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Electrical properties of Ga_2O_3-based dielectric thin films prepared by plasma enhanced atomic layer deposition (PEALD)

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Abstract Ga_2O_3 and Ga_2O_3-TiO_2 (GTO) nano-mixed thin films were prepared by plasma enhanced atomic layer deposition with an alternating supply of reactant sources, $[(CH_3)_2GaNH_2]_3$, $Ti(N(CH_3)_2)_4$ and oxygen plasma. The uniform and smooth Ga_2O_3 and GTO thin films were successfully deposited. Excellent step coverage of these films was obtained by chemisorbed chemical reactions with oxygen plasma on the surface. The dielectric constant of GTO thin film definitely increased compared to Ga_2O_3 film, and the leakage currents of GTO films were comparable to Ga_2O_3 films. The leakage current density of a 40-nm-GTO film annealed at 600°C was approximately 1×10^{-7} A/cm^2 up to about 600 kV/cm.

Keywords Ga_2O_3-TiO_2 · PEALD · Dielectric constant · Leakage current

1 Introduction

As device size becomes scaled down, numerous dielectrics with high permittivity have attracted much attention for future application of nanoscale device. Alternative materials with a permittivity higher than that of SiO_2 are needed for use in thicker gate dielectrics to achieve the required capacitance without tunneling currents, and allow evolution toward higher integration densities to continue. The replacement of SiO_2 with high-permittivity dielectrics presents a significant challenge in which the basic research and the near future needs of the semiconductor industry merge [1, 2]. The reduction of thin film to nanometer dimension for new technologies requires precise control of film thickness, conformallity, crystallinity and morphology. A lower deposition temperature is also required because interlayer diffusion may destroy the properties of nanoscale devices. Many of these requirements can be achieved by growth controlled to within single atomic layers by means of binary reaction sequence chemistry [3–6]. Furthermore, since the plasma introduction into atomic layer deposition (ALD) process can improve the film quality and enlarge the process window of ALD to lower temperature direction through the enhancement of chemical reaction compared to conventional ALD film, plasma enhanced atomic layer deposition (PEALD) has recently received much attention [7–9].

Since Ga_2O_3 is a wide band gap material with good chemical and thermal stability, Ga_2O_3 thin film has been studied as a promising dielectric material for various device applications due to its somewhat high dielectric constant (10–14) and large band gap (~5 eV). Ga_2O_3 thin films have been used in luminescent phosphors, high temperature sensors, deep-UV transparent oxides and dielectric coatings for solar cells [10, 11, 16]. On the other hand, TiO_2 is also an attractive material because of its high dielectric constant (>100) and moderate band gap [12, 13]. Therefore, the composite Ga_2O_3-TiO_2 (GTO) nano-mixed thin film is an interesting material. In this study, Ga_2O_3 and GTO nano-mixed thin films were prepared by using PEALD process, and their properties were investigated.

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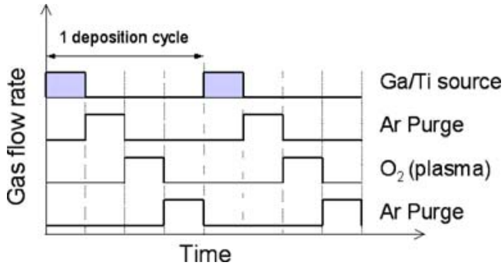

Fig. 1 Gas flow rate with time. One deposition cycle consists of four pulses. $[(CH_3)_2GaNH_2]_3$ or $Ti(N(CH_3)_2)_4$ vapor pulse with 100 sccm Ar carrier gas for 0.1 s, Ar purge gas pulse for 2 s, O_2 plasma gas pulse for 1 s, and Ar purge gas pulse for 0.4 s. The periodic cycle is repeated until the desired film thickness is obtained

2 Experimental procedure

The PEALD was used to deposit the dielectric Ga_2O_3 and GTO thin films in this study. The PEALD system consists of a warm-wall reactor, a gas-switching system, pumping system an RF-generating system, and injector (manufactured by Genitech Co. Ltd, Korea). The plasma was generated to activate oxygen gas during the O_2 gas pulse and the RF plasma power was 60 Watt. The deposition temperature was maintained at a substrate temperature of 200°C and the chamber pressure was maintained at 1.0 Torr.

The Ga_2O_3 thin film was deposited on Si (100) wafer with an alternating supply of $[(CH_3)_2GaNH_2]_3$ and oxygen plasma. While the GTO thin film was deposited on Si (100) wafer with an alternating supply of $[(CH_3)_2GaNH_2]_3$, O_2 plasma, $Ti(N(CH_3)_2)_4$ and O_2 plasma. One deposition cycle consists of four pulses: $[(CH_3)_2GaNH_2]_3$ or $Ti(N(CH_3)_2)_4$ vapor pulse with 100 sccm Ar carrier gas for 0.1 s, Ar purge gas pulse for 2 s, oxygen plasma gas pulse for 1 s, Ar purge gas pulse for 0.4 s. These four pulses were defined as one deposition cycle. A schematic diagram of the deposition process is shown in Fig.1. During deposition, this cycle was repeated until the desired thickness was obtained. The thicknesses of Ga_2O_3 and GTO thin films were measured by a surface profile measurement system and were approximately 50 nm and 40 nm, respectively. After deposition, the as-deposited Ga_2O_3 and GTO thin films were annealed in a furnace in ambient oxygen gas for 30 min. The annealing temperatures were 600, 700, and 800°C, respectively.

The coverage properties and surface morphologies of the thin films were investigated by scanning electron microscopy (FE-SEM, HITACHI S-4200, Hitachi Co.) and atomic force microscopy (AFM, SPA-400, Seiko Instruments). The scanning area in AFM measurements was 500 × 500 nm^2. The compositions of the thin films were investigated by auger electron spectroscopy (AES, MICROLAB 350, VG Scientific Co.). An X-ray diffractometer (XRD, D/MAX 2100H, Rigaku, Japan, 40 kV, 30 mA) was used to investigate the structural properties of the thin films.

To investigate the electrical properties of the metal-film-substrate (MFS) structures, the Pt top electrodes were

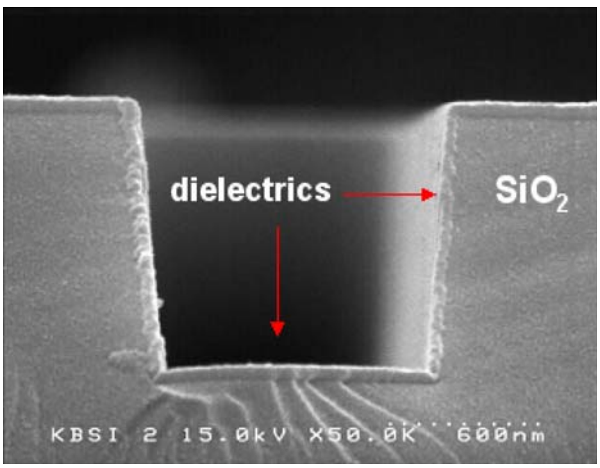

Fig. 2 Cross-sectional SEM micrograph of a Ga_2O_3 thin film on a patterned SiO_2/Si structure deposited at 200°C by using PEALD

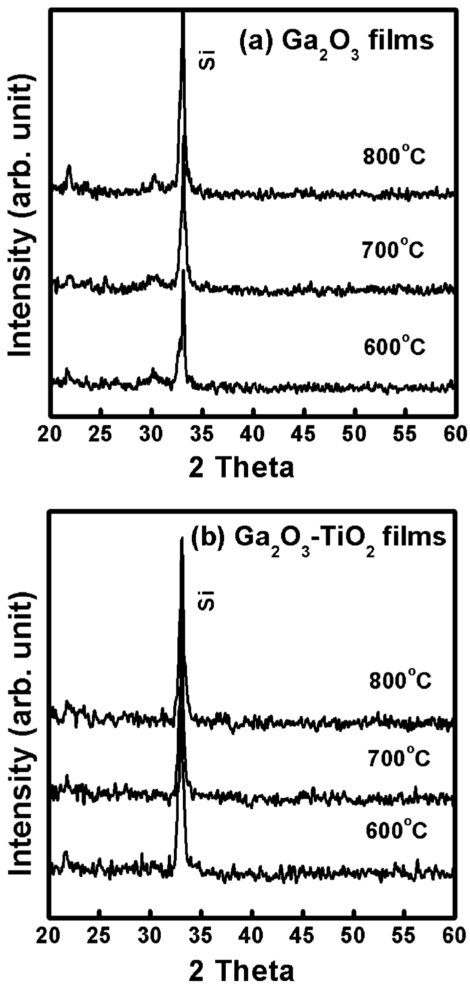

Fig. 3 XRD patterns of Ga_2O_3 (a) and Ga_2O_3-TiO_2 (b) thin films annealed at different temperatures. All of the thin films were annealed in oxygen atmosphere for 30 min

prepared by dc magnetron sputtering and then patterned using lift-off lithography. The measured capacitor size was 100 $\times$ 100 μm^2. The Capacitance-voltage curves, dielectric constant and leakage current characteristics were measured using an HP 4275A LCR meter at a frequency of 100 kHz and an HP 4145B semiconductor parameter analyzer, respectively. The interface trap density of the thin films was measured by a high-frequency method developed by Terman [14].

3 Results and discussion

When the thickness of a thin film is decreased to nanometer scale, poor step coverage can lead to structures containing voids. Good step coverage is of major important in device fabrication. Voids are generally unacceptable, since they can be opened during etching [6, 7]. The best way to avoid such problems is to use a deposition method that can produce step coverage as high as possible. Figure 2 shows the cross-sectional SEM micrograph of Ga_2O_3 thin film on a patterned SiO_2/Si structure deposited at 200°C using PEALD. The film morphology is completely continuous and the film coverage is conformal around the sidewall and bottom of the patterned structure. The step coverage of Ga_2O_3 films produced by PEALD is excellent above 90%. The PEALD process has great potential for step coverage and conformal coating procedures, which are often required in ULSI device manufacturing due to the nature of its required surface control.

Figure 3(a) shows the X-ray-diffraction patterns of the as-deposited and annealed Ga_2O_3 thin films (600, 700, and 800°C, respectively). And Fig. 3(b) shows the X-ray-diffraction patterns of the as-deposited and annealed GTO thin films (600, 700, and 800°C, respectively). Two types of thin films, Ga_2O_3 and GTO, exhibited no specific peak even annealed at temperature as high as 800°C. And there is no secondary phase observed in the XRD patterns of the thin films. This amorphous nature could bring desired insulating property for the thin films.

The surface morphologies of the thin films were measured using a scanning probe microscope (SPA-400) in the AFM mode. Figure 4(a), (b), (c) and (d) show the AFM images of the as-deposited and the annealed Ga_2O_3 thin films (600, 700, and 800°C, respectively). Figure 4(e), (f), (g) and (h) show the AFM images of the as-deposited and annealed GTO thin films (600, 700, and 800°C, respectively). As shown in Figs. 4(a) and (e), the surface morphology of as-deposited thin films is very smooth. The root mean square (RMS) values for the as-deposited thin films are about 0.2–0.4 nm. Furthermore, the surface roughness of the thin films slightly increased with annealing temperature. All annealed samples have very smooth surface with RMS values smaller than 1 nm. It was also revealed that the surface roughness and grain size of GTO thin films was relatively smaller than those of Ga_2O_3 thin films.

The AES depth profiles of Ga_2O_3 and GTO films on Si substrates deposited at 200°C are presented in Fig. 5. For the GTO films, Ga and Ti elements were uniformly distributed in entire thin film layer. Since ALD is normally performed at a relatively low temperature, so only monolayer of the reactant is chemisorbed on the substrate, the impurity incorporation into the thin films may be observed. However, it is revealed that, even for the as-deposited ones, no carbon is incorporated in Ga_2O_3 and GTO thin films. Except for carbon detection on film surface that was resulted from contamination. It may

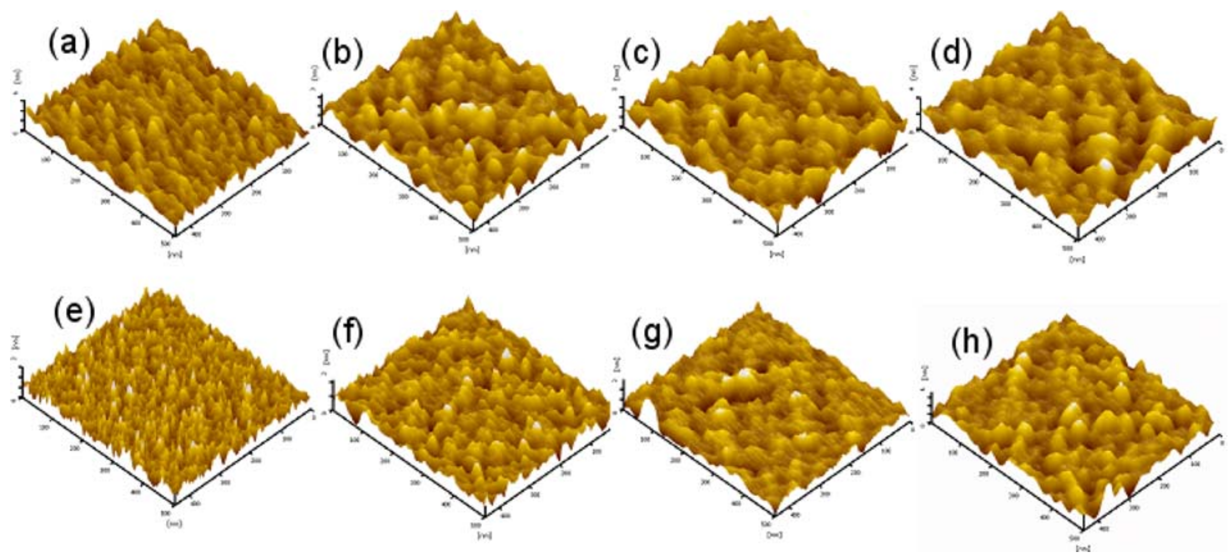

Fig. 4 AFM images of Ga_2O_3 and Ga_2O_3-TiO_2 thin films on Si substrates deposited at 200°C using PEALD and annealed at various temperatures. As-deposited Ga_2O_3 film (a), and Ga_2O_3 thin films annealed at 600°C (b), 700°C (c), and 800°C (d). As-deposited Ga_2O_3-TiO_2 thin film (e), and Ga_2O_3-TiO_2 thin films annealed at 600°C (f), 700°C (g), and 800°C (h)

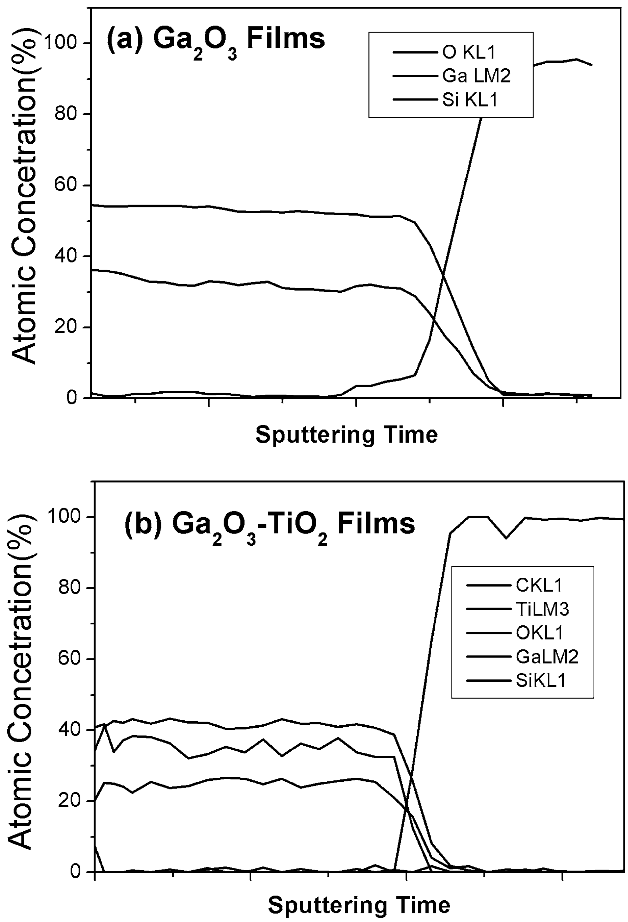

Fig. 5 AES depth profiles of Ga_2O_3 (a) and Ga_2O_3-TiO_2 (b) thin films on Si substrates deposited at 200°C by using PEALD

be considered that the amount of impurities of carbon and others could be reduced by plasma enhancement compared with the conventional ALD.

In order to investigate the electrical properties of the dielectric thin films, a Pt top electrode patterned by lithography process was prepared. Capacitance-voltage (C-V) characteristics of Ga_2O_3 and GTO thin films annealed at 700°C were measured as the voltage was swept up and down. The two curves are shown in Fig. 6. The capacitance value on the accumulation region increased in GTO thin films compared to Ga_2O_3 thin films. Furthermore, while the flat-band voltage of the Pt/GTO/Si structure exists in the zero voltage regions, the Pt/Ga_2O_3/Si structure exhibits a large positive shift of flat-band voltage in the C-V curve. It is well known that the positive shift in flat-band voltage in metal-oxide-semiconductor (MOS) systems resulted from the negative charge in the oxide layer [15]. It may be possible that the SiO_2 layer is formed at the interface between Ga_2O_3 and Si during annealing in oxygen ambient. This would result in the generation of oxygen vacancies, and the extra electrons could be produced by the oxygen vacancies. The exact mechanisms of flat-band voltage shift, due to the introduction of TiO_2 into Ga_2O_3 thin films, have been still under the investigation. The interface trap density around the midgap for the Pt/GTO/Si system is in the range of $10^{11} - 10^{12}$ cm^{-2} eV^{-1}.

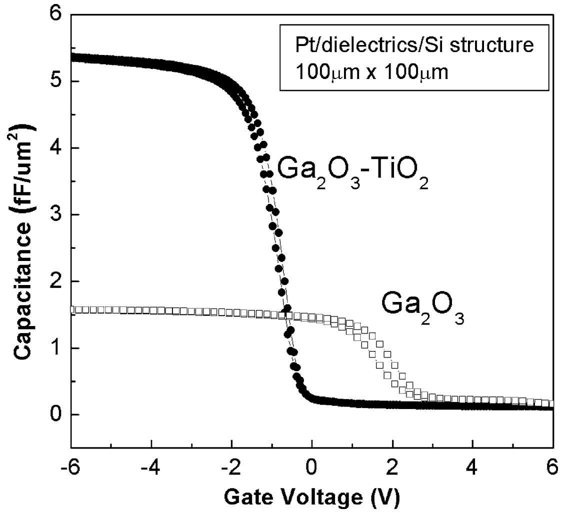

Fig. 6 Capacitance-voltage characteristics of Ga_2O_3 and Ga_2O_3-TiO_2 thin films annealed at 700°C

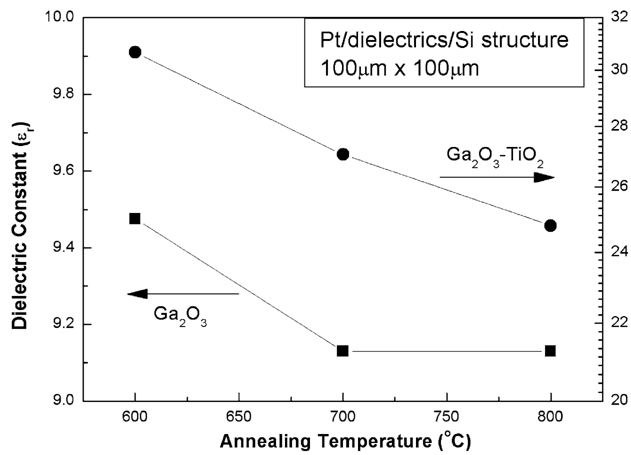

Fig. 7 Dielectric constants of Ga_2O_3 and Ga_2O_3-TiO_2 thin films as function of annealing temperature

The dielectric constants of Pt/Ga_2O_3/Si and Pt/GTO/Si structures with the annealing temperature were measured and shown in Fig. 7. The dielectric response at a frequency of 100 kHz was measured by applying a small signal of 10 mV in amplitude. The dielectric constant of the thin film decreased with increasing annealing temperature. This could be considered that an interfacial layer with lower permittivity was formed at high annealing temperature in O_2 ambient. The dielectric constant of GTO thin films is definitely higher than that of Ga_2O_3 thin films. This means that the incorporation of TiO_2 into Ga_2O_3 thin films results in the improvement of dielectric characteristics. Dielectric constant of GTO thin film annealed at 600°C at a frequency of 100 kHz is about 30.

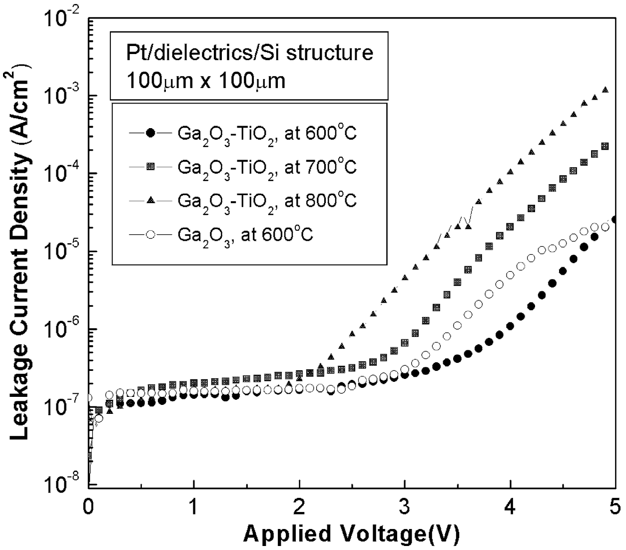

Fig. 8 Leakage current densities of Ga_2O_3 and Ga_2O_3-TiO_2 thin films annealed at various annealing temperature

The leakage current densities of Ga_2O_3 and GTO thin films annealed at various temperatures are presented in Fig. 8. As can be from Fig. 8 that, leakage current densities of GTO thin films remained at almost the same level at low voltage regions and gradually increased at high voltage regions with increasing annealing temperature.

Comparing the leakage current of Ga_2O_3 and GTO thin films at identical annealing temperature, I–V curves for the two thin films exhibited the similar behavior. And the leakage current densities of approximately 1×10^{-7}A/cm^2 were maintained up to an applied field of 600 kV/cm. Then the leakage current density increased rapidly when the applied field was above 600 kV/cm. These good insulating properties could be resulted from an improved film-quality prepared by PEALD technique.

4 Conclusions

Ga_2O_3 and GTO thin films were prepared by PEALD with an alternating supply of reactant sources, $[(CH_3)_2GaNH_2]_3$, $Ti(N(CH_3)_2)_4$ and O_2 plasma. The smooth and conformal thin films were successfully deposited on Si substrates. The grain size of GTO thin film was relatively smaller than that of Ga_2O_3 thin films. The dielectric constant of GTO thin film was definitely higher than that of Ga_2O_3 thin film. The leakage current densities of GTO thin films and Ga_2O_3 thin films were comparable. The leakage current density of a 40 nm-GTO thin film on Si substrate annealed at 600°C was approximately 1×10^{-7} A/cm^2 up to an applied field of 600 kV/cm.

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References

1. R.A. McKee, F.J. Walker, and M.F. Chisholm, *Phys. Rev. Lett.*, **81**, 3014 (1998).
2. J.W. Klaus, O. Sneh, and S.M. George, *Science*, **278**, 1934 (1997).
3. P.A. Packan, *Science*, **285**, 2079 (1999).
4. M. Ritala, K. Kukli, A. Rahtu, P.I. Raisanen, M. Leskela, T. Sajavaara, and J. Keinonen, *Science*, **288**, 31 (2000).
5. T. Watanabe and H. Funakubo, *Jpn. J. Appl. Phys.*, **39**, 5211 (2000).
6. M. Leskela and L. Niinisto, in *Atomic Layer Epitaxy*, edited by T. Suntola and M. Simpson (Blackie, London, 1990), p. 1.
7. W.J. Lee, I.K. You, S.O. Ryu, B.G. Yu, K.I. Cho, S.G. Yoon, and C. Su. Lee, *Jpn. J. Appl. Phys.*, **40**, 6941 (2001).
8. W.J. Lee, W.C. Shin, B.G. Chae, S.O. Ryu, I.K. You, S.M. Cho, B.G. Yu, and B.C. Shin, *Integr. Ferroelectr.*, **46**, 275 (2002).
9. S. Yamamoto and S. Oda, *Chem. Vap. Deposition*, **7**, 7 (2001).
10. M. Fleischer, W. Hanrieder, and H. Meixner, *Thin Solid Films*, **190**, 93 (1990).
11. M. Orita, H. Ohta, and M. Hirano, *Appl. Phys. Lett.*, **77**, 4166 (2000).
12. M.F. Al-Kuhaili, S.M.A. Durrani, and E. Khawaja, *Appl. Phys. Lett.*, **83**, 4533 (2003).
13. D.R. Lide (Ed.), *Handbook of Chemistry and Physics* (CRC, New York, 1999), p. 12.
14. L.M. Terman, *Solid-State Electron*, **5**, 285 (1962).
15. E.H. Nicollian and J.R. Brews, *MOS Physics and Technology* (John Wiley & Sons, New York, 1982), pp. 319–491.
16. F.K. Shan, G.X. Liu, W.J. Lee, G.H. Lee, I.S. Kim, and B.C. Shin, *J. Appl. Phys.*, **98**, 023504 (2005).