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Growth of Vertically-Aligned GaN Nanowires by Metal Organic Chemical Vapor Deposition Utilizing Trimethygallium and Tertiarybutylhydrazine

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The vertically-aligned GaN nanowires (NWs) were grown on Au coated α-Al_2O_3(001) and GaN(002)/α-Al_2O_3(001) substrates by metal organic chemical vapor deposition technique using trimethygallium and tertiarybutylhydrazine (TBHy) as sources. The growth tempearuture of the GaN NWs were reduced to under 700°C due to the low decomposition temperature of TBHy. The vertically-aligned GaN NWs were grown by controlling diameter of Au droplets in the nucleation stage. The GaN NWs grown on α-Al_2O_3 exhibited (101) preferred orientation, while GaN NWs on the GaN(002)/α-Al_2O_3(001) substrate retained [0001] growth direction.

Keywords Synthesis; MOCVD; Vertical GaN Nanowires; Chemical Vapor Deposition.

1. Introduction

One-dimensional (1D) nanostructures, such as nanotubles, nanowires, nanorods have been regarded as the most promissing building block for nanoscale electronic and optoelectronic devices due to the efficient transport of electrons and excitons. [1–5] Shine 1D nanostructures have unique electrical, thermal, mechanical and optical properties that vary from their respective bulk material, fundamental understanding of 1D nanostructures is important for technological progress. As an important III-V semiconductor, GaN is well-know for its excellent optoelectronic properties with direct and wide bandgap, high mobility, and excellent thermal stability. [6, 7] To improve the performance and efficiency of vertically-aligned GaN nanowires (NWs) the development of new methods for fabricating nanowires have attracted much attention. There have been many researches on the formation of 1D GaN structures using a number of advanced techniques by serveral groups. [8–10] However a

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new process for large quantities of 1D GaN at low costs, and high-volume production still have challenges.

GaN NWs preparation is typically based on the vapor-liquid-solid (VLS) growth mechanism by using catalysts such as Au, Ni, Pt, Fe or In, [11–13] or without using catalyst. [14–16] The catalysts create a hightly selective growth environment occuring only in the areas activated by the metal catalysts and the size and position of the NWs are determined by the metal catalysts. It is also important to point out that the catalyst droplets play critical roles in NWs growth by VLS mechanism. Therefore, well-controlled particles size and uniform distribution over the substrate surface are needed in the nucleation stage to get well aligned and uniform GaN NWs. Gold is the most frequently used metal for the VLS process due to such advatages as high chemical stability, non-oxidizing in air, and non-toxicity. [17] The reported synthetic schemes for GaN based materials to date have used molecular-beam epitaxy, [18, 19] hydride phase epitaxy, [20, 21] and metal-organic chemical vapor deposition (MOCVD). [22, 23] Most of these processes use trimethygallium (TMGa) and amonia as the precusors for Ga and N sources, respectively. The growth of GaN NWs require high temperature ($\sim$850°C or above) due to high decomposition temperature of amonia. Moreover, amonia is known as one of the coportant leading to the corrosion of the system. For this reason tertiarybutylhydrazine (TBHy) is known as an ideal nitrogen source alternative to amonia, which can be decomposed at low temperature of 400°C. [24]

Our previous works were in valved the growth of GaN layers on sapphire by using TMGa and TBHy as the precursors. [25, 26] In this work we report the synthesis of vertically-aligned GaN NWs by applying the VLS growth mechanism. Emphasis was placed upon growth direction control of GaN NWs and the feasibility of the low temperature reaction system. The results showed well-alligned wurtzite GaN NWs growth on α-Al_2O_3(001) and GaN(002)/α-Al_2O_3(001) substrates.

2. Experimental Section

All α-Al_2O_3(001) and a 2μm GaN(002)/α-Al_2O_3(001) substrates were cleaned by sonication in acetone for 5 min followed by ethanol for another 5 min, then rinsed with millipore water and blown dry by nitrogen. Then, Au catalysts were deposited on substrates via sputtering with an Emitech K550 sputer coater, followed by heating up to 700°C. Au nanoparticales were formed on the substrate surface during the heating. Then, GaN NWs were grown on thus prepared substrates using the reaction of TMGa (US Epichem) and TBHy (Japan Pionics) at 700°C with the V/III ratios was 53.2 and growth time for 2 hours. Nitrogen was used as the carrier gas. The total pressure during GaN growth was kept at 0.4 Torr.

The synthesized GaN NWs were characterized by several analysis techniques. The morphology of the NWs were observed by Field-Emission Scanning Electrong Microscopy (FESEM), JEOL JSM-6500F. The crystallinity and epitaxial orientation of the NWs were studied by X-ray diffraction (XRD) (Rigaku Dmax-B, Japan) using a Cu-Kα source that was operated at 40 kV and 100 mA with $\lambda = 1.5405$ Å. The diffraction angle (2θ) was taken from 30 to 60 degrees. The structural properties of GaN NWs were characterized by Raman spectroscopy (Reinishaw in Via Raman microscope system) at room temperature with polarized light of He-Ne laser at 633 nm, and the photoluminesence (PL) measurement using He-Cd laser at wavelength 325 nm was also performed to study the optical property.

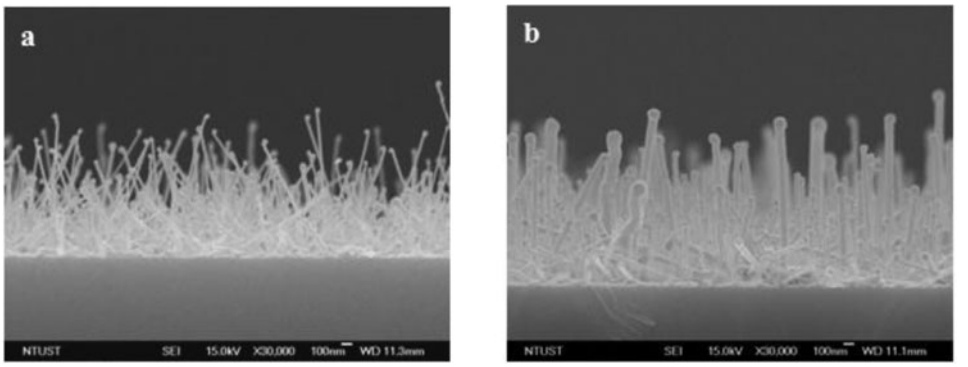

Figure 1. SEM images of GaN NWs growth on different substrates: (a) α-Al_2O_3(001), (b) GaN(002)/α-Al_2O_3(001).

3. Results and Discussion

The growth of GaN NWs on different substrates at 700°C are shown on the Figure 1. Figure 1(a)–1(b) show scanning electron microscope (SEM) images in the cross-sectional of GaN NWs grown on gold-coated α-Al_2O_3(001) and GaN(002)/α-Al_2O_3(001) substartes, respectively.

All these NWs were nucleated using 3 nm thick Au layers. In Figure 1(a), a large number of GaN NWs with diameter ranging from 50 to 100 nm and up 1 μm in length were grown randomly. On the contrary, Figure 1(b) shows that most of the NWs are vertically oriented with respect to the GaN(002)/α-Al_2O_3(001) substrate; this is due to the excellent symmetry and lattice match between the NWs and substrate structure. Moreover the size of GaN in both α-Al_2O_3(001), GaN(002)/α-Al_2O_3(001) substrates were not uniform due to sizes of catalyst were different (Fig. 2a). In addition, we obserbed the NWs with the size over 50 nm are easy to growth vertically (Fig. 1b). Therefore, the nucleation of gold on substrate need to be more uniform and size bigger than 50 nm. An approach was carried out by sputting 5 nm of gold on α-Al_2O_3(001) substrate, this mean the gold enough to form a uniform size droplets on the surface.

The SEM images in Figure 2(a)-2(b) show the forming of Au droplets on α-Al_2O_3(001) with different thickness, as can be seen the nucleation sizes of Au were not uniform when the thickness of Au was 3 mn (Fig. 2a), this reason caused the GaN NWs were not homogeneous which mean the sizes of the catalyst droplets were changed during the NWs growth. On the other hand, the migration of smaller catalyst droplets to larger ones caused the NW shorter or longer. [27] Figure 2(c)–2(d) show a high uniform and well-aligned GaN NWs grown on α-Al_2O_3(001) substrate using 5 nm thickness of Au catalysts. The preferred orientation of the NWs confirm that epitaxial growth of 1D GaN nanostructures on α-Al_2O_3(001) and GaN(002)/α-Al_2O_3(001) substrates are possible. Furthermore, longer or shorter NWs could be achieved by varying the growth time.

XRD analysis from an as-grown sample is used to examine the crystal structure of GaN NWs, and the spectrum is shown on Figure 3. Figure 3 shows a typical XRD pattern of the straight and well-aligned GaN grown on α-Al_2O_3(001), and GaN(002)/α-Al_2O_3(001) substrates. The peak indexed on three substrates as (002) and (101) of the hexagonal wurtzite structure of GaN NWs with the lacttice constants $a = 0.318$ nm and $c = 0.518$ nm, well consistent with the reported values for wurtzite structure GaN. [28] It is interesting

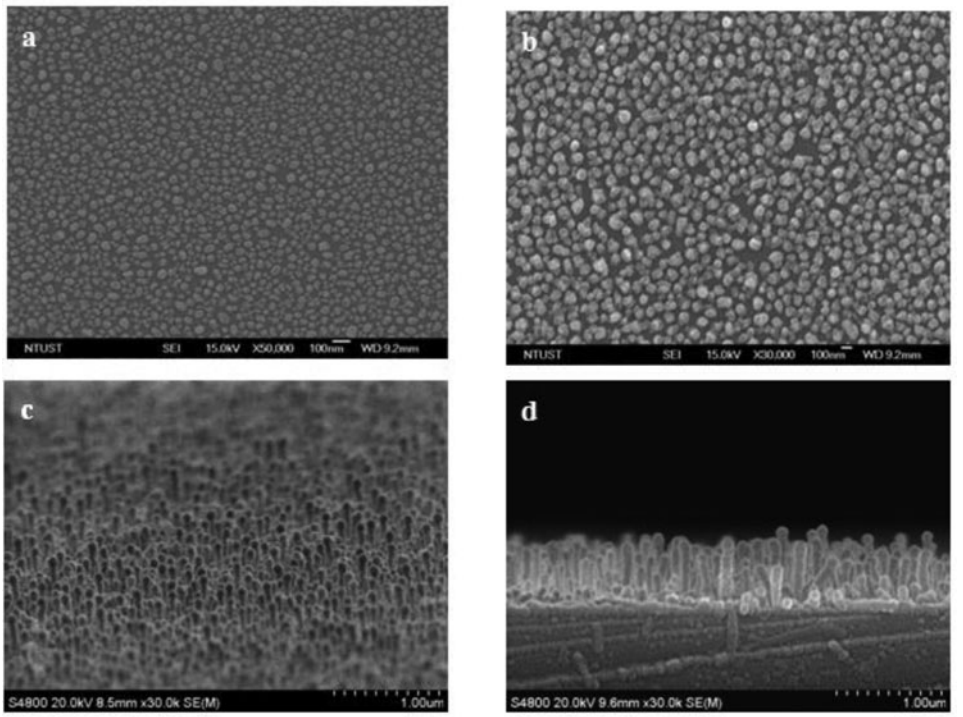

Figure 2. SEM images of Au droplets on α-Al_2O_3(001) with different Au thickness: (a) 3 nm (b) 5 nm. And SEM images of GaN growth on 5 nm of gold coated α-Al_2O_3(001) substrate (c), (d).

to note that is an apparent in orientation of GaN NWs. The GaN NWs prefer orientation (002) on GaN substrate (Fig. 3b), (101) on α-Al_2O_3(001) (Fig 3a). However, the different in orientation of GaN NWs can be explain as the different from lattice mismatch and thermal expansion between two substartes with GaN NWs. Furthermore, only peak from GaN NWs are observed, indicating a good alignment of NWs and the epitaxial relationship of GaN NWs on these substrates.

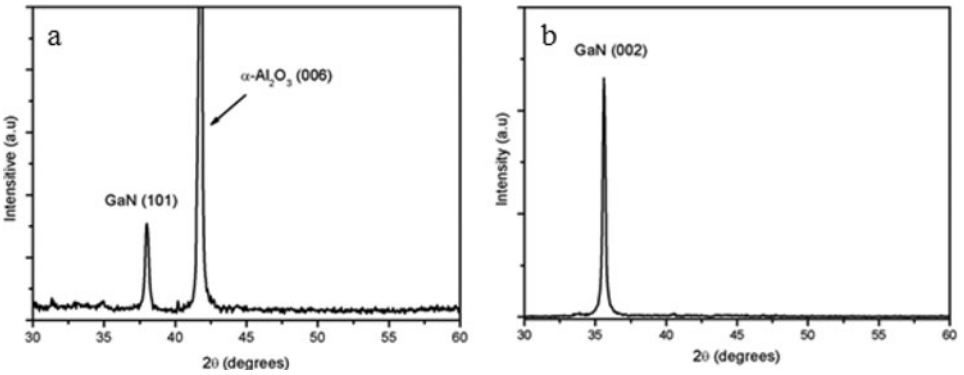

Figure 3. XRD pattern of GaN NWs on: (a) 5 nm of Au coated on α-Al_2O_3(001) substrate, and (b) 3 nm of Au coated on GaN(002)/α-Al_2O_3(001) substrate.

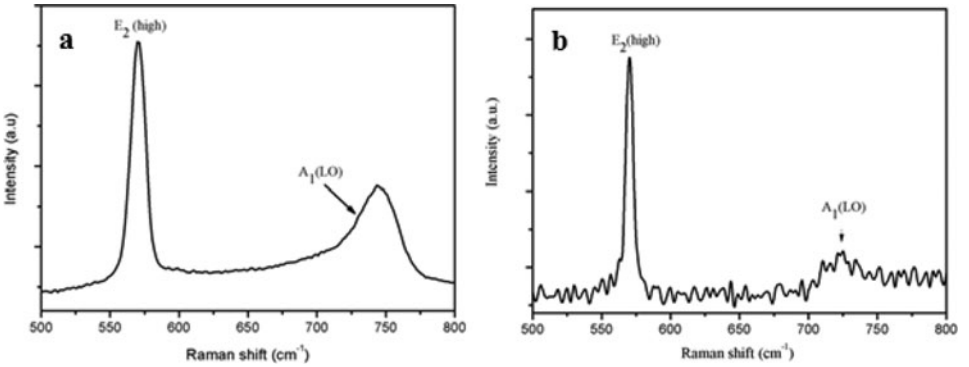

Figure 4. Raman scattering of GaN NWs on: (a) 5 nm of Au coated on α-Al_2O_3(001) substrate, and (b) 3 nm of Au coated on GaN(002)/α-Al_2O_3(001) substrate.

Figure 3 shows a typical Raman spectrum of an as grown of GaN NWs. Theory pridicts and experiments confirm that single crystalline GaN substructures possess eight sets of optical phonon modes near the zone center. [29–31] Among the GaN phonon mode $A_1\,(z) + 2B_1 + E_1(x,y) + 2E_2$, where x, y, z refer to the direction of the phonon polarization, the A_1, E_1, and E_2 mode are Raman-active, whereas the $2B_1$ modes are Raman-inactive and infrared-active $(A_1 + E_1)$. GaN is noncentrosymmetric, so that the A_1 and E_1 modes are split into LO (longitudinal optical) and TO (transverse optical) components due to the macroscopic electrical field associated with the longitudinal vibration. From the results show in Figure 4 at ~569 cm^{-1} (Fig. 4a) and at ~570 cm^{-1} (Fig. 4b) have symmetric E_2 (high). However, the position of A_1 (LO) and A_1 (TO) modes are significantly softer in both α-Al_2O_3(001) and GaN(002)/α-Al_2O_3(001) substrates. The peak at ~750 cm^{-1} on Figure 4a was belong to α-Al_2O_3(001) substrate. [32] The intensity of $I(E_2)/I(A_1) > 1$ is an agreement with the usally observed high intensity of $I(E_2)/I(A_1)$. Additionally, the strong E_2 (high) phonon line in the Raman spectrum is characteristic of the wurtizite phase of GaN. The Raman shift, the full width at half maximum (FWHM) of E_2 (high) 12.7 cm^{-1} (Fig. 4a) was larger than the FWHM E_2 (high) 6.5 cm^{-1} (Fig. 4b) that mean the NWs

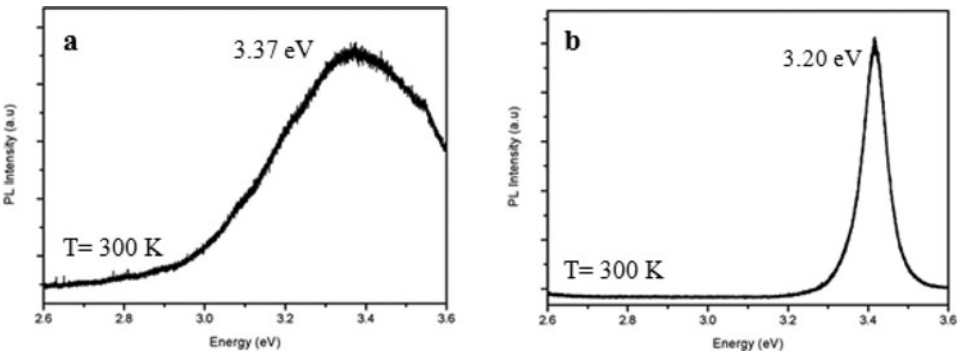

Figure 5. PL spectrum of the as-grown GaN NWs at room temperature (300 K) on different substrates: (a) 5 nm of Au coated on α-Al_2O_3(001) substrate, and (b) 3 nm of Au coated on GaN(002)/α-Al_2O_3(001) substrate.

growth on GaN(002)/α-Al_2O_3(001) substrate had higher quality than those growth on α-Al_2O_3(001) substrate.

A study of the optical properties of GaN NWs are desirable, due to their optical properties are directly linled to their potential optoelectronic applications. The PL spectrum of GaN NWs were detected with He-Cd laser as the excitation source (with wave length of 325 nm) at room temperature (300 K). Figure 5 shows the PL of GaN NWs synthesis at 700°C, a broad emission band ranging from 3.2 eV to 3.6 eV (Fig. 5a), with its maximum intensity centered at 3.37 eV is observed for those GaN NWs grown on α-Al_2O_3(001). Figure 5(b) shows a small and shape of PL of GaN NWs grown on GaN(002)/α-Al_2O_3(001) substrate. The PL peak broadening and red shift 30 meV in Figure 5(a) may be due to point-defect incoporation in the NWs, in contrary the blue shift 20 meV in Figure 5(b) due to the quantum confinment effect.

4. Conclusion

In summary well-aligned GaN NWs were grown on α-Al_2O_3(001) and GaN(002)/α-Al_2O_3(001) substrates by MOCVD method by using TMGa and TBHy as precursors at 700°C. The effect of Au droplets to the growth of the GaN NWs was confirmed that the uniform Au droplet with size larger than 50 nm could grow vertically-aligned GaN NWs. The GaN NWs grown on GaN(002)/α-Al_2O_3(001) substrate exhibited better quality than those grown on α-Al_2O_3(001) substrate.

References

[1] Xia, Y., Yang, P., Sun, Y., Wu, Y., Mayers, B., Gates, B., Yin, Y., Kim, F., & Yan, H. (2003). *Adv. Mater. 15*, pp. 353–389.
[2] Noy, A., Artyukhin, A. B., & Misra, N. (2009). *Materialstoday. 12*, pp. 22–31.
[3] Thelander, C., Agarwal, P., brongersma, S., Eymery, J., Feiner, L. F., Forchel, A., Scheffle, M., Riess, W., Ohlsson, B. J., Gosele, U., & Samuelson, L. (2006). *Materialstoday. 9*, pp. 28–35.
[4] Li, Y., Qian, F., Xiang, J., & Lieber, C. M. (2006). *Materialstoday. 9*, pp. 18–27.
[5] Pauzauskie, P. J., & Yang, P. (2006). *Materialstoday. 9*, pp. 36–45.
[6] Morkoc, H., Strite, S., Gao, G. B., Lin, M. E., Sverdlov, B., & Burns, M. (1994). *J. Appl. Phys. 76*, pp. 1363–1398.
[7] Nakamura, S., Senoh, M., & Mukai, T. (1993). *Appl. Phys. Lett. 62*, pp. 2390–2392.
[8] Kishino, K., Sekiguchi, H., & Kikuchi, A. (2009). *J. Cryst. Growth. 311*, pp. 2063–2068.
[9] Hersee, S. D., Sun, X., & Wang, X. (2006). *Nano Lett. 8*, pp. 1808–1811.
[10] Kim, H. M., Kim, D. S., Kim, D. Y., Kang, T. W., Cho, Y. H., & Chung, K. S. (2002). *Appl. Phys. Lett. 81*, pp. 2193–2195.
[11] Lee, Y. M., Navamathavan, R., Song, K. Y., Park, J. H., Kim, D. W., Kissinger, S., Kim, J. S., Lee, C. R. (2010). *J. Cryst. Growth. 312*, pp. 2339–2344.
[12] Chen, C. C., yeh, C. C., Chen, C. H., Yu, M. Y., Lin, H. L., Wu, J. J., Chen, K. H., Chen, L. C., peng, J. Y., & Chen, Y. F. (2001). *J. Am. Chem. Soc. 123*, pp. 2791–2798.
[13] Zhang, J., & Zhang, L. (2003). *J. Vac. Sci. Technol. B 21*, pp. 2415–2419.
[14] Chen, X. J., Perillat-Merceroz, G., Sam-Giao, D., Durand, C., & Eymery, J. (2010). *Appl. Phys. Lett. 97*, pp. 151909.
[15] Lin, C., Yu, G., Wang, X., Cao, M., Lu, H., Gong, H., Qi, M., & Li, A. (2008). *J. Phys. Chem. C 112*, pp. 18821–18824.
[16] Sohn, Y., & Kim, C. (2009). *App. Sur. Sci. 256*, pp. 1078–1081.
[17] Schmidt, V., Wittemann, J. V., Senz, S., & Gösele, U. (2009). *Adv. Mater. 21*, pp. 2681–2702.
[18] Park, C. Y., Lim, J. M., Yu, J. S., & Lee, Y. T. (2010). *Appl. Phys. Lett. 96*, pp. 151909.

[19] Calarco, R., Meijers, R. J., Debnath, R. K., Stoica, T., E. S, & Luth, H. (2007). *Nano Lett*. *8*, pp. 2248–2251.
[20] Kwon, H. Y., Shin, M. J., Choi, Y. J., Moon, J. Y., Ahn, H. S., Yi, S. N., Kim, S., Ha, D. H., & Park, S. H. (2009). *J. Cryst. Growth*. *311*, pp. 4146–4151.
[21] Kim, H. M., Kim, D. S., Park, Y. S., Kim, D. Y., Kang, T. W., & K. S. (2002). *Chung. Adv*. Mater. *14*, pp. 991–993.
[22] Ra, Y. H., Navamathavan, R., Lee, Y. M., Kim, D. W., Kim, J. S., Lee, I. H., & Lee, C. R. (2010). *J. Cryst. Growth. 312*, pp. 770–774.
[23] Wang, G. T., talin, A. A., Werder D. J., Creifhton, J. R., Lai, E., Anderson, R. J., & Arslan, I. (2006). *Nanotechnology 17*, pp. 5773–5780.
[24] Nishide, S., Yoshimura, T., Takamatsu, Y., Ichige, A., Pak, K., Ohshima, N., & Yonezu, H. (1998). *J. Cryst. Growth*. *189/091* pp. 923–523.
[25] Hsu, Y. J., Hong, L. S., & Tsay, J. E. (2003). *J. Cryst. Growth. 252*, pp. 144–151.
[26] Hsu, Y. J., Hong, L. S., Jiang, J. C., & Chang, J. C. (2004). *J. Cryst. Growth. 266*, pp. 347–353.
[27] hannon, J. B., Kodambaka, S., Ross, F. M., & Tromp, R. M. (2006). *Nature 440*, pp. 69–71.
[28] Han, W., Fan, S., Li, Q., & Hu, Y. (1997). *Science 277*, pp. 1287–1289.
[29] Miwa, K., & Fukumoto, A. (1993). *Phys. Rev. B 48*, pp. 7897–7902.
[30] Kozawa, T., Kachi, T., Kano, H., Taga, Y., Hashimoto, M., Koide, N., & Manabe, K. (1994). *J. Appl. Phys. 75*, pp. 1098–1101.
[31] Song, D. Y., Nikishi, S. A., Holtz, M., Soukhoveev, V., Usikov, A., & Dmitriev, V. (2007). *J. Appl. Phys*. *101*, pp. 053535.
[32] Hushur, A., Manghnani, M. H., & Narayan, J. (2009). *J. Appl. Phys*. *106*, pp. 054317.