Electric, dielectric and optical properties of Ga_2O_3 grown by metal organic chemical vapour deposition

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Abstract. Thin film (15-130 nm) of gallium oxide were grown by the industry relevant metal organic chemical vapour deposition (MOCVD) technique on p-type Si to check the possibility for integration of newly rediscovered wide bandgap material with the Si technology. Electric, dielectric and optical properties were studied and analyzed. To perform electrical characterization, Ga_2O_3 films were integrated into Al/Ga_2O_3/*p*-Si metal–oxide–semiconductor (MOS) capacitors. Relative dielectric permittivity, flat-band voltage shift and effective oxide charge density were obtained from C-V measurements. Spectroscopic ellipsometry measurements reveal that Ga_2O_3 deposited by MOCVD is a direct bandgap material with a large optical bandgap of about 5.1 eV. Both ellipsometrical and electrical results show formation of a thick interfacial SiO_2.

1. Introduction

Gallium oxide has attracted significant attention as material due to its very interesting physical and electrical properties. Depending on growth conditions, β-Ga_2O_3 can be an insulator or a semiconductor; growing under oxidizing conditions results in insulating β-Ga_2O_3, whereas that growing under reducing conditions is conductive [1]. Intentionally doped with IV-group elements β-Ga_2O_3 also attains semiconducting properties [2-4]. Ga_2O_3 is considered as a promising material for various applications such as: optoelectronic devices in deep UV range, gas sensing, transparent electronic devices, metal-oxide- semiconductor (MOS) capacitors, resistive switching memory devices, antireflection coatings due to its favorable properties - wide band gap(about 5 eV), medium dielectric constant, good dielectric strength and deep-UV (<300 nm) transparency [3, 5]. Since many of these devices have been and will likely continue to utilize silicon, it is important to investigate the properties of Ga_2O_3 integrated into a Si device. Although the properties of Ga_2O_3 as a wide bandgap semiconductor attracts more interest, its potential as a dielectric material has also been considered and studied [6-8]. For example, Ga_2O_3 metal-oxide semiconductor field effect transistors (MOSFETs) with high breakdown voltages, large ON/OFF ratios, and high temperature operation have been recently demonstrated [9, 10]. Variety of thin film deposition methods such as different physical vapor deposition techniques, sol-gel, pulsed laser deposition, atomic layer deposition and chemical vapour deposition (CVD) were implemented to achieve better quality of Ga_2O_3 thin films. CVD is the method of choice in this paper since it is applicable for growth of a large number of metals, elemental or compound semiconductors and dielectric thin films with structure ranging from amorphous to polycrystalline and single-crystalline [11,12]. It is an industry-relevant technique combining high material quality with reasonable costs due to the ability to deposit various materials homogeneously on a large-scale.

In this work, dielectric, electrical and optical properties of MOS capacitor with Ga_2O_3 grown by MOCVD on Si substrate have been investigated.

2. Experimental procedure

p-type Si (100) wafers were used as substrates in the deposition process. They were chemically cleaned and etched just before loading in the reactor to control the thickness of the native SiO_2.Thin films of Ga_2O_3 were grown at 750 °C by MOCVD in a horizontal cold-wall reactor employing the metal-organic compound trimethylgallium (TMGa) and oxygen as precursors for Ga and oxygen, respectively. The TMGa bubler was kept at temperature of 10 ^{o}C. Argon was used as a transport gas. No special buffer layers or substrate pretreatments were employed on the Si substrates.

Ga_2O_3 films with different thickness in the range of 15-130 nm were deposited. Metal-Oxide-Si (MOS) capacitors with an area S=2.8x10^{-3} cm^2 are formed by evaporating Al through a shadow mask. The electrical properties were studied by capacitance–voltage (*C–V*) measurements. The measurements were carried out in a dark chamber employing Agilent 4980A LCR meter. Characterization by spectroscopic ellipsometry is also performed to obtain information about the optical constants and the thicknesses of layers. The ellipsometry measurements were performed using J.A. Woollam Co., Inc. M2000D rotating compensator spectroscopic ellipsometer with a CCD spectrometer with wavelength range from 193 to 1000 nm. Experimental data were acquired at angles of incidence of 65, 70 and 75 degrees and were modelled using the CompleteEASE Woollam Co., Inc. software.

3. Results and Discussion

The typical frequency dependent *C-V* curves for thinnest (15 nm) Ga_2O_3 sample are presented in figure 1 (a). Similar very strong dependence of capacitance on the frequency is observed also for thicker samples. In figure 1 (b) the capacitance in accumulation in dependence on frequency is presented for samples with different thicknesses. As is seen for thicker samples the dependence is weaker. The *C-V* curves of different samples measured at 1 kHz are compared in figure 1 (c). The parameters extracted from 1 kHz curves – effective dielectric constant, ε_{eff}, flat-band voltage, V_{fb}, effective oxide charge,Q_{eff}, are presented in table 1. Here, thicknesses are determined ellipsometrically using a single layer model. The effective oxide charge (Q_{eff}) is calculated from the *C-V* curves using the flat-band voltage shift and is found to be negative with a density in the order of 4x10^{12} cm^{-2}and is only slightly dependent on the thickness. Net negative oxide charge in Ga_2O_3 layers has been observed also in other works [8]. It should be pointed-out that most of the metal oxides used as high-k dielectrics (e.g. HfO_2, ZrO_2, Ta_2O_5, etc.) in nanoelectronic devices exhibit effective positive oxide charge. Therefore, Ga_2O_3 may be considered as a possible dopant of high-k dielectrics in applications where compensation of oxide charges, hence low net oxide charge is needed. As is seen in figure 1 (a) with decreasing frequency the curves shift to more positive voltages, which also reveals negative charge trapping. Therefore, the frequency behavior of *C-V* curves implies existence of electron traps with significant density. The shift of *C-V* curves and the hysteresis can be attributed to the combined effect of the slow and fast interface states. In this context, the lack of hysteresis and the steeper *C-V* curve measured for 15 nm Ga_2O_3 films implies the better interface quality of the thinnest samples. The decreased slope of the curves for thicker films is a clear indication of increased density of fast interface states. The thicker samples demonstrate also significant hysteresis, which reveals charge exchange between Si substrate and electrically active traps in the dielectric stack.

As is seen from table 1 the effective permittivity of layers depends on the thickness and decreases very strongly with decreasing thickness. This strong dependence is assigned to the growth of interfacial SiO_2 and formation of a double-layer structure. In this case the structure could be represented by two capacitors C_{SiO} and C_{GaO} with SiO_2 and Ga_2O_3 dielectrics, connected in series and the total capacitance

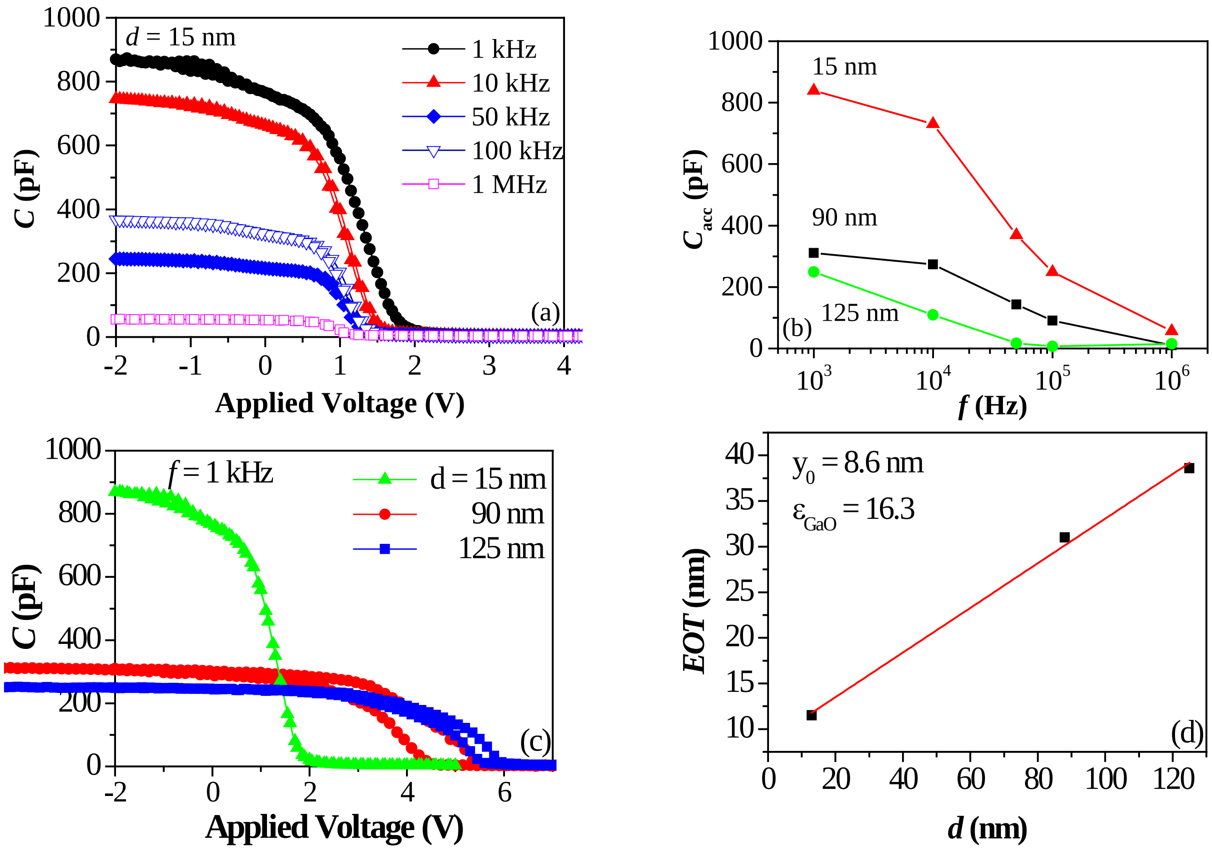

Figure 1. (a) C-V curves of 15 nm Ga_2O_3 layers measured at different frequencies; (b) frequency dependence of capacitance in accumulation for Ga_2O_3 layers with various thicknesses; (c) comparison of 1 kHz C-V curves of Ga_2O_3 layers with various thicknesses; (d) dependence of equivalent oxide thickness on physical thickness.

Table 1. Effective dielectric constant ε_{eff}, flat-band voltage shift V_{fb} and effective oxide charge Q_{eff} as obtained from 1 kHz C-V curves for Ga_2O_3 films with different thickness.

Thickness, nm	ε_{eff}	V_{fb} Volts	Q_{eff} cm^{-2}
15	4.4	2.1	$-4.5x10^{12}$
90	11.4	5.4	$-4.0x10^{12}$
125	12.6	6.2	$-3.6x10^{12}$

could be written as:

$$\frac{1}{C} = \frac{1}{C_{SiO}} + \frac{1}{C_{GaO}}, \quad (1)$$

which can be re-written also as:

$$\frac{EOT}{\varepsilon_{SiO}} = \frac{d_{SiO}}{\varepsilon_{SiO}} + \frac{d_{GaO}}{\varepsilon_{GaO}}, \quad (2)$$

where the equivalent oxide thickness of the stack EOT is evaluated from the capacitance in accumulation of *C–V* curves. d_{SiO} and d_{GaO} are the thicknesses of SiO_2 and Ga_2O_3 layers and ε_{SiO} and ε_{GaO} - their permittivities. In figure 1(d), the *EOT* vs Ga_2O_3 thickness (d_{GaO}) dependence is presented. As is seen from equation (2) this dependence should be a straight line and d_{SiO} could be found from its intercept with the y-axis, and the slope of the curve gives the permittivity of Ga_2O_3 dielectric. The fitting gives a value of SiO_2 thickness d_{SiO} = 8.6 nm. Therefore, electrical measurements reveal formation of very thick SiO_2 at the Ga_2O_3/Si interface. The permittivity of Ga_2O_3 is estimated to be about 16.3, which is slightly larger than the reported values of about 10-15 by other authors [8, 13].

The reasons for the strong frequency dispersion (figure 1 (a)) can be: i) underoxidized films in which oxygen deficiency leads to poor insulating properties [14]. In the case of existence of defective conductive regions interspersed in insulating material a dramatic increase of dielectric constant with decreasing frequency is observed and the obtained permittivity at low frequencies is unrealistically large [14]. In our case although the same behaviour of capacitance with frequency is observed, the values of ε_{GaO} at low frequency are consistent with values typically reported. Also, as will be seen below, the results from spectroscopic ellipsometry reveal well oxidized layers; ii) Maxwell-Wagner polarization which arise from charge accumulation at the interface between two materials which have different conductivities [15]. Having in mind the results obtained, this is the most probable reason for the large frequency dispersion in the samples under consideration. The binary metal oxides are inherently thermally unstable in contact with Si and formation of thin interfacial SiO_2 layer is unavoidable. In most of the cases, however, the thickness of this interfacial layer is less than 3 nm and the obtained here thickness of about 8 nm is very surprising. Therefore, we performed spectroscopic ellipsometry measurements to determine the thicknesses of Ga_2O_3 and interfacial SiO_2.

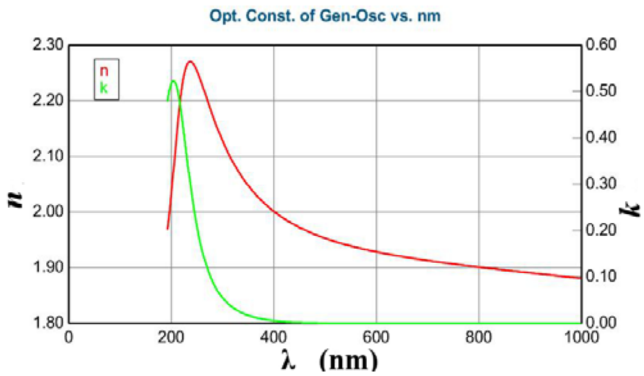

Figure 2. Refractive index *n* and the extinction coefficient *k* as a function of wavelength for Ga_2O_3 layer with a thickness of about 130 nm.

For ellipsometric modelling a three-layer model was used to represent the sample, consisting of a silicon substrate, a silicon oxide layer (as a 1st layer), a Ga_2O_3 layer as a second layer and a roughness layer as a third layer. For the silicon substrate and the silicon oxide layer we used the models from the CompleteEASE software database. The experimentaly obtained parameters Ψ and Δ were then fitted in the transparent area from 500 to 1000 nm using the Cauchy model. The Ga_2O_3 layer was then parametrised using first the b-spline model and then the General oscillator model with one Cody-Lorentz oscillator. The thicknesses of the silicon native oxide layer and the Ga_2O_3 layer were determined in the transparent area from 500 to 1000 nm and fixed. The dispersion of the dielectric functions was then determined by fitting Ψ and Δ in the entire wave length (λ) range from 193 to 1000 nm. The General oscillator parametrization ensures Kramers-Kroning consistent optical properties [16, 17]. The roughness layer was modeled by Bruggeman's EMA (Effective Medium Approximation) of 50% voids and 50% bulk material [16]. The values for the thickness as determined from the above described model are: 128.8 nm for the Ga_2O_3 layer and 7.7 nm for the silicon oxide layer. The roughness of the Ga_2O_3

layer as determined from the model is 1.67 nm. Therefore, the spectroscopic ellipsometry results are in a very good agreement with electrical results and also confirm formation of very thick interfacial SiO_2. This implies a strong thermodynamic instability of Ga_2O_3 in contact with Si. The SiO_2 formation is obviously stimulated by a high deposition temperature (750 ºC) of MOCVD process.

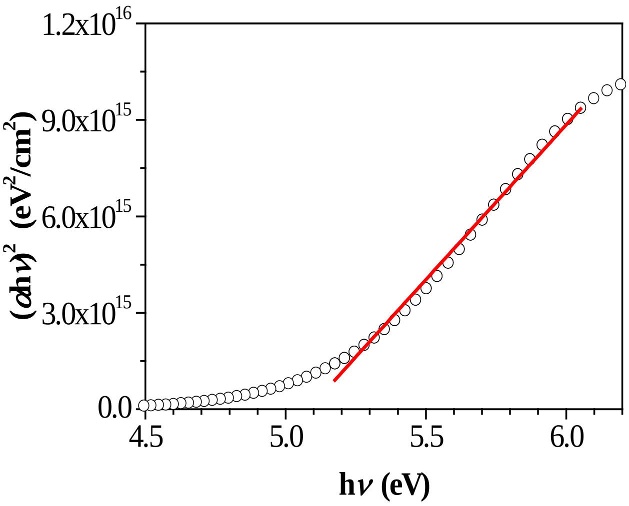

Figure 3. Tauc plot for Ga_2O_3 layer with a thickness of about 130 nm.

The dispersions of the refractive index *n* and the extinction coefficient *k* are presented in figure 2. The values of n, especially its maximum value (~ 2.27), are larger than the reported by other authors [18]. As the higher n indicates more dense films without pores, this means that the MOCVD technique results in denser Ga_2O_3 layers. This can explain also the higher dielectric constant as compared to films deposited by other techniques.

The optical bandgap can be derived from the relation: $\alpha h\nu \sim (h\nu - Eg)^h$, where $\alpha = 2\pi k/\lambda$ is the absorption coefficient at photon energy $h\nu$ and h depends on the type of transition (h=1/2 for direct bandgap and h=2 – for indirect) [19]. Figure 3 shows that linear fit is obtained for h=1/2, which reveals a direct bandgap. The extrapolation of the linear part of the curve to zero yields E_g = 5.1 eV. The bandgap of Ga_2O_3 layers is reported to be in the range 4.3 – 5.1 eV depending on its thickness and crystalline status [18]. Also, the better oxidation results in increase of E_g and better insulating properties of Ga_2O_3 [18]. Therefore, the large E_g = 5.1 eV obtained for our films reveals good oxidation, i.e. the strong frequency dispersion of capacitance is not due to poor oxidation.

4. Conclusion

The following conclusions could be drawn from the results obtained. Ga_2O_3 layers deposited on Si by MOCVD exhibit better dielectric and optical properties – larger relative dielectric constant of ~16, larger optical bandgap of ~5.1 eV and larger refractive index (revealing more dense films) as compared to the reported values for Ga_2O_3 layers deposited by other techniques. However, the high deposition temperature (750 °C) of MOCVD process stimulates formation of a very thick SiO_2 interfacial layer which could be a serious problem to integrate Ga_2O_3 on Si. The different conductivities of Ga_2O_3 and SiO_2 layers resulting in an accumulation of charge at the Ga_2O_3/SiO_2 interface is the most probable reason for the observed strong frequency dispersion of capacitance. Technological approaches to eliminate or suppress formation of SiO_2 should be found in order to successfully integrate Ga_2O_3 in Si technology.

References

[1] Nakano Y and Jimbo T 2003 *Appl. Phys. Lett.* **82** 218–220

[2] Gogova D, Schmidbauer M and Kwasniewski A 2015 *CrystEngComm.* **17** 6744-6752
[3] Higashiwaki M, Sasaki K, Kuramata A, Masui T and Yamakoshi S 2012 *Appl. Phys. Lett.* **100** 013504.
[4] Gogova D, Wagner G, Baldini M, Schmidbauer M, Irmscher K, Schewski R, Galazka Z, Albrecht M and Fornari R 2014 *J. Crystal Growth* **401** 665–669.
[5] Wager J F, 2003 *Science* **300**(**5623**) 1245–1246.
[6] Passlack M, Schubert E F, Hobson W S, et al 1995 *J. Appl. Phys* **77** 686-693
[7] Dakhel A A and Alnaser W E 2013 *Microel. Reliab.* **53** 676
[8] Altuntas H, Donmez I, Ozgit-Akgun C and Biyikli N 2014 *J Vac. Sci. Technol. A* **32** 041504
[9] Higashiwaki M, Sasaki K, Kamimura T, Wong M H, Krishnamurthy D, Kuramata A, Masui T, and Yamakoshi S 2013 *Appl. Phys. Lett.* **103** 123511
[10] Hwang W S, Verma A, Peelaers H, Protasenko V, et al 2014 *Appl. Phys. Lett.* **104** 203111
[11] Pierson H O, 1999 *Handbook of Chemical Vapor Deposition (CVD): Principles, Technology, and Applications* (Norwick, New York: Noyes Publ.)
[12] Gogova D, Siche D, Fornari R, Monemar B, Gibart P, Dobos L, Pécz B, Tuomisto F, Bayazitov R and Zollo G 2006 *Semicond. Sci. Technol.* **21** 702-706
[13] Fu D and Kang T W 2002 *Jpn. J. Appl. Phys.* **41** L1437
[14] Ramanathan S, Park C-M and McIntyre P C 2002 *J. Appl. Phys.* **91** 4521
[15] Jameson J R, Griffin P B, Plummer J D and Nishi Y 2006 *IEEE Trans. Electr. Dev.* **53** 1858
[16] *CompleteEASE® Software Manual, J.A.Woollam Co. Inc*
[17] Hilfiker J N, Singh N, Tiwald T, Convey D, Smith S M, Baker J H and Tompkins H G 2008 *Thin Solid Films* **516** 7979-7989
[18] Al-Kuhaili M F, Durrani S M A and Khawaja E E 2003 *Appl. Phys. Lett.* **83** 4533
[19] Pankove J I, 1971 *Optical Processes in Semiconductors (*New York: Dover)