Ferroelectric properties of lightly doped La:HfO_2 thin films grown by plasma-assisted atomic layer deposition

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M. G. Kozodaev,[1] A. G. Chernikova,[1] E. V. Korostylev,[1] M. H. Park,[2] U. Schroeder,[2] C. S. Hwang,[3] and A. M. Markeev[1,a)]
[1]*Moscow Institute of Physics and Technology, Institutskii per. 9, 141700 Dolgoprudny, Moscow region, Russia*
[2]*NaMLab gGmbH/TU Dresden, Noethnitzer Strasse 64, 01187 Dresden, Germany*
[3]*Department of Materials Science and Engineering and Inter-University Semiconductor Research Center, Seoul National University, Seoul 08826, South Korea*

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The structural and ferroelectric properties of lightly La-doped (1 mol. %) HfO_2 thin films grown by plasma-assisted atomic layer deposition were examined. An annealing temperature as low as 400 °C crystallized the film into the desired orthorhombic phase, which resulted in it displaying promising ferroelectric performance. The remanent polarization (P_r) increased with annealing temperature, but the performance enhancement seemed to saturate at 500 °C. A slight decrease in the dielectric constant, which was associated with the preferential formation of a polar orthorhombic phase at higher temperatures, was also observed. The long-term wake-up effect, i.e., a marked rise in the $2P_r$ value during field cycling, was demonstrated for films processed at all annealing temperatures. The presence of domain groups with opposite internal electric biases was found in the pristine state, while the internal bias distribution became more uniform during wake-up. The endurance of up to 4×10^8 switching cycles without marked fatigue using bipolar pulses with a duration of 600 ns, and an amplitude of ±3 MV/cm was demonstrated. *Published by AIP Publishing.*
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The recent discovery of ferroelectricity in doped hafnium oxide (HfO_2)[1] demonstrated the possibility to overcome technical challenges facing conventional perovskite ferroelectrics.[2] Both ferroelectric HfO_2-based layers and electrodes, typically TiN, can be grown by atomic layer deposition (ALD) with excellent conformality,[3] which means that they are fully compatible with complementary metal-oxide-semiconductor (CMOS) technology and allow the potential of three-dimensional structure formation.[4] However, the TiN/HfO_2 interface is usually imperfect and contains a high density of defects (e.g., oxygen vacancies). Because interfacial and bulk defects are considered as the root of several undesired effects such as wake-up, fatigue, imprint, and early breakdown, the use of inert electrodes could be required, as has proved effective in the case of perovskite materials.[5] In this regard, ALD can also be applied to Ir[6] or Ru[7] growth.

It has been suggested that the ferroelectricity in doped HfO_2 films is caused by the formation of the polar orthorhombic phase (o-phase, space group $Pca2_1$) under certain conditions.[8,9] Incorporation of dopants with a large atomic radius (e.g., Y, La, and Gd) into HfO_2 has been proven experimentally to be one of the most effective methods to promote the formation of the o-phase[10–13] and consequently provide promising ferroelectric responses. In particular, the combination of a relatively high double remanent polarization ($2P_r$) value (~33 $\mu C/cm^2$) and endurance following 10^8 switching cycles without any fatigue (decrease in the $2P_r$ value with cycling) was recently demonstrated for La-doped HfO_2 (La:HfO_2).[11] Unfortunately, La:HfO_2 films possess a higher crystallization temperature than that of pure HfO_2 for the same thickness (or grain size), which might be because La is an amorphization dopant in HfO_2.[14] As a result, the use of La:HfO_2 thin films in a standard back-end-of-line (BEOL) process for ferroelectric random access memory is quite challenging compared to that of other doped HfO_2 or $Hf_xZr_{1-x}O_2$ ferroelectrics, which possess crystallization temperatures as low as 400–450 °C over a wide thickness range down to 2.5 nm.[15–19] Indeed, even a relatively low level of La doping (2.1 at. %) resulted in 10-nm-thick La:HfO_2 films retaining their amorphous state after annealing at temperatures below 550 °C. These results indicate that a lower La doping level may result in a lower crystallization temperature, as predicted by the literature.[20] Therefore, this work explores the possibility of lowering the crystallization temperature of La:HfO_2 to a BEOL-compatible level (400 °C) by decreasing its La content while maintaining the preferential formation of the o-phase.

It has been shown that the dielectric layer should be kept in an amorphous state before rapid thermal annealing (RTA) to induce crystallization or during top electrode deposition to avoid undesirable preliminary crystallization and consequently achieve a high remanent polarization (P_r).[21,22] However, conventional ALD or chemical vapor deposition processes for TiN top electrode fabrication require a rather high deposition temperature (400–450 °C),[23] which may induce the crystallization of even ultrathin HfO_2-based films.[16] Plasma-assisted atomic layer deposition (PAALD) allows the deposition temperature to be lowered to ~300 °C[4,24] and, therefore, can be applied for this task.

We utilized PAALD to prepare a set of 10-nm-thick La:HfO_2 films with a low La concentration (1 mol. %) in order to investigate their ferroelectric and structural properties

a)Electronic mail: markeev.am@mipt.ru

after rapid thermal annealing (RTA) at 400–500 °C. The structural properties of the annealed La:HfO_2 films were examined by grazing-incidence X-ray diffraction (GIXRD). The ferroelectric properties of annealed complete MFM structures were investigated by the positive-up–negative-down (PUND) technique. The detailed description of sample preparation and experimental techniques is presented in the supplementary material.

First, the crystalline structure of La:HfO_2 films annealed at different temperatures was investigated [Fig. 1(a)]. All films, including those annealed at 400 °C, were polycrystalline with clear diffraction peaks, which were attributed to the o-phase and/or tetragonal phase (t-phase, space group $P4_2/nmc$).

The diffraction peak located at ≈30.4° could consist of $[111]_o$ and $[111]_t$ peaks, while more precise identification is quite challenging due to the structural identity of mentioned phases. The presence of the cubic phase (c-phase, space group Fm3m) could also not be completely excluded, but according to the literature data, it becomes stable only at a high La concentration.[14,26] It is worth noting that the peak near ∼30.4° shifted monotonically to lower the 2θ value with increasing RTA temperature, whereas that near 35.5° shifted to a higher 2θ value [Fig. 1(b)] under identical RTA conditions, which indicates the variation of the lattice parameters of the films with changing RTA temperature. The extracted lattice parameters from these peak positions are presented in Fig. 1(c). Here, the lattice parameter "c" refers to the longest axis (a for the o-phase and c for the t-phase), while "a" refers to the two shorter axes (b and c for the o-phase and a for the t-phase). The aspect ratio (c/a for the t-phase and 2a/(b + c) for the o-phase) increases from 1.023 to 1.028 with rising annealing temperature from 400 to 500 °C, which is similar to those one observed for Si-, Al-, and Gd-doped HfO_2 thin films with strong ferroelectricity.[27] Therefore, the La:HfO_2 film could be ferroelectric after RTA at just 400 °C according to the presented structural analysis. At the same time, an increase in the relative fraction of the o-phase with rising annealing temperature can be expected because of the corresponding increase in the aspect ratio of the unit cell.

The presence of a small amount of the monoclinic phase (m-phase) was also identified for the films crystallized all RTA temperatures because weak peaks located at ∼28.5° and ∼31.6°, attributed to $[-111]_m$ and $[111]_m$ reflections, respectively, were found in all GIXRD patterns presented in Fig. 1(a). The precise calculation of the m-phase fraction is quite difficult given the proximity of the peak positions from different phases and rather broad diffraction peaks. Therefore, only the relative ratio (R_m) of the integrated area of the peaks, corresponding to the m-phase, to the sum of all peak intensities in the 2θ region 27–33°, is presented, which might be sufficient to justify the following analysis. The R_m value is ∼20% for the film annealed at 400 °C and decreases slightly to ∼15% for films annealed at 450 and 500 °C. However, the R_m increase is expected at higher annealing temperature because of the possible increased grain size, which decreases the surface energy contribution. The surface/grain boundary/interface energy is the critical factor affecting the stabilization of the o-phase.[8,27] To get insights into this seemingly contradictory result, scanning electron microscopy (SEM) was used to examine the grain size distribution in the samples. The estimated median grain radius is 9.4 nm, and it is almost constant for films annealed at different temperatures (the related SEM images are presented in the supplementary material), which could be related to the rather narrow range of RTA temperatures used here and the strong ability of La to suppress grain growth.[28] It is speculated that the slight decrease in R_m observed in Fig. 1(a) arises from the presence of remaining amorphous regions (e.g., near the ferroelectric/electrode interfaces) after RTA

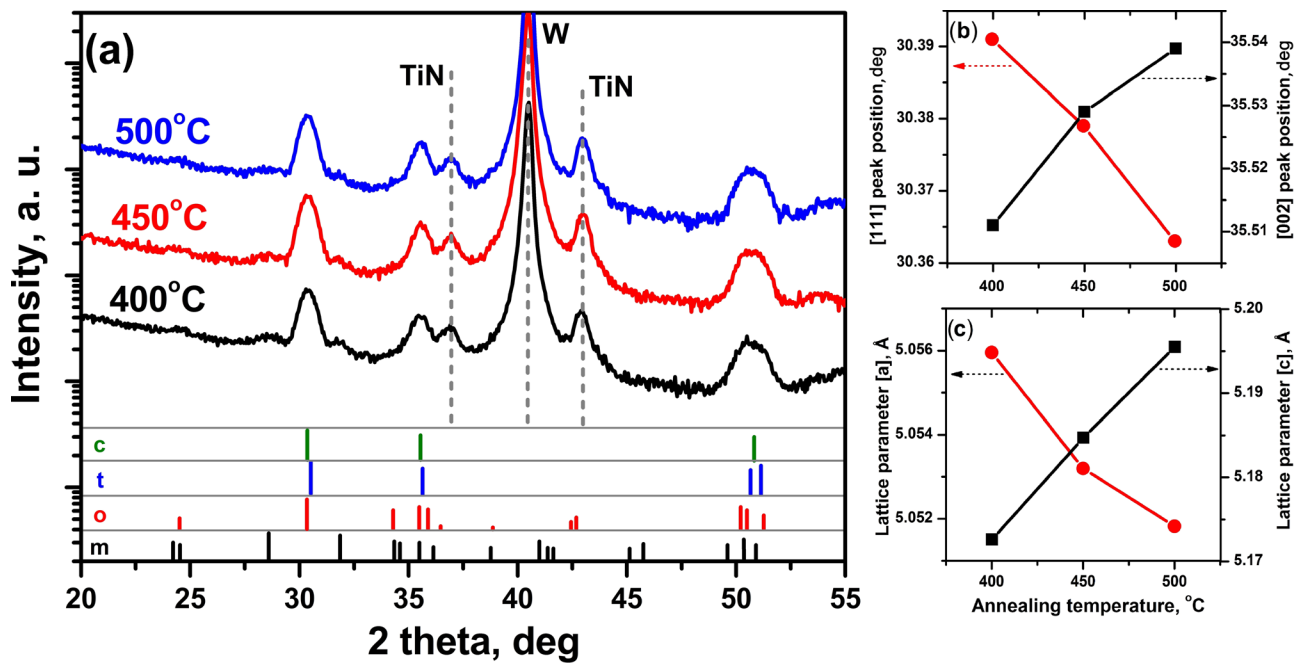

FIG. 1. (a) GIXRD spectra, collected from La:HfO_2 films, annealed at 400, 450, and 500 °C with calculated powder diffraction patterns;[8,25] (b) [111] and [002] peak positions as a function of annealing temperature; (c) variations in the lattice parameters as a function of annealing temperature.

at 400 °C. The remaining amorphous material will crystallize into the o-phase (or partially into the t-phase) by heterogeneous nucleation at the amorphous/o-phase interface during RTA at 450 or 500 °C because the major crystalline phase after RTA at 400 °C is the o-phase.

The ferroelectric response of the films was analyzed. Dynamic switching current-electric field (I-E) measurements of film, annealed at 400 °C, in the pristine (i.e., before field cycling) state showed current peaks both at negative and positive voltages, which is typical for ferroelectric materials [Fig. 2(a)]. However, multiple current peaks in response to the first voltage sweep on the pristine structure were observed both at positive and negative voltages, which is clearly attributed to the switching non-uniformity of the ferroelectric film and is caused by the presence of groups of domains with different internal (built-in) biases.[29] The voltage sweep schemes used for their distinction are presented in Figs. 2(c) and 2(e), while the related current responses are presented in Figs. 2(d) and 2(f). The repeated application of triangular sweeps with the same amplitude and direction of the electric field provided test results compatible with those from the PUND tests. According to Figs. 3(c) and 3(d), after the first ND-PU cycle with an amplitude of ±3 MV/cm, all switchable ferroelectric domains in the film become polarized to the "positive" direction. After that, by applying a ND

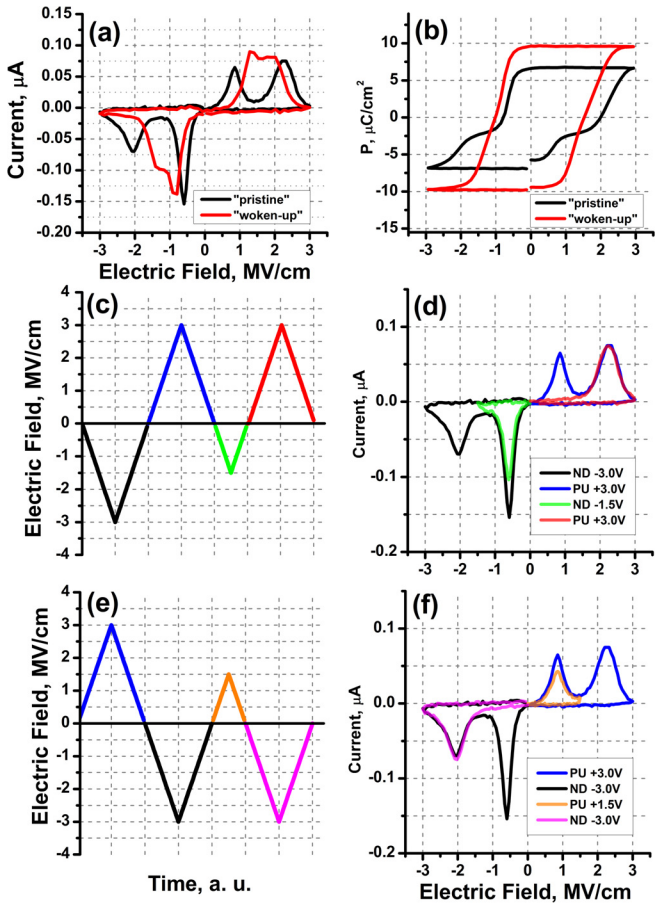

FIG. 2. (a) I-E characteristics of the La:HfO_2 film, annealed at 400 °C, in "pristine" (black) and "woken-up" (10^5 switching cycles at ±3 MV/cm) states (red) with the corresponding P_r-E loops (b). (c) and (e) P-U-N-D measurement voltage sweep and (d) and (f) corresponding I-E characteristics of the same film (the colors of the voltage sweep curves correspond to related current responses).

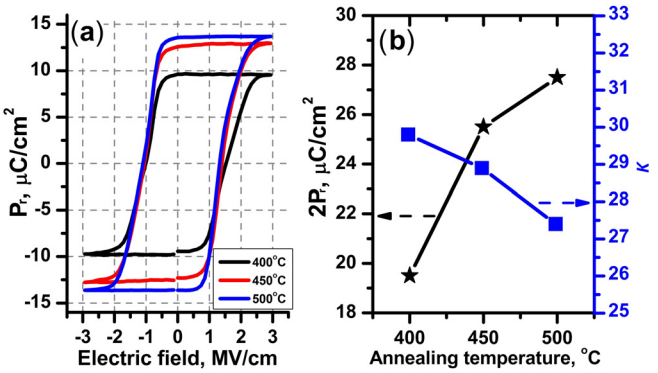

FIG. 3. (a) P_r-E hysteresis loops, measured from La:HfO_2 films, annealed at 400, 450, and 500 °C, after 10^5 switching cycles at ±3 MV/cm. (b) $2P_r$ and k value as a function of RTA temperature.

voltage sweep with a smaller amplitude of −1.5 MV/cm, only one group of the domains (with a lower relative switching field E_s of ∼−0.56 MV/cm) switches to the "negative" direction. The subsequent PU sweep with an amplitude of +3 MV/cm revealed the back-switching field E_{bs} of this group of domains, which was relatively high (E_{bs} ∼ +2.36 MV/cm). A schematic picture, illustrating the described procedure, is presented in the supporting material. The peak at +0.84 MV/cm, which can be clearly observed after the first ND-PU cycle with an amplitude of ±3 MV/cm, disappeared after the last procedure. It becomes obvious that this peak originates from the switching of domains belonging to another group. Therefore, the first group of domains has a hysteresis curve that is shifted toward the positive direction along the electric field axis. This shift can be presented as a function of the internal bias field E_{bias}, while the average coercive field E_c of these domains can also be roughly evaluated from E_s and E_{bs} peak positions.

The following equations were used to estimate E_{bias} and E_c:

$$E_c = \left| \frac{E_s - E_{bs}}{2} \right|, \tag{1}$$

$$E_{bias} = \frac{E_s + E_{bs}}{2}. \tag{2}$$

According to these equations, the E_{bias} of ∼0.90 MV/cm and the E_c of ∼1.45 MV/cm were calculated for the first group of domains from the dynamic current curve presented in Fig. 2(d). A similar procedure was used to reveal the E_{bias} and E_c of the second group of domains [Figs. 2(e) and 2(f)]; the E_{bias} of ∼−0.55 MV/cm and E_c of ∼1.40 MV/cm were found for this case.

The presence of two types of ferroelectric domains with almost equal E_c and different E_{bias} in the pristine state, which was also observed earlier for hard Pb(Ti, Zr)O_3 ceramics,[30] may be caused by interfacial defects (possibly oxygen vacancies) near both top and bottom film interfaces. The generation of oxygen vacancies could be caused by oxygen migration to the TiN layers, and they can diffuse to the domain wall regions and pin the domains.[30] Multiple switches could result in a more uniform defect distribution across the ferroelectric layer and a change in their occupancy, which was earlier observed during the wake-up process for other HfO_2-based

ferroelectrics.[31–33] A similar behavior was also observed here: after the wake-up cycling (i.e., after 10^5 switches by pulses with a duration of 600 ns and an amplitude of 3 MV/cm), the multiple current peaks moved toward each other [Fig. 2(a)]. However, even after this procedure, the resulting current response contained multiple components, which indicates that only partial internal bias relaxation occurred. Almost full relaxation of the internal bias occurred for the second group of domains, while the internal bias decreased to ~0.5 MV/cm for the first. The same procedure was performed for the films annealed at higher temperatures with a similar qualitative result. The extracted coercive fields and biases for the pristine and woken-up states are presented in the supplementary material.

The $2P_r$ value, which was extracted from P_r-E hysteresis curves [Fig. 2(b)], increased markedly following the wake-up process from ~12 to ~20 $\mu C/cm^2$. Besides the partial relaxation of the built-in bias during wake-up, the previously inactive (or pinned) domains in the pristine state (presumably related to defects) became involved in the switching process after the wake-up process. The transformation from the t- to o-phase near the ferroelectric/electrode interface, as shown previously for other HfO_2-based ferroelectrics, could be among the reasons for such behavior.[31,32]

The improvement of the ferroelectric properties of the films with increasing annealing temperature was subsequently examined. The P_r-E hysteresis loops for films after RTA at 400, 450, or 500 °C and 10^5 wake-up cycles are presented in Fig. 3(a).

The $2P_r$ value increases from ~20 to ~25 $\mu C/cm^2$ with rising RTA temperature from 400 to 450 °C. A further increase in the RTA temperature caused a minor $2P_r$ rise of only ~7%, indicating a tendency to saturation. According to the structural analysis presented above, the observed initial increase in the $2P_r$ value can be attributed to increased crystallization of the film into the o-phase. The formation of the o-phase was further confirmed by the analysis of the small-signal C-V curves measured after 10^5 switches. Figure 3(b) shows the variation of the extracted k values along with the $2P_r$ values with increasing RTA temperature. Here, the k-values were taken at an electric field strength of +3 MV/cm, i.e., outside the switching regions, to represent only the linear dielectric contribution. "The k value decreased monotonically from ~30.0 to ~27.5 with increasing RTA temperature from 400 to 500 °C. According to the literature data, the o-phase is characterized by a k-value of ≈30, while the one for the t-phase is ≈35. For the m-phase, it is in the range of ≈15–20, which is close to that of the amorphous HfO_2. All these phases can be present in the La:HfO_2 films, and their relative portion can change with the RTP temperature increase. The GIXRD showed a slight decrease in the m-phase relative ratio (R_m) with the increasing RTP temperature, which could have increased the k value. However, the observed considerable increase in P_r with the RTP temperature indicates the effective transition of the t-phase to the o-phase, which is consistent with the k value decrease in the overall film. This means that the t- to o-phase transition has a more pronounced role in the k evolution compared to the decrease in amorphous and m-phase portion with the increasing RTP temperature."

Finally, the endurance characteristics of the La:HfO_2 films were examined. The change in $2P_r$ with the increasing number of switching cycles is presented in Fig. 4. A marked wake-up effect is observed up to almost 10^6 switching cycles irrespective of the RTA temperature. After such prolonged wake-up, slight fatigue (decrease in $2P_r$ by ~10%) was detected. Overall, the endurance performance of the samples was rather limited. The film annealed at 400 °C could be cycled up to 4×10^8 times, but then a hard breakdown occurred. A slight endurance decrease (down to $\sim 2 \times 10^8$) was also observed with increasing RTA temperature. It is worth noting that lowering the switching pulse amplitude to 2.5 MV/cm resulted in a significant endurance improvement up to 1×10^{10} cycles with no hard breakdown (Fig. 4). However, the lower switching field resulted in a lower maximum $2P_r$ value (~13 $\mu C/cm^2$ at 500 °C). Also, the samples showed noticeable fatigue (decrease in $2P_r$ by ~60%) after ~10^7 switching cycles. It is believed that such limited endurance might be caused by imperfect interfacial layers between the ferroelectric and electrodes because oxygen vacancies are known to facilitate breakdown mechanisms in HfO_2.[33] Therefore, inert electrode utilization may overcome this problem.

In conclusion, feasible ferroelectric performance was achieved by PAALD-grown La:HfO_2 films with a La concentration of 1 mol. % even when RTA was performed at just 400 °C, which is compatible with standard BEOL processes. The obtained $2P_r$ value was ~20 $\mu C/cm^2$, and the film could endure up to 4×10^8 switching cycles under applied bipolar pulses of ±3 MV/cm and 600 ns. Interestingly, increasing the RTA temperature up to 500 °C slightly decreased the undesirable m-phase content by transformation into the ferroelectric o-phase. As a result, the $2P_r$ value of the film was increased to ~27 $\mu C/cm^2$. The current results may be compared with those of a previous study of La:HfO_2 films with a slightly higher La concentration.[11] The decrease in the La content resulted in a sizable annealing temperature decrease from ~550 to 400 °C while keeping a rather high $2P_r$ value. Moreover, promising endurance characteristics were also achieved. Furthermore, because of its low crystallization temperature, 1 mol. % La:HfO_2 competes with the well-studied $Hf_{0.5}Zr_{0.5}O_2$, which can be processed at a similar RTA temperature. However, $Hf_{0.5}Zr_{0.5}O_2$ films demonstrated the marked fatigue (decrease in $2P_r$ by ~20% after 1×10^8 switching cycles)[34] compared with that for the La:HfO_2 films in this work. Nonetheless, methods to further improve the endurance characteristics of

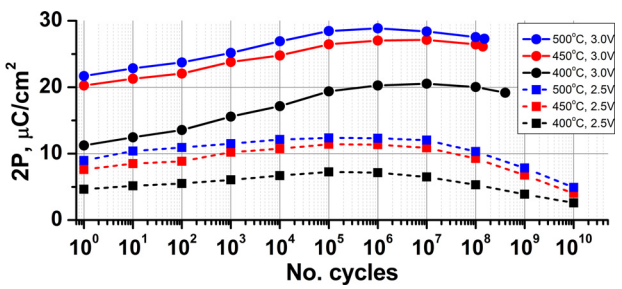

FIG. 4. Endurance characteristics of La:HfO_2 films, annealed at 400, 450, and 500 °C (±3.0/2.5 MV/cm, 600 ns). A hard breakdown occurred after the maximum switching cycles for an applied switching field of 3 MV/cm (circle symbols), which was not the case for 2.5 MV/cm (square symbols).

such films are still highly desired to make the material compatible with the requirements for a universal memory.

See supplementary material for the details of sample preparation, measurement techniques, grain size analysis (SEM images), and the information related to the internal biases calculation.

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