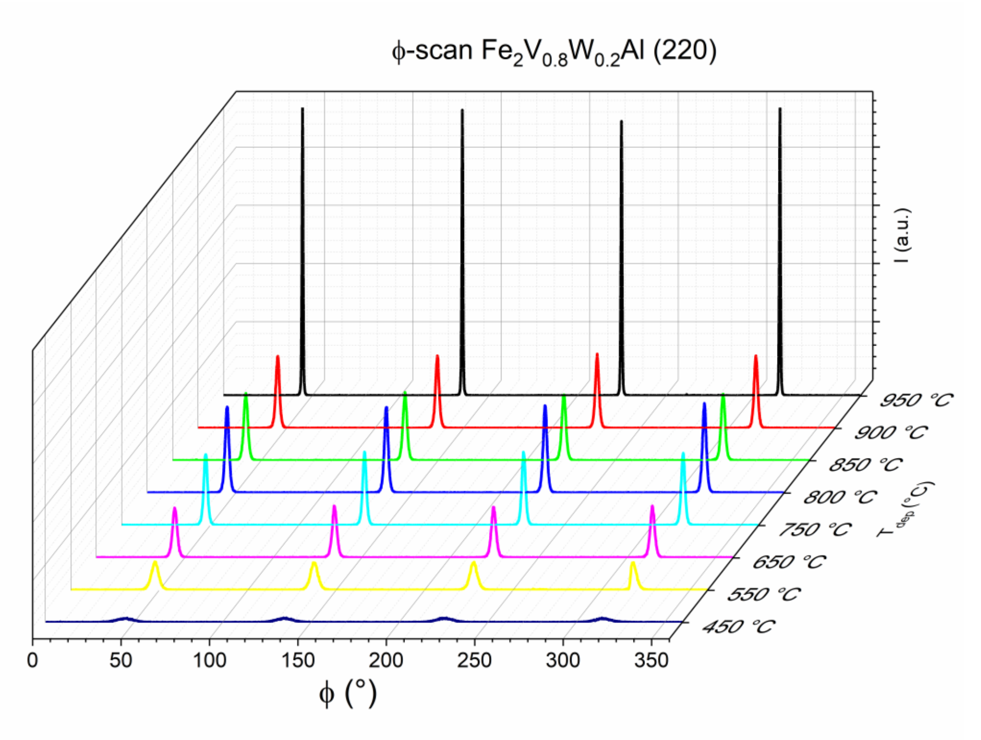


SI 5: Off-specular (ψ=45°) X-Ray θ/2θ vs γ 2D maps for $Fe_2V_{0.8}W_{0.2}Al$ films at all deposition temperatures (T_{dep}) deposited on MgO substrate.

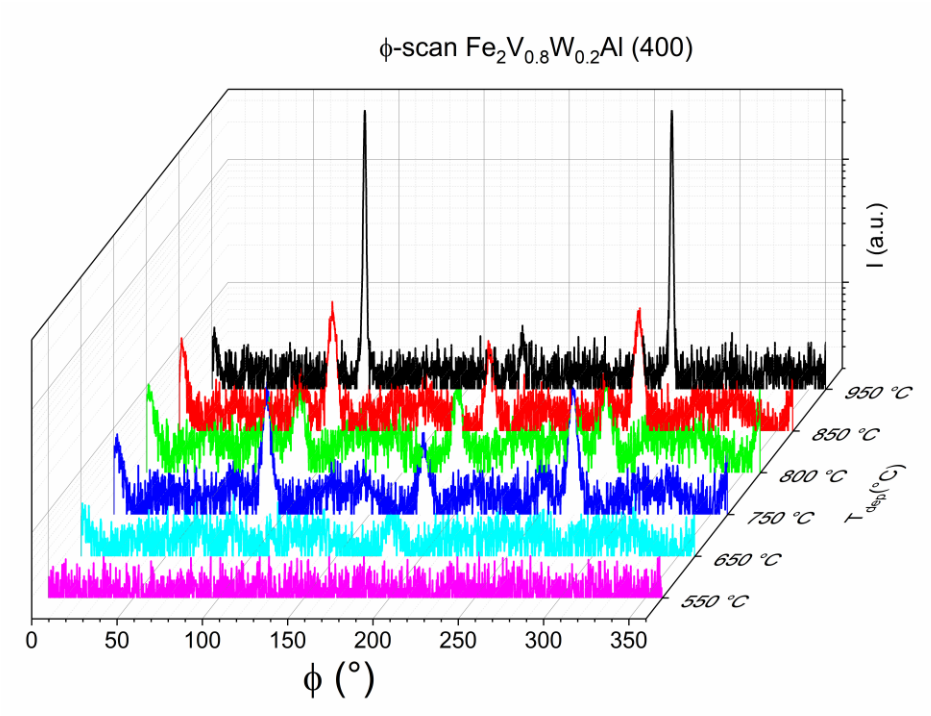


SI 6: Off-specular (ψ=54.7°) X-Ray $\theta/2\theta$ vs γ 2D maps for $Fe_2V_{0.8}W_{0.2}Al$ films at all deposition temperatures (T_{dep}) deposited on MgO substrate.

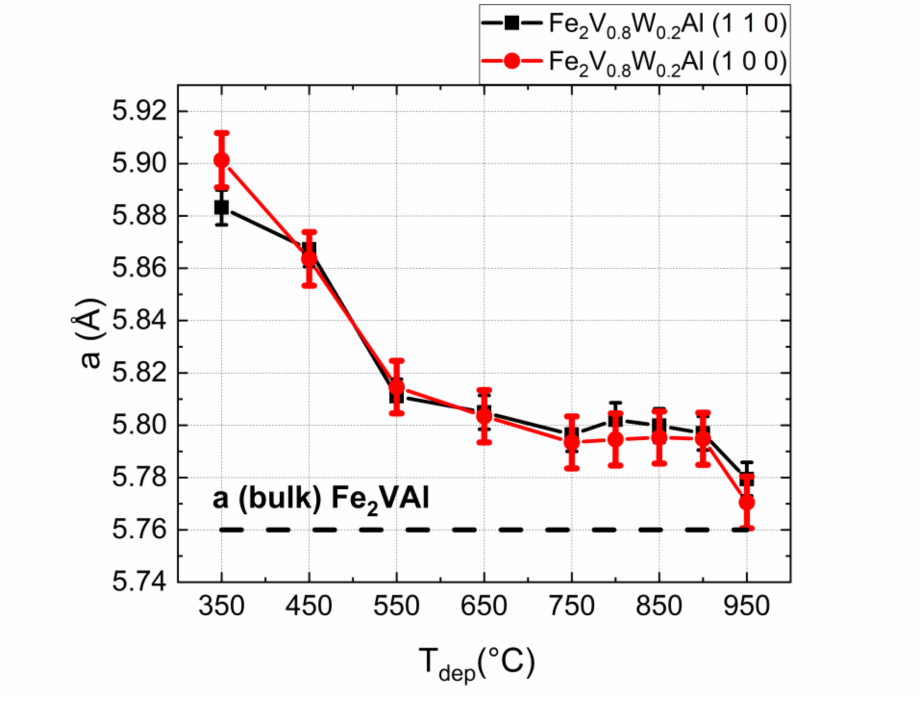
Phi scans, lattice parameter and crystallite size



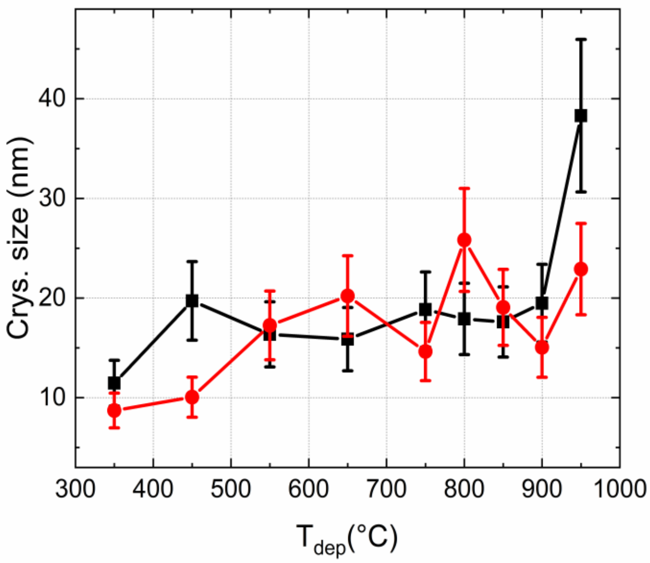
SI 7: ϕ-scan of (2 2 0) diffraction peak of $Fe_2V_{0.8}W_{0.2}Al$ films deposited on MgO for various $T_{dep.}$



SI 8: *ϕ-scan of (4 0 0) diffraction peak of $Fe_2V_{0.8}W_{0.2}Al$ films deposited on Al_2O_3 for various T_{dep}.*



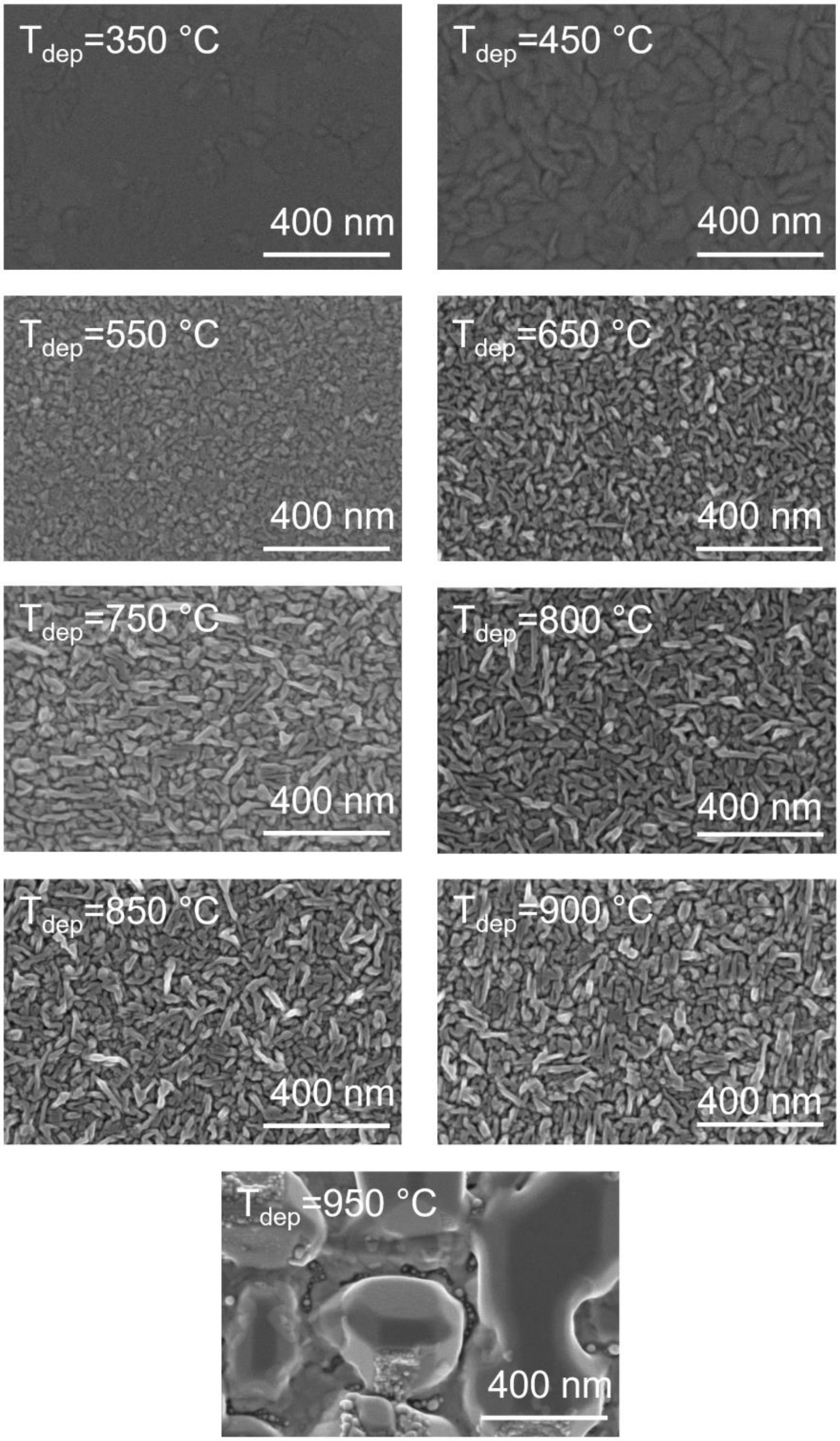
SI 9: *Out-of-plane lattice parameter on specular ($\psi=0°$) $\theta/2\theta$ measurements for $Fe_2V_{0.8}W_{0.2}Al$ deposited on MgO (red) and Al_2O_3 (black). The measured distances are compared with the bulk lattice parameter of Fe_2VAl from [1].*



SI 10: Out-of-plane crystallite size obtained from Scherrer's formula of the specular (ψ=0°) θ/2θ measurements of $Fe_2V_{0.8}W_{0.2}Al$ *(1 0 0) and (1 1 0) films.*

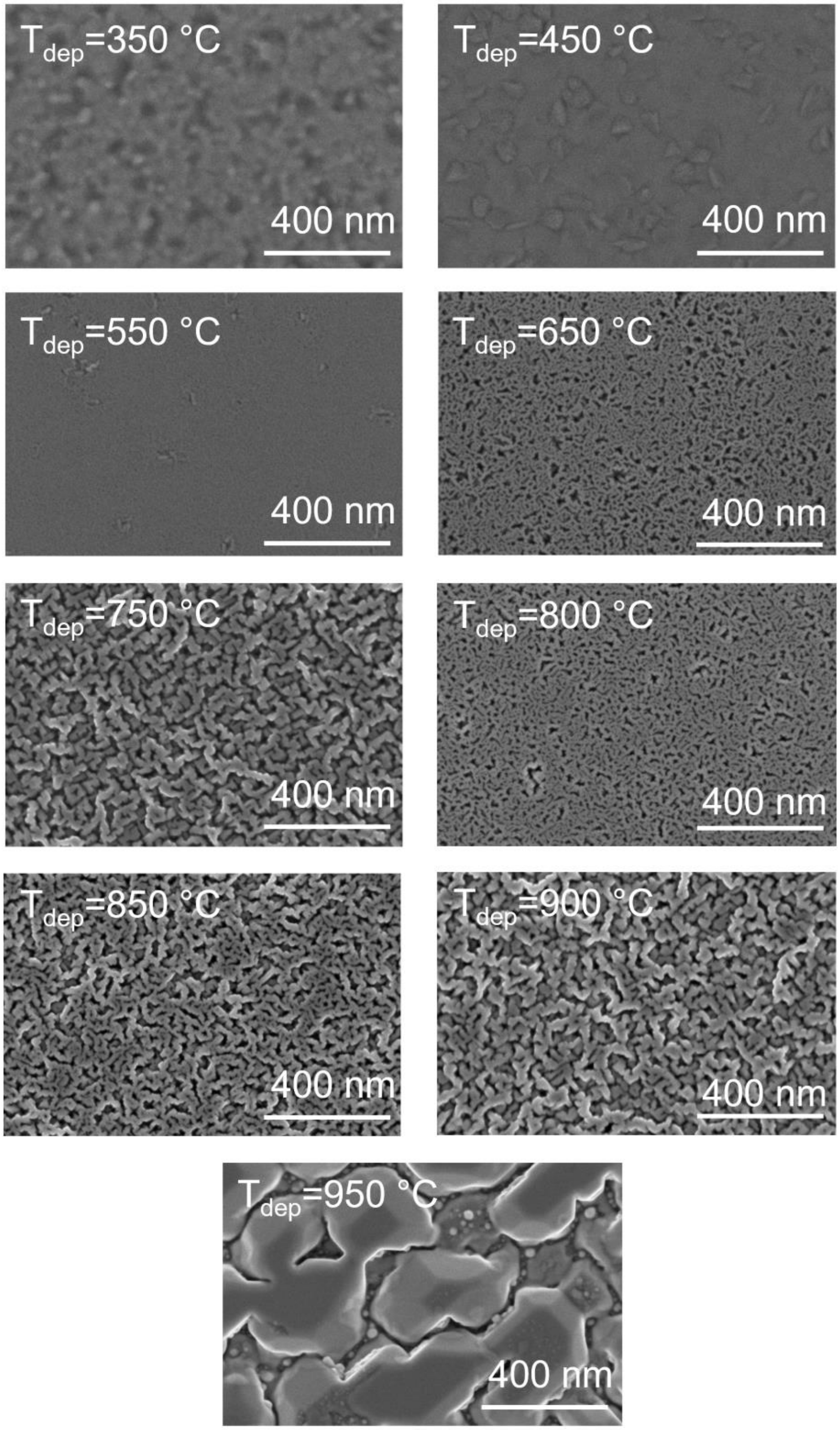
SEM

Al_2O_3 substrate:



SI 11: SEM micrographs of $Fe_2V_{0.8}W_{0.2}Al$ *films deposited on* Al_2O_3 *at all* T_{dep}*.*

MgO substrate:



SI 12: SEM micrographs of $Fe_2V_{0.8}W_{0.2}Al$ *films deposited on MgO at all* T_{dep}.

Additional simulations

Reproducibility statements

This work consists of one deposited series (on Al_2O_3 and MgO substrates) with deposition temperatures ranging from 350°C to 950°C. In order to avoid temporal drifts in the deposition system each sample series was deposited in a random order of T_{dep} (i.e., chronologically the samples were deposited with T_{dep} covering in a random fashion the T_{dep} range). The whole deposition spanned for two and a half months, showing the stability of the process. Besides some minor differences in the thermoelectric values between concrete cases of the general tendency of $L2_1$ boost in the Seebeck coefficient and in the thermoelectric power factor is reproduced. Moreover, the sample for the thermal conductivity determination was deposited more than twelve months after the main series, since a thicker sample is required for optical measurements of thermo-reflectance. These considerations ensure the reproducibility and stability of the deposition procedure.