Superior Piezo-/Ferro-Electricity in Antiferroelectric $Ag_xNbO_{3-\delta}$ Thin Films by Nanopillar Local Structure Design

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However, harnessing their superior properties presents a significant challenge due to the delicate balance required between their various states. In this study, through the unique design of nanopillar structures to alleviate the local polar heterogeneity, we have achieved significantly improved piezo-/ferro-electricity in classic lead-free antiferroelectric Ag_xNbO_{3- $\delta}$} (x = 1, 0.9, and 0.8) epitaxial thin films. The effective piezoelectric coefficient reaches 440 pm V⁻¹, 1 order of magnitude larger than the stoichiometric AgNbO₃, rivaling classic lead zirconate titanate piezoelectrics. Atomic-scale electron microscopy investigations unravel the underlying mechanisms. The nanopillars, characterized by antisite occupancy of both Ag and Nb atoms and forming out-of-phase boundaries with the matrix, reduce the local



crystal symmetry via interphase strain. This leads to the creation of flexible multinanodomain structures that significantly facilitate polarization rotation, thus substantially enhancing the piezoelectric performance. This study demonstrates the feasibility of engineering local heterogeneity through nanopillar design, offering a generally applicable method for property improvement of a wide range of antiferroelectrics.

KEYWORDS: ferroelectric, piezoelectric, AgNbO₃, nanopillar, interphase strain

1. INTRODUCTION

Antiferroelectrics, a crucial category of functional materials, are distinguished by their antiparallel electric dipole alignment, which results in unique double hysteresis curves.¹ These materials display diverse properties such as high dielectric permittivity,² strain induced by phase transitions,³ and distinct thermal behaviors.^{4,5} This range of characteristics renders them exceptionally suitable for various applications, including energy storage,^{6,7} sensors,⁸ and actuators.⁹ More importantly, they have emerged as fundamental building blocks crucial for advancing lead-free piezoelectric and ferroelectric technologies, as they generally have intricate lattice dynamics and structural distortions and include delicate competing among different states, including centrosymmetric, antiferroelectric (AFE), and ferroelectric (FE) states.^{10–14} Thus, this fundamental nature of antiferroelectrics makes understanding and precisely controlling their material properties a challenging task.

Typical antiferroelectrics encompass a range of materials, including lead-based perovskites, like PbZrO₃ and PbHfO₃,^{15,16} lead-free perovskites, such as AgNbO₃ and NaNaO₃,^{17,18} and certain binary oxides, like ZrO₂.¹⁹ Among them, the lead-free AFE perovskite AgNbO₃ stands out not only for its environmentally friendly, lead-free nature but also for its ferrielectric-like ground states, capable of exhibiting an

exceptionally large polarization of 52 μ C cm⁻² under electric fields.²⁰ What sets AgNbO₃ apart even more is its intriguing phase transition behavior, which can be finely tuned by varying temperature,²¹ pressure,²² and composition.²³ It has been demonstrated that, within only a 200-degree temperature range, AgNbO₃ can undergo complex phase transitions, traversing several phases (including M1, M2, and M3) with striking phase similarities.^{24,25} This is attributed to its surprisingly low free energy difference between centrosymmetric (nonpolar) and noncentrosymmetric (polar) states, which is only 0.1 meV f.u.^{-1,11} Therefore, centrosymmetric AFE, and noncentrosymmetric FE states are nearly energy degenerate within this system. These unique attributes render AgNbO₃ highly sensitive to external perturbations like defects,^{26,27} dopants,^{23,28} nonstoichiometry,^{29,30} and lattice strain,^{31,32} which provides a fertile ground for the exploration of exotic properties finely manipulating the delicate balance

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between competing states. However, despite its promising potential, comprehensive studies exploring the tunability of AgNbO₃'s ground states and the spectrum of properties that can be induced remain scarce and are still limited, largely due to the material's inherent complexity. Therefore, it underscores the need for an in-depth investigation into external perturbations' effects to more effectively tailor and engineer AgNbO₃ for desired applications and to synthesize the material in a controlled manner for optimal property manifestation. Particularly, recent advances in NaNbO₃ and PbZrO₃ have demonstrated that tailored adjustments in chemical composition can significantly influence the ground states and local structures, leading to the emergence of novel properties.^{33,34} This has further sparked interest in exploring the untapped potential in AgNbO₃.

In this study, we successfully manipulated the AFE-FE phase stability in $Ag_xNbO_{3-\delta}$ epitaxial thin films by finely tuning the film stoichiometry (x = 0.8, 0.9, and 1). These films feature unique, well-defined nanopillar structures and demonstrate pronounced ferroelectricity up to 540 K. Remarkably, they achieved a piezoelectric response as high as 440 pm V^{-1} , rivaling the classic system like lead zirconate titanate (PZT) $(d_{33} \sim 408 \text{ pm V}^{-1})$.³⁵ The robust macroscopic ferroelectric properties and significant piezoelectric response of these films were validated through comprehensive ferroelectric hysteresis measurements and piezoelectric force microscopy (PFM) analysis. By using atomic-scale scanning transmission electron microscopy (STEM), the microscopic origin of the superior properties has been unraveled, which is rooted in the antisite occupation of Nb atoms at Ag sites within the nanopillar regions (NPRs). This occupation leads to local structural distortions, which in turn generate notable off-site displacements and dipoles. Besides, through the construction of local heterogeneity by forming NPRs, the multidomain structure was confirmed by the polar mapping analysis, resulting in the obvious enhancement of the piezoelectric response. Our findings not only shed light on the mechanisms driving the phase transition between AFE and FE states in these materials but also open up new avenues for innovative strategies for harnessing and manipulating phase stability for advanced material applications.

2. EXPERIMENTAL PROCEDURES

2.1. Target Synthesis and Thin Film Deposition. A series of the Ag_xNbO_{3- δ} targets with different Ag contents were prepared by Ag₂O and Nb₂O₅ powders through a conventional solid-state reaction, where the Ag₂O/Nb₂O₅ molar ratios were maintained at 1:1, 1.1:1, and 1.3:1, respectively. To inhibit the high-temperature decomposition of Ag_2O , all samples were sintered under an oxygen atmosphere. These targets were presintered at 900 °C for 6 h and then sintered at 1050 °C for 6 h. Thin films were fabricated on (001)oriented single-crystal SrTiO₃ substrates by pulsed laser deposition. A KrF excimer laser with a wavelength of 248 nm was used to ablate the $Ag_{r}NbO_{3-\delta}$ targets at a repetition rate of 5 Hz and an energy density of 1.25 J cm⁻² for depositing the Ag_xNbO_{3- δ} films. During the deposition, the oxygen pressure and substrate temperature were controlled at 15 Pa and 550 °C, respectively. After deposition, the film was in situ annealed for 15 min under an oxygen pressure of 15,000 Pa, and then the temperature was reduced to room temperature at a cooling rate of 15 °C min⁻¹.

2.2. Composition Characterization. The film chemistry was determined by energy dispersive spectrometry from scanning electron microscopy (LEO1530, ZEISS SUPRA 55, Oberkochen, Germany) and X-ray photoelectron spectrometry (ESCALAB Xi+, Thermo Fisher Scientific).

2.3. Structural Characterization and Analysis. The macrostructure of the thin film was examined by high-resolution X-rays (Rigaku SmartLab) with Cu K α radiation. The cross-sectional microstructure was characterized by STEM using a double aberration-corrected FEI Titan Themis G2 microscope operated 3 at 300 kV. The collection angle is 12-45 mrad and 48-200 mrad for ABF and HAADF, respectively. To extract the precise atom positions, 2D Gaussian peaks were employed to fit each atomic column profile in STEM images using in-house MATLAB codes. We set the coordinate system such that the horizontal and vertical directions correspond to the X-axis and Y-axis, respectively, with the coordinate origin located at the left top corner. The specific lattice parameters for out-of-plane (c) and in-plane (a) were quantified for each unit cell of the structure based on the determined atom positions. The unit-celllevel c/a ratio was calculated as $(c_1 + c_2)/(a_1 + a_2)$ by using the nearest-neighbor Ag column positions. The polar vector map was calculated from the relative displacement of the Nb cation position with respect to the centroid of the surrounding four Ag atoms.

2.4. Electric Measurements. For electrical property measurements, circular Pt top electrodes with a diameter of 50 μ m were deposited by using a shadow mask by magnetron sputtering. The electrode area was measured by using an optical microscope equipped with a scale ruler. The bottom electrode was a conductive 0.7 weight % Nb-doped SrTiO₃ substrate. Hysteresis loop measurements were performed by using a ferroelectric analyzer (TF Analyzer 1000, aixACCT, Germany). Surface morphology, switching of ferroelectric domains, and piezoelectric response were measured by PFM (MFP-3D, Asylum Research, USA, and Dimension Icon, Bruker, Germany). The temperature-dependent dielectric spectra were performed using an Agilent E4980A (Agilent Technologies Company, Palo Alto, CA, USA).

2.5. Chemical Valence, Composition, and Electronic Structure Analyses. X-ray photoelectron spectroscopy data and depth profiling analyses were collected using an X-ray photoelectron spectrometer (ESCALAB Xi+, Thermo Fisher Scientific). Soft X-ray absorption spectra were recorded at the 4B9B beamline of BSRF and the BL07U beamline of SSRF. All XPS spectra were also calibrated according to the 1s peak of carbon, and all X-ray absorption spectroscopy (XAS) spectra were calibrated using a Au standard sample.

2.6. First-Principles Calculations. Theoretical calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) type. The energy profile of the ANO system with a nanopillar structure was modeled with 14 Ag, 14 Nb, and 38 O atoms and determined using the variable cell nudged elastic band (VC-NEB) technique implemented in the USPEX code. The parameters for the ANO nanopillar structure were optimized using a plane-wave cutoff of 550 eV and an energy convergence threshold of 10^{-6} eV. A k-point spacing of 0.3 and 0.7 Å⁻¹ was used for structural optimizations and VC-NEB calculations, respectively. The stopping criterion for searching the minimum energy pathway connecting two nanopillar structures with opposite polarization states was set when the rootmean-square forces on images were less than 0.03 eV Å⁻¹, with the spring constant between neighboring images set within a range of $3.0-6.0 \text{ eV } \text{Å}^{-2}$.

3. RESULTS AND DISCUSSION

We fabricated the epitaxial AgNbO₃ (ANO) films by pulsed laser deposition on (001)-oriented SrTiO₃ (STO) substrates with varying Ag content (Ag_xNbO_{3- δ}, A_xNO, x = 1, 0.9, 0.8, 0.75, and 0.7) and a thickness of 350 nm (Figure S1a and Table S1). Experimental results indicate that very low Ag content (A_{0.75}NO and A_{0.70}NO) would introduce the Nb₂O₅ impurity phase (Figure S2), which can cause the films to lose their perovskite structure, adversely affect the ferroelectric properties, and deteriorate the piezoelectric response. Therefore, we primarily focus on the A_xNO films with x = 1, 0.9, and

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Figure 1. Structural characterization of A_x NO (x = 1, 0.9, and 0.8) films. (a) Out-of-plane high-resolution XRD pattern of A_x NO films grown on STO substrates. (b) RSM near the (103) spot of the substrate from ANO and $A_{0.8}$ NO films, where *H* and *L* represent the (*h*00) and (00*l*) Miller indices, respectively. (c) Dependence of the tetragonality (c/a) on the Ag content in A_x NO (x = 1, 0.9, and 0.8) films. (d) Low-mag cross-sectional HAADF-STEM image of the $A_{0.8}$ NO film. (e) Atomic-scale HAADF-STEM image of the $A_{0.8}$ NO film, showing the nanopillars embedded vertically in the matrix. (f) Schematic structural model for the $A_{0.8}$ NO film containing matrix and NPRs, which is constructed based on atomic-scale observations.



Figure 2. Electrical properties of the A_xNO films (x = 1, 0.9, and 0.8). (a,b) *P-E* loops of ANO and A_{0.8}NO films with the corresponding out-ofplane PFM phase images shown in the bottom right insets. (c,d) Dependence of dielectric permittivities on the temperature of ANO and A_{0.8}NO films, where the transitions between M₁-M₂ and M₂-M₃ are indicated by solid and dashed arrows, respectively. (e) M phase diagram built according to the temperature dependence of dielectric permittivity from A_xNO films. (f) Piezoelectric coefficient (d₃₃) obtained in this work compared with other common systems.^{23,33,35,39-45} Error bar is the standard deviation.

0.8 in this study. Figure 1a shows the typical high-resolution Xray diffraction (XRD) patterns of these A_xNO films, where only (00*l*) diffraction peaks, including (001) and (002) peaks, are observed. This suggests the high epitaxy and crystallinity of the films. By employing the reciprocal space mapping (RSM) technique, the in-plane lattice matching relationship between the A_xNO films and the STO substrate was determined. As illustrated in Figure 1b, the RSM results around the (103) spot reveal a well-matched in-plane lattice of the thin films with the STO substrate lattice. This congruence is observed consistently across all variations of the Ag content in the films (Figures 1b and S3a), highlighting the robustness of the epitaxial relationship between the films and the SrTiO₃ substrates. Besides, we note that the (103) reflection splits into two, which could result from the different *c* parameters of the matrix and NPRs due to the strain relaxation away from the coherent interface. Notably, a reduction in the Ag content leads to a slight decrease in the tetragonality (c/a ratio) of the A_xNO films, as shown in Figure 1c. This alteration in tetragonality is primarily due to a decrease in the out-of-plane lattice constant *c*, suggesting the structural distortions induced by the nonstoichiometry and underscoring the nuanced relationship between composition and epitaxial film characteristics.

Cross-sectional aberration-corrected STEM investigations were performed to elucidate the microstructure of the $A_{0.8}$ NO film. As shown in the low-magnification, high-angle annular dark-field (HAADF-STEM) image in Figure 1d, the thin film features distinct NPRs (indicated by red arrows) embedded



Figure 3. Atomic-scale characterization of the $A_{0.8}$ NO film. HAADF-STEM image of the $A_{0.8}$ NO film viewed along the (a) [100] zone axis and (b) [110] zone axis. The insets are the enlarged view from the rectangle-frame regions in (a,b), respectively. (c) Out-of-phase boundary schematic diagram consisted of a normal unit cell (U_N) and an abnormal unit cell (U_{AN}) (marked by the blue and red frame, respectively), from which the simplified graph of the front view and top view is shown on the right. (d) Color-mapped *c/a* ratio of the nanopillar region (NPR) and matrix in the $A_{0.8}$ NO film. (e) Polar vector mapping superposed with the color-mapped polarization angle from the white rectangle-frame regions in panel (d), where the overlaid polar vectors indicate the off-centering movement of Ag and Nb atoms. (f) Average line profile of the *c/a* ratio and polarization angle of the rectangle-frame regions in panel (d) across the interface of NPRs and matrix, where the error bars are the standard deviation, and the intensity profiles of atomic columns of Ag atom shown in the bottom, where the Ag nanopillars are denoted by red arrows.

vertically in the matrix regions. Such NPRs extend throughout the thickness of the film. More importantly, as further highlighted by the enlarged HAADF-STEM image in Figure 1e, they have coherent and atomically sharp interfaces with both the surrounding matrix regions and the STO substrate. The nanopillars are uniformly sized, with a lateral dimension of approximately 2 nm. Correlating these observations with XRD results and detailed atomic-scale quantitative analysis (as elaborated in Figure 3), we constructed the structural model for the $A_{0.8}$ NO film comprising both matrix and NPRs. Noteworthily, this structure bears a striking resemblance to that observed in sodium-deficient NaNbO₃ thin films, as reported in previous studies.³³

The room-temperature electrical properties of the A_xNO films (x = 1, 0.9, and 0.8) were evaluated and are compared in Figure 2. As shown in Figure 2a, the polarization-electric field (P-E) loop of the stoichiometric ANO thin film exhibits double hysteresis characteristics, suggesting its AFE-like feature. Meanwhile, it is noteworthy that the residual polarization (P_r) is not zero ($P_r \sim 1.7 \ \mu C \ cm^{-2}$). This feature aligns with previous measurements and is likely due to the coexistence of the polar phase $(Pmc2_1)$ and nonpolar phase (Pbcm) at room temperature.^{21,36} The previous study also indicates that the ground states of ANO can be ferrielectric rather than perfect AFE.³⁶ As the Ag content decreases, the ferroelectric characteristics increasingly dominate, as evidenced in Figures 2b and S3. For the $A_{0.8}$ NO film, it exhibits a typical ferroelectric hysteresis P-E loop with a significantly enhanced polarization of $P_r \sim 12.4 \ \mu C \ cm^{-2}$ compared to the ANO. This level of polarization is comparable to that of some classical ferroelectrics, such as BaTiO₃ and HfO₂.^{37,38} Additionally, the switchable nature of the A_{0.8}NO film is confirmed through PFM, as illustrated in the inset of Figure 2b. The evident reversal of phase contrast during polling demonstrates that the

orientation of spontaneous polarization within the ferroelectric domains can be effectively altered by application of external electric fields. Moreover, the $A_{0.8}NO$ film demonstrates remarkable fatigue resistance, enduring over 10^7 switching cycles (Figure S4).

Bulk AgNbO₃ undergoes complex phase transitions with temperature, primarily driven by the coupling between the tilting of NbO₆ octahedra and local displacements of Ag and Nb atoms.⁴⁶ As evidenced in the temperature-dependent dielectric spectra in Figure 2c, the epitaxial ANO thin film exhibits consistent phase transitions analogous to those in the bulk material,²¹ including the M_1-M_2 phase transition at around 325 K ($T_{\rm M_1-M_2}$) and $\rm M_2-M_3$ phase transition at around 625 K $(T_{M_2-M_2})$ at 50 kHz. Variations in the Ag content lead to changes in the phase transition behavior, particularly in terms of transition temperatures and frequency-dependent properties. With the decrease in Ag content, the enhanced frequency dependency in the A_{0.8}NO film is primarily due to the domain wall motion within the multidomain structure caused by nanopillars (as shown in Figure 2d).³³ Comprehensive measurements have allowed us to construct an Ag-content and temperature phase diagram based on the dielectric spectrum recorded at 1000 kHz (as shown in Figures 2c,d and S3), with details depicted in Figure 2e. It can be seen that $T_{M_1-M_1}$ remains relatively constant across A_x NO films. However, $T_{M_1-M_2}$ moves to a higher temperature range when going from the ANO to A_{0.8}NO film. Note that the M₂ phase is exclusively nonpolar (*Pbcm*), whereas the M_1 phase presents a mix of polar $(Pmc2_1)$ and nonpolar (Pbcm) phases.¹² In this sense, the $T_{M_1-M_2}$ transition generally serves as a key indicator of the stability of the polar phase.^{47–49} Therefore, the observed increase in T_{M,-M2} suggests enhanced stability of the polar phase at room temperature in Ag-deficient AgNbO₃ films.



Figure 4. Lattice dynamics and electronic structure analysis. (a) O K-edge and (b) Nb M-edge XAS spectra of A_x NO (x = 1 and 0.8) films which have been normalized to the edge jump. Absorption peaks of Ag 4d orbitals are noted as A. (c) Initial and relaxed ANO model with the nanopillar structure. (d) Energy profile of ANO with the nanopillar structure system.

The observed changes in phase transition behaviors significantly alter the relative stability of AFE and FE phases, consequently affecting the ground states of the system. This, in turn, has a direct impact on the physical properties, particularly piezoelectricity, considering the emergence of a noncentrosymmetric polar phase.⁵⁰ We conducted piezoelectric tests on all A_xNO films and found that Ag-deficient A_xNO (x = 0.9 and 0.8) films demonstrated a markedly enhanced piezoelectric response. It is found that the piezoelectric constant showed a consistent increase with a reduction in Ag content, as detailed in Figure S5. The peak value is observed in the A_{0.8}NO composition, with d_{33} reaching around 440 pm V⁻¹. This value is notably higher by an order of magnitude compared to the AFE ANO and can even rival the piezoelectric properties of the well-known piezoelectric material PZT film, as shown in Figure 2f.

To elucidate the origin of the enhanced properties in Agdeficient ANO thin films, we performed a quantitative atomicscale analysis of the A08NO thin film using sphericalaberration-corrected STEM, particularly focusing on the critical role of the NPRs. Figure 3a,b shows the atomically resolved HAADF-STEM images at the interface of matrix and NPR, viewed along the [100] and [110] zone axes, respectively. It can be seen that within the matrix region, the thin film displays a conventional perovskite structure (the unit cell of this structure is referred to as U_N hereafter and marked by a blue frame), as corroborated by the superimposed ANO structure model. Within the NPRs, however, additional intensities are observed between Ag and Nd columns. These intensities indicate the presence of an overlapping perovskite unit cell (hereafter termed the U_{AN}, marked by a red frame) that exhibits a phase shift relative to the standard perovskite unit cell in the matrix. In the [110] zone axis image, the NPRs and matrix largely share the same atomic arrangement, and only the slight elongation of atomic columns within the NPRs

is observed, indicating the edge-on boundary between NPRs and the matrix in this zone axis. Combining these observations, we can deduce the phase shift between the two unit cells as < a/2, b/2, δc >, where "a" and "b" are the unit vectors along the in-plane directions, and " δc " is along the out-of-plane direction, representing a small fraction of the unit cell length. This shift essentially corresponds to Nb atoms occupying positions originally held by Ag and Ag atoms taking over positions initially occupied by Nb. The schematic model of such an interface is depicted in Figures 3c and S6 (plane-view schematic model). The proposed model effectively captures the experimental observations, particularly regarding the relatively weaker intensities of the UAN due to the fewer number of atoms in each column and the distinctive edge-on boundary observed between NPRs and the matrix along the [110] zone axis.

These structural characteristics of the $A_{0.8}$ NO thin film show high similarities to those observed in sodium-deficient NaNbO₃ thin films, which are known for their exceptional piezoelectric properties.³³ These properties have been demonstrated to be closely related to the unique domain structures induced by this out-of-phase boundary between NPRs and the matrix. In our case, the local structural distortions and unique domain structure have been unambiguously revealed through atomic-scale quantitative analysis, as shown in Figures 3d,e. It can be seen that within the NPRs, the lattice exhibits an increased tetragonality, which has been caused by the interphase strain from out-of-phase boundaries in NPRs, evident from higher c/a ratios compared to the matrix area.

Besides, this observation is further supported by the average line profile extending from the NPRs to the matrix, as illustrated in Figure 3f. These tetragonal distortions induced by interphase strain can prompt atoms to deviate from their original positions, accompanied by the distortion of oxygen octahedra (Figures S7 and S8), which eventually can lead to significant alterations in the polarization configurations. Based on fitting each atomic column to a two-dimensional Gaussian peak, we quantified the polarization displacement within each unit cell. Figure 3e presents the distribution of polarization displacement near an NPR-matrix boundary, revealing distinct net polarizations in both the matrix and NPRs, which correspond to tetragonal c domains and monoclinic domains (Figure S9), respectively. This polarization configuration significantly diverges from that of stoichiometric ANO, where polarizations are either aligned antiparallel in an AFE fashion or partially antiparallel in a ferrielectric fashion. More importantly, there is a substantial polarization angle difference between the NPRs and the matrix, improving the construction of a heterogeneous polar structure from interphase strain in NPRs, as emphasized by the line profile in Figure 3f. This characteristic significantly facilitates the rotation of polarization under external electric fields, serving as the fundamental structural origin for the enhanced piezoelectric response.

To further investigate the correlation between the out-ofphase boundary-tuned microstructure and superior properties, we analyzed the electronic structures of the A_{0.8}NO thin film through XAS and first-principles calculations. As shown in Figure 4a,b, the XAS of the O K-edge and Nb M-edge have been displayed. According to crystal field theory, the 4d orbitals split into high-energy e_g and low-energy t_{2g} orbitals in an ideal oxygen octahedron. 51 The nanopillars in the $A_{0.8}\rm NO$ film are mainly from the antisite occupancy of Nb atoms, which leads to the decreases of the Nb valence states to keep the system electrically neutral (Figure S10).⁵² In low-valence Nb (lower than +5), more electrons could occupy the lower energy t_{2g} orbitals, thus causing the lower intensity of the t_{2g} peak in the A_{0.8}NO film than that in the ANO film shown in Figure 4a. Besides, the coupling between Ag and O bonds becomes weaker in the $A_{0.8}NO$ film, confirmed by the lower intensity of the A peak indicating the hybridization between Ag 4d and O 2p,⁵³ which would promote the formation of antisite Nb_{Ag} deficiencies. Two regions of M_3 (2p_{3/2}) and L_2 (2p_{1/2}) are displayed in the Nb M-edge XAS (Figure 4b).³³ Each of them is split by a crystal field into t_{2g} and e_g . Due to the Jahn–Teller effect, the degenerate triplet t_{2g} and doublet e_g orbitals will be further split caused by lattice strain, and the difference between the e_g and t_{2g} orbitals represents the crystal-field splitting energy (Δ).⁵¹ For the A_{0.8}NO film, the out-of-phase boundaries cause lattice structure elongation in NPR. To alleviate the NbO₆ oxygen octahedral distortion from the outof-plane elongation, the Nb atoms are further shifted. Owing to the displacement of Nb atoms along the out-of-plane direction, the hybridization between Nb and O1 (O ions in the out-ofplane direction) is relatively strengthened, while that between Nb and O_2 (O ions in the in-plane direction) becomes weaker, which eventually decreases the splitting energy (Δ) (Figures 4b and S8). Therefore, the interphase strain from the out-ofphase boundaries can promote polar transformation and lead to the construction of multidomain polar structures.

To reproduce the experimental observation, the ANO structural model concluding the NPR and matrix has been established. As shown in Figure 4c, the initial model has been displayed, where the constructed structure is consistent with our previous experimental findings. After structural relaxation, the features of the nanopillar structure are maintained, indicating the phase stability of the nanopillar heterogeneous structure in the $A_{0.8}$ NO film. The polar vector distribution

around the NPR was analyzed and is displayed in Figure S11. Wherein, the multipolar domain structure was also established, proving the favorable formation of multidomain structures facilitated by NPR construction. To further understand the nanopillar structure, first-principles DFT calculations were conducted. As the movement of Nb atoms, the completely opposite polarization states with inverse polarization displacement are in the lowest energy state, and the total energy of the system features a double-well potential similar to that of perovskite-type ferroelectrics.⁵¹ Compared to the AFE phase with the triple-well potential energy curve, the double-well potential curve indicates the polar phase of the nanopillar structure, in which the polar ferroelectric phase could be stabilized by nanopillar structure construction.⁴⁸ We note that certain local variations in crystal and electronic structures as well as boundary conditions cannot be fully captured by theoretical calculations, leading to imperfect reproduction of experimental results. Nevertheless, the calculation results preserve the fundamental characteristics of the NPRs observed experimentally, such as the nested two perovskite unit cells $(U_N \text{ and } U_{AN})$ and the polarization displacement.

4. CONCLUSIONS

In summary, we successfully manipulated the stability between AFE and FE phases in $Ag_x NbO_{3-\delta}$ epitaxial thin films by precisely adjusting the film stoichiometry and local structural heterogeneity (x = 0.8, 0.9, and 1). Notably, in the A_{0.8}NO thin film, we achieved a substantial enhancement in ferroelectricity, with P_r reaching up to 12.4 μ C cm⁻² compared to 1.7 μ C cm⁻² in stoichiometric ANO. Besides, a pronounced piezoelectric response has been realized, reaching as high as 440 pm V^{-1} , which can rival the classic PZT system. Advanced electron microscopy investigations revealed the underlying mechanisms. The nanopillars, characterized by the antisite occupancy of both Ag and Nb atoms and the formation of out-of-phase boundaries with the matrix, can induce the interphase strain, which would lead to local structural distortions and, in turn, generate significant off-site displacements and dipoles. The multidomain structure constructed by nanopillars could facilitate polarization rotation, thus enhancing the piezoelectric performance substantially. This study not only elucidates the mechanisms underlying the AFE-ferroelectric phase transition but also establishes novel approaches to local heterogeneity engineering for controlling and utilizing phase stability, thereby unlocking emergent properties and enabling advanced material applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.4c08183.

Additional electron microscopy images, structural and electrical characterizations, XPS results, structural models, and chemical analysis and quantitative results of atomic displacements (PDF)

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Notes

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