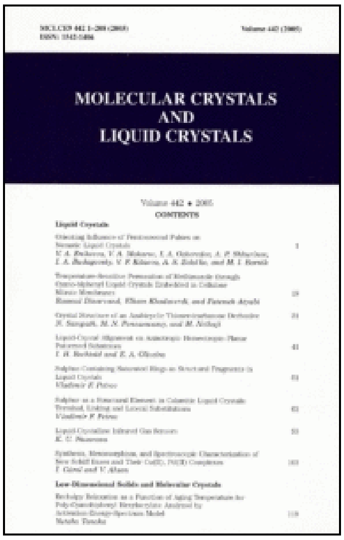

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644168

Low-Voltage Driving of Liquid Crystals Vertically Aligned by Ion-Beam Bombardment on High-*k* HfO_2 Surface

Lee-Gon Kim[a]; Won-Kyu Lee[a]; Byeong-Yun Oh[a]; Ji-Hun Lim[a]; Hyun-Jae Na[a]; Hong-Gyu Park[a]; Young-Hwan Kim[a]; Byoung-Yong Kim[a]; Young-Ku Kang[a]; Chul-Ho Ok[a]; Jeoung-Yeon Hwang[a]; Jeong-Min Han[b]; Dae-Shik Seo[a]
[a] Department of Electrical & Electronic Engineering, College of Engineering, Yonsei University, Seodaemoon-gu, Seoul, Korea [b] Department of Electronic, Seoil University, Jungnang-gu, Seoul, Korea

First published on: 12 November 2010

To cite this Article Kim, Lee-Gon , Lee, Won-Kyu , Oh, Byeong-Yun , Lim, Ji-Hun , Na, Hyun-Jae , Park, Hong-Gyu , Kim, Young-Hwan , Kim, Byoung-Yong , Kang, Young-Ku , Ok, Chul-Ho , Hwang, Jeoung-Yeon , Han, Jeong-Min and Seo, Dae-Shik(2010) 'Low-Voltage Driving of Liquid Crystals Vertically Aligned by Ion-Beam Bombardment on High-*k* HfO_2 Surface', Molecular Crystals and Liquid Crystals, 529: 1, 115 — 121

To link to this Article: DOI: 10.1080/15421406.2010.495885

URL: http://dx.doi.org/10.1080/15421406.2010.495885

Mol. Cryst. Liq. Cryst., Vol. 529: pp. 115–121, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.495885

Low-Voltage Driving of Liquid Crystals Vertically Aligned by Ion-Beam Bombardment on High-*k* HfO_2 Surface

LEE-GON KIM,[1] WON-KYU LEE,[1]
BYEONG-YUN OH,[1] JI-HUN LIM,[1] HYUN-JAE NA,[1]
HONG-GYU PARK,[1] YOUNG-HWAN KIM,[1]
BYOUNG-YONG KIM,[1] YOUNG-KU KANG,[1]
CHUL-HO OK,[1] JEOUNG-YEON HWANG,[1]
JEONG-MIN HAN,[2] AND DAE-SHIK SEO[1]

[1]Department of Electrical & Electronic Engineering, College of Engineering, Yonsei University, Seodaemoon-gu, Seoul, Korea
[2]Department of Electronic, Seoil University, Jungnang-gu, Seoul, Korea

Ion-beam irradiation (IB) on HfO_2 surface induced high-performance liquid crystal (LC) driving at a 1-V threshold with vertical alignment of liquid crystals (LC). The high-k materials Atomic layer deposition was used to obtain LC orientation on ultra-thin and high-quality films of HfO_2 layers. To analyze surface morphological transition of HfO_2 which can act as physical alignment effect of LC, atomic force microscopy images are employed with various IB intensities. The contact angle was measured to elucidate the mechanism of vertical alignment of LC on HfO_2 with IB irradiation. Contact angle measurements show the surface energy changes via IB intensity increasing.

Keywords HfO_2; ion-beam irradiation; liquid crystals

Introduction

The uniformly aligned liquid crystal (LC) molecules on a polyimide (PI) is an important factor in the manufacture of LC displays (LCDs). Mechanical rubbing is the industry standard process for achieve this [1–4]. A PI layer with an anisotropic surface [5–8] which can create a pretilt angle between liquid crystal and its surface is essential for operating the LCDs with optically transparent and chemically stable insulating characteristics [9]. However, the rubbing process for LC alignment has major demerits such as debris generation, local defects, and electrostatic discharge [10,11]. To decrease these defects, a cleaning process which slows down the manufacturing

Address correspondence to Prof. Dae-Shik Seo, Information Display Device Laboratory, Department of Electrical and Electronic Engineering, 262 Seongsanno, Seodaemoon-gu, Seoul 120-749, Republic of Korea. Tel.: 82-2-1213-7727; Fax: 82-2-3147-1351; E-mail: dsseo@yonsei.ac.kr

process and reduces its cost effectiveness have to be required in rubbing process. Also, the quality of the displays produced is degraded during the rubbing process. Over the past several years, several alternative alignment techniques have been investigated for inducing anisotropy on LC alignment layer surfaces by noncontact method [12] including oblique deposition [13], plasma treatment [14], photoalignment [10], and nanostructured alignment surfaces [9,10]. Above all, ion beam (IB) bombardment is a noncontact alignment method that provides reliability, controllability, a continuous manufacturing process, and high resolution displays. Depending on these non-contact alignment methods, many optically transparent insulators such as diamondlike carbon [15], SiC [16], SiO_x [17], SiN_x [18], γ-Fe_2O_5 [5] have been reported as potential candidates for inorganic alignment materials. Even so, LC orientation on a brand new material with upgraded capacity is required to produce high-performance displays. Many inorganic materials with high permittivities can reduce the voltage losses due to the LC alignment layers that are a trade-off for its capacitance. The lower voltage for LC operation can be applied to the LC under low external voltage by using high-k materials. This means that low power operation for LCD applications can be accomplished using a high-k alignment structure where the LC can be operated effectively with a low threshold voltage. In this reasons, it has been intensively investigated in our previous work with optically transparent high-k insulating inorganic materials such as Al_2O_3 [19], Ta_2O_5 [11] and HfO_2 [20] for LCDs applications. The LC alignment mechanism is explained by a random network model of the atomic arrangement in the inorganic films surface. However, despite many efforts to find a simple low-cost method and different alignment materials, the LC orientation mechanism by IB bombardment is still not completely revealed. In our previous work, we reported a technique for the homogeneous alignment of LCDs on IB bombarded Ta_2O_5, and showed the mechanism that the creation of the pretilt angle was due to the IB bombardment breaking Ta-O and O-Ta bonds. The orientational order was thus generated by directional IB [11].

Among the many other potential high-k materials, HfO_2 is considered as one of the most promising materials to satisfy considerably large band gap (5.68 eV), high dielectric constant ($k \sim 30$). In particular, IB bombarded LC alignment layers grown by atomic layer deposition (ALD) was studied in our group which reported that the non-stoichiometric HfO_2 surface transformed to fully oxidized HfO_2 by ion-bombardment. The IB bombardment might induce activation of Hf dangling bonds on the film surface, which can easily be transformed to Hf-O bonding by supplying atmospheric oxygen. The strong van der Waals interactions between the HfO_2 surfaces and LC molecules, which are more effective than LC molecular interactions, are thought to have induced a random LC alignment before IB bombardment. When HfO_2 surfaces were stabilized with ion bombardment to induce surface oxidization, the van der Waals interactions between HfO_2 and LC decreased to a smaller value that was sufficiently weak to make a good balance with LC molecular interactions for vertical alignment [20]. In this study, we investigated about physical alignment effect and the thermal stabilities on HfO_2 surface which is modified by IB bombardment. This is the series of our experiments about ultra thin HfO_2 as a vertical alignment layers. Based on the chemical structure transition of HfO_2 surface by IB bombardment revealed in our previous work, we studied on the topological transformation and wetting property analysis which is major tools for understanding of inorganic LC alignment layers. Also, we conducted thermal stability test which is important factor of LCDs reliabilities.

Experimental

HfO_2 thin films 10 nm thick were deposited on the ITO-coated glass substrates via ALD using trimethylaluminum [$Al(CH_3)_3$] and water at a deposition temperature of 300°C. The films 10 nm thick were exposed to Ar^+ IB plasma with dosages of 10^{14}–10^{15} ions/cm^2 at an incident angle of 45 degree from the surface normal for 2 min at various energy intensities 0 eV, 600 eV, 1000 eV, 1500 eV, 2400 eV, 3000 eV. A current density in a beam of positive charged particles measures from a Faraday cup system was 3.7 mA/cm^2 and a plasma ion density measured by the double Langmuir probe tips was of approximately 10^{11} cm^{-3}. As illustrated in Figure 1, the IB system used to align the LC molecules in this study was based on a direct-current DuoPIGatron-type gun with a hot-filament ion source. The glass substrates with the HfO_2 layer on the ITO electrodes were assembled in an anti-parallel configuration with a cell gap of 60 μm to observe the pretilt angles, and VA-LCDs were prepared with a cell gap of 5 μm to examine the voltage-transmittance analysis. The cells were then filled with negative LCs (MJ98468; Merck) with a dielectric anisotropy ($\Delta\varepsilon$) of −4; refractive indices in the ordinary and extraordinary axes of 1.4742 and 1.5512, respectively; and isotropic transition temperature of 75°C. The surface morphology of the samples was observed by atomic force microscopy (AFM) before (0 eV) and after (600 eV, 2400 eV) IB bombardment which can explain the possible LC alignment behavior. The contact angle of each surface was measured by the sessile drop technique with de-ionized water using a Phoenix 300 surface angle analyzer (SEO) and analyzed with IMAGE PRO 300 software. Then the fabricated LC cells were put on the hot plate for the thermal stability test. The temperature of the hot plate was changed from 50°C to 250°C with the increment of 50°C. Then, each LC cell was observed by the polarized optical microscope.

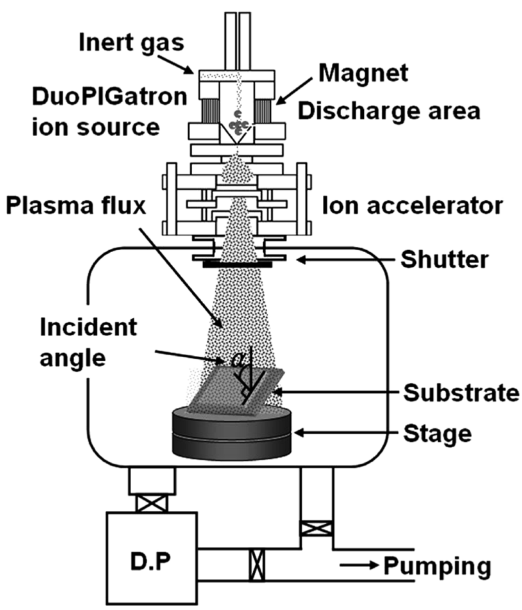

Figure 1. DuoPIGatron-type ion-beam system.

Results and Discussion

Contact angle measurement can be considered a gauge of the relationship between liquid and the surface characteristics of a solid on which the liquid is placed. Figure 2 shows the variation in contact angle on the HfO_2/ITO films for various IB intensities at an incident angle of 45 degree and an exposure time of 2 min. The measured contact angle is 70, 53.8, 50.5, 50.5, 43.3, 50.5 degree with the incident IB intensity of 0 (before IB bombardment), 600, 1000, 1500, 2400 and 3000 eV, respectively. From this result, we can confirm that the measured contact angle decreases with IB bombardment which means that the surface energy is increasing. Furthermore, the films lost their hydrophobicity with increasing IB bombardment. We can also obtain the measured value of 50.5 degree which is limited contact angle for vertical alignment of LC molecules on the IB bombarded HfO_2 surface.

To elucidate the physical alignment effect of LC on HfO_2 surface, we employed AFM analysis which can reveal the morphological transition on the HfO_2 surface by IB bombardment.

Figures 3(a), 3(b) and 3(c) exhibit the AFM images of the HfO_2 thin films before (Fig. 3(a)), IB intensity of 600 eV (Fig. 3(b)) and IB intensity of 2400 eV (Fig. 3(c)). The surface rms roughnesses were 3.5, 5.18 and 5.5 nm with IB intensity of 0, 600, 2400 eV, respectively. In the previous work at the same experimental conditions, there are random LC orientations with the IB intensity of 0 eV and 600 eV which has the rms roughness of under 5.5 nm. However, when the IB intensity increases, the rms roughness is increasing over 5.5 nm which is suitable for good LC alignment states. From this result, it is found that the surface topological transition is progressed with IB bombardment and the minimum value of surface rms roughness is existing which is essential for vertical alignment of LC molecules as an physical alignment effect. As the contact angle is also related to the surface morphology, it can be thought that the increased rms roughness of HfO_2 nano-structure increases the surface energy of HfO_2 which can be detected by contact angle decreasing. This series of nano-structure related surface energy variations can be considered as physical alignment factor which contributes to vertical alignment of LCs.

Figure 4 show the voltage-transmittance curve of HfO_2 based VA-LCDs. The ion energy intensity, incident angle, and exposure time were 2400 eV, 45 degree, and 120 s, respectively. (We did same experiments again for confirm the reliability of our previous work.) The performance of existing VA-LCDs on IB bombarded

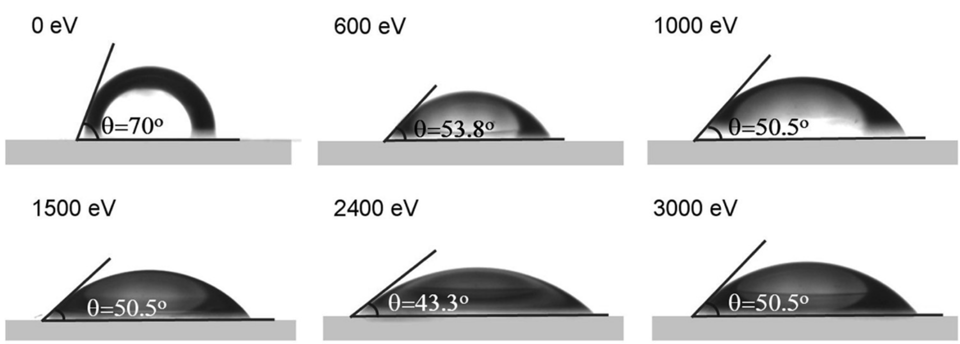

Figure 2. Contact angles on the IB-bombarded HfO_2 films with various IB energy intensity.

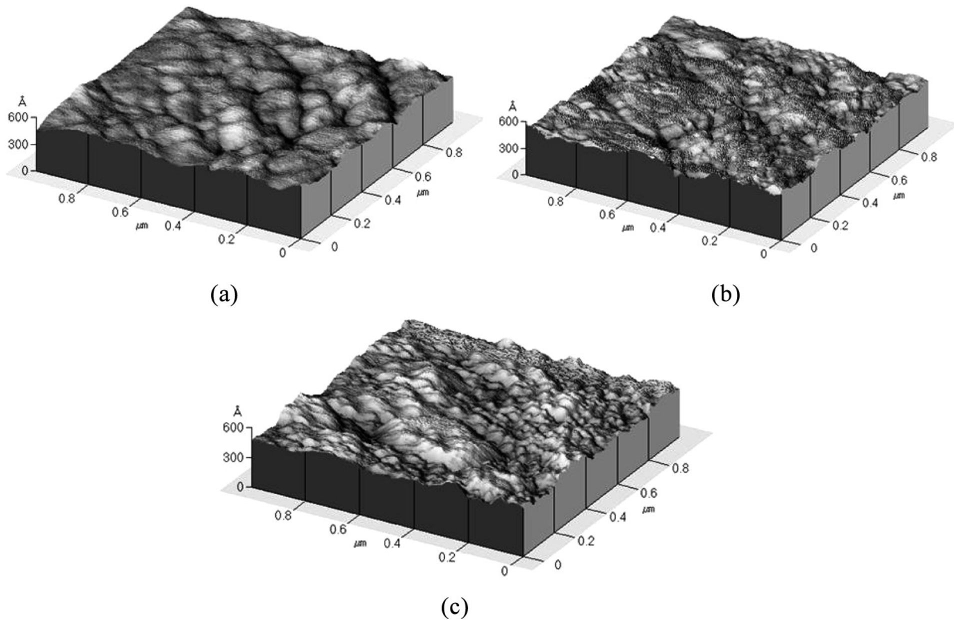

Figure 3. AFM images of HfO_2 thin films: (a) before IB bombardment (random alignment of LC), (b) IB intensity of 600 eV (random alignment of LC) and (c) IB intensity of 2400 eV (vertical alignment of LC).

PI is shown for comparison. The superior performance of *V-T* characteristics obtained with threshold voltage of 1 V while the IB bombarded PI based VA-LCDs had the threshold voltage of 3.3 V. The capacity of 10 nm thick alignment layer is one of the most reasonable factor for explaining this result. The total capacitance can be expressed in simplified form as a linear combination of the alignment layer

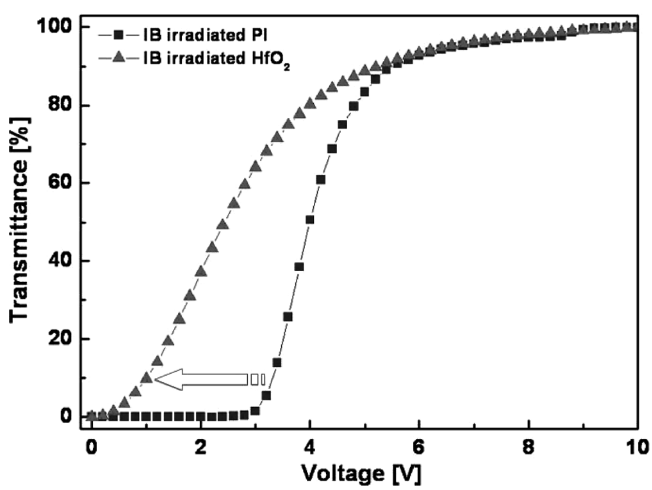

Figure 4. *V-T* characteristics of HfO_2 based VA-LCDs.

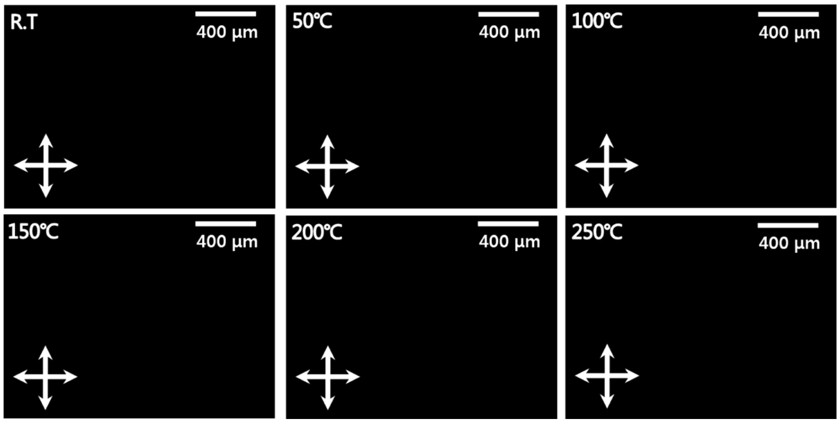

Figure 5. Thermal stability test of LC cells on HfO_2 thin film in the high temperatures.

capacitance and the LC capacitance. The high-k HfO_2 alignment layers can dramatically increase the capacitance of alignment layers which can reduce voltage losses due to LC alignment layers. Also, the thickness of HfO_2 can be another factor of increasing the capacitance of LC alignment layers. The 10 nm thick alignment layers by ALD can reduce the alignment layer related voltage losses. From this result, we can concluded that HfO_2 based VA-LCDs can drop the threshold voltage which is essential for the low power operation of device.

Moreover, the thermal stability of the HfO_2 based LC cells were examined. Thermal stability is one of the best merits of the inorganic alignment layer because the organic alignment layer results in a change of the pretilt angle and alteration of electro optical properties due to its deterioration by thermal stress and does not secure a long lifetime. To evaluate the thermal stability in the HfO_2 layers, the LC cells were exposed to high temperatures. As seen in Figure 5, the HfO_2 alignment layers did not deteriorate at high temperatures owing to robust properties of the inorganic materials. Eventually, they showed stable alignment properties, which secured the long lifetime of the advanced LCDs.

Conclusions

In summary, VA-LCDs based on HfO_2 layers with IB bombardment were embodied in this work. The 10 nm ultra-thin alignment layers were deposited by ALD process which can suppress the voltage losses due to the capacitance of thick LC alignment layers. The IB bombardment can induce the certain surface states of nano-structure which can vertically align the LC molecules. The nano-structure variation by IB bombardment can change the surface energy which is related to the vertical alignment of LCs. The HfO_2 based VA-LCDs have merits of low power operation and stability under harsh conditions such as high temperatures.

Acknowledgments

This research was supported by the MKE (The Ministry of Knowledge Economy), Korea under the ITRC (Information Technology Research Center) Support program supervised by the NIPA (National IT Industry Promotion Agency) (NIPA-2009-C1090-0902-0018).

References

[1] Kim, Y. J., Zhuang, Z., & Patel, J. S. (2000). *Appl. Phys. Lett.*, *77*, 513.
[2] Toney, M. F., Russell, T. P., Logan, J. A., Kikuchi, H., Sands, J. M., & Kumer, S. K. (1995). *Nature*, (London) *374*, 709.
[3] Huang, C. Y., Lin, C. H., Wang, J. R., Huang, C. W., Tsai, M. S., & Fuh, A. Y. G. (2002). *J. Appl. Phys.*, *92*, 7231.
[4] Hoogboom, J., Rasing, T., Rowan, A. E., & Nolte, R. J. M. (2006). *J. Mater. Chem.*, *16*, 1305.
[5] Wu, H. Y., & Pan, R. P. (2007). *Appl. Phy. Lett.*, *91*, 074102.
[6] Chaudhari, P., Lacey, J. A., Lien, S. C. A., & Speidell, J. L. (1998). *Jpn. J. Appl. Phys., Part 2*, *37*, L55.
[7] Geary, J. M., Goodgy, J. W., Kmetz, A. R., & Patel, J. S. (1987). *J. Appl. Phys.*, *62*, 4100.
[8] Kim, J. H., & Rosenblatt, C. (2000). *J. Appl. Phys.*, *87*, 155.
[9] Yeung, F. S., Ho, J. Y., Li, Y. W., Xie, F. C., Tsui, O. K., Sheng, P., & Kwok, H. S. (2006). *Appl. Phys. Lett.*, *88*, 051910.
[10] Kim, J. B., Lim, J. R., Park, J. S., Ahn, H. J., Lee, M. J., Jo, S. J., Kim, M., Kang, D., Lee, S. J., Kim, Y. S., & Baik, H. K. (2008). *Adv. Funct. Mater.*, *18*, 1340.
[11] Kim, J. Y., Oh, B. Y., Kim, B. Y., Kim, Y. H., Han, J. W., Han, J. M., & Seo, D.-S. (2008). *Appl. Phy. Lett.*, *92*, 043505.
[12] Ho, J. Y. L., Chigrinov, V. G.., & Kwok, H. S. (2007). *Appl. Phys. Lett.*, *90*, 243506.
[13] Lu, M. (2004). *Jpn. J. Appl. Phys., Part 1*, *43*, 8156.
[14] Lee, C. Y., Liu, Y. L., Wu, K. Yi., Chen, M. Y., & Hwang, J. C. (2008). *Jpn. J. Appl. Phys.*, *47*, 226.
[15] Choi, J. H., Ham, M. H., Oh, B. Y., Hwang, J. Y., Choi, S. H., Seo, D.-S., & Myoung, J. M. (2006). *Liq. Cryst.*, *33*, 947.
[16] Kim, J. B., Kim, K. C., Ahn, H. J., Hwang, B. H., Hyun, D. C., & Baik, H. K. (2007). *Appl. Phys. Lett.*, *90*, 043515.
[17] Janning, J. L. (1972). *Appl. Phys. Lett.*, *21*, 173.
[18] Lee, S. K., Kim, J. H., Oh, B. Y., Kang, D. H., Kim, B. Y., Han, J. W., Kim, Y. H., Han, J. M., Hwang, J. Y., Ok, C. H., & Seo, D.-S. (2007). *Jpn. J. Appl. Phys., Part 1*, *46*, 7711.
[19] Park, H. G., Kim, Y. H., Ph, B. Y., Lee, W. K., Kim, B. Y., & Seo, D.-S. (2008). *Appl. Phys. Lett.*, *93*, 233507.
[20] Lee, W. K., Oh, B. Y., Lim, J. H., Park, H. G., Kim, B. Y., Na, H. J., & Seo, D.-S. (2009). *Appl. Phys. Lett.*, *94*, 223507.