Interface Quality of High-Pressure Reactive Sputtered and Atomic Layer Deposited Titanium Oxide Thin Films on Silicon

S. Dueñas[1], H. Castán[1], H. García[1], J. Barbolla[1], E. San Andrés[2], I. Mártil[2], G. González-Díaz[2], K. Kukli[3] and J. Aarik[4]

[1]Departamento de Electricidad y Electrónica, E.T.S.I. Telecomunicación, Universidad de Valladolid, Campus "Miguel Delibes", 47011 Valadolid, Spain. Phone: +34983423679. Fax: +34983423675. e-mail: sduenas@ele.uva.es.
[2]Departamento de Física Aplicada III (Electricidad y Electrónica), Facultad de Ciencias Físicas, Universidad Complutense, 28040 Madrid, Spain.
[3]Institute of Experimental Physics and Technology, University of Tartu, Tahë 4, 51010 Tartu, Estonia.
[4]Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia.

Abstract

A comparison between interface quality of several temperatures thermal annealed HPRS TiO_2 films and 750 °C annealed ALD TiO_2 films has been established. Our attention has been focused on the interfacial state and disordered induced gap state densities. From our results, HPRS films submitted to in situ 900 ° C thermal annealing in oxygen atmosphere exhibit the best characteristics, with D_{it} density being the lowest value measured in this work ($5 - 6 \times 10^{11}$ cm^{-2} eV^{-1}), and undetectable conductance transients within our experimental limits.

1. Introduction

Titanium dioxide has been one of the most extensively studied oxides because of its remarkable optical and electrical properties [1-5]. Because of its high dielectric constant, it may used as a thin film capacitor. Also, it is a prototypical alternate gate dielectric for deep-submicron MOSFETs due to the acceptance of titanium in most modern CMOS fabrication facilities. Studies of thin films of TiO_2 typically report dielectric constants that range from 40 to 86. It is believed that this variability is related to the presence of low-permittivity interfacial layers and to the dependence of permittivity on crystalline phase. Titanium dioxide forms in a number of phases. By far the most common are anatase and rutile, which normally forms at temperatures above 800 °C. The bandgap of the material is reported to be between 3.0 and 3.5 eV, depending on the crystalline phase. The anomalously high permittivity of TiO_2, which arises through a strong contribution from soft phonons involving Ti ions, is not exhibited by the other group IVB metal oxides. On the other hand, Ti has several stable oxidation states of Ti^{3+} and Ti^{4+} which lead to a well-known problem with materials containing Ti-O bonds: a reduced oxide. Such a reduced oxide has many oxygen vacancies which act as carrier traps and high leakage paths [6].

Another important concern related to titanium dioxide is the electron effective mass value. Monticone et al. taked the anatase TiO_2 electron effective mass to be equal to $m_e = 10\ m_0$ [7]. On the other hand, J. Pascual and co-workers obtained $m_e = 3\ m_0$ [8], whereas M. D. Stamate recently reported a value of $m_e = (0.71 - 1.26)$ m_0 [9].

The present work deals with the interface quality of TiO_2-based metal-insulator-semiconductor (MIS) structures, with TiO_2 being fabricated by using two different methods: high-pressure reactive sputtering (HPRS) and atomic layer deposition (ALD).

2. Experimental

Some films were grown by atomic layer deposition (ALD) [10] in a flow-type low-pressure (250 Pa) reactor. TiO_2 films were deposited from three different precursor systems employing titanium tetrachloride ($TiCl_4$) and titanium ethoxide ($Ti(OC_2H_5)_4$) as the metal precursors, and water (H_2O) and hydrogen peroxide (H_2O_2) vapors as the oxygen precursors. In all cases an ALD cycle consisted of metal precursor pulse (t_1), purge (t_2), oxygen precursor pulse (t_3) and another purge (t_4). Nitrogen was used as the carrier of precursor as well as the purging gas. The growth temperatures (T_G) and time parameters of the deposition process are listed in Table 1.

The n-type Si(1 0 0) substrates used in our experiments were etched in HF and then rinsed in deionized water immediately before loading them into the reactor. The TiO_2 films were grown on the bare substrates without using any buffer layers. The thickness value of the

0-7803-8810-0/05/$20.00 ©2005 IEEE.

Table 1. ALD process parameters used for growing TiO_2 films and thickness values obtained.

Sample	Precursors	T_G, °C	t_1–t_2–t_3–t_4, s	Cycles	Thickness, nm
1012	$TiCl_4$-H_2O	225	0.5–2–2–2	330	20
1018	$Ti(OC_2H_5)_4$-H_2O	275	2–2–2–2	300	20
1025	$Ti(OC_2H_5)_4$-H_2O_2	225	2–2–2–2	360	20
1024	$Ti(OC_2H_5)_4$-H_2O_2	275	2–2–2–2	330	20

films deposited for electrical measurements was 20 nm. These films were too thin for reliable composition analysis. However EPMA measurements performed for thicker films grown under similar conditions demonstrated that the concentration of residual chlorine did not exceed 0.1 atomic % in the TiO_2 films grown from $TiCl_4$ and H_2O at 200-275°C [11] and the concentration of residual carbon was 0.5–1.0 atomic % or lower in the films grown from $Ti(OC_2H_5)_4$ and H_2O at 200°C and higher temperatures [12, 13].

The TiO_2 films were too leaky in their as-grown stage. Therefore thermal annealing was used to improve dielectric properties of those films. The annealing has been carried out at 750 °C in purified oxygen (99.999%) under atmospheric pressure for 10 min. After the film deposition and also after annealing procedures, aluminium dot electrodes were e-beam evaporated through shadow mask on the top of dielectric films. The area of Al dots was 0.204 mm^2. The backsides of the silicon substrates were etched in HF and metallized by evaporating the Al electrodes to provide nearly ohmic contact to silicon. The thickness of the Al electrodes was 120-150 nm.

On the other hand, HPRS TiO_2/SiO_2 dielectric thin films stacks were grown on n-type silicon substrates. First, a 7 nm SiO_2 film was grown by ECR-CVD. After, 77.5 nm TiO_2 films were grown in a HPRS system at a pressure of 1 mbar during 3 hours, the growing temperature was kept at 200°C and the RF power was 600 W. Finally, the samples were in situ annealed in oxygen atmosphere at temperatures ranging from 600 to 900°C.

Electrical characterization was carried out by using capacitance—voltage (C-V), deep-level transient spectroscopy (DLTS) and conductance transient (G-t) measurements.

3. Results and Discussion

Figure 1 shows capacitance-voltage curves obtained at liquid nitrogen temperature (a) and at room temperature (b). As for C-V measured at 77 K, we see that unannealed films deposited by HPRS show positive flat-band voltage shift which means negative trapped charge in the insulator. Also, C-V curves have a considerable stretch-out as well as hysteresis behaviour, thus indicating that interface states distribution follows the disordered induced gap-state (DIGS) model [14]. However, annealed films both atomic layer deposited and high-pressure sputtered show flat band voltage values very near to 0 V, and their C-V shape are much less distorted, thus indicating better interface quality. It is worth to point out that flat-band voltage shift corresponding to ALD samples clearly diminishes in C-V curves measured at 77 K to respect those measured at room temperature, indicating that some defects are frozen at low temperatures.

Deep level transient spectroscopy (DLTS) measurements allow us to obtain interfacial state density, as it is shown in Figure 2. Unannealed HPRS films and annealed ALD films have D_{it} densities of 5 x

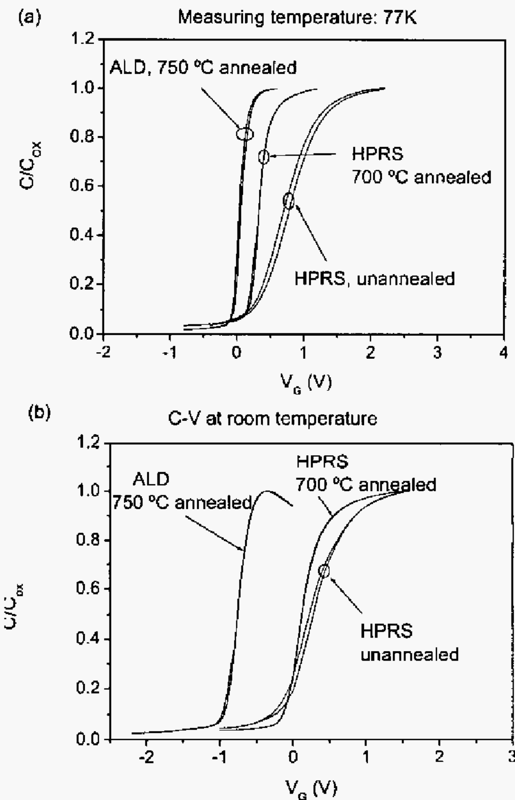

Fig.1. 1 MHz C-V curves measured at 77 K (a) and at room temperature (b) corresponding to HPRS and ALD TiO_2 MIS devices.

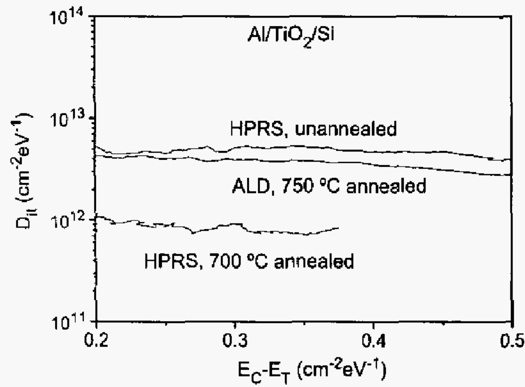

Fig.2. DLTS profiles for HPRS and ALD TiO_2 MIS devices.

10^{12} cm^{-2} eV^{-1} and 4 x 10^{12} cm^{-2} eV^{-1}, respectively. However, for 700 °C annealed HPRS films we obtain lower D_{it} values (1 x 10^{12} cm^{-2} eV^{-1}). No great differences are observed between DLTS spectra corresponding to all the samples in Table 1.

Moreover, from experimental conductance transients we can obtain the DIGS state density as a function of the spatial distance to the interface and of the energy position, as it has been described elsewhere [15, 16]. To evaluate the spatial coordinate, we must know the effective mass value. Differences of a factor of 3 have been obtained by using the values provided in references [7-9], but they only affect to the value of the spatial distance to the interface and not to the DIGS density values. So, the intermediate value (m_e = 3 m_0) has been considered through all this work.

Figure 3 shows three-dimensional DIGS profiles of 750 °C annealed ALD (a) and 700 °C annealed HPRS (b) TiO_2 films. Despite their low values of D_{it} obtained by DLTS, we clearly see that DIGS density is higher for 700 °C annealed HPRS films (2.5 x 10^{11} cm^{-2} eV^{-1}) than for 750 °C annealed ALD films (DIGS density is less than 1 x 10^{11} cm^{-2} eV^{-1}).

HPRS films submitted to different annealing temperatures exhibit lower DIGS densities, as we can

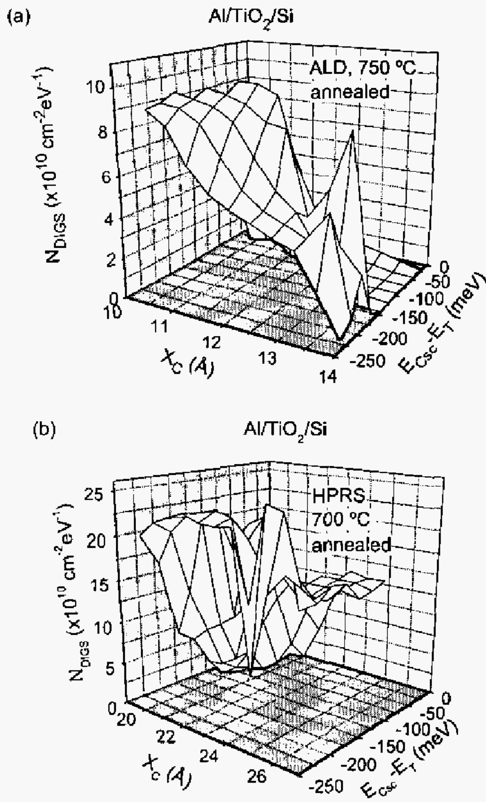

Fig.3. Three-dimensional DIGS profiles of 750 °C annealed ALD (a) and 700 °C annealed HPRS (b)

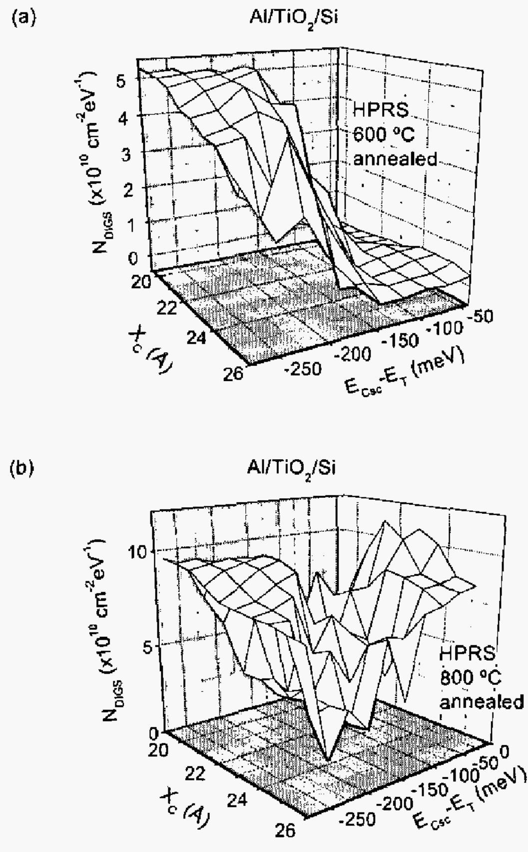

Fig.4. Three-dimensional DIGS profiles of 600 °C (a) and 800 °C annealed (b) HPRS TiO_2 MIS devices.

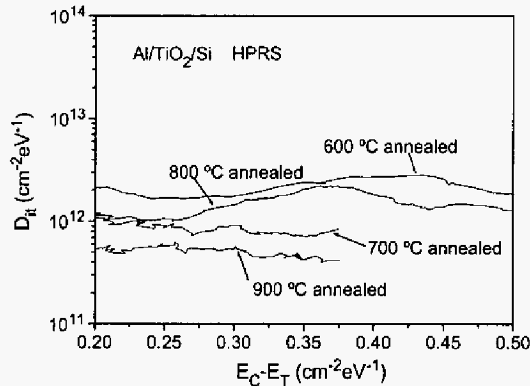

Fig.5. DLTS profiles for several annealing temperatures HPRS

see in Figure 4: we obtain 5×10^{10} cm^{-2} eV^{-1} in the cases of 600 °C annealing (a) and 1–1.2 x 10^{11} cm^{-2} eV^{-1} in the 800 °C cases (b). Within our experimental resolution, conductance transients have not been detected for 900 °C annealed HPRS samples. However, at this point it is worth to compare DIGS and D_{it} densities. Figure 5 indicates that samples submitted to 600 °C and 800 °C annealing exhibit greater interfacial state densities than those submitted to 700 °C annealing. Also, the lowest value of D_{it} is obtained for 900 °C annealed HPRS films.

4. Conclusions

In summary, an electrical characterization of TiO_2-based MIS structures, with TiO_2 being fabricated by using two different methods: high-pressure reactive sputtering (HPRS) and atomic layer deposition (ALD) has been carried out, by means of C-V, DLTS and G-t techniques. A comparison between several temperatures thermal annealed HPRS films has been established. Our results show that annealed HPRS films exhibit better interface quality than 750 °C annealed ALD ones in terms of interfacial state density. However, DIGS density is greater for 700 °C annealed HPRS films than for 750 °C annealed ALD TiO_2 films, whereas 800 ° C annealing offers DIGS density values similar to ALD cases. Annealing temperature of 600 °C provides HPRS films with DIGS density as low as 5×10^{10} cm^{-2} eV^{-1}. 900 °C annealing seems to be the best, with D_{it} density being the lowest value measured in this work (5 - 6 x 10^{11} cm^{-2} eV^{-1}), and undetectable conductance transients within our experimental limits.

References

[1] W. D. Brown and W. W. Grannemann, "C-V characteristics of metal-titanium dioxide-silicon capacitors", *Solid State Electron.*, vol. 21, p. 837, 1978.

[2] T. Fuyuki and H. Matsunami, "Electronic properties of the interface between Si and TiO_2 deposited at very low temperatures", *Jpn. J. Apl. Phys.*, vol. 25, p. 1288, 1986.

[3] N. Rausch and E. P. Burte, "Thin TiO_2 films prepared by low pressure chemical vapor deposition", *J. Electrochem. Soc.*, vol. 140, p. 145, 1993.

[4] J. Yan, D. C. Gilmer, S. A. Campbell, W. L. Gladfelter, and P. G. Schmid, "Structural and electrical characterization of TiO_2 grown from titanium tetrakis-Isopropoxide (TTIP) and TTIP/H_2O ambients", *J. Vac. Sci. Technol. B*, vol. 14, p. 1706, 1996.

[5]S. A. Campbell, H.-S. Kim, D. C. Gilmer, B. He, T. Ma, and W. L. Gladfelter, "Titanium dioxide (TiO_2)-based gate insulators", *IBM J. Res.Develop.*, vol. 43, no. 3, pp. 383-392, May 1999.

[6] G.D. Wilk, R.M. Wallace, and J.M. Anthony, "High-k gate dielectrics: current status and materials properties consideration", *J. Appl. Phys.* vol. 89, no. 10, pp. 5243-5275, May 2001.

[7] S. Monticone, R. Tufeu, A. V. Kanaev, E. Scolan, and C. Sanchez, "Quantum size effect in TiO_2 nanoparticles: does it exist?", *Appl. Surf. Sci.*, vol. 162-163, pp. 565-570, 2000.

[8] J. Pascual, J. Camassel, and H. Mathieu, "Resolved quadrupolar transition in TiO_2", *Phys. Rev. Lett.*, vol. 39, no. 23, pp. 1490-1493, December 1977.

[9] M. D. Stamate, "On the non-linear I-V characteristics of dc magnetron sputtered TiO_2 thin films", *Appl. Surf. Sci.*, vol. 205, pp. 353-357, (2003).

[10] M. Ritala, and M. Leskelä, "Handbook of thin film materials, Vol. 1, Deposition and processing of thin film materials", Academic, San Diego, p. 104, 2002.

[11] J. Aarik, A. Aidla, H. Mändar, and T. Uustare, "Atomic layer deposition of titanium dioxide from $TiCl_4$ and H_2O: investigation of growth mechanism", *Appl. Surf. Sci.*, vol. 172, pp. 148–158, 2001.

[12] J. Aarik, A. Aidla, V. Sammelselg, T. Uustare, M. Ritala, and M. Leskelä, "Characterization of titanium dioxide atomic layer growth from titanium ethoxide and water", *Thin Solid Films*, vol. 370, pp. 163-172, 2000.

[13] V. Sammelselg, E. Rauhala, K. Arstila, A. Zakharov, J. Aarik, A. Kikas, J. Karlis, A. Tarre, A. Seppälä, J. Asari, and I. Martinson, "Study of thin oxide films by electron, ion and synchrotron radiation beams", *Mikrochimica Acta*, vol.139, pp. 165-169, 2002.

[14] L. He, H. Hasegawa, T. Sawada, and H. Ohno, "A self-consistent computer simulation of compound semiconductor MIS C-V curves based on the disorder-induced gap-state model", *J. Appl. Phys.* vol. 63, no. 6, pp. 2120-2130, March 1988.

[15] S. Dueñas, R. Peláez, H. Castán, R. Pinacho, L. Quintanilla, J. Barbolla, I. Mártil, and G. González-Díaz, "Experimental observation of conductance transients in Al/SiN_x:H/Si metal-insulator-semiconductor structures", *Appl. Phys. Lett.* vol. 71, no.6, pp. 826-828, August 1997.

[16] H. Castán, S. Dueñas, J. Barbolla, E. Redondo, N. Blanco, I. Mártil, and G. González-Díaz, "Interface quality study of ECR-deposited and rapid thermal annealed silicon nitride Al/SiN_x:H/InGaAs structures by DLTS and conductance transient techniques", *Microelectron. Rel.* vol. 40, pp. 845-848, 2000.