

## Dielectric properties of thin Cr<sub>2</sub>O<sub>3</sub> films grown on elemental and oxide metallic substrates

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In an attempt to optimize leakage characteristics of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> thin films, its dielectric properties were investigated at local and macroscopic scale. The films were grown on Pd(111), Pt(111), and V<sub>2</sub>O<sub>3</sub> (0001), supported on Al<sub>2</sub>O<sub>3</sub> substrate. The local conductivity was measured by conductive atomic force microscopy mapping of Cr<sub>2</sub>O<sub>3</sub> surfaces, which revealed the nature of defects that formed conducting paths with the bottom Pd or Pt layer. A strong correlation was found between these electrical defects and the grain boundaries revealed in the corresponding topographic scans. In comparison, the Cr<sub>2</sub>O<sub>3</sub> film on V<sub>2</sub>O<sub>3</sub> exhibited no leakage paths at similar tip bias value. Electrical resistance measurements through e-beam patterned top electrodes confirmed the resistivity mismatch between the films grown on different electrodes. The x-ray analysis attributes this difference to the twin free Cr<sub>2</sub>O<sub>3</sub> growth on V<sub>2</sub>O<sub>3</sub> seeding.

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### I. INTRODUCTION

The use of an applied electric field to manipulate magnetism in the absence of dissipative electric currents has recently drawn much attention. It promises a new class of low-power spintronic devices taking advantage of nonvolatile magnetic order [1,2]. A promising scheme for such manipulation involves the electrical control of magnetization via the exchange bias (EB) [3] effect, which can be used to switch the remnant magnetization of a ferromagnetic thin film. EB arises from exchange coupling at the interface between an antiferromagnet and a ferromagnet and causes the hysteresis loop of the ferromagnet to shift along the field axis. Chromia (Cr<sub>2</sub>O<sub>3</sub>) is a magnetoelectric (ME) antiferromagnet [4,5] that can be used to realize a particular variation of the ordinary EB effect known as voltage-controlled EB. Chromia has a Néel temperature ( $T_N$ ) of 307 K. Isothermal voltage control of EB has been demonstrated at room temperature utilizing bulk single crystals of this insulating antiferromagnet [6,7]. B-doped chromia may even be a candidate for high- $T_N$  magnetoelectrics [8], while both intrinsic and B-doped forms of this material are of interest for use in low-power magnetic random access memory [4,5]. Practical device applications require a thin-film implementation of this material. Voltage control of EB has been achieved in magnetic heterostructures incorporating thin-film chromia [9–13]. However, reversible electrical switching of EB between positive and negative EB fields larger than the coercivity of the loop with applied magnetic fields lower in magnitude than the coercive fields remains a significant challenge. Optimization of the magnetic and electrical properties of the magnetoelectric films is required in order to overcome this challenge.

The central concept that lies at the heart of utilizing chromia for the electrical control of magnetism involves reversing the

polarity of the EB generated at its interface with a ferromagnet. In the isothermal version of this switching, static electric ( $E_{\text{iso}}$ ) and magnetic ( $H_{\text{iso}}$ ) fields are applied simultaneously across the chromia along its  $c$  axis. The EB has first been initialized via a ME field-cooling procedure, i.e., cooling from above the Néel temperature ( $T_N = 307$  K) to below it, with the simultaneous applications of static electric and magnetic fields. The field product ( $E_{\text{iso}}H_{\text{iso}}$ ) determines the condition under which switching occurs [7,14]. It is therefore possible to achieve switching for weak magnetic fields by increasing  $E_{\text{iso}}$  accordingly. This should effectively allow for the practical control of magnetism via purely electrical means. The small required symmetry-breaking magnetic field can be utilized, for instance, from the fringe magnetic fields emanating from the fixed ferromagnetic film in a magnetic tunnel junction (MTJ) used for readout. The MTJ uses tunnel magnetoresistance to read the bit in a ME magnetic random access memory (ME-MRAM) architecture [1]. The difficulty with this approach, however, is that it requires the chromia films to be able to support large electric fields ( $> 10$  kV/mm), without exhibiting significant leakage. It would not only obviate any potential power gains expected to arise from the voltage-based control of magnetism but also induce dielectric breakdown of the ME film. It is worth mentioning that all thin-film heterostructures require much higher field products for switching than their bulk counterparts. The reason for this is the fact that, in thin films, one must overcome additional exchange coupling in one direction (while the switching is supported by exchange in the other direction). This makes the switching product more asymmetric, while the reduced volume of the antiferromagnet additionally means that less ME energy is available to switch the ferromagnet. Under such conditions, the switching-field product is no longer an intrinsic property of chromia but is rather strongly affected by its coupling to the ferromagnet [13].

The preceding discussion implies that a critical parameter for evaluating the performance of chromia films is their

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electrical resistivity. For the EB-based applications that we have described, it is essential that current leakage through the biased films should be reduced to an absolute minimum. In bulk, at least, chromia has a measured band gap of 3.3 eV [15] that provides it with high intrinsic resistivity,  $\rho \sim 10^{12} \Omega \text{ cm}$  at 300 K [16]. Thin films produced previously, via a variety of different techniques, approach nowhere near this optimal value, with reported resistivities ranging from  $10^2$  to  $10^9 \Omega \text{ cm}$  [11,12,17]. Generally, in the case of transition-metal oxides, it is known that, regardless of the specific growth method used, proper choice of metal substrate can have a profound effect on the surface structure of the resulting oxide film and its electrical properties [18]. Motivated by this understanding, in this article we explore the structural and electrical properties of chromia films prepared on Pd(111), Pt(111), and  $\text{V}_2\text{O}_3$  (0001) seed layers. In most studies cited in this work, Pt and Pd have remained the choice materials to be used as both seed layers and bottom electrode. In contrast,  $\text{V}_2\text{O}_3$  grown by sputtering was recently pioneered in Ref. [19] as the seed layer and the bottom gate material for chromia. The rationale for studying chromia on three distinct seed layers is to elucidate the role of different degrees of crystalline twinning and lattice deformation on the electric conduction pattern in a top-to-bottom device configuration. Our investigation reveals that the benefits of using  $\text{V}_2\text{O}_3$  as the seed layer is twofold. First,  $\text{V}_2\text{O}_3$ , as opposed to the cubic materials Pd and Pt, is isostructural with the corundum  $\text{Al}_2\text{O}_3$  (space group  $R\bar{3}c$ ) substrate. This pseudohomoeptaxy promotes growth of films that are free of rotational defects but are unavoidable in the growth of Pd and Pt on  $\text{Al}_2\text{O}_3$  [20]. These rotational domains are discussed in further detail later. Second,  $\text{V}_2\text{O}_3$  is used because of the small lattice mismatch ( $\sim 0.1\%$ ), as compared with Pd (3.9%) and Pt (3.1%), with chromia that minimizes the strain on the chromia films. The  $\text{V}_2\text{O}_3$  films are grown at a thickness above the critical thickness for relaxation [21] to avoid significant strain in the chromia films. These relationships emphasize the benefits in using  $\text{V}_2\text{O}_3$  as bottom electrode to optimize the properties of chromia thin films for device applications. It is also important to note that  $\text{V}_2\text{O}_3$  thin films exhibit a metal-insulator transition (MIT) at about 150 K [21]. Below this temperature, an antiferromagnetic insulating state is observed. It is characterized by a several-order-of-magnitude increase in resistivity. At temperatures above 200 K,  $\text{V}_2\text{O}_3$  behaves like a bad metal with virtually constant resistivity of about  $10^{-3} \Omega \text{ cm}$ . The MIT is shifted towards lower temperature with decreasing film thickness. This is beneficial for device applications that utilize the metallicity of  $\text{V}_2\text{O}_3$  as bottom contact and substrate for defect-free growth of chromia.

In addition to performing a variety of structural characterizations on these films, we also investigate their electrical properties via electrical resistivity measurements and conductive atomic force microscopy (C-AFM). Lithographic patterning is used to form electrical contacts on chromia with sizes ranging from  $1 \mu\text{m}^2$  to close to  $1 \text{ mm}^2$  and is found to reveal dramatic differences in current leakage based on metallic seed layer. More specifically, Pd-based films exhibit wide and uncontrolled variations in leakage at levels that vary by many orders of magnitude and show pinhole-based inhomogeneity, whereas Pt-based films, though more homogenous in resistivity,

demonstrate low values as well. The aforementioned problems are absent in the  $\text{V}_2\text{O}_3$ -based films. Microscopic insight into the reasons for these very different behaviors is provided by using C-AFM to correlate leakage in the films to the presence of microscopic defects in their surfaces. In this way we identify the presence of a class of defects which mediate leakage in the Pd-based films. C-AFM also presents an improved topography and reduced leakage in the case of Pt-based films but demonstrates the presence of an extremely smooth surface of  $\text{V}_2\text{O}_3$ -based films with insulating surface shown in the corresponding conductivity mapping. This result is supported by our x-ray diffraction (XRD) studies. These studies reveal a dominant presence of  $60^\circ$  rotational domains in Pd-based films, a significant reduction of these domains for Pt-based films, and a total absence of these domains in  $\text{V}_2\text{O}_3$ -based films. By demonstrating the critical influence that the metal seed layer may exert on the dielectric properties of the resulting chromia layers, our results represent a crucial step towards the realization of electrically contacted chromia films with virtually bulk-like resistivity critical for the realization of voltage-controlled spintronic applications.

## II. EXPERIMENT

The samples studied consist of 5-, 20-, 40-, and 300-nm chromia films grown onto (0001) sapphire substrates. Prior to chromia film growth, a bottom metallic electrode (Pd, Pt, or  $\text{V}_2\text{O}_3$ ) was deposited. The sapphire substrates were cleaned using a modified Radio Corporation of America protocol [22] and introduced into an ultrahigh-vacuum chamber. For Pd electrode, 1 nm of it was first deposited on sapphire (0001) via molecular beam epitaxy at  $300^\circ\text{C}$  substrate temperature and the deposition rate was 0.5 nm/min. Additional Pd was then grown in a three-step growth process [23]: (1) a seed layer of 7 nm was grown at  $650^\circ\text{C}$ ; (2) the sample was then cooled to  $50^\circ\text{C}$ , and an additional 33 nm of Pd was deposited at a rate of 0.008 nm/s; and (3) to crystallize the Pd, the temperature was raised to  $650^\circ\text{C}$ . This process minimized the roughness of the final film.

Pt electrodes were deposited using dc magnetron sputtering. The films were fabricated at room temperature using a power of 20 W in an Ar atmosphere of 3 mTorr from a base pressure of about  $1 \times 10^{-7}$  Torr and the deposition rate was about 0.4 nm/min. The Pt films were then annealed at  $600^\circ\text{C}$  to smoothen the surface and ensure good crystallinity.

The  $\text{V}_2\text{O}_3$  electrodes were deposited using pulsed laser deposition (PLD). The substrates were heated to  $750^\circ\text{C}$  during the deposition. A KrF excimer laser with pulse energies of 170 mJ, a spot size of about  $6 \text{ mm}^2$ , and a pulse width of 20 ns (at a repetition rate of 6 Hz) was used to ablate a  $\text{V}_2\text{O}_3$  target. The target-to-substrate distance was kept at about 9 cm and the substrate rotation rate was at 3 rpm.

$\text{Cr}_2\text{O}_3$  was then grown on the resulting substrates (described above) *ex situ* using PLD. The pulse energy was 200 mJ and the frequency was 10 Hz from a  $\text{Cr}_2\text{O}_3$  target. The temperature of the substrate was maintained at  $500^\circ\text{C}$  during deposition of the chromia films. The growth rate of  $\text{Cr}_2\text{O}_3$  ( $\text{V}_2\text{O}_3$ ) was about 0.025 nm/s (0.017 nm/s). For samples with Pd electrodes, chromia was grown on four substrates, with thicknesses of

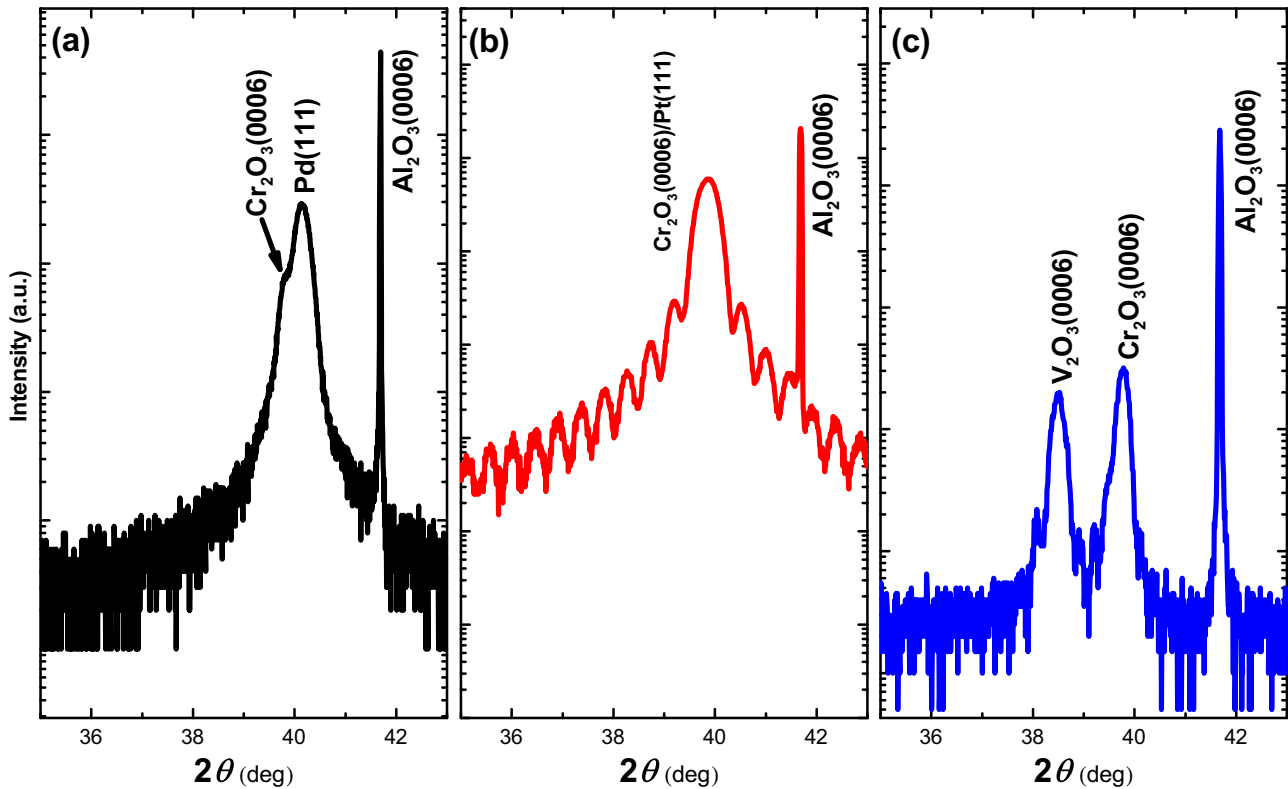


FIG. 1. Out-of-plane x-ray diffraction measurements of (a) Cr<sub>2</sub>O<sub>3</sub> (300 nm)/Pd(40 nm)/Al<sub>2</sub>O<sub>3</sub>, (b) Cr<sub>2</sub>O<sub>3</sub> (300 nm)/Pt(20 nm)/Al<sub>2</sub>O<sub>3</sub>, and (c) Cr<sub>2</sub>O<sub>3</sub> (20 nm)/V<sub>2</sub>O<sub>3</sub>(20 nm)/Al<sub>2</sub>O<sub>3</sub>. The Laue oscillations in (b) are from the Pt layer and not from the chromia film. It is also important to note that Laue oscillations are present in (c) for both the Cr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>3</sub> films.

5, 20, 40, and 300 nm. These samples were compared with a 300-nm-thick chromia film grown on 25-nm-thick Pt and a 20-nm chromia film grown on 20-nm-thick V<sub>2</sub>O<sub>3</sub>.

XRD was used to study the structural properties of the films. Cu  $K\alpha_1$  x-ray radiation with a wavelength of 1.54 Å was used to perform x-ray analysis in various modes. Those are  $\theta$ - $2\theta$  Bragg reflection for out-of-plane scans,  $\phi$  scans for determining rotational domains, and in-plane  $2\theta_{\chi/\phi}$  diffraction. Electrical leakage measurements were performed on lithographically formed contacts using a Keithley 2400 sourcemeter.

C-AFM studies were performed under ambient conditions using a Bruker Icon atomic force microscope in tunneling AFM (TUNA) mode, with a current sensing C-AFM module. PtIr-coated Si tips with a nominal radius of 20–40 nm and a spring constant of 2.8 N/m were used. The current sensitivity was set at 20 pA/V. To ensure a dry environment, all topography and electrical measurements were recorded under a constant flow of N<sub>2</sub>. Since the structure of the tip, including its shape and radius, can be worn out both mechanically and electrically as successive scans are performed, care was taken to acquire images with fresh tips whenever such degradation was noticeable. Usually, during current mapping by scanning probe, the observed variations depend greatly on cantilever deflection and the tip condition. A constant cantilever deflection set point of 30 nN was utilized during all imaging. The dc voltage was applied between the bottom electrode and tip, with the latter acting as a virtual ground.

### III. RESULTS AND DISCUSSION

In Fig. 1, we show the results of the out-of-plane XRD  $\theta$ - $2\theta$  scans for [Fig. 1(a)] chromia(300)/Pd(40)/Al<sub>2</sub>O<sub>3</sub>, [Fig. 1(b)] chromia(300)/Pt(20)/Al<sub>2</sub>O<sub>3</sub>, and [Fig. 1(c)] chromia(20)/V<sub>2</sub>O<sub>3</sub>(20)/Al<sub>2</sub>O<sub>3</sub> heterostructures (where the numbers in parentheses represent film thickness in nanometers). Full scans were performed to confirm the (0001) orientation of the chromia and V<sub>2</sub>O<sub>3</sub> films, and the (111) texture for Pd and Pt films. For clarity, we only show the first-order Bragg diffraction peaks. Due to the inability to distinguish the first-order diffraction peaks of chromia and Pt, in-plane  $2\theta_{\chi/\phi}$  diffraction was performed on this sample to confirm the epitaxy of the chromia layer. It is important to note that the Laue oscillations in the data of Fig. 1(b) are from the Pt film and not from the chromia film. We attempted to fit the data and the fit provides a thickness close to the expected 20-nm value. Also, the data shown in Fig. 1(c) exhibit Laue oscillations for both the Cr<sub>2</sub>O<sub>3</sub> (20) and V<sub>2</sub>O<sub>3</sub> (20) films.

$\phi$  scans were performed to investigate the presence of 60° rotational domains in the films, as shown in Fig. 2. In these measurements, the samples were tilted such that the scattering vector is normal to the (10 $\bar{1}$ 4) planes for the chromia and V<sub>2</sub>O<sub>3</sub> films. For the Pd and Pt films, the samples were tilted so that the scattering vector is normal to the (11 $\bar{1}$ ) planes. Following this alignment, the samples were rotated about the sample normal with the source and detector fixed at the appropriate Bragg angles for each film. This type of scan manifests the presence

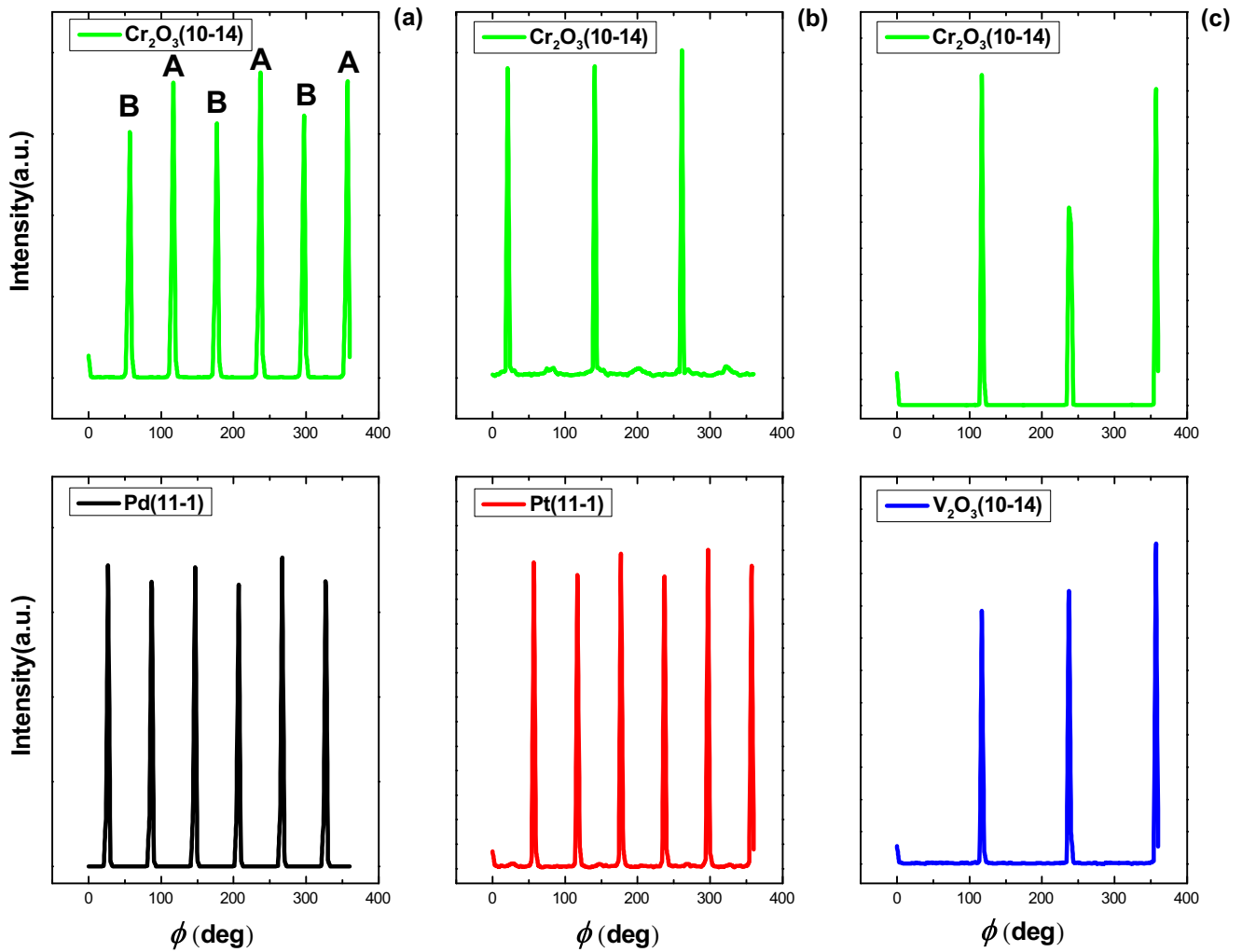


FIG. 2.  $\phi$  scans of the  $(10\bar{1}4)$  pole of (a) chromia grown on Pd, (b) chromia grown on Pt, and (c) chromia on  $V_2O_3$ . In (a), the in-plane rotational domains are labeled with A or B for the chromia  $\phi$  scan. Each diffraction peak is separated by  $60^\circ$  for films with two domains and  $120^\circ$  for films with a single domain. For Pt and Pd films, the  $\phi$  scans are done from the  $(11\bar{1})$  planes.

of in-plane rotational domains in thin films. Figures 2(a)–2(c) show the  $\phi$  scans for chromia growth on Pd, Pt, and  $V_2O_3$ , respectively. Both the Pd and Pt films exhibit essentially no preference in growth. This is indicated by the sixfold symmetry of the  $\phi$  scans with each peak nearly equally intense and separated by  $60^\circ$ . A  $(111)$ -oriented Pd or Pt single crystal would have threefold symmetry in this type of scan. These rotational domains are formed at the Pd (or Pt)/ $Al_2O_3$  interface and propagate vertically through the heterostructure. The growth of cubic structured Pd/Pt on a hexagonal plane of  $Al_2O_3$  with epitaxial relationship  $[111]_{\parallel}[0001]_{\perp}$  has no preference in the two rotational domain formations [20]. In contrast, the  $V_2O_3$  film has no indication of rotational domains. Additionally, the  $\phi$  scans of chromia for each sample show fairly similar behavior as the seed layer. For example, in Fig. 2(a), each rotational domain is labeled A or B. Corresponding domain peaks are separated by  $120^\circ$ . For the sample with a Pd seed layer, the chromia shows a nearly equal presence of these domains, whereas the sample with Pt shows a significant reduction of these domains. Finally, the chromia film grown on  $V_2O_3$  eliminates these domains completely. It should be noted that, in this type of

scan, it is impossible to distinguish whether these domains are twins or other types of domains involving  $60^\circ$  rotation.

Next, we present and discuss the electrical conduction and topography of these films via scanning probe studies. Figure 3 compares the results of lateral topographic, and corresponding current, mapping of two Pd-based chromia films, of thicknesses 5 nm [Fig. 3(a)] and 20 nm [Fig. 3(b)]. The topographic image of the 5-nm film [Fig. 3(a)] reveals the clear presence of flat planes that are unconnected to one another. These unconnected flat planes are referred to as r-planes and their formation is a consequence of the low surface energy of chromia [24]. An analysis of a  $100 \times 100 \text{ nm}^2$  area on a single plane reveals a root-mean-square (rms) surface roughness of  $\sim 0.24 \text{ nm}$ . Also, there are spaces between flat planes and they maintain a depth of around 5 nm, indicating that the bottom Pd electrode is being exposed in these areas. This is further confirmed in the corresponding C-AFM mapping in Fig. 3(b), which yields a current level of several picoamperes on these low-lying areas, whereas the chromia planes are completely insulating at a tip bias of 1 V. Figure 3(c) shows a topographic image of a 20-nm chromia film formed on Pd.



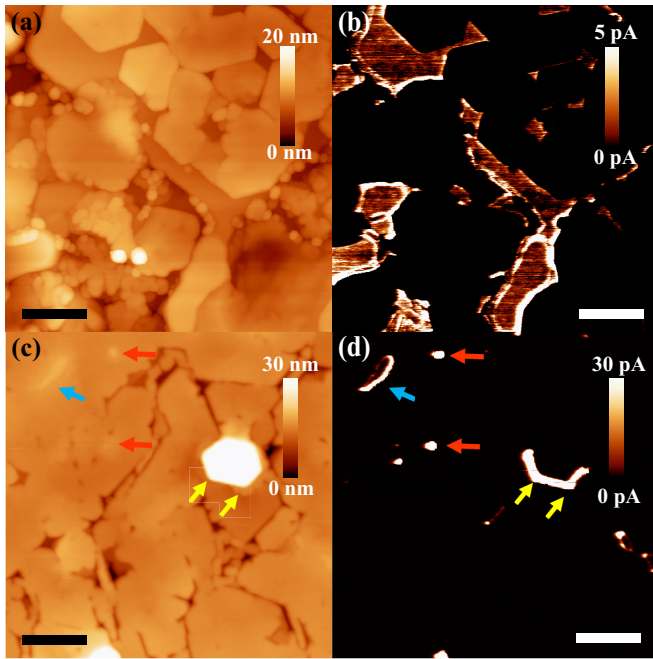


FIG. 3. (a), (c) Topography and (b), (d) conduction mapping of (a) 5-nm and (c) 20-nm Cr<sub>2</sub>O<sub>3</sub> (0001) film on Pd on Al<sub>2</sub>O<sub>3</sub> substrate. The *r*-planes mentioned in the main text are seen in the topographic image in (a) as the flat planes with defined angles. The colored arrows in (b) and (d) point to various types of defects. Tip bias voltage for C-AFM is 1.0 V. Arrows in (c) and (d) point to various defects on the surface. Scale bar: 200 nm.

One can observe here that the flat planes join together to form a more continuous surface, although some pinholes are left in between them. One noticeable feature that now starts to appear is the presence of high structures (typically a few tens of nanometers high), referred to here as mesas, which display similar edge orientations to the chromia planes. In Fig. 3(d), which shows the corresponding current map of Fig. 3(c), the mesas are mostly leaky at their edges, although it is not clear whether this leakage is intrinsic. There are other types of surface defects, which are present in abundance, that are responsible for excessive leakage. These defects appear as small dots in the topographic image of Fig. 3(c) and are correlated directly to the highly conductive spots in the C-AFM image of Fig. 3(d). Such conduction spots are not uncommon in transition-metal oxides, in which they are generally considered to represent the location of conducting filaments in the oxide [25–28]. There have been numerous studies of current sensing in contact mode using scanning probe microscopy, on resistive switching memories based on transition-metal oxides, where the migration of O<sub>2</sub><sup>−</sup> ions and the remaining oxygen vacancies are responsible for the formation of conducting nanofilaments [29]. C-AFM can detect the presence of these filaments and can even be used to bias them in low- or high-resistive states. Figures 4(a) and 4(b) show topographic and conductive maps, respectively, for a 40-nm-thick Pd-based chromia film. As can be clearly seen, the flat planes are now joined together but the conducting filaments and mesas still exist. The corresponding C-AFM map now shows leakage that is predominantly mediated through the spots.

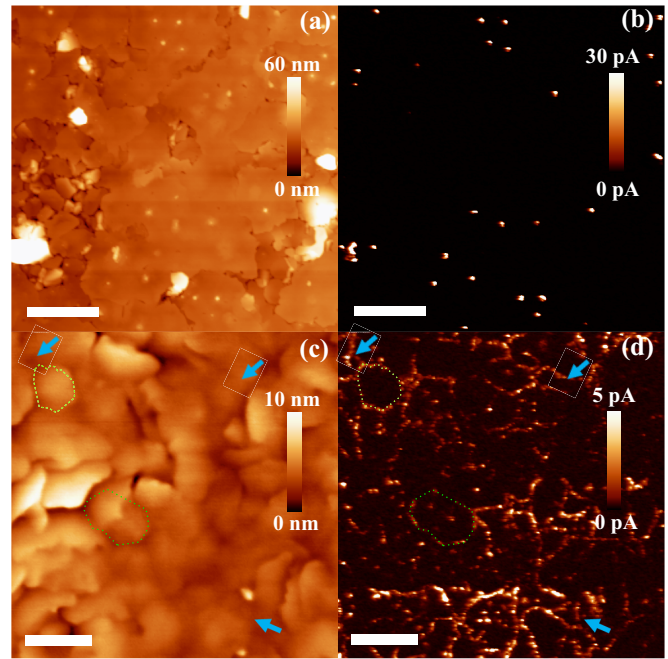


FIG. 4. (a), (c) Topography and (b), (d) conduction mapping of (a) 40-nm and (c) 300-nm Cr<sub>2</sub>O<sub>3</sub> (0001) film on Pd on Al<sub>2</sub>O<sub>3</sub> substrate. Tip bias voltage for C-AFM is 1.0 V. Arrows in (c) and (d) point to smaller-sized domains, whereas the area marked by the dotted line represents an individual grain. Scale bar: (a), (b) 800 nm and (c), (d) 200 nm.

Turning now to thicker films, in Figs. 4(c) and 4(d) we show topographic and C-AFM maps, respectively, obtained for a 300-nm-thick Pd-based chromia film. It is notable that the topographic features obtained in this case resemble those exhibited by the 40-nm film, with flat planes that are completely joined together. Both the height and the abundance of the aforementioned mesas are also reduced as compared to thinner films. The corresponding conductive mapping shows some remarkable features. The boundaries between the flat planes clearly exhibit enhanced leakage and can be readily correlated with the topographic grain boundaries. Upon close inspection, one observes that these are individual conducting dots lined along the grain boundaries. The dotted line indicated in the topographic image follows the shape of one such boundary. Leakage at grain boundaries is not uncommon and has been observed in C-AFM studies of other oxides [30]. The leakage has been explained by considering that the nanoscale conducting paths formed at the grain boundaries can serve as channels for easy diffusion for oxygen vacancies. In other cases of resistive switching, consideration has been given to models based on charge-carrier trapping [31], and of a Mott transition that is induced by carrier doping at the oxide-metal interface [31]. A structural study performed by our collaborators on 300-nm Pd-based chromia films helps explain the leakage through the grain boundaries [32]. They have combined advanced scanning transmission electron microscopy (STEM) characterization and density functional theory to correlate structure and structural defects with their respective electronic properties. By using high-angle annular dark field STEM imagery, vertical

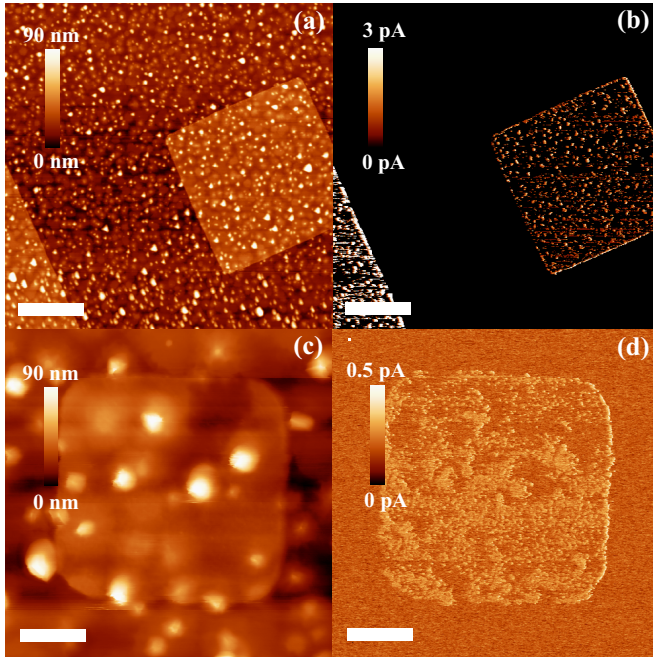


FIG. 5. (a) Topography and (b) conduction mapping of electrodes of sizes  $5 \times 5 \mu\text{m}^2$  and one portion of  $10 \times 10 \mu\text{m}^2$  Ti/Au top electrodes on  $\text{Cr}_2\text{O}_3$  (0001) film on Pd on  $\text{Al}_2\text{O}_3$  substrate. (c) AFM topographic image of  $1 \times 1 \mu\text{m}^2$  Ti/Au pad on  $\text{Cr}_2\text{O}_3$  (0001) film on Pd on  $\text{Al}_2\text{O}_3$  substrate. The C-AFM image in this case (d) represents almost negligible current of  $\sim 0.1$  pA. Tip bias voltage for C-AFM is 1.0 V. Scale bar: (a), (b)  $2 \mu\text{m}$  and (c), (d)  $300 \text{ nm}$ .

planar grain boundaries with substantially reduced electronic band gap have been revealed [32]. They are prone to dielectric breakdown once electrons in the presence of an applied electric field gain sufficient energy to cross the reduced band gap. This explains the observed high conduction points along the boundaries of flat planes in our 300-nm films. Although the lateral resolution of the AFM tip is less than that in STEM, and so is consequently unable to capture the  $<50$ -nm grains, the C-AFM mapping does show certain features that are not discernible in the corresponding topography map. The blue arrows in Fig. 4(d), for example, point to some of the smallest grains, for which C-AFM shows measurable structure even though the corresponding topographic features are not well resolved.

To shed further light on the conduction behavior of the 300-nm films, both photolithography and electron-beam lithography were used to fabricate Cr/Au electrodes on top of Pd-based chromia. The contact sizes vary from  $500 \times 500$  to  $1 \times 1 \mu\text{m}^2$ , thereby allowing us to control the number of leakage filaments in contact with the electrode. C-AFM was then used to characterize the current profile of these pads. Figures 5(a) and 5(b) are the topographic and C-AFM images, respectively, obtained by scanning over a  $5 \times 5 \mu\text{m}^2$  electrode, and a portion of a  $10 \times 10 \mu\text{m}^2$  pad. At a scanning-tip voltage of 1.0 V, different current strengths of  $\sim 3$  and  $0.5$  pA are clearly seen for these two electrodes. This difference in current strength indicates that the number of conducting paths in contact with any given electrode varies in accordance with its size. To further illustrate this point, in Table I we indicate the value of the current determined for contact pads of varying size, clearly

TABLE I. Current measured by C-AFM tip for various electrode sizes.

Pad size ( $\mu\text{m}^2$ )	Current at $V_{\text{tip}} = 1.0 \text{ V}$ (nA)
$300 \times 300$	1.1
$120 \times 120$	0.9
$70 \times 70$	0.7
$50 \times 50$	0.4
$20 \times 20$	0.15

revealing a direct relationship between this current and the contact area. This current is the total current determined over the total time that the tip remains in contact with the surface. To draw a comparison between two representative electrode areas, we calculated resistivity of  $5 \times 5$  and  $10 \times 10 \mu\text{m}^2$  electrodes and the corresponding values are  $4.9 \times 10^9$  and  $3.3 \times 10^9 \Omega \text{ cm}$ , which indicate a trend towards scaling, as will be more clear by the discussion in the next paragraph. This scaling of resistivity is traced to electrodes of very small sizes such as  $1 \mu\text{m}^2$  as shown in Fig. 5(c) (topography) and Fig. 5(d) (conductivity mapping) for the  $1 \mu\text{m}^2$ -sized electrode; where an average current of a few tens of femtoamperes at 1.0 V bias is discernible from the noise range of the instrument and depicts a very high resistivity, a strong indication of a lesser number of filaments in contact with this electrode.

In Fig. 6, we show the results of a detailed comparison of the leakage resistance of more than a hundred different electrodes of varying size formed on 300-nm chromia films on Pd, Pt, and  $\text{V}_2\text{O}_3$  substrates. The ordinate of this figure provides the measured resistivity versus electrode areas. For all three film types, and for the largest pad size ( $500 \times 500 \mu\text{m}^2$ ) studied, it is clear that there is significant leakage, placing an upper limit on the area over which chromia films can be synthesized with satisfactory dielectric properties. For smaller pad sizes,

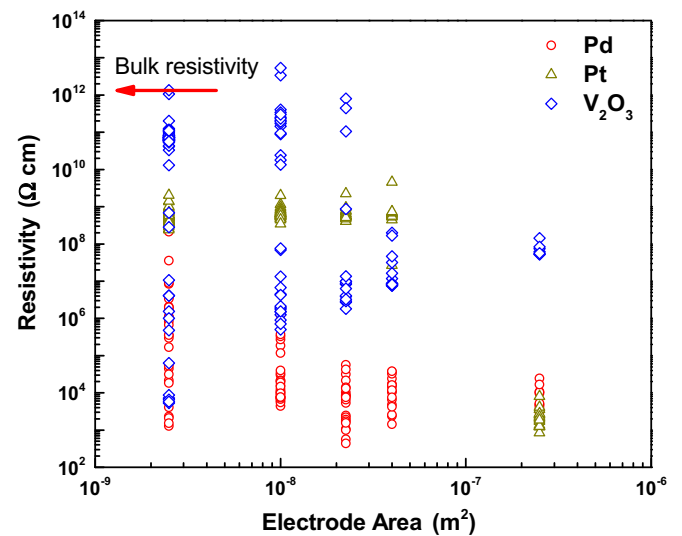


FIG. 6. Resistivity for electrodes of various sizes plotted as a function of electrode area with Pd (red circles), Pt (olive triangles), and  $\text{V}_2\text{O}_3$  (blue diamonds) under layers. The red arrow marks the resistivity of bulk chromia.



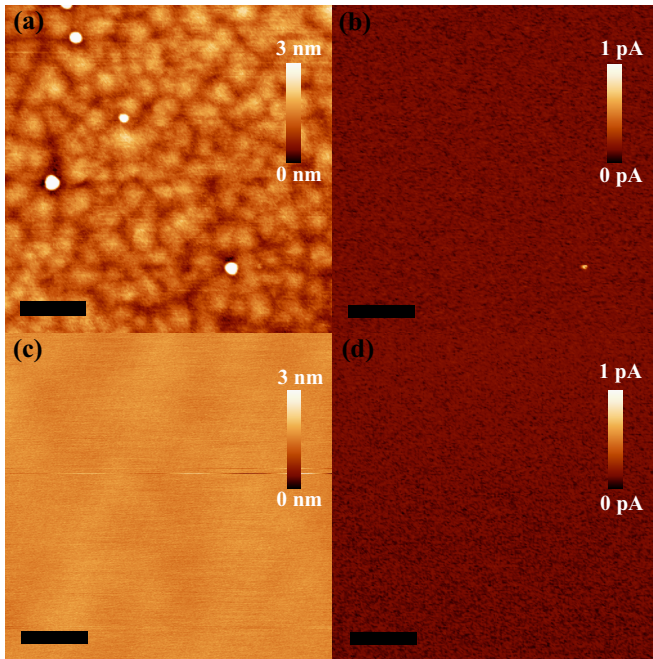


FIG. 7. (a) Topography and (b) conduction mapping of 300-nm Cr<sub>2</sub>O<sub>3</sub> (0001) film on Pt seeding layer on Al<sub>2</sub>O<sub>3</sub> substrate. Tip bias: 1.0 V. (c) Topography of ultrasmooth surface of Cr<sub>2</sub>O<sub>3</sub> (0001) on V<sub>2</sub>O<sub>3</sub> (0001) seeding layer and (d) its corresponding conductive mapping. Tip bias: 3.0 V. Scale bar: 200 nm.

however, the difference between films on all three seeding layers becomes clearer. Pd-based films are more leaky and subject to large statistical variations in resistivity. For Pd-based chromia with a contact size of  $50 \times 50 \mu\text{m}^2$ , resistance values range from just 1 k $\Omega$  to as much as 1 G $\Omega$ , with the latter value implying a leakage level of 1 nA at 1 V bias. The tendency for the Pd-based films to show increasing resistivity value with decreasing contact size appears to be consistent with the results of our corresponding current-mapping studies, which hint at the reduced number of shunting paths in direct contact with the electrodes. On the other hand, Pt-based films exhibit a large and uniform resistivity; this makes them a candidate for more reliable contacts as the resistivity values are more stable, albeit remaining low at around  $10^9 \Omega \text{ cm}$ . V<sub>2</sub>O<sub>3</sub>-based films again exhibit a wider spread in resistivity for smaller contacts. However, the striking feature is that the measured resistivity is larger than  $10^{12} \Omega \text{ cm}$ , which is comparable to that of chromia bulk at room temperature.

While we have largely focused thus far on the topography and two-dimensional conductivity mapping of Pd-based films, we repeated similar measurements on 20-nm Pt and V<sub>2</sub>O<sub>3</sub> seed layers. Figure 7(a) displays the topography of 300-nm chromia films on a Pt seeding layer. The topography shows that the aforementioned r-planes are absent in these films, while the grains are much smaller ( $\sim 50$ – $100$  nm) than those exhibited by the Pd-based films. Consistent with this, the rms roughness of the films is  $\sim 0.15$  nm. The corresponding current scan in Fig. 7(b) indicates almost no leakage at the surface, with only a few leakage spots being present, in which the current remains at

subpicoampere levels. These spots appear relatively high in the topographic scans and likely represent surface contaminants, rather than any capping of the conducting filaments. The absence of significant leakage in the results of Fig. 7(b) appears consistent with the behavior shown in Fig. 6, in which the Pt-based films show a far more uniform resistivity. Figure 7(c) shows a topographic scan of 20-nm-thick chromia on V<sub>2</sub>O<sub>3</sub> and it can be readily observed that an ultrasmooth surface has been grown as compared to the metal-based samples. The rms roughness is estimated to be  $< 0.1$  nm, characterized by an absence of surface features observed in the abovementioned films. The corresponding conductive mapping that was taken at a tip bias of 3.0 V is essentially featureless as well, to mention the completely insulating nature of the surface. This is a direct result of an absence of in-plane rotational domains as explained earlier. Thus, from our topographic and electrical studies, we infer that the Pt- and V<sub>2</sub>O<sub>3</sub>-based chromia films show significantly lower density of leakage sites than their Pd-based counterparts. More specifically, based on our XRD studies, this dramatic improvement is attributed to the absence of leakage pinholes associated with twinning and  $60^\circ$  rotated planes, which were found to be abundant in chromia on Pd.

#### IV. CONCLUSIONS

In this work, we have compared the morphology and accompanying electrical properties of thin-film chromia formed on Al<sub>2</sub>O<sub>3</sub> substrates with different seed layers (Pd, Pt, and V<sub>2</sub>O<sub>3</sub>) and at various thicknesses. Through XRD studies, we found that the appearance of rotational domains is strongly dependent upon the choice of underlying seed layer. C-AFM measurements further reveal the source of current leakage to be the existence of nanoscale conducting paths at grain boundaries. Although this work does not establish any correlation between the rotational domains and the nanoscale conducting paths, we found that rotational domains, as well as the resulting electrical leakage, are strongly suppressed when chromia is grown on Pt and V<sub>2</sub>O<sub>3</sub>, which is in agreement with our electrical study shown in Fig. 6. Furthermore, very thin (20-nm) chromia films grown on V<sub>2</sub>O<sub>3</sub> present a completely revolutionized result where the films are able to sustain high electric fields with reduced top-to-bottom applied voltage. Our results suggest that the all-oxide approach has great promise for implementation in ultralow-power ME-MRAM and spintronic logic devices.

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- [1] P. A. Dowben, C. Binek, and D. E. Nikonov, in *Nanoscale Silicon Devices*, edited by S. Oda and D. K. Ferry (CRC Press, Boca Raton, FL, 2015).
- [2] C. Binek and B. Doudin, *J. Phys. Condens. Matter* **17**, L39 (2005).
- [3] J. Nogués and I. K. Schuller, *J. Magn. Magn. Mater.* **192**, 203 (1999).
- [4] W. Kleemann and C. Binek, *Magnetic Nanostructures*, edited by H. Zabel and M. Farle (Springer, Berlin, 2013).
- [5] N. Wu, X. He, A. L. Wysocki, U. Lanke, T. Komesu, K. D. Belashchenko, C. Binek, and P. A. Dowben, *Phys. Rev. Lett.* **106**, 087202 (2011).
- [6] P. Borisov, A. Hochstrat, X. Chen, W. Kleemann, and C. Binek, *Phys. Rev. Lett.* **94**, 117203 (2005).
- [7] X. He, Y. Wang, N. Wu, A. N. Caruso, E. Vescovo, K. D. Belashchenko, P. A. Dowben, and C. Binek, *Nat. Mater.* **9**, 579 (2010).
- [8] M. Street, W. Echtenkamp, T. Komesu, S. Cao, P. A. Dowben, and C. Binek, *Appl. Phys. Lett.* **104**, 222402 (2014).
- [9] W. Echtenkamp and C. Binek, *Phys. Rev. Lett.* **111**, 187204 (2013).
- [10] S. M. Wu, S. A. Cybart, D. Yi, J. M. Parker, R. Ramesh, and R. C. Dynes, *Phys. Rev. Lett.* **110**, 067202 (2013).
- [11] J. T. Heron, J. L. Bosse, Q. He, Y. Gao, M. Trassin, L. Ye, J. D. Clarkson, C. Wang, J. Liu, S. Salahuddin, D. C. Ralph, D. G. Schlom, J. Íñiguez, B. D. Huey, and R. Ramesh, *Nature (London)* **516**, 370 (2014).
- [12] T. Ashida, M. Oida, N. Shimomura, T. Nozaki, T. Shibata, and M. Sashashi, *Appl. Phys. Lett.* **106**, 132407 (2015).
- [13] K. Toyoki, Y. Shiratsuchi, A. Kobane, C. Mitsumata, Y. Kotani, T. Nakamura, and R. Nakatani, *Appl. Phys. Lett.* **106**, 162404 (2015).
- [14] T. Martin and J. Anderson, *IEEE Trans. Magn.* **2**, 446 (1966).
- [15] P. J. Brown, J. B. Forsyth, E. Lelièvre-Berna, and F. Tasset, *J. Phys. Condens. Matter* **14**, 1957 (2002).
- [16] C.-P. Kwan, R. Chen, U. Singisetti, and J. P. Bird, *Appl. Phys. Lett.* **106**, 112901 (2015).
- [17] S.-H. Lim, M. Murakami, S. E. Lofland, A. J. Zambano, L. G. Salamancariba, and I. Takeuchi, *J. Magn. Magn. Mater.* **321**, 1955 (2009).
- [18] K.-J. Lee, L.-W. Wang, T.-K. Chiang, and Y.-H. Wang, *Materials* **8**, 7191 (2015).
- [19] T. Kosub, M. Kopte, R. Hühne, P. Appel, B. Shields, P. Maletinsky, R. Hübner, M. O. Liedke, J. Fassbender, O. G. Schmidt, and D. Makarov, *Nat. Commun.* **8**, 13985 (2017).
- [20] M. Grundmann, *Phys. Status Solidi B* **248**, 805 (2011).
- [21] L. Dillemans, T. Smets, R. R. Lieten, M. Menghini, C.-Y. Su, and J.-P. Locquet, *Appl. Phys. Lett.* **104**, 071902 (2014).
- [22] D. Zhang, Y. Wang, and Y. Gan, *Appl. Surf. Sci.* **274**, 405 (2013).
- [23] T. Wagner, G. Richter, and M. Rühle, *J. Appl. Phys.* **89**, 2606 (2001).
- [24] T. Nozaki, Y. Sato, T. Ashida, N. Shiomomura, and M. Sashashi, *Appl. Phys. Express* **7**, 093006 (2014).
- [25] R. Waser and M. Aono, *Nat. Mater.* **6**, 833 (2007).
- [26] K. Szot, W. Speier, G. Bihlmayer, and R. Waser, *Nat. Mater.* **5**, 312 (2006).
- [27] M. Hwan Lee and C. Seong Hwang, *Nanoscale* **3**, 490 (2011).
- [28] Y.-M. Kim and J.-S. Lee, *J. Appl. Phys.* **104**, 114115 (2008).
- [29] M.-J. Lee, S. Han, S. H. Jeon, B. H. Park, B. S. Kang, S.-E. Ahn, K. H. Kim, C. B. Lee, C. J. Kim, I.-K. Yoo, D. H. Seo, X.-S. Li, J.-B. Park, J.-H. Lee, and Y. Park, *Nano Lett.* **9**, 1476 (2009).
- [30] V. Iglesias, M. Porti, M. Nafria, X. Aymerich, P. Dudek, and G. Bersuker, *J. Vac. Sci. Technol. B* **29**, 01AB02 (2011).
- [31] A. Sawa, *Mater. Today* **11**, 28 (2008).
- [32] C. Sun, Z. Song, A. Rath, M. Street, W. Echtenkamp, J. Feng, C. Binek, D. Morgan, and P. Voyles, *Adv. Mater. Interfaces* **4**, 1700172 (2017).