Integrated Ferroelectrics, 57: 1163–1173, 2003
Copyright © Taylor & Francis Inc.
ISSN: 1058-4587 print/ 1607-8489 online
DOI: 10.1080/10584580390259579

Taylor & Francis
Taylor & Francis Group

Comparison of Hafnium Precursors for the MOCVD of HfO_2 for Gate Dielectric Applications

A. R. TEREN,[1] P. EHRHART,[1] R. WASER,[1] J. Q. HE,[1] C. L. JIA,[1] M. SCHUMACHER,[2] J. LINDNER,[2] P. K. BAUMANN,[2] T. J. LEEDHAM,[3] S. R. RUSHWORTH,[3] and A. C. JONES[3]

[1]*Institut für Festkörperforschung, Forschungzentrum Jülich GmbH, D-52425 Jülich, Germany*
[2]*AIXTRON AG, Aachen, Germany*
[3]*Epichem Limited, Bromborough, UK*

(Received April 20, 2003; in final form July 21, 2003)

Hafnium oxide films were deposited on Si (100) substrates using metal-organic chemical vapor deposition (MOCVD) and evaluated for gate dielectric applications. For this study, two types of precursors were tested: an oxygenated one, Hf butoxide-mmp, and an oxygen-free one, Hf diethyl-amide. Depositions were carried out in the temperature range of 350–650°C. However, the discussion is focused on amorphous films. The films were compared on the basis of growth rate, phase development, density, interface characteristics, and electrical properties. A similar amorphous to polycrystalline phase transition temperature was found for both precursors. For low deposition temperatures the growth rate for the amide precursor was significantly higher than for the butoxide-mmp precursor and films prepared with the amide precursor contained a lower carbon impurity content than with the butoxide-mmp one. The dielectric constant was slightly higher for amorphous HfO_2 deposited from the amide precursor than for the butoxide-mmp one. Only in respect to the trap density does the butoxide precursor seem advantageous.

Keywords: Gate dielectric; MOSFET; high k; HfO_2

INTRODUCTION

For future generations of metal-oxide-semiconductor field-effect transistors (MOSFET), the current gate oxide layer SiO_2 (or SiO_xN_y) will need to be replaced with a material possessing a higher dielectric constant ($\kappa > 3.9$). HfO_2 is a potential candidate for MOS, as well as metal-insulator-metal (MIM), applications due to its high bulk dielectric constant ($\kappa \approx 25$–30) [1]. The other relevant properties of HfO_2 are good thermal and chemical

stability on Si, relatively large bandgap (5.7 eV), sufficiently high value for the Si/HfO_2 barrier height, and compatibility with n^+ polysilicon gate electrodes.

Recently, HfO_2 films have been investigated using several deposition techniques including atomic layer deposition (ALD) [2], sputtering [3], pulsed laser deposition [4], and thermal [5, 6] and plasma—enhanced [7] chemical vapor deposition. Chemical vapor deposition has the advantages of uniform thickness over large substrate areas and good conformal step coverage. In contrast to ALD, it is relatively easy to dope the HfO_2 using CVD, which may be necessary for future gate dielectrics. In previous studies of CVD-deposited HfO_2, several types of precursors have been evaluated, including hafnium-tetra-tert-butoxide $Hf(C_4H_9O)_4$ [8], hafnium nitrate $Hf(NO_3)_4$ [9] and hafnium diethyl amide $Hf(NEt_2)_4$ [5, 6] at deposition temperatures of 250–550°C. In one study of MOCVD of $Hf_{1-x}Si_xO_2$ films, a comparison of growth and structural properties was made of an oxygen-based precursor, $Hf(O\text{-}iPr)_2thd_2$, and a nitrogen-based precursor, $Hf(NEt_2)_4$ [10]. In this paper, we report on a study in which HfO_2 was deposited under similar conditions using an oxygenated precursor, Hf tertiary butoxide-mmp [11] and an oxygen-free precursor, Hf diethyl amide. We present both structural and electrical characterization of the films. Amorphous films are preferred candidates for next-generation device applications, due to the expected more homogeneous electrical properties. However, these amorphous films can have worse electrical properties, e.g., the actual dielectric constant has been observed to be lower ($\kappa \approx 12$–14) [12]. Nevertheless, we will concentrate on these amorphous films as these data are considered as a base for the anticipated stabilization of the amorphous phase by alloying.

EXPERIMENTAL

HfO_2 films were deposited by liquid-injection metal-organic chemical vapor deposition (MOCVD) on p-type Si(100) wafers. The MOCVD system consists of an Aixtron AIX200 horizontal quartz reactor and a liquid-delivery TRIJET^{TM} vaporizer. The precursors investigated were hafnium diethyl amide, Hf-$[N(C_2H_5)_2]_4$, and hafnium butoxide methoxy methyl propanolate, Hf-$[(OC_4H_9)_2(mmp)_2]$, which was dissolved in octane to make a 0.05 M solution. The precursors were kept at room temperature in a glass ampule, and were injected into the vaporizer via high-speed electro-mechanical valves. Evaporation temperatures of 200°C were used. The precursors were pulse injected with a 500 msec period and 0.8 msec injector opening times (yielding

an average flow rate of $\sim 5 \times 10^{-7}$ mol/sec). The films were deposited under 2 mbar pressure over the temperature range of 350–650°C. Argon was used as the carrier gas, with a flow of 200 sccm, and oxygen as the oxidant, with a flow of 50 sccm. Based on the precursor injection rate for the butoxide-mmp precursor and the oxygen flow, we estimated that the ratio of O atoms in the gas stream relative to the mmp molecule was ~30. The silicon substrates, which were 1 in^2 in size, were used with a native oxide layer, as previous investigations of $SrTiO_3$ on Si depositions did not show an improvement of the interfacial layer with a HF-last treatment [13]. Prior to deposition, they were ultrasonically cleaned in acetone and propanol, rinsed with deionised water, and dried with nitrogen.

The phase determination of the films was carried in a Philips MRD X-ray diffractometer, using a glancing incidence geometry. Thickness and density was determined from X-ray reflectivity scans, which were measured in a Brucker AXS X-ray reflectometer.

TEM and HRTEM investigations were carried out in a JEOL 4000EX electron microscope operated at 400 kV. Both cross-sectional and plan-view specimens were prepared by conventional methods.

For electrical measurements, Pt electrode pads were sputter deposited on top of the HfO_2 films and patterned using lift-off lithography, providing areas of 1 mm^2, 0.049 mm^2 and 0.018 mm^2. A GaIn eutectic paste was applied manually to make an ohmic backside contact. The resulting film stack was $Pt/HfO_2/p\text{-}Si/Ga_{0.85}In_{0.15}$. Capacitance-voltage curves were measured on an HP # 4284 LCR meter using a frequency of 100 kHz.

RESULTS

A. Film Growth

Figure 1 shows the growth rate (nm/min) versus both deposition temperature and inverse temperature for both precursors. For the amide precursor, the growth rate increases from 2 nm/min to as high as 20 nm/min as the temperature is increased from 300°C to 450°C. In this temperature range, the growth can be described as kinetically-controlled. Above $T_{dep} = 450°C$, the growth rate saturates, indicating a transport-controlled process. For the butoxide precursor, the growth rate is significantly lower than for the amide at low temperatures. Even at 450°C, the growth rate is only 2 nm/min. It is apparent that for this precursor, the growth is kinetically controlled up to about 600°C. At this temperature, the growth rate for both precursors is approximately the same. Thus, for deposition at low temperatures,

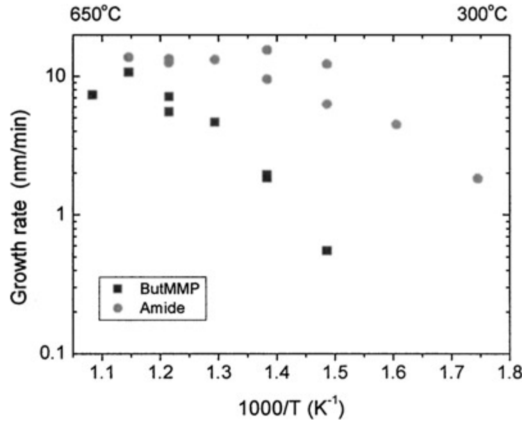


FIGURE 1 Growth rate versus inverse temperature for the two different precursors.

which are required for obtaining amorphous films, the amide precursor is preferable.

B. Structural Characterization

Figure 2 shows the grazing-incidence two-theta X-ray diffraction patterns of the HfO_2 deposited at different temperatures with both precursors. In Fig. 2(a) the phase development of the HfO_2 is seen for the butoxide-mmp precursor. The hafnium oxide appears weakly crystallized at a deposition temperature of 450°C. By $T_{dep} = 500°C$, the film is fully crystallized, with all peaks belonging to the monoclinic crystal structure. For the amide precursor,

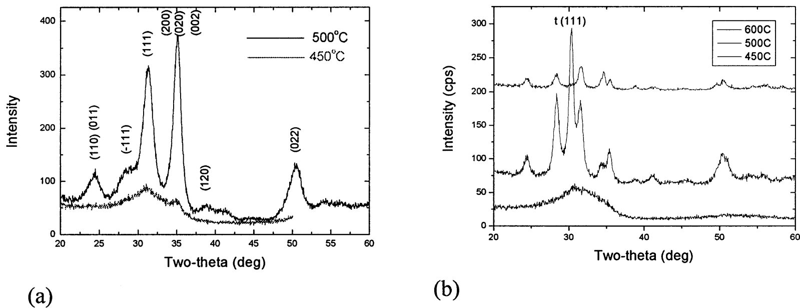


FIGURE 2 Grazing-incidence X-ray diffraction patterns of HfO_2 deposited with (a) butoxide-mmp and (b) diethyl-amide precursors.

the films are also well crystallized by $T_{dep} = 500°C$. However, in addition to the reflections for the monoclinic structure, there is a peak at $2\theta = 30°$ which corresponds to the tetragonal (111) reflection as confirmed by selected area electron diffraction (SAED). Although this peak is not distinguishable in the XRD spectrum for the butoxide film, the broadening of the (111)m peak suggests there could be a contribution. This second phase has also been observed in hafnium oxide films deposited by CVD [6] and ALD [2]. As T_{dep} is increased to 600°C (Fig. 2(b)), this peak is no longer present, indicating that the film consists primarily of the monoclinic phase.

X-ray characterization was also used to determine the density and thickness of the films. Figure 3(a) shows a representative X-ray reflectivity experimental curve along with the corresponding simulation. The thickness is determined from the spacing of the fringes and the density is related to the critical incidence angle for total reflection by the equation $\vartheta_c \propto \rho^{1/2}$. Figure 3(b) shows a plot of the density versus deposition temperature for both precursors. There is a general increase of the density with increasing temperature, which must be due in part to the crystallization of the films. An increase in density is also likely due to a reduction in carbon impurity content as the temperature is raised, as demonstrated by SIMS analysis (Fig. 4). A similar behavior was observed by Schaeffer et al. [6] for HfO_2 deposited by MOCVD using the same precursor, Hf diethyl amide. The highest density (9.7 g/cm^3) was obtained with the butoxide-mmp precursor at a deposition temperature of 600°C. This value is close to the theoretical

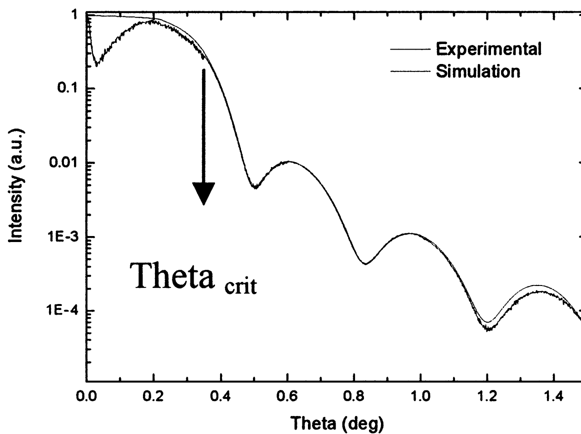


FIGURE 3a X-ray reflectivity curve and corresponding simulation for a 12 nm—thick HfO_2 film.

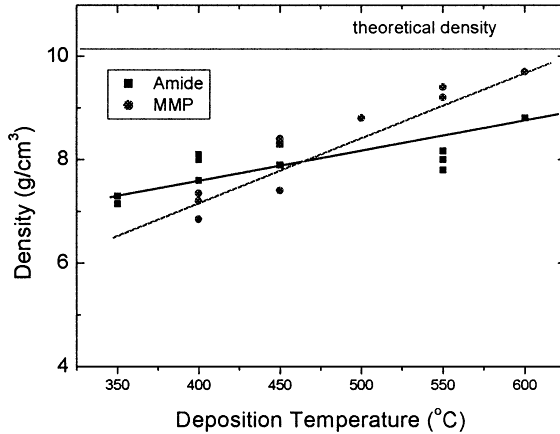


FIGURE 3b Density of as-deposited films obtained from simulation of reflectivity curves.

density of 10.1 g/cm^3. However, for the amide precursor, the density did not approach the theoretical density as was the case for the study by Schaeffer et al. The different behavior may perhaps be due to the fact that for our experiments the Hf precursor was dissolved in octane. However, although the additional octane could be a source for a greater impurity content, we

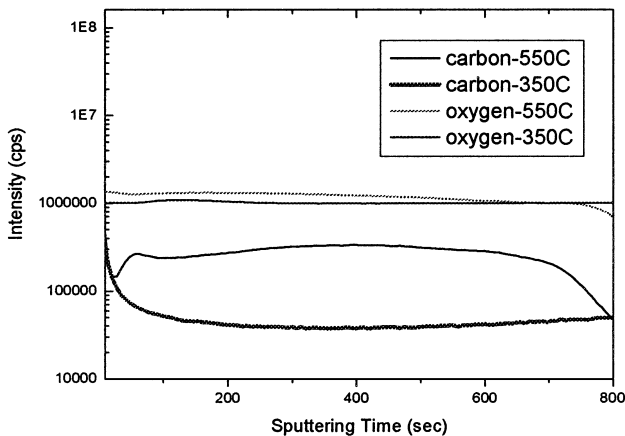


FIGURE 4a SIMS depth profiles showing reduction in carbon impurity levels by increasing deposition temperature from 350°C to 550°C for the amide precursor.

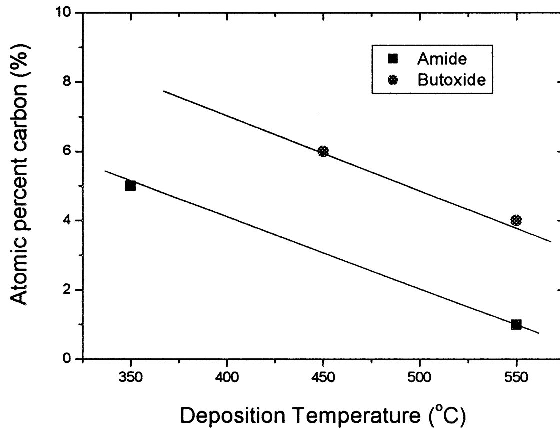


FIGURE 4b Comparison of carbon content for the two precursors at different deposition temperatures.

obtained a 1 at.% C content for $T_{dep} = 550°C$, which was not significantly greater than the 0.5 at% obtained by Schaeffer et al.

In this study, we also compared with SIMS the carbon impurity content for both precursors. As seen in Fig. 4(b), the carbon concentration is higher for the butoxide precursor than for the amide one. This can be likely attributed to the butoxide precursor having a higher number of carbon atoms in the molecule. For a low deposition temperature of 400°C, the higher carbon concentration corresponds to a lower film density for the butoxide precursor.

However, for a high deposition temperature of 600°C, the density is higher for the butoxide-mmp, despite the higher carbon content, something, which requires further investigation.

The interface properties of the HfO_2 were investigated by means of cross-sectional TEM. In Fig. 5, the cross-sectional images are shown only for a deposition temperature of 400°C for (a) the butoxide-mmp and (b) amide precursors. While XRD did not show any peaks for this temperature, the TEM micrographs reveal that there is a mixture of amorphous and nanocrystalline phases. It can be observed that an amorphous interlayer (SiO_2 or Hf silicate) is present between the Si and the HfO_2, as is typically observed for HfO_2 deposited by CVD and by other methods. The thickness of this interlayer is about 3 nm for both precursors. This is significantly higher than that for the native oxide, ~1 nm, which demonstrates that the native oxide is not stable. However, for films grown at 550°C, making them polycrystalline, the interfacial layer was as low as 1 nm for both precursor types (data not shown).

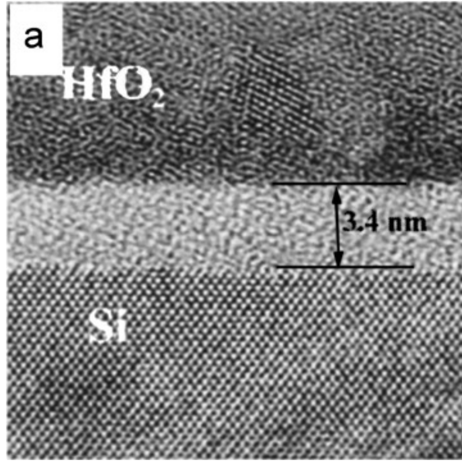


FIGURE 5a Cross-sectional TEM of HfO_2 deposited with butoxide-mmp precursor at 400°C.

This suggests that at higher deposition temperatures the Hf atoms are more reactive with O than are the Si ones. This hypothesis is also supported by experiments which showed that the interfacial layer at the HfO_2/Si interface is reduced in thickness at post-annealing temperatures $>500°C$ [14].

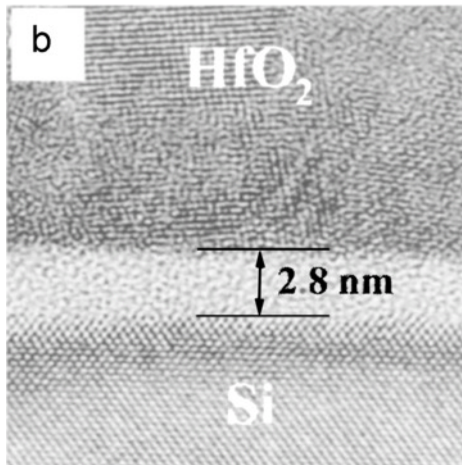
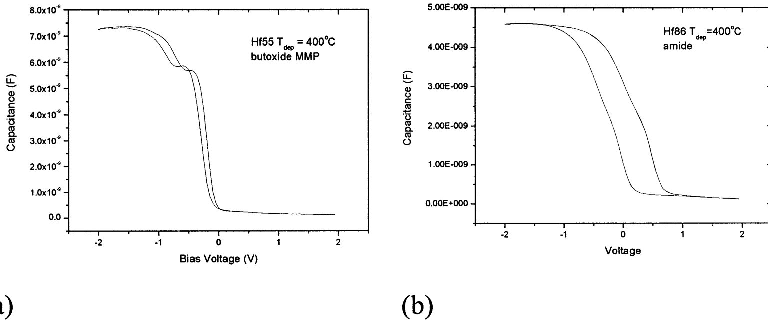


FIGURE 5b Cross-sectional TEM of HfO_2 deposited with amide precursor at 400°C.



(a) (b)

FIGURE 6 Typical C-V curves for as-deposited films prepared at 400°C (amorphous) with (a) butoxide-mmp (thickness = 11 nm) and (b) diethyl-amide precursors (thickness = 15 nm).

C. Electrical Characterization

Figure 6(a) shows a typical C-V curve for an as-deposited film prepared with the butoxide-mmp precursor, and Fig. 6(b) shows one for the amide precursor. Two main differences between the films prepared with the two precursors are the flatband voltage (V_{fb}) and the hysteresis (ΔV) values. The hysteresis is related to the density of rechargeable trap states in the oxide film, N_{ot}. For the amide precursor, the hysteresis is significantly larger (0.4–0.7 V), compared with the butoxide (0.02–0.2 V). For the butoxide-deposited films, N_{ot} was typically in the range of 10^{10}–10^{11}/cm^2, whereas for the amide-deposited films, N_{ot} was 10^{11}–10^{12}/cm^2. It was noted that for the butoxide-mmp—deposited HfO_2, the flatband voltage was typically close to zero for films deposited at 400°C (amorphous). However, for higher temperatures V_{fb} is typically positive shifted by several tenths of a volt, indicating a higher negative fixed charge. In contrast, for the amide-deposited HfO_2, the V_{fb} is more strongly positive-shifted and is shifted for both amorphous (400°C) and crystalline (500–550°C). It can be noticed in Fig. 6(a) that for the mmp-derived HfO_2, there is a shoulder in both the forward and reverse voltage sweeps, this feature is seen in all curves. Such a plateau has also been observed in sputtered HfO_2 [3] and more recently in MOCVD deposited HfO_2 [15]. In the Si/SiO_2 system the presence of a shoulder, similar to the Fig. 6(a) C-V profile, is typically attributed to the presence of unpassivated silicon dangling bonds, which are interface defects known as P_b centers.

A graph of the equivalent oxide thickness versus the physical thickness for films prepared with the mmp and amide precursors at 400°C is shown

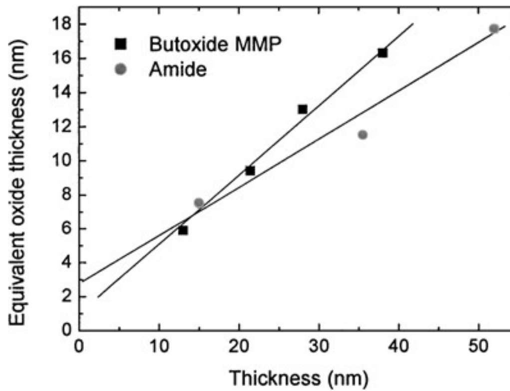


FIGURE 7 Equivalent oxide thickness versus physical thickness for films deposited at 400°C with both butoxide-mmp and amide precursors.

in Fig. 7. From the slope of the linear fit, a dielectric constant of 10 is obtained for the HfO_2 layer deposited with the butoxide-mmp precursor and a dielectric constant of 14 for the amide precursor. The higher dielectric constant may be due to the lower carbon content in the amide-prepared films. These values are lower than reported for bulk crystalline HfO_2 ($\varepsilon = 25$–30) and more characteristic of amorphous HfO_2. As pointed out by Conley et al. [12], the reduced dielectric constant may be due to the presence of excess oxygen in the HfO_2. A likely additional source of the dielectric lowering is the substantial carbon impurity content.

CONCLUSIONS

The structural and electrical properties were investigated for HfO_2 deposited by MOCVD using two different precursors. For both precursors, the HfO_2 films were X-ray amorphous at low temperatures and crystallized between 450–500°C, with the monoclinic structure being the dominant phase at high temperatures. The detailed differences are discussed for the amorphous films. The Hf diethyl-amide precursor produced at low temperatures a significantly higher growth rate than Hf-butoxide-mmp. In addition, for the amide-deposited films, the carbon impurity content was several percent lower than for the butoxide-deposited ones. Hence, this precursor is advantageous for deposition the amorphous films. In contrast there was no noticeable difference in the amorphous interlayer thickness. For films deposited with

the amide precursor, the dielectric constant was ∼14 for amorphous films, compared with ∼10 for butoxide-prepared films. However, for the amide precursor, the number of trap states was found to be higher than for the butoxide-mmp precursor.

ACKNOWLEDGMENTS

The authors would like to acknowledge R. Ganster and M. Gebauer for building up the MOCVD system, D. Vukelic for the Pt electrode preparation, U. Brewer for the SIMS, and W. Krumpen for XRF analysis.

REFERENCES

[1] G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.* **89**, 5243 (2001).
[2] J. Aarik, A. Aidla, H. Mandar, T. Uustare, K. Kukli, and M. Schuisky, *Applied Surface Science* **173**, 15 (2001).
[3] A. Callegari, E. Cartier, and M. Ribelyuk, *J. Appl. Physics* **90**, 6466 (2001).
[4] H. Ikeda et al., *Jpn. J. Appl. Phys.* **41**, 2476 (2002).
[5] Y. Ohshita, A. Ogura, A. Hoshino, T. Suzuki, S. Hiiro, and H. Machida, *J. Crystal Growth* **235**, 365 (2002).
[6] J. Schaeffer et al. *J. Electrochemical Society* **150**, F67 (2003).
[7] K.-J. Choi, W.-C. Shin, J.-B. Park, and S.-G. Yoon, *Integrated Ferroelectrics* **48**, 13 (2002).
[8] S. Sayan, S. Aravamudhan, B. W. Busch, W. H. Schulte, F. Cosandey, G. D. Wilk, T. Gustafsson, and E. Garfunkel, *J. Vac. Sci. Tech A* **20**, 507 (2002).
[9] R. C. Smith, N. Hoilien, J. Roberts, S. A. Campbell, and W. L. Gladfelter, *Chemistry of Materials* **14**, 474 (2002).
[10] B. C. Hendrix et al. *Mat. Res. Soc. Proc.* **716**, B.6.7.1 (2002).
[11] P. A. Williams, J. L. Roberts, A. C. Jones, P. R. Chalker, N. L. Tobin, J. F. Bickley, H. O. Davies, L. M. Smith, and T. J. Leedham, *Chem. Vapor. Deposition* **8**, 163 (2002).
[12] J. F. Conley, Y. Ono, D. J. Tweek, W. Zhuang, and R. Solanki, *J. Appl. Phys.* **93**, 712 (2003).
[13] J.-Q. He, S. Regnery, C. L. Jia, Y. L. Qin, F. Fitsilis, P. Ehrhart, R. Waser, K. Urban, and R. H. Wang, *J. Appl. Phys.* **92**, 7200 (2002).
[14] J. Park, B.-K. Park, M. Cho, C.-S. Hwang, K. Oh, and D.-Y. Yang, *J. Electrochemical Society* **149**, G89 (2002).
[15] B. J. O'Sullivan, E. O'Connor, P. K. Hurley, H. Roussel, M. A. Audier, and J. P. Senateur, abstract in the 2002 Electrochemical Society Meeting.