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Letter

Charged domains in ferroelectric, polycrystalline yttrium manganite thin films resolved with scanning electron microscopy

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Abstract

We have investigated ferroelectric charged domains in polycrystalline hexagonal yttrium manganite thin films ($\text{Y}_1\text{Mn}_1\text{O}_3$, $\text{Y}_{0.95}\text{Mn}_{1.05}\text{O}_3$, $\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$, and $\text{Y}_{0.94}\text{Mn}_{1.05}\text{Ti}_{0.01}\text{O}_3$) by scanning electron microscopy (SEM) in secondary electron emission mode with a small acceleration voltage. Using SEM at an acceleration voltage of 1.0 kV otherwise homogenous surface charging effects are reduced, polarization charges can be observed and polarization directions ($\pm P_z$) of the ferroelectric domains in the polycrystalline thin films can be identified. Thin films of different chemical composition have been deposited by pulsed laser deposition on Pt/SiO₂/Si structures under otherwise same growth conditions. Using SEM it has been shown that different charged domain density networks are existing in polycrystalline yttrium manganite thin films.

Keywords: charged domains, ferroelectric domains, polycrystalline, yttrium manganite thin films, scanning electron microscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Rare earth hexagonal manganites belong to the group of multiferroics, in which magnetic and ferroelectric properties co-exist. Multiferroic materials received much attention due to the applications in the field of non-volatile memories [1] and nanosensors [2]. In hexagonal YMnO_3 (*h*- YMnO_3) the Mn^{3+}



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ions are coordinated with five oxide ions (three in-plane and two apical). Non-connected layers of MnO_5 bipyramids are separated by Y^{3+} ions along the z -axis, which are coordinated by eight oxide ions [3, 4]. Ferroelectricity induced in $h\text{-YMnO}_3$ is due to electrostatic and geometrical effects. It emerges in two steps [5, 6]: In a two-step transition, at the Curie temperature, $T_C = 1270$ K, the centrosymmetric crystal structure $P6_3/mmc$ is lowered to $P6_3cm$ by the condensation of K_3 nonplanar mode [7, 8] and a secondary mode provides the ferroelectric polarization by corrugation of Y^{3+} planes with spontaneous polarization of $5.6 \mu\text{C cm}^{-2}$ [8, 9]. Ferroelectricity in hexagonal manganites also has been claimed to emerge in a single-step transition together with a trimerizing lattice distortion [10, 11]. The Curie temperatures reported are in the range of 910 K to 1270 K [4, 10–15]. Ferroelectric, polycrystalline hexagonal yttrium manganite thin films can be grown at temperatures below the Curie temperature [16].

In $h\text{-YMnO}_3$, unit-cell tripling leads to three trimerization antiphase's ($\alpha^\mp, \beta^\mp, \gamma^\mp$) and subsequent ionic displacement leads to two different ferroelectric polarization (upward polarization ($+P_z$) and downward polarization ($-P_z$)) [17]. Merging of alternative ferroelectric polarization and trimerization results in two possible domain sequence: $\alpha^+, \beta^-, \gamma^+, \alpha^-, \beta^+, \gamma^-$ (vortex) and $\alpha^+, \gamma^-, \beta^+, \alpha^-, \gamma^+, \beta^-$ (anti-vortex) [17]. In periodic lattice, it has six different phases rotated by 60° with respect to each other. Ferroelectric domain walls are firmly locked with magnetic domain walls in multiferroic hexagonal manganites. Transmission electron microscopy (TEM) [18, 19] and scanning probe microscopy (SPM) [20] investigations reveal ‘cloverleaf’ vortex like domain pattern in single crystalline $h\text{-YMnO}_3$, with a feature size of $1\text{--}2 \mu\text{m}$. On the other hand, there exists only a few reports on ferroelectric domains and domain structure in polycrystalline and atomic substituted $h\text{-YMnO}_3$ [21, 22]. It is also reported that annular domains, stripe domains [23] can appear in certain temperature range and often co-exist with vortex like domains for Fe substituted at Mn-site in polycrystalline $h\text{-YMnO}_3$ [22]. In single crystalline $\text{Y}_{0.67}\text{Lu}_{0.33}\text{MnO}_3$ topological four state domain pattern was observed [23]. Ti^{4+} substitution of Mn-site in $h\text{-YMn}_{1-x}\text{Ti}_x\text{O}_3$ single crystals for $0 < x < 0.30$ drastically changes the ferroelectric domain size [21, 24]. Domain structure of oxygen deficient YMnO_3 and $\text{YMnO}_{3-\delta}$ single crystals were investigated by Chen *et al* using piezoresponse force microscopy (PFM) [25]. Instead of domain vortex structure in stoichiometric crystals, $\text{YMnO}_{3-\delta}$ exhibits a random domain configuration with straight domain walls [25]. Density of vortices in different RMnO_3 ($R = \text{Y, Dy, Er, Tm}$) single crystals cooled down below the ferroelectric ordering temperature was investigated by Meier *et al* [26] with piezoresponse force microscopy (PFM) in dependence on the cooling rate and revealed a linear dependence of vortex density on cooling rate in logarithmic scale [26]. In addition to PFM, surface and polarization charges of ferroelectric materials have also been investigated with nanoscale resolution by Kelvin probe force microscopy (KPFM) and by Charge gradient microscopy (CGM) [27–30]. The effect of film thickness in single and polycrystalline and of grain size in polycrystalline films on

peculiarities of surface and polarization charges films with KPFM, PFM, and CGM has not been addressed in literature.

In this letter, we report on the observability of ferroelectric charged domains in polycrystalline hexagonal yttrium manganite thin films ($\text{Y}_1\text{Mn}_1\text{O}_3$, $\text{Y}_{0.95}\text{Mn}_{1.05}\text{O}_3$, $\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$, and $\text{Y}_{0.94}\text{Mn}_{1.05}\text{Ti}_{0.01}\text{O}_3$) using scanning electron microscopy (SEM). SEM is a non-destructive method with high spatial resolution and easy sample preparation. Because ferroelectrics are good insulators, typically their surfaces get charged under electron beam irradiation. To reduce the electrostatic charging effect or to keep it minimal, the SEM cathode acceleration voltage is kept as low as 1.0 kV. An electrostatic charge is homogenous and would mask the local charges of the charged domain walls.

2. Thin film deposition and experimental technique

Yttrium manganite ceramic targets ($\text{Y}_1\text{Mn}_1\text{O}_3$, $\text{Y}_{0.95}\text{Mn}_{1.05}\text{O}_3$, $\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$, and $\text{Y}_{0.94}\text{Mn}_{1.05}\text{Ti}_{0.01}\text{O}_3$) have been prepared by conventional solid-state reaction sintering process. High purity powders of Y_2O_3 , MnO_2 and TiO_2 weighted according to stoichiometric proportions (depending on the composition of the targets), were thoroughly wet grinded to a powder of about $200 \mu\text{m}$ particle size and the mixture has been dried for 2 d. The mixture is preheated at 1000°C for 5 h and the resulting powders were reground, pressed into pellets, and sintered at 1350°C for 10 h (heating rate: 300°C h^{-1} and cooling rate: 200°C h^{-1} in air) and furnace cooled to room temperature. All the mentioned procedures were performed in air. Using energy-dispersive x-ray (EDX) spectroscopy, Ti contamination has been detected in the metalized substrates from Hefei Kejing Materials (China). Possibly, due to this Ti contamination the Pt bottom electrode (150 nm) remains stable on SiO_2 (500 nm)/Si. After reaching a base pressure of 10^{-6} mbar in the deposition system, the substrate temperature has been increased at a heating rate of 30 K min^{-1} to 800°C . The deposition of yttrium manganite thin films began immediately after the substrate temperature stabilized at 800°C by using a KrF excimer laser operating at 248 nm wavelength. Laser energy E , pulse repetition rate f , substrate temperature T_s , and oxygen partial pressure p_{O_2} have been kept constant for the PLD deposition process at $E = 2.5 \text{ J cm}^{-2}$, $f = 3 \text{ Hz}$, $T_s = 800^\circ\text{C}$, and $p_{\text{O}_2} = 0.18 \text{ mbar}$. Besides oxygen no additional gas has been introduced into the PLD chamber. The number of laser pulses is 6000 for all samples presented in this paper. The cooling process began immediately after the deposition process. Oxygen is continuously admitted and an oxygen partial pressure of 1 mbar has been built up in the PLD chamber. The temperature is reduced to 100°C at a programmed cooling rate of 20 K min^{-1} . Samples are then taken out at a temperature of around 100°C and then placed in the desiccator. The re-oxidation of the deposited thin films takes place during the cooling process in the PLD chamber and is caused by the diffusion of oxygen from the thin film surface into the film towards the film substrate interface. Therefore, the oxygen stoichiometry is expected to be slightly

inhomogeneous within the yttrium manganite thin films, with a larger oxygen concentration at the surface compared to the bulk [31]. However, the oxygen concentration may also be influenced by the composition of the used target.

A Bruker D8 Advance x-ray diffractometer equipped with a Goebel mirror has been used to identify the crystalline structure of thin films ($\text{Y}_1\text{Mn}_1\text{O}_3$, $\text{Y}_{0.95}\text{Mn}_{1.05}\text{O}_3$, and $\text{Y}_{0.94}\text{Mn}_{1.05}\text{Ti}_{0.01}\text{O}_3$). A GE Seifert 3000PTS x-ray diffractometer (also with parallel beam optics and an additional monochromator crystal) has been used to investigate the crystalline structure of $\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$ thin film. The diffraction patterns of yttrium manganite thin films deposited on Pt/SiO₂/Si have been recorded with a fixed small incident angle $\omega = 0.5^\circ$, called grazing incidence (GI). We used Kelvin probe force microscopy (KPFM) and Scanning electron microscopy (SEM) to investigate polarization charges of the ferroelectric domains in the polycrystalline yttrium manganite thin films. Both, KPFM and SEM, are sensitive to any kind of surface charge. Surface charging effects may dominate the electrostatic gradient field influencing the oscillating movement of the conducting KPFM tip during KPFM measurements and the scattering of electrons during SEM measurements. Therefore, surface charges have to be smaller than polarization charges in order to realize dominating electrostatic gradient fields from the ferroelectric domains. Surface potentials of the thin films were characterized with a Level-AFM from Anfattec Instruments AG, operated under nitrogen atmosphere in dark conditions. During the KPFM measurements topography and electrical signals were probed simultaneously in amplitude modulation mode using Pt coated n-type Si cantilevers (MikroMasch HQ:NSC18/Pt, resonance frequency: $f_{\text{res}} = 75$ kHz, spring constant: $k = 2.8$ N m⁻¹) with a typical tip radius of less than 30 nm. The topography was measured at the 1st eigenmode (≈ 75 kHz) and Kelvin bias was measured at the 2nd eigenmode (≈ 450 kHz) of the cantilever with an excitation voltage of $V_{\text{AC}} = 1.0$ V. A Carl Zeiss NTS field emission scanning electron microscope was used to investigate the ferroelectric domains in yttrium manganite thin films. An in-lens detector is used to map the sample surface. The benefit of using an in-lens detector is its high detection efficiency of the secondary electrons. In particular, at low acceleration voltages and small working distances, images with high contrast can be obtained. In-addition to the information about the morphology and surface topography, the in-lens detector images differences in the work function i.e. electronic variations on the sample with high lateral resolution. In case of images recorded by the conventional secondary electron detector, the topographic information of ferroelectric, polycrystalline thin films is dominant and their charged domain walls cannot be detected.

3. Results and discussion

GI-XRD patterns (figure 1) of as-grown polycrystalline thin films are assigned to h -YMnO₃ with a space group $P6_3cm$. GI-XRD patterns are indexed by the respective Miller indices (hkl) and correspond to the Crystallography Open Database

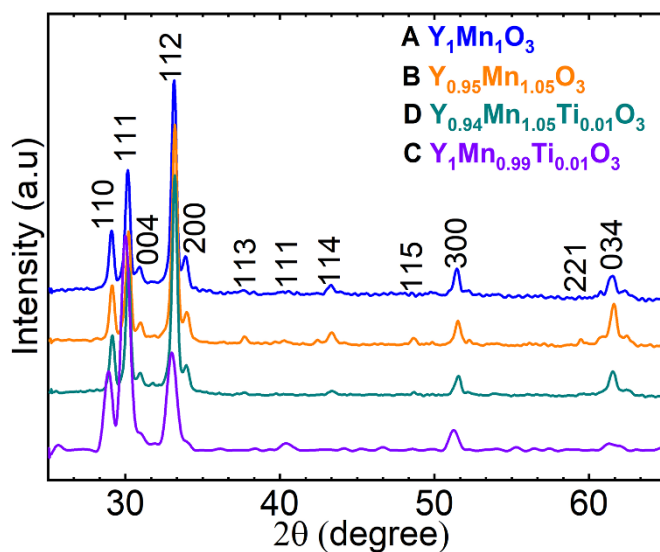


Figure 1. Grazing incidence XRD data of the samples A ($\text{Y}_1\text{Mn}_1\text{O}_3$), B ($\text{Y}_{0.95}\text{Mn}_{1.05}\text{O}_3$), C ($\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$), and D ($\text{Y}_{0.94}\text{Mn}_{1.05}\text{Ti}_{0.01}\text{O}_3$) grown on Pt bottom electrode and SiO₂/Si substrate with a constant incident angle of $\omega = 0.5^\circ$. For a better visibility the XRD lines are stacked by different Y offsets. Reflections are assigned to h -YMnO₃ and respective Miller indices hkl .

(COD) entry 2011820 for h -YMnO₃. Substitution levels are nominal and no additional phases have been observed. Sample C ($\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$) has a small crystallite size [32] and diffraction pattern with relatively low intensities. When fitting the XRD data of sample C with Rietveld method, an additional background peak at around $2\theta = 31.6^\circ$ is added, which accounts for crystallite sizes smaller than 3 nm. This is a common method for analyzing XRD data with the Rietveld method.

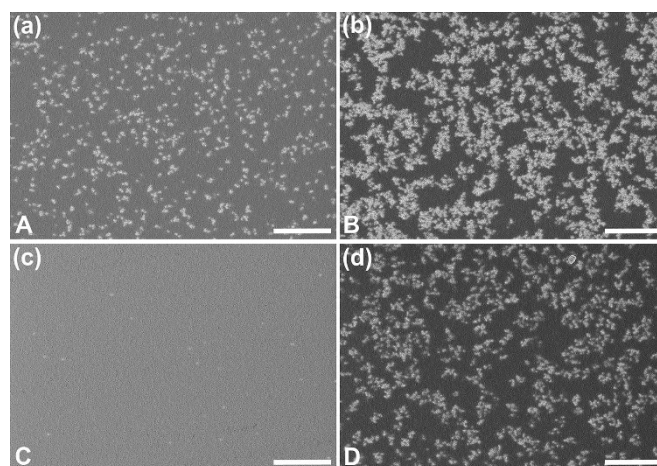
Figures 2(a)–(d) show the secondary electron images of polycrystalline yttrium manganite thin films (table 1) measured with an in-lens detector. The bright and dark contrasts of the SEM images are due to different secondary electron emission current from the virgin thin films and refer to different polarization ($\pm P_z$) directions. Scan time of the image is 72 s (figures 2(a)–(d)). When an electron beam is irradiated on the observed region a portion of this energy is used to excite the secondary electrons with emission coefficient (δ). Except the energy taken by secondary electrons and back-scattered electrons, the remaining energy of the incident electrons is absorbed by the sample and turned into thermal energy. The temperature in the irradiated region rises and then the pyroelectric effect results in a change of the surface potential. The dwell time (τ_d), length of time that the primary electron beam dwells on the specimen is 10^{-7} s. The conductivity is given by the equation $\sigma = J/E$ where, σ is the conductivity, J is the current density and E is the electric field. The current densities are extracted at a low voltage (0.1 V) and taken from our work [32]. The thickness of the thin films is 200 nm. By using the equation $\sigma = J/E$ the conductivity of the thin films has been calculated (table 1). Maxwell relaxation time constant ($\tau_m = \epsilon\epsilon_0/\sigma$, where ϵ is relative dielectric

Table 1. Sample ID, target composition, current density at 0.1 V, conductivity and Maxwell relaxation time constant of the yttrium manganite thin films.

Sample	Target composition	Current density [32] (10^{-2} A m $^{-2}$)	Conductivity [32] (10^{-7} S m $^{-1}$)	Relaxation time (τ_m) (10^{-4} s)
A	Y ₁ Mn ₁ O ₃	7.0	1.4	0.13
B	Y _{0.95} Mn _{1.05} O ₃	10.0	2.0	8.85
C	Y ₁ Mn _{0.99} Ti _{0.01} O ₃	6.0	1.2	0.16
D	Y _{0.94} Mn _{1.05} Ti _{0.01} O ₃	9.0	1.8	9.83

constant of YMnO₃ [33], ε_0 is permittivity of vacuum and σ is conductivity (S m $^{-1}$) of yttrium manganite thin films) is an intrinsic property of the thin films and depends only on the conductivity ($\sigma = J/E$). Using the dielectric constant of YMnO₃, i.e. $\varepsilon = 20$ [33], and conductivity calculated from previous report by Rayapati *et al* [32] the Maxwell relaxation time constant is calculated (table 1) for all yttrium manganite thin films. Thin films show $\tau_d < \tau_m$, which means the bombarded electrons on the sample are unable to relax. If $\tau_d > \tau_m$, the incident electrons on the samples are relaxed. In this letter $\tau_d < \tau_m$. Therefore, the accumulated charges cannot be completely screened within the dwell time. Increase in local temperature due to the pyroelectric effect gives rise to surface potential i.e. negative potential for local polarization vector with upward polarization components and positive potential for local polarization vector with downward polarization components [34, 35]. Positive surface potential and pyroelectric effect strongly affect the intrinsic secondary electron emission from ferroelectric domains [34]. Secondary electron emission yield from local polarization vector with upward polarization components is larger than from the local polarization vector with downward polarization components. The number of secondary electrons arriving at the detector is large for local polarization vector with upward polarization components, making them brighter. For local polarization vector with downward polarization components, the yield of secondary electrons is less and the contrast of the domain is dark. Different contrasts of ferroelectric domains characterized by SEM are observed in KTiOPO₄ [34], LiTaO₃ [35] and single crystalline YMnO₃ [36, 37].

Ferroelectric charged domain network formation in case of sample B (Y_{0.95}Mn_{1.05}O₃) is dense and close compared to the remaining samples in this work. Sample A (Y₁Mn₁O₃) and Sample D (Y_{0.94}Mn_{1.05}Ti_{0.01}O₃) reveal an extended domain network. In case of Mn rich composition, Sample B (Y_{0.95}Mn_{1.05}O₃) and Sample D (Y_{0.94}Mn_{1.05}Ti_{0.01}O₃), the polycrystalline yttrium manganites show an increase in formation of dense domain network compared to sample A (Y₁Mn₁O₃) and sample C (Y₁Mn_{0.99}Ti_{0.01}O₃). However, in case of sample C (Y₁Mn_{0.99}Ti_{0.01}O₃), small isolated domains are observed. Sample C (Y₁Mn_{0.99}Ti_{0.01}O₃) shows a smaller crystallite sizes [27], grain sizes (figure 3(k)) and with an amorphous contribution in the thin film. Ferroelectric domains observed in YMnO₃ are in general appearing due to the trimerizing tilt of the trigonal bipyramids and corrugation of Y³⁺ planes. The type of the domains observed depends on the temperature at which the thin films were deposited and on the film composition. For example, domain vortex structure was

**Figure 2.** $11 \times 8 \mu\text{m}^2$ large SEM images with in-lens detector and small acceleration voltage in samples (a) A (Y₁Mn₁O₃), (b) B (Y_{0.95}Mn_{1.05}O₃), (c) C (Y₁Mn_{0.99}Ti_{0.01}O₃), and (d) D (Y_{0.94}Mn_{1.05}Ti_{0.01}O₃). The bright regions correspond to local polarization vector with upward polarization components (+P_Z) and dark regions to local polarization vector with downward polarization components (−P_Z). The scale bar is 2 μm .

observed in stoichiometric YMnO₃ single crystals and random domain configuration with straight domain walls was observed in YMnO_{3- δ} single crystals [25]. Due to the enhanced oxygen concentration at the surface compared to the bulk and the influence of dopants on grain growth and their size distributions (figures 3(i)–(l)) a different domain density network is observed. These effects may influence the trimerizing tilt of the trigonal bipyramids and corrugation of Y³⁺ planes. For as grown films Y₁Mn₁O₃, Y_{0.95}Mn_{1.05}O₃, Y₁Mn_{0.99}Ti_{0.01}O₃, and Y_{0.94}Mn_{1.05}Ti_{0.01}O₃ films we estimated a domain density of approx. $5.13 \mu\text{m}^{-2}$ (Sample A, figure 2(a)), $8.56 \mu\text{m}^{-2}$ (Sample B, figure 2(b)), $0.13 \mu\text{m}^{-2}$ (Sample C, figure 2(c)), and $6.41 \mu\text{m}^{-2}$ (Sample D, figure 2(d)) from the number of small bright spots (compare bright spots in figure 2(a)) in SEM images with in-lens detector and small acceleration voltages. The observed domain density network is homogenous over the whole area ($1 \times 1 \text{ cm}^2$) of the investigated thin films.

Figure 3 shows the topography (figures 3(a)–(d)) and probed electrical signal images (figures 3(e)–(h)) with AFM and KPFM, respectively. In samples A (Y₁Mn₁O₃), B (Y_{0.95}Mn_{1.05}O₃) and D (Y_{0.94}Mn_{1.05}Ti_{0.01}O₃) charging effects can be observed (table 1). The dark contrast of KPFM image corresponds to more negative surface potential. Even though with visible ferroelectric domains from KPFM images,

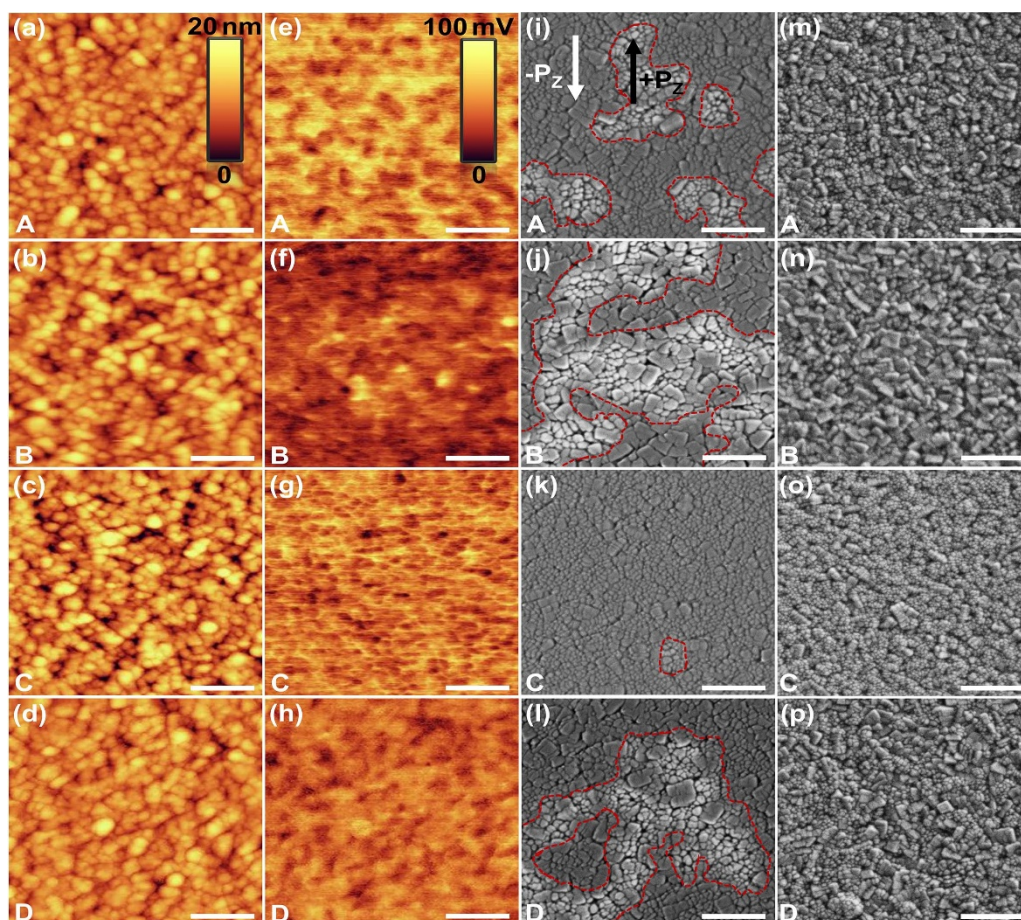


Figure 3. $1 \times 1 \mu\text{m}^2$ large AFM (a)–(d), KPFM (e)–(h), SEM with with an in-lens detector, and SEM with conventional secondary electron detector (m)–(p) images of samples A ($\text{Y}_1\text{Mn}_1\text{O}_3$), B ($\text{Y}_{0.95}\text{Mn}_{1.05}\text{O}_3$), C ($\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$), and D ($\text{Y}_{0.94}\text{Mn}_{1.05}\text{Ti}_{0.01}\text{O}_3$). Ferroelectric domains are only clearly visible in the SEM images with an in-lens detector (i)–(l), where bright regions correspond to local polarization vector with upward polarization components ($+\text{P}_z$) and dark regions to local polarization vector with downward polarization components ($-\text{P}_z$). The arrows indicate the z -component of the vector (out-of-plane). Note, that the individual x , y , z components of the polarization vector are not known. The AFM, KPFM, and SEM scale bar is 250 nm. The positions of AFM and KPFM and of SEM with an in-lens detector and SEM with conventional secondary electron detector are the same. Note that the position of AFM/KPFM and of SEM are not the same.

identification of the respective domains requires further work. Sample C ($\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$), which shows faint ferroelectric domains in SEM (figure 3(k)), does not show the charging effects like the remaining samples in KPFM. SEM image with an in-lens detector and at higher magnification in figures 3(e)–(h) show the distribution of ferroelectric regions with local polarization vector with upward polarization components ($+\text{P}_z$) and local polarization vector with downward polarization components ($-\text{P}_z$). SEM image with conventional secondary electron detector in figures 3(m)–(q) show only the topographic information. Whereas, using SEM with an in-lens detector differences in the work function i.e. electronic variations, can be detected on the samples.

4. Conclusion

In this work, we have resolved charged ferroelectric domains in polycrystalline hexagonal yttrium manganite thin films deposited by pulsed laser deposition using scanning electron

microscopy in secondary emission mode. The observed dependency of different compositions to the charged domain density network in yttrium manganite thin films is influenced by different factors: stoichiometry gradient, oxygen, dopant concentration and the resulting grain structure. A dense domain network is observed for Mn-rich samples ($\text{Y}_{0.95}\text{Mn}_{1.05}\text{O}_3$ and $\text{Y}_{0.94}\text{Mn}_{1.05}\text{Ti}_{0.01}\text{O}_3$) in comparison to $\text{Y}_1\text{Mn}_1\text{O}_3$. Especially $\text{Y}_1\text{Mn}_{0.99}\text{Ti}_{0.01}\text{O}_3$ with very small grains show isolated charged domains. Transmission electron microscopy, kelvin probe force microscopy, piezoresponse force microscopy, and conductive atomic force microscopy are time intensive to characterize the charged ferroelectric domains. We demonstrated that scanning electron microscopy with in-lens detector and small acceleration voltages is a fast and versatile technique/alternative to determine the charged ferroelectric domains in polycrystalline hexagonal yttrium manganite thin films. It is expected that SEM can also be applied to investigate the ferroelectric domain structure in other polycrystalline hexagonal manganite thin films.

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