

Epitaxial (001) Bi Fe O 3 membranes with substantially reduced fatigue and leakage

H. W. Jang, S. H. Baek, D. Ortiz, C. M. Folkman, C. B. Eom, Y. H. Chu, P. Shafer, R. Ramesh, V. Vaithyanathan, and D. G. Schlom

Citation: [Applied Physics Letters](#) **92**, 062910 (2008); doi: 10.1063/1.2842418

View online: <http://dx.doi.org/10.1063/1.2842418>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/92/6?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Enhanced fatigue and ferroelectric properties in multiferroic \(Ba_{0.7}Sr_{0.3}\)TiO₃/\(Bi_{1.05}La_{0.05}\)FeO₃ epitaxial heterostructures](#)

Appl. Phys. Lett. **102**, 232902 (2013); 10.1063/1.4809932

[Role of dual-laser ablation in controlling the Pb depletion in epitaxial growth of Pb\(Zr_{0.52}Ti_{0.48}\)O₃ thin films with enhanced surface quality and ferroelectric properties](#)

J. Appl. Phys. **111**, 064102 (2012); 10.1063/1.3694035

[Electrical reliability and leakage mechanisms in highly resistive multiferroic La_{0.1}Bi_{0.9}FeO₃ ceramics](#)

Appl. Phys. Lett. **98**, 152902 (2011); 10.1063/1.3580604

[Reversible plasma switching in epitaxial BiFeO₃ thin films](#)

Appl. Phys. Lett. **96**, 202902 (2010); 10.1063/1.3431585

[Switching kinetics in epitaxial BiFeO₃ thin films](#)

J. Appl. Phys. **107**, 084111 (2010); 10.1063/1.3392884

An advertisement for Oxford Instruments' Asylum Research AFM. The background is dark blue. On the left, there is a vintage mobile phone and a vintage desktop computer. In the center, there is a modern AFM. Text on the left asks 'You don't still use this cell phone or this computer'. Text in the center asks 'Why are you still using an AFM designed in the 80's?'. Text on the right says 'It is time to upgrade your AFM' and 'Minimum \$20,000 trade-in discount for purchases before August 31st'. Below that, it says 'Asylum Research is today's technology leader in AFM'. At the bottom right, there is the Oxford Instruments logo and the tagline 'The Business of Science®'. An email address 'dropmyoldAFM@oxinst.com' is also present.

You don't still use this cell phone or this computer

Why are you still using an AFM designed in the 80's?

It is time to upgrade your AFM

Minimum \$20,000 trade-in discount for purchases before August 31st

Asylum Research is today's technology leader in AFM

OXFORD INSTRUMENTS
The Business of Science®

dropmyoldAFM@oxinst.com

Epitaxial (001) BiFeO₃ membranes with substantially reduced fatigue and leakage

H. W. Jang,¹ S. H. Baek,¹ D. Ortiz,¹ C. M. Folkman,¹ C. B. Eom,^{1,a)} Y. H. Chu,²
P. Shafer,² R. Ramesh,² V. Vaithyanathan,³ and D. G. Schlom³

¹Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

²Department of Physics and Department of Materials Science and Engineering, University of California, Berkeley, California 94720, USA

³Department of Materials Science and Engineering, Pennsylvania State University, Pennsylvania 16802-5005, USA

(Received 20 December 2007; accepted 20 January 2008; published online 14 February 2008)

We report substantially reduced fatigue and electrical leakage in BiFeO₃ membranes fabricated by releasing epitaxial (001) BiFeO₃ films from the Si substrates on which they were grown. Fatigue-free switching behavior of up to 10¹⁰ cycles was observed for BiFeO₃ membranes with Pt top electrodes, while as-grown films break down at ~10⁹ cycles. This is attributed to the low coercive field of BiFeO₃ membranes and their being free from substrate clamping. In contrast, (111) BiFeO₃ films exhibit significant fatigue at the same electric field. Epitaxial (001) BiFeO₃ membranes with low coercive field are very promising for lead-free ferroelectric memory and magnetoelectric devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.2842418]

The lead-free perovskite BiFeO₃ has received considerable attention for nonvolatile memory applications because of its large polarization of ~100 μC/cm² along the [111] direction.¹⁻⁴ Epitaxial growth of BiFeO₃ on silicon has been demonstrated using an intervening epitaxial SrTiO₃ buffer layer.⁵ The critical challenges remaining to be overcome before BiFeO₃-based films will be candidates for integrated microelectronic devices are lowering its coercive field (E_c) and leakage current and demonstrating its reliability.⁶ Additionally, the multiferroic nature of BiFeO₃ offers the very exciting possibility of manipulating magnetic state by an electric field at room temperature.⁶ Recently, Zhao *et al.* showed evidence of coupling between the ferroelectric and magnetic order parameters in BiFeO₃.⁷ The magnetoelectric coupling in BiFeO₃ has also been suggested to enable the switching of a ferromagnetic material such as (La,Sr)MnO₃ or Co coupled to the multiferroic through exchange interactions.⁸

In this paper, we demonstrate that the ferroelectric properties of epitaxial (001) BiFeO₃ thin films can be significantly enhanced by releasing them from the underlying Si substrate and transferring them onto a new substrate. (001) BiFeO₃ membranes with Pt top electrodes exhibit significantly lower E_c , lower leakage current, and improved fatigue in comparison to as-grown films. After release, fatigue-free switching behavior to 10¹⁰ cycles was achieved for BiFeO₃ membranes. The mechanism of fatigue-free behavior in a (001) BiFeO₃ membrane is discussed and compared with both clamped (001) and (111) BiFeO₃ films.

Epitaxial (001) BiFeO₃ films were grown by off-axis radio-frequency (rf) magnetron sputtering³ on (001) Si substrates miscut by 4° toward [110]. Prior to the deposition of the BiFeO₃ films, an epitaxial 15-nm-thick SrTiO₃ buffer layer and 100-nm-thick SrRuO₃ bottom electrode were deposited on the 50-μm thick Si substrates by molecular-beam

epitaxy⁹ and 90° off-axis rf magnetron sputtering,^{10,11} respectively. The fabrication process of epitaxial (001) BiFeO₃ membranes is described with schematic diagrams in Fig. 1. After epitaxial growth of BiFeO₃ films on the SrRuO₃/SrTiO₃/Si templates, Pt top electrodes (50-nm-thick and 100 μm in diameter) were formed on the BiFeO₃ film by rf sputtering and photolithography. After measurement of the electrical properties of the capacitors with the Pt top electrodes, the underlying Si substrate was completely removed by dry etching. In the etch process, the bottom SrTiO₃ and SrRuO₃ layers were used as etch stop layers. In order to handle the BiFeO₃ membranes, 25-μm-thick Au platforms were formed on the thin-film membranes using electroplating. In this way, capacitors of BiFeO₃ membranes with the same original Pt top electrodes were obtained and tested.

The lattice parameters and symmetries of the BiFeO₃ films before and after lift-off were determined by reciprocal

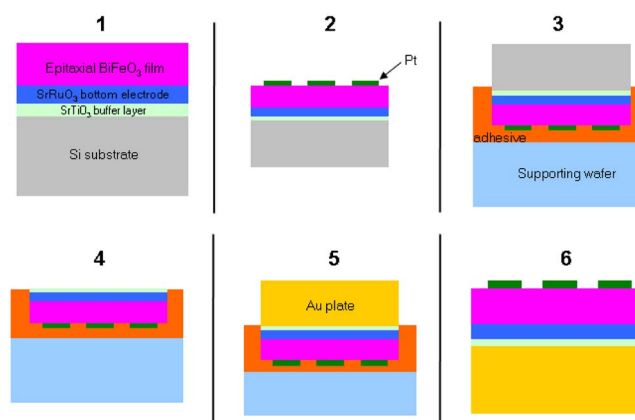


FIG. 1. (Color online) Schematic diagrams showing the fabrication process of strain-free BiFeO₃ membranes: (1) epitaxial growth of BiFeO₃/SrRuO₃/SrTiO₃/Si heterostructures; (2) deposition of Pt top electrodes; (3) bonding the capacitor structure onto a supporting wafer; (4) removal of the Si substrate by inductive plasma etching; (5) Au electroplating; and (6) final structure after detachment of the membrane from the supporting wafer by dissolving the adhesive in acetone.

^{a)} Author to whom correspondence should be addressed. Electronic mail: eom@engr.wisc.edu.

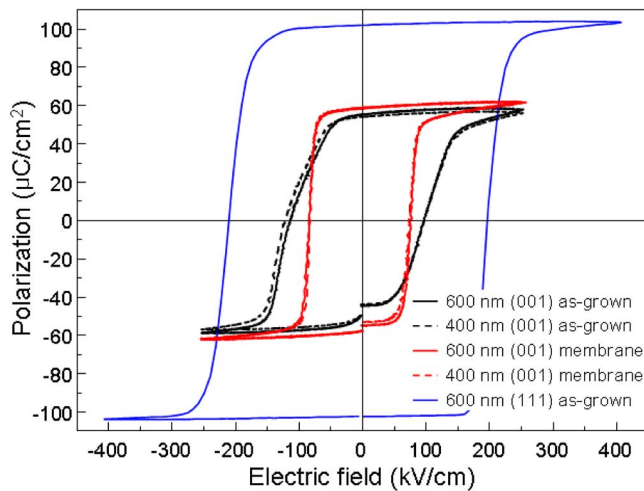


FIG. 2. (Color online) P - E hysteresis loops of the 400-nm- and 600-nm-thick (001) BiFeO₃ as-grown films and membranes. Both loops were obtained from the same Pt top electrode before and after lift-off. The P - E hysteresis loop of a 600-nm-thick (111) BiFeO₃ film on (111) SrTiO₃ is shown for comparison.

space mapping using high-resolution x-ray diffraction; the details are reported elsewhere.¹² The as-grown films are subjected to biaxial tensile strains due to the large mismatch in the thermal expansion coefficients of Si and BiFeO₃.⁵ For the membranes, the out-of-plane and in-plane lattice parameters are the same as those of bulk BiFeO₃, indicating that the BiFeO₃ membranes are fully relaxed and strain-free. The strain relief accompanying lift-off results in a symmetry change of the BiFeO₃ films from monoclinic for the as-grown strained films to rhombohedral for the membranes.

The ferroelectric properties were characterized by polarization-electric field (P - E) measurements. Figure 2 shows the P - E hysteresis loops measured on 400-nm- and 600-nm-thick (001) BiFeO₃ films on Si before and after lift-off. It should be noted that we measured the *same* Pt top electrode before and after lift-off, which excludes all other variables affecting P - E hysteresis loops. It is apparent that the membranes display significantly enhanced ferroelectric properties, including increased remanent polarization (P_r) and reduced E_c . The 400-nm-thick film on Si has a higher coercive field than the 600-nm-thick one. Both the 400-nm- and 600-nm-thick membranes, however, have almost the same coercive fields, which are 25%–30% lower than the clamped films. Achieving such low E_c values is a key to the use of BiFeO₃ in nonvolatile memories. Notably, the E_c (80 kV/cm) of the membranes is the lowest ever reported for epitaxial BiFeO₃ films^{1–3} and comparable to those of epitaxial Pb(Zr,Ti)O₃ films.¹¹ This observation implies that the relatively high E_c reported for epitaxial BiFeO₃ thin films originates from a substrate-clamping effect. Meanwhile, (111)-oriented epitaxial BiFeO₃ films on (111) SrTiO₃ substrates show a large P_r (102 $\mu\text{C}/\text{cm}^2$) and very high E_c (200 kV/cm²).

To confirm the low E_c of the BiFeO₃ membranes, we conducted piezoelectric force microscopy (PFM) measurements.¹³ The results (not shown) revealed a two-domain stripe pattern with stripes separated by 71° domain walls in both the as-grown film and the BiFeO₃ membrane, consistent with transmission electron microscopy analysis.³ Furthermore, the lower E_c of the membrane is observed via

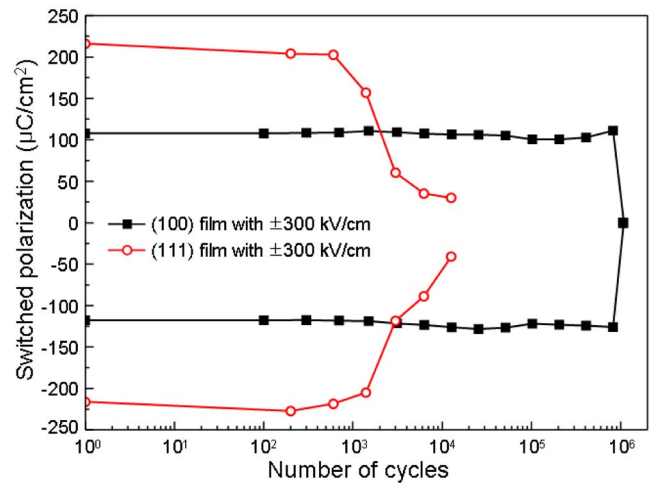


FIG. 3. (Color online) Fatigue characteristics of 600-nm-thick (001) BiFeO₃/(001) Si and (111) BiFeO₃/(111) SrTiO₃ films. The width and frequency of switching pulses were 10 μs and 100 Hz, respectively.

dc poling by the PFM tip. The polarization of the membrane was switchable by ± 12 V, whereas the bias had to be increased to ± 20 V to complete switching in the clamped film. This decrease in E_c for the membrane as determined by PFM poling is commensurate with the decrease observed in the P - E loops. The discrepancy between both measurements is a result of switching on a local scale (PFM) versus the average switching observed under a patterned electrode (P - E loop).^{3,13}

Fatigue is one of the most important factors in determining the reliability of ferroelectric and magnetoelectric devices. We carried out fatigue tests on as-grown (001) and (111) BiFeO₃ films by applying 5 μs wide pulses with a repetition frequency of 100 Hz to the top Pt and bottom SrRuO₃ electrodes, as shown in Fig. 3. The cycling voltage was selected to be ± 300 kV/cm, which gives complete switching for both films, as shown in Fig. 2. The capacitor of the (001) BiFeO₃ film on Si shows no fatigue up to 9×10^5 cycles and an abrupt break down at 1×10^6 cycles. In contrast, the (111) BiFeO₃ film on (111) SrTiO₃ substrates exhibits a significant degradation in switching after 10^4 cycles, which is similar to the fatigue behavior typically seen in Pb(Zr,Ti)O₃.¹⁴ The completely different fatigue behaviors between (001) and (111) films are consistent with the previous report on fatigue anisotropy. Bornand *et al.*¹⁵ showed that (001)-oriented thin films of the rhombohedral relaxor ferroelectric Pb(Yb_{1/2}Nb_{1/2})O₃-PbTiO₃ have no fatigue ($2P_r \sim 50 \mu\text{C}/\text{cm}^2$) up to 10^{11} cycles, while (111) films exhibit a marked fatigue by voltage cycling. 71° domain switching occurs in the (001) BiFeO₃ film, as shown in Fig. 3, while only 180° domain switching occurs in the (111) BiFeO₃ film. This difference in domain switching leads to the fatigue anisotropy.^{15,16}

We also conducted fatigue tests on the (001) BiFeO₃ as-grown films and membranes at a switching field of ± 160 kV/cm. Figure 4(a) shows the fatigue characteristics of a 400-nm-thick (001) as-grown film and membrane. The amplitudes of the switched polarization for the as-grown films and membranes are very close to the $2P_r$ values shown in Fig. 2, indicating that the switching field of ± 160 kV/cm provides complete switching in both cases. The capacitor of the as-grown film shows no fatigue up to 9×10^8 cycles but

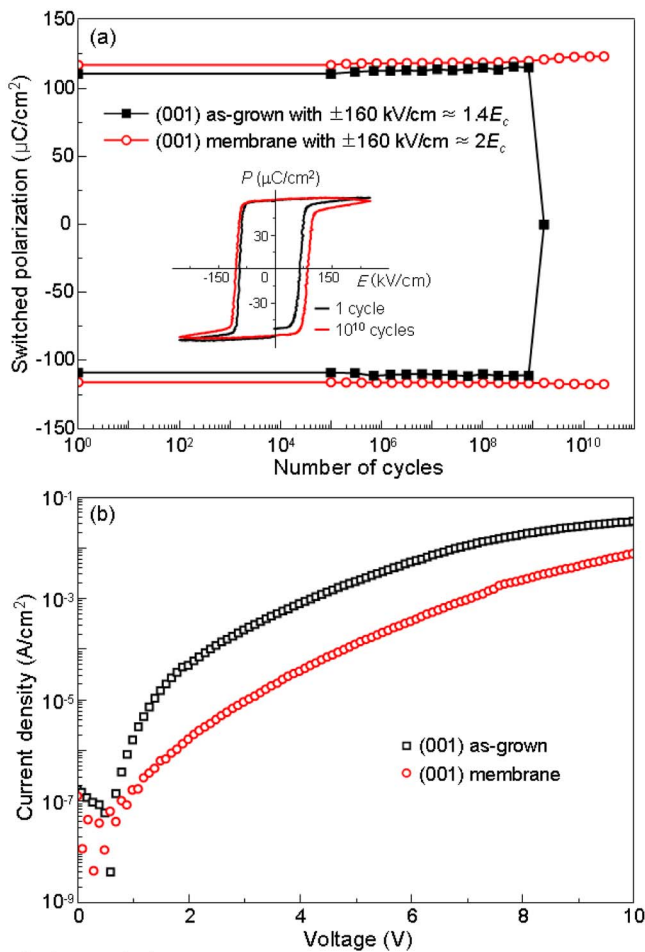


FIG. 4. (Color online) (a) Fatigue characteristics of a 400-nm-thick BiFeO₃ film and membrane. The width and frequency of the switching pulses were 5 μ s and 100 kHz, respectively. The inset shows P - E hysteresis loops of the BiFeO₃ membrane before and after 10^{10} cycles with a switching field of ± 160 kV/cm. (b) Forward leakage current characteristics as a function of applied voltage of 400-nm-thick BiFeO₃ thin film capacitors before (film) and after lift-off (membrane).

breakdown at 1×10^9 cycles. In combination with the result in Fig. 4, we conclude that the lower switching field suppresses the breakdown of the film during the voltage cycling. In contrast, the BiFeO₃ membrane with Pt top electrodes remains fatigue-free to 2.4×10^{10} cycles. It is remarkable that $2P_r$ of the BiFeO₃ membrane is as high as $116 \mu\text{C}/\text{cm}^2$, significantly higher than that of Pb(Zr_{0.53}Ti_{0.47})O₃,¹⁴ SrBi₂Ta₂O₉,¹⁷ and Bi_{3.75}La_{0.25}Ti₃O₁₂.¹⁸ For the 600-nm-thick membranes, we observed a very similar result, confirming the fatigue-free behavior of the BiFeO₃ membranes.

It is widely accepted that oxygen vacancies formed during growth, cause a portion of the Fe³⁺ ions to become Fe²⁺, which is responsible for the high leakage current in BiFeO₃.¹⁹ From this, we suggest that the breakdown during the fatigue test could be due to the formation of conducting filaments as they gather mobile defects such as oxygen vacancies. After breakdown, observation under an optical microscope revealed a small dark spot on the Pt top electrode, which supports the formation of conducting filaments. Figure 4(b) shows that the membrane has a lower leakage current than the as-grown film. We believe that the reduction in the leakage current and easy domain wall motion that arises from freeing the BiFeO₃ film from substrate clamping prevents breakdown during the fatigue test and, thus, leads to

the observed fatigue-free behavior. Further study is needed to identify the mechanism responsible for the lower leakage current in the BiFeO₃ membranes.

In conclusion, we have demonstrated a significant enhancement of the ferroelectric properties of (001) BiFeO₃ thin films by removing the constraint of the underlying substrate. The reduction of both coercive field and leakage current and fatigue-free switching behavior over 10^{10} cycles were achieved in strain-free BiFeO₃ membranes. This work presents a route to overcome some of the major challenges involved in applying BiFeO₃ thin films to nonvolatile memories and magnetoelectric devices. Another promising application of BiFeO₃ membranes is microelectronics built on flexible substrates. Using wafer bonding technology,²⁰ freestanding BiFeO₃ thin films can be integrated on any kind of flexible substrates, making it available for applications in displays, solar cells, smart cards, and rf tags.

The authors gratefully acknowledge the financial support of the National Science Foundation through grants ECCS-0708759 and DMR-0507146 and the Office of Naval Research through grants N00014-07-1-0215 and N00014-04-1-0426 monitored by Colin Wood.

¹J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).

²J. F. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruetter, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, *Appl. Phys. Lett.* **84**, 5261 (2004).

³R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, F. Zavaliche, S. Y. Yang, R. Ramesh, Y. B. Chen, X. Q. Pan, X. Ke, M. S. Rzchowski, and S. K. Streiffer, *Appl. Phys. Lett.* **88**, 242904 (2006).

⁴D. Lebeugle, D. Colson, A. Forget, and M. Viret, *Appl. Phys. Lett.* **91**, 022907 (2007).

⁵J. Wang, H. Zheng, Z. Ma, S. Prasertchoung, M. Wuttig, R. Droopad, J. Yu, K. Eisenbeiser, and R. Ramesh, *Appl. Phys. Lett.* **85**, 2574 (2004).

⁶R. Ramesh and N. A. Spaldin, *Nat. Mater.* **6**, 21 (2007).

⁷T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, *Nat. Mater.* **5**, 823 (2006).

⁸Y.-H. Chu, L. W. Martin, M. B. Holcomb, and R. Ramesh, *Mater. Today* **10**, 16 (2007).

⁹L. V. Goncharova, D. G. Starodub, E. Garfunkel, T. Gustafsson, V. Vaithyanathan, J. Lettieri, and D. G. Schlom, *J. Appl. Phys.* **100**, 014912 (2006).

¹⁰C. B. Eom, R. J. Cava, R. M. Fleming, J. M. Phillips, R. B. Vandover, J. H. Marshall, J. W. P. Hsu, J. J. Krajewski, and W. F. Peck, *Science* **258**, 1766 (1992).

¹¹C. B. Eom, R. B. Vandover, J. M. Phillips, D. J. Werder, J. H. Marshall, C. H. Chen, R. J. Cava, R. M. Fleming, and D. K. Fork, *Appl. Phys. Lett.* **63**, 2570 (1993).

¹²H. W. Jang, S. H. Baek, D. Ortiz, C. M. Folkman, R. R. Das, Y. H. Chu, P. Shafer, J. X. Zhang, S. Choudhury, V. Vaithyanathan, Y. B. Chen, X. Q. Pan, D. G. Schlom, L. Q. Chen, R. Ramesh, and C. B. Eom (unpublished).

¹³F. Zavaliche, P. Shafer, R. Ramesh, M. P. Cruz, R. R. Das, D. M. Kim, and C. B. Eom, *Appl. Phys. Lett.* **87**, 252902 (2005).

¹⁴H. N. Alshareef, A. I. Kingon, X. Chen, K. R. Bellur, and O. Auciello, *J. Mater. Res.* **9**, 2968 (1994).

¹⁵V. Bornand, S. Troler-McKinstry, K. Takemura, and C. A. Randall, *J. Appl. Phys.* **87**, 3965 (2000).

¹⁶J. F. Scott and M. Dawber, *Appl. Phys. Lett.* **76**, 3801 (2000).

¹⁷C. P. de Araujo, J. Cuchiaro, L. McMillan, M. Scott, and J. Scott, *Nature (London)* **374**, 627 (1995).

¹⁸B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, *Nature (London)* **401**, 682 (1999).

¹⁹X. Qi, J. Dho, R. Tomov, M. G. Blamire, and J. L. MacManus-Driscoll, *Appl. Phys. Lett.* **86**, 062903 (2005).

²⁰F. Niklaus, G. Stemme, J.-Q. Lu, and R. J. Gutmann, *J. Appl. Phys.* **99**, 031101 (2006).