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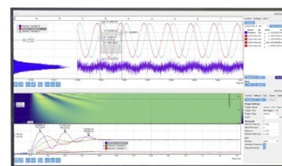

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Substrate biasing effect on the electrical properties of magnetron-sputtered high-*k* titanium silicate thin films

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We report on the effect of substrate biasing on the properties of high-dielectric constant (high-*k*) titanium silicate ($Ti_xSi_{1-x}O_2$) thin films deposited with a room-temperature magnetron-sputtering process. The composition, microstructure, and electrical properties of the $Ti_xSi_{1-x}O_2$ films were systematically characterized, as a function of the substrate bias voltage (V_S), by means of various complementary techniques, including x-ray photoelectron spectroscopy, x-ray reflectivity, Rutherford backscattering spectrometry, and appropriate electrical characterizations. We show, in particular, that depositing the $Ti_xSi_{1-x}O_2$ films with a relatively small biasing voltage ($V_S \approx -15$ V) leads not only to a significant reduction of their porosity but more interestingly to a marked improvement of their electrical properties. A further increase of the negative bias voltage (from 20 to 110 V) was, however, found to increase progressively the leakage current through the $Ti_xSi_{1-x}O_2$ films. Such a degradation of the electrical properties at high V_S values is shown to be associated with some resputtering and defects generation caused by the rather energetic bombardment conditions. In contrast, the "soft hammering" induced by the relatively low-energy ion bombardment densifies the films and improves their properties. Under the optimal substrate biasing conditions ($V_S \sim -15$ V), the room-temperature deposited titanium silicate films are shown to exhibit a highly attractive combination of electrical properties, namely a *k* value as high as ~17, a dissipation factor <0.01, a leakage current as low as 5×10^{-9} A/cm^2 at 1 MV/cm, and a breakdown field higher than 4 MV/cm. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2759196]

I. INTRODUCTION

The development of high-quality electronic thin films is essential to fuel the continuing scaling down of microelectronic components.[1] A salient example is the high-dielectric constant (high-*k*) materials that are required to replace the traditional dielectrics, such as SiO_2 (k=3.9) or Si_3N_4 (k=7), in advanced complementary metal–oxide–semiconductor devices.[2–14] The integration of high-*k* materials is indeed a clever way to circumvent the exponential increase of the leakage current associated with the scaling down of the classical gate dielectric of metal–oxide–semiconductor field-effect transistors.[2–7] Furthermore, new high-*k* materials are also required for the development of metal–insulator–metal (MIM) capacitors that can simultaneously meet the stringent criteria of a high capacitance density, a low leakage current, and very stable operation characteristics in analog/mixed signal and radio-frequency (rf) circuits.[7–14] Moreover, as MIM capacitors are generally integrated at the backend of the circuit fabrication process, the low thermal budget (i.e., $T < 400$ °C) is an additional constraint to be considered in order to be compatible with the Cu interconnects technology.[1,8,13] Consequently, low deposition temperature processes are highly desirable for the growth of high-quality replacement dielectrics.

Among the various high-*k* materials investigated for microelectronic applications, the silicates (i.e., mixtures of SiO_2 with a metal oxide) are among the most promising candidates.[2–6,15–22] They indeed offer the interesting advantage of combining a dielectric constant higher than that of SiO_2 (because of the presence of the metal oxide), with a reduced leakage current density and a higher band gap compared to pure metal oxide films.[2,3,18] However, most of the silicates provide only a moderate increase of the dielectric constant compared to the traditional dielectrics. For example, zirconium and hafnium silicates, which have been widely investigated for gate dielectric applications, have a *k* value limited to the 10–13 range, even when the films are exposed to high temperature annealings.[2,5,6] An exception to this general trend is the titanium silicates (i.e., $Ti_xSi_{1-x}O_2$), which offer the possibility of achieving *k* values higher than those of other silicates. Indeed, due to the very high polarizability of the Ti atoms, a dielectric constant higher than 20 can be achieved for $Ti_{0.5}Si_{0.5}O_2$ films, while keeping leakage currents much lower than those of TiO_2 films.[6,16–22]

Titanium silicate thin films have been prepared by various methods including chemical vapor deposition (CVD),[6,21–24] pulsed-laser ablation,[15,17] sol-gel,[20,25,26] and sputtering.[16,18,19,27,28] Some of these, however, require high thermal budget (firing, etc.) which may limit their compatibility with backend applications. The CVD based techniques offer the prospect of a high throughput, but they generally

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lead to a large incorporation of hydrogen (or other impurities originating from the precursor gases) in the films, particularly for low deposition temperatures.[29] Magnetron sputtering arises as the most suitable technique to grow highly dense films with a high purity even at low deposition temperatures.[30,31] Moreover, this latter technique generally offers the possibility to use an additional substrate biasing to tune further the properties of the sputtered films.[31–34] The aim of the present work is thus to take advantage of the additional substrate biasing in order to grow, at room temperature, high-k titanium silicate films that meet the aggressive criteria needed for MIM capacitor applications.

In the present article, we report the results of a systematic investigation of the effect of substrate biasing on the electrical and structural properties of titanium silicate thin films grown using a magnetron sputtering deposition process at room temperature. We were thus able to demonstrate that, by applying a moderate bias voltage, both the leakage currents and dielectric losses of the titanium silicate films were significantly reduced. In contrast, higher bias voltages are found to rather deteriorate the electrical properties of the films. Interesting correlations are pointed out between the electrical properties of the films, their density, composition, and the degree of resputtering caused by the substrate biasing induced ion bombardment.

II. EXPERIMENT

The titanium silicate films were grown from the 13.56 MHz rf magnetron sputtering of a 3 in.-diameter TiO_2/SiO_2 (50/50 at. %) composite target (99.9% purity) at a power of 250 W. The system was first cryopumped to a base pressure of $\sim 10^{-8}$ Torr. The sputtering deposition process was then performed at a pressure of 1.5 mTorr in a mixture of high purity Ar (99.999%) and O_2 (99.995%) gases. The flow rates for Ar and O_2 were adjusted to a ratio of 80/20 to minimize the presence of oxygen vacancies in the films.[16] The titanium silicate films were deposited simultaneously on Si (100) and Pt-coated Si substrates. The substrates were mounted on a substrate holder and placed at a distance of about 20 cm from the target. Before the deposition, the target was cleaned by presputtering for 15 min with the shutters closed. All the depositions were carried out without any heating of the substrates (even when the plasma deposition is on, the measured substrate temperature was below 40 °C for all the investigated deposition conditions.) No postdeposition annealing treatment was performed. The thickness of the films was *in situ* monitored by means of a calibrated quartz crystal microbalance and *ex situ* measured by x-ray reflectivity (XRR) and Rutherford backscattering (RBS). For this study, the thickness of the titanium silicate films was in the 75–90 nm range (unless otherwise specified), which corresponds to a deposition duration of 90 min.

The substrate bias voltage was controlled by applying a 13.56 MHz rf power to the substrate using an independent rf-power source synchronized with the main sputtering source using a common exciter. By applying a rf power to the substrate, a negative direct current (dc) component self-polarizes the substrate and creates a controlled bombardment

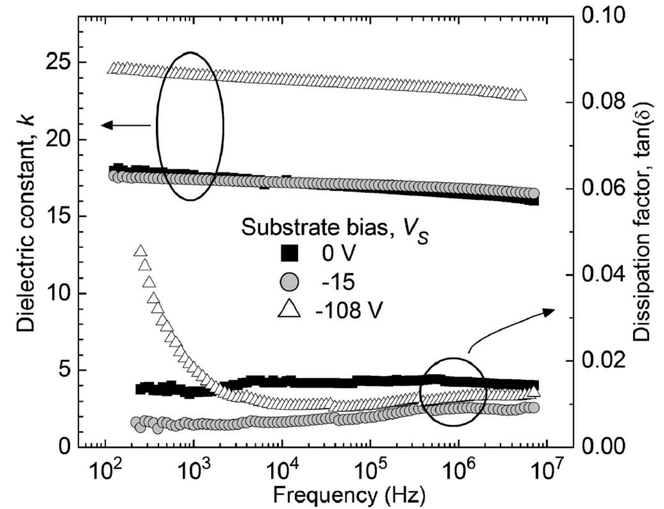

FIG. 1. Frequency dependence of both the dielectric constant and the dissipation factor tan(δ) of sputtered titanium silicate thin films grown at various substrate bias voltages.

of positively charged Ar ions on the surface of the film being grown. The dc substrate bias voltage (V_S) is defined here as the dc potential measured when the bias rf power is applied on the substrate from which the self-polarization potential (i.e., about +7 V above the ground, when no rf power is applied) is subtracted. The effect of the substrate bias voltage was investigated for V_S values in the 0 to −110 V range.

For the electrical and dielectric characterizations of the sputtered titanium silicate films, $Si/SiO_2/Ti/Pt/Ti_xSi_{1-x}O_2/Al$ MIM capacitors were fabricated. The current-voltage characteristics of the devices were acquired by using an HP4145A pA meter. An HP4192A was used to measure the complex impedance of the devices in the 1 kHz–10 MHz frequency range. The dielectric constant and dissipation factor [tan(δ)] of the titanium silicate films were then derived from the complex impedance measurements. The thickness and the density of the films were characterized by XRR. The XRR spectra were acquired by means of a high resolution Philips X'pert diffractometer (angular resolution of 10^{-4} deg) using Cu K_α radiation. Prior to the measurements, the samples were precisely aligned along the diffractometer axes. Thus, the critical angle of the reflectivity curves can be determined repeatedly within $\sim 10^{-3}$ deg. Grazing incidence x-ray diffraction (GIXRD) measurements were also performed with the same diffractometer. X-ray photoelectron spectroscopy (XPS) analyses were carried out in order to characterize the chemical composition and bonding states of the films. The XPS spectra were collected using the Al K_α (1486.6 eV) monochromatic x-ray source of an ESCALAB 220I-XL spectrophotometer. The RBS experiments were carried out using both 1 and 2 MeV He^+ ions beams. The incident and scattering angles were set, respectively, to 7° and 169° while the detector has a ~20 keV energy resolution and a 6.69 mSr solid angle of detection. Finally, the morphology of the films was investigated by scanning electron microscopy (SEM) observations and their surface roughness evaluated through atomic force microscopy (AFM) measurements.

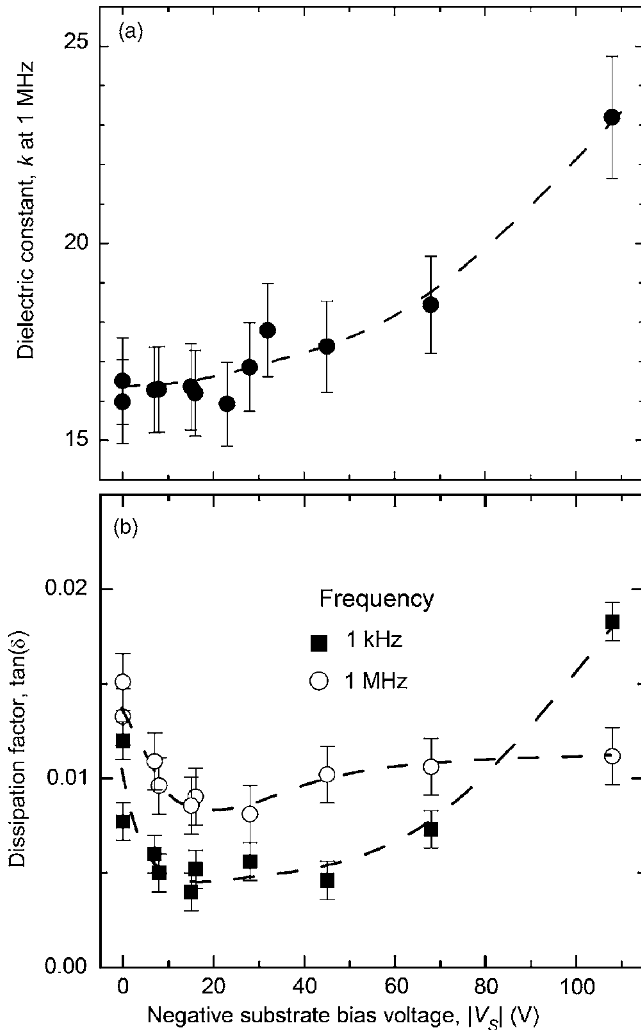

FIG. 2. Effect of the substrate bias voltage on (a) the dielectric constant measured at a frequency of 1 MHz and (b) the dissipation factor tan(δ) measured at 1 kHz and 1 MHz.

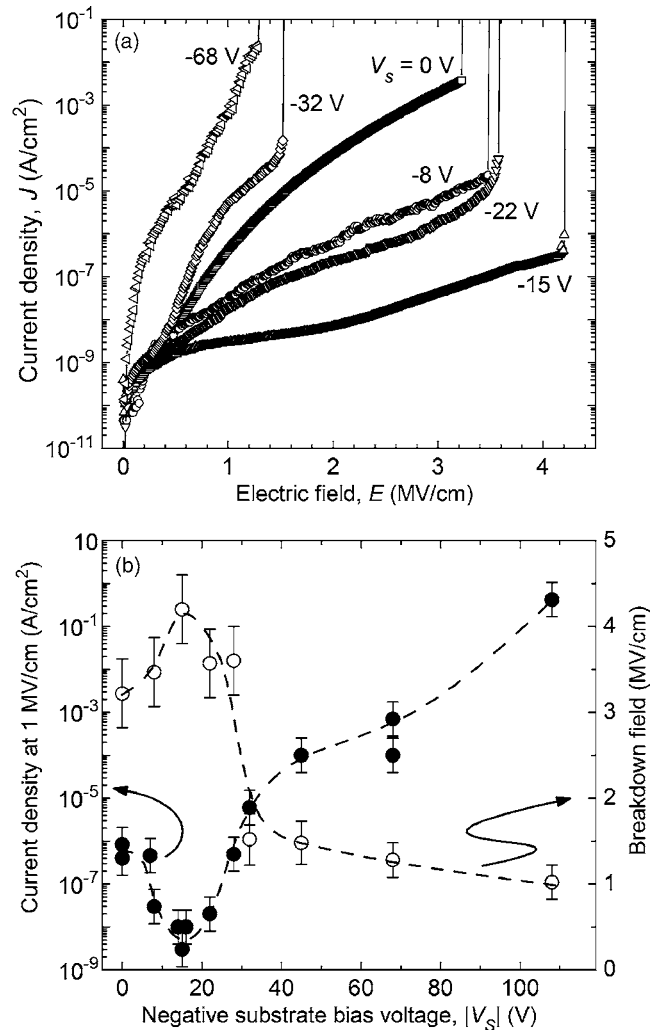

FIG. 3. (a) Leakage current density vs electric field curves of sputtered titanium silicate thin films grown at various substrate bias voltages. (b) Substrate bias voltage dependence of both the leakage current density (at an electric field of 1 MV/cm) and the breakdown field of the titanium silicate films.

III. RESULTS AND DISCUSSION

A. Electrical properties

Figure 1 shows the dielectric constant (k) as a function of frequency for the titanium silicate thin films sputter deposited at V_S=0, −15, and −108 V. It is seen that the k-versus-frequency curves are almost constant with a very low dispersion. For the films deposited at low bias values (i.e., V_S=0 and −15 V), the dielectric constant is found to be of about 17. On the other hand, when a high bias voltage (V_S=−108 V) is applied, k increases significantly up to a value of 23. Figure 2(a) shows the variation of the dielectric constant (at 1 MHz) with the increasing negative bias voltage. It is seen that the k value of the films remains constant (around a value of ~17) up to V_S~−35 V, and then increases with V_S to reach a value of 23 at −108 V. The k values obtained here for the titanium silicates films are seen to be comparable with the highest values reported for high-k pure metal oxide dielectrics integrated into MIM devices [i.e., k~15–18 for HfO_2,[8,9] k~22 for ZrO_2,[10] k~7 for Y_2O_3,[11] k~9 for Al_2O_3,[12] k~24 for Ta_2O_5,[13] k~23 for La_2O_3 (Ref. 14)]. On the other hand, Fig. 1 also shows that all the titanium silicate films have a low dissipation factor [i.e., tan(δ)<0.02] over all the investigated frequency range, particularly for the low V_S biasing conditions. Indeed, the titanium silicate films deposited with a V_S of −15 V were found to possess the lowest dissipation factor [tan(δ) <0.01] over the entire frequency range (Fig. 1). Those deposited with a V_S=−108 V, however, exhibited a dissipation factor that increases at low frequencies. This latter behavior is thought to be caused by the presence of higher leakage currents in these highly-biased films, as it will be discussed latter on (see Fig. 3). Figure 2(b) summarizes the variation of tan(δ) as a function of the bias voltage (for frequencies of 1 kHz and 1 MHz). It is clearly seen that tan(δ) reaches its minimum values (either at 1 kHz or at 1 MHz) for a V_S value around −15 V.

Figure 3 shows the leakage current density-versus-electric field characteristics of titanium silicate films deposited at various V_S values. For the films deposited without substrate biasing (i.e., V_S=0 V), a low leakage current of about 5×10^{-7} A/cm^2 is obtained at an electric field of 1 MV/cm, along with a breakdown field of about 3 MV/cm.

When a small negative bias ($V_S \sim -8$ V) is applied during the film growth, its electrical properties are found to improve significantly. This improvement is seen in Fig. 3 to reach its maximum at $V_S = -15$ V. Indeed, at $V_S = -15$ V, the leakage currents of the titanium silicate films is reduced down to a value as low as 5×10^{-9} A/cm^2 at 1 MV/cm and the breakdown field reaches a high value of ~ 4.2 MV/cm. A further increase of the negative bias voltages, ($|V_S| > 20$ V), is found to be accompanied with a gradual deterioration of the electrical properties of the films (Fig. 3). In particular, the leakage current of the films grown with $|V_S|$ values exceeding 40 V are unacceptably high for MIM capacitor applications. The variations of the leakage current density and the breakdown field of the films with V_S are summarized in Fig. 3(b). The optimal V_S value that minimizes the leakage currents while maximizing the breakdown field of the films is found to be of about -15 V; a bias voltage for which the films exhibited also the lowest dispersion and dissipation factor values (Fig. 1 and 2). Thus, the earlier discussed results clearly point up the bias voltage $V_S = -15$ V as the optimal biasing condition that lead to the growth of titanium silicate films combining a dielectric constant as a high as 17, a very low leakage current density of 5×10^{-9} A/cm^2 at 1 MV/cm, a breakdown field in excess of 4 MV/cm, and a very low dissipation factor < 0.01. Additionally, the process developed here offers the advantage of a very low thermal budget with a deposition at room temperature. Thus, the achieved titanium silicate based MIM capacitors are highly attractive for backend integration into microelectronic devices. These results highlight the crucial role of substrate biasing to optimize the microstructure and, hence, the electrical properties of the titanium silicate films.

B. Structural properties

The structural properties of the titanium silicate films were characterized in order to better understand the effect of substrate biasing on their microstructure and electrical properties. First, the general morphological characteristics of the titanium silicate films were examined using AFM and SEM. On the SEM micrographs, all the titanium silicate films appear to be densely packed and homogeneous without any apparent porosity or distinguishable features [as illustrated in Fig. 4(a)]. No significant difference can be noticed between the films deposited at various bias voltages. Also, from the AFM characterizations, the films were found to be very smooth with a root-mean-square (rms) roughness of ~ 0.3 nm, which is found to be insensitive to V_S [Figs. 4(b) and 4(c)]. Finally, the amorphous character of the films, regardless of the V_S value, was confirmed by the GIXRD measurements (not shown) as no diffraction peak can be found in the spectra.

Figure 5 shows typical XPS spectra for the O 1*s*, Si 2*p*, and Ti 2*p* core levels of titanium silicate thin films. The O 1*s* peak position is found to be of 531.5 eV, which is an intermediate value between the binding energy positions of the O 1*s* peaks in SiO_2 (533 eV) and TiO_2 (530 eV),[18,25,35] respectively. This indicates that both Ti and Si atoms are present in the first coordination shell of the O atoms. Also, the Si 2*p*

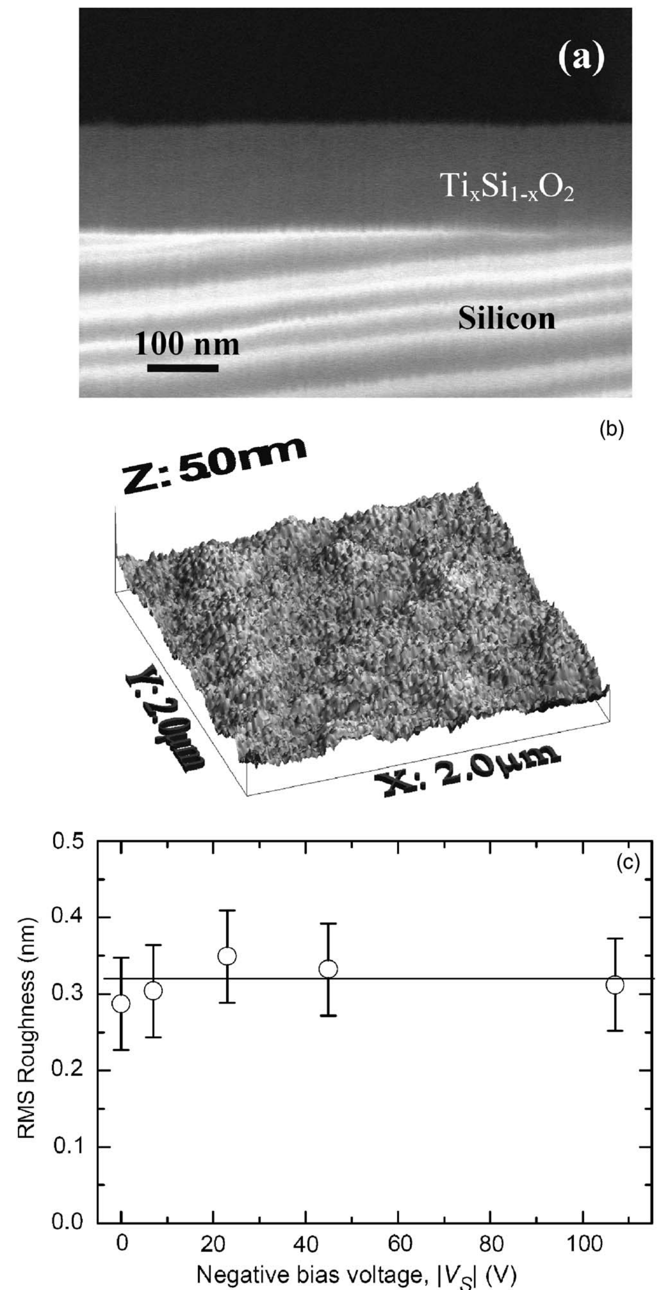

FIG. 4. (a) Typical SEM cross-sectional micrograph of a ~ 160 nm-thick titanium silicate thin film grown on a silicon substrate. (b) AFM three-dimensional view of a 2×2 μm micrograph for a titanium silicate thin film. (c) rms roughness of the titanium silicate thin films as a function of the applied substrate bias voltage.

peak position is centered at a lower energy (~ 102 eV) compared to its position in SiO_2 (103.3 eV).[18,25,35] This shift indicates that the charge on the Si atoms is affected by the presence of Ti atoms in their close neighborhood. Conversely, the position of the Ti 2*p* peak (~ 459 eV) is slightly higher than that of Ti in pure TiO_2 (~ 458.7 eV) [18,25,35] because of the influence of nearby Si atoms. The measured peak positions for O 1*s*, Si 2*p*, and Ti 2*p* thus confirm that the SiO_2 and the TiO_2 components of the target were mixed at the molecular level during the deposition process leading thereby to the formation of Ti-O-Si types of environments in the films, which constitute the fingerprint of the titanium

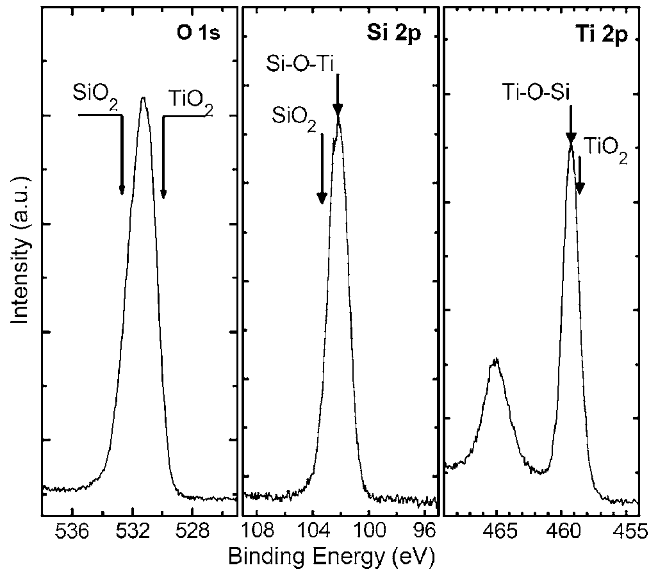

FIG. 5. Typical O 1*s*, Si 2*p*, and Ti 2*p* core-level high resolution XPS spectra of the sputtered titanium silicate thin films.

silicate phase. On the other hand, the XPS spectra of the films deposited at various biasing values were found to be very similar with no significant difference in their peak positions.

Figure 6 shows a typical RBS spectrum acquired with 1 MeV He^+ ions for a titanium silicate thin film grown on Si with its corresponding simulated spectrum. The theoretical spectrum was built by assuming a single layer with a uniform distribution of the elements in the depth. This assumption is confirmed by the good fit between experimental and theoretical spectra (see Fig. 6). The films were also characterized with a 2 MeV He^+ beam in order to be able to separate Ar and Ti signals in the RBS spectra. (The 1 MeV He^+ beam offers a better depth resolution but does not permit

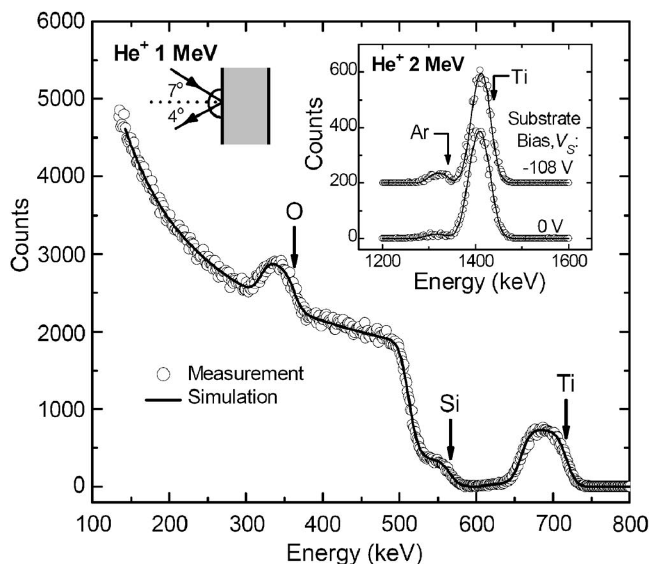

FIG. 6. Typical RBS spectrum acquired with a 1 MeV He^+ ion beam for sputtered titanium silicate thin films with its corresponding simulated curve. The inset shows the 1200–1600 keV region of spectra acquired with a 2 MeV He^+ ion beam for films deposited at 0 and −108 V substrate bias voltage.

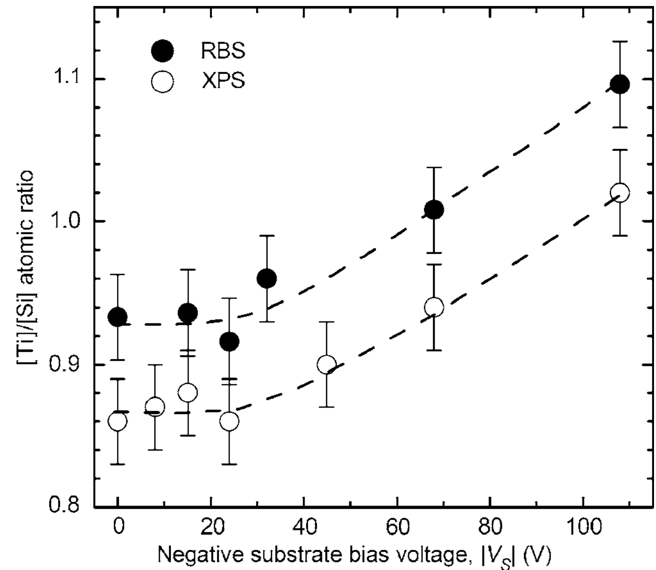

FIG. 7. Effect of the substrate bias voltage on the [Ti]/[Si] atomic ratio of the titanium silicate thin films as measured by both the XPS and RBS techniques.

direct deconvolution of Ti and Ar signals.) As illustrated in the inset of Fig. 6, the spectra acquired at 2 MeV revealed that some argon can be trapped in the films during the sputtering deposition process. Indeed, the Ar content of the films was found to increase significantly with the substrate bias voltage (from <1 at. % at 0 V to about 2.5 at. % at −108 V), as a consequence of the more intense Ar ion bombardment at high substrate biasing.

On the other hand, the [Ti]/[Si] atomic ratio of the films was determined from RBS analyses, as a function of V_S, and compared to its corresponding XPS surface values (see Fig. 7). The [Ti]/[Si] atomic ratio is found to increase from ~0.9 at low substrate biasing ($0<|V_S|<30$ V) to a value slightly above 1 at a $V_S=-108$ V. Even if the XPS data are seen to be slightly lower than their RBS counterpart, both characterization techniques show the same trend for the V_S dependence of the [Ti]/[Si] ratio. Indeed, Fig. 7 shows that the [Ti]/[Si] atomic ratio remains constant up to a V_S of about −30 V and then continuously increases with $|V_S|$. It is worthy to note here that the observed Ti enrichment of the films with substrate biasing occurs in conjunction with the increase of the dielectric constant shown in Figs. 2(a). Indeed, a higher Ti content increases the amount of the highly polarizable atoms of the films and thus leads to an increase of the dielectric constant.[18] As it will be discussed latter on, the observed Ti enrichment of the films with substrate biasing is believed to arise from a preferential resputtering of the Si in the films at high bias voltages.

On the other hand, although the compositions obtained from XPS and RBS measurements exhibited the same variation as a function of V_S, a small systematic shift between the two techniques can be noticed (Fig. 7). The XPS technique can indeed lead to a systematic underestimation of the surface Ti content in the case of TiO_2/SiO_2 mixtures, as reported in Ref. 25. Thus it is highly likely that the actual film composition is more accurately reflected by the RBS measurements. One should also note that the films deposited at

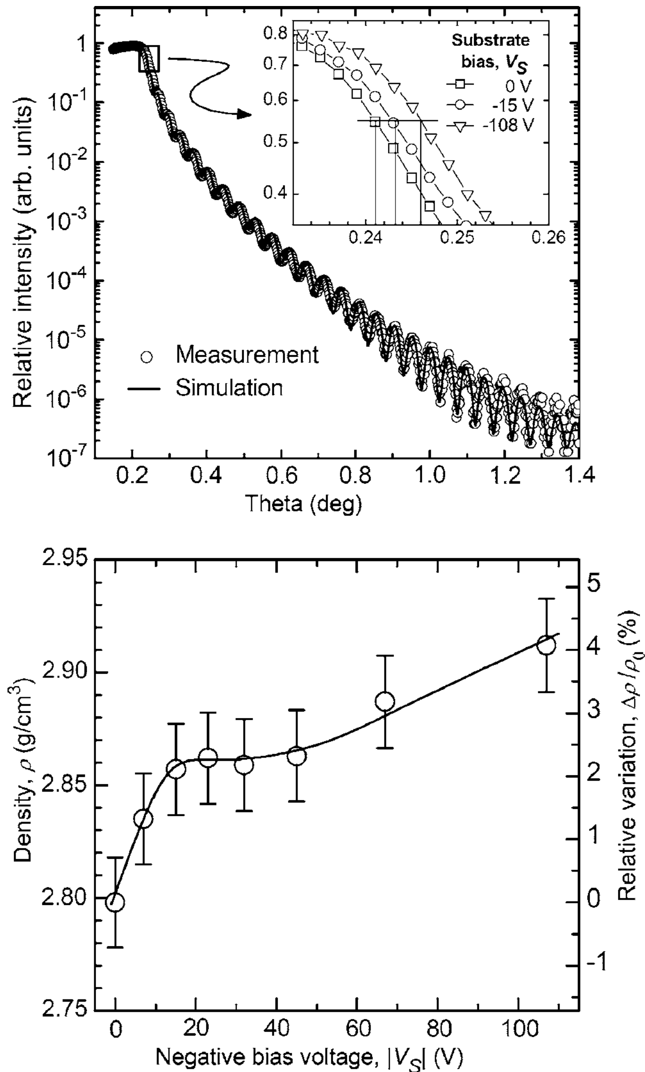

FIG. 8. (a) Typical XRR spectrum of a sputtered titanium silicate thin film with its corresponding calculated curve. The inset shows a region of the XRR spectra near the critical angle for films deposited at various substrate bias voltages. (b) Variation of the density of the titanium silicate thin films with the substrate bias voltage.

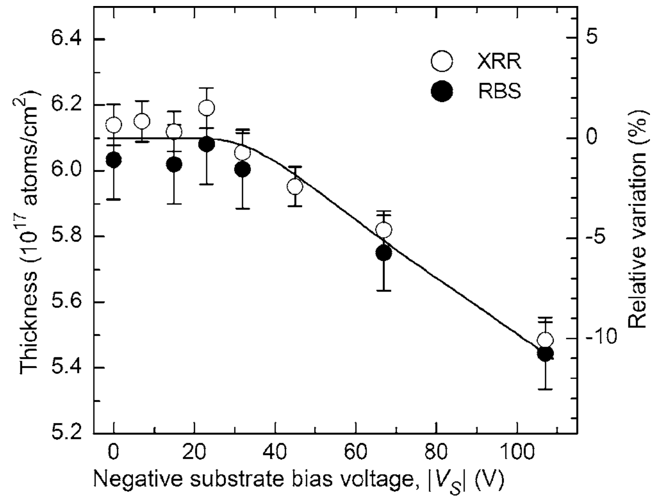

FIG. 9. Variation of the thickness of sputtered titanium silicate thin films, as measured by both RBS and XRR techniques, as a function of the applied substrate bias voltage.

low substrate biasing voltages are slightly SiO_2 rich ([Ti]/[Si]$\sim$0.9) compared to the target (which has a [Ti]/[Si] ratio of 1). Such a difference between the composition of the target and the films is indeed commonly observed during the sputtering of multicomponent targets and can be caused by several mechanisms (for example, it can be due to the preferential sputtering of one element of the target combined with some plasma-induced diffusion in the target[32]).

Figure 8(a) shows a typical XRR spectrum for a titanium silicate film deposited on a Si substrate. The simulated spectra were obtained by a least square fitting technique with a simple model consisting of a single layer on Si. The fitting parameters consisted of the density, roughness, and thickness of the top layer and the roughness of the substrate/film interface. The simulated spectra were found to be in very good agreement with the measurements [Fig. 8(a)], indicating that the titanium silicate films can be fairly well represented by a single layer model of constant density (in agreement with the results obtained from RBS). Also, the XRR analyses permitted the precise determination of the physical thickness [in nanometers (nm)] of the films from the clearly visible fringes on the spectra. On the other hand, although the films exhibit similar XRR spectra, a significant increase of the critical angle (i.e., the angle at which the reflected intensity abruptly decreases) was observed with increasing negative bias values (see inset of Fig. 8). This variation indicates that the films deposited at higher negative bias values have a higher density.[36] Figure 8(b) shows the variation of the mass density of the titanium silicate films as a function of V_S. (The density was calculated using the RBS-determined composition of the films and the appropriate atom form factor for Ti, Si, and O.) As $|V_S|$ is increased from 0 to 15 V, the density is found to increase significantly from 2.80 up to 2.86 g/cm^3. Then, it remains unchanged around 2.86 g/cm^3 even if $|V_S|$ is further increased up to $\sim$50 V. For higher biasing voltages ($|V_S| > 60$ V), the density is found to increase slowly until it reaches a value of $\sim$2.91 g/cm^3 at $V_S = -108$ V.

The increase of the density with substrate biasing indicates that the ion bombardment favors the growth of more densely packed films and reduces the presence of pores and microvoids. The density increase observed with $|V_S|$ values of up to 20 V is believed to be a result of the beneficial "soft-hammering" effect of ion bombardment, which can contribute to increase the mobility of the adatoms at the surface of the films. In contrast, the additional increase of the density observed for $|V_S| > 60$ V can be attributed to the TiO_2 phase enrichment of the films (i.e., increasing [Ti]/[Si] ratio; see Fig. 7). Indeed, as the [Ti]/[Si] ratio is increased, the density of the films is expected to increase toward the ultimate density of amorphous TiO_2 films ($\sim$3.8 g/cm^3).[18]

Figure 9 shows the effect of V_S on the thickness of the films (in $atoms/cm^2$ units) as determined by both XRR and RBS measurements.[37] The thickness values obtained from both techniques are in good agreement. It is clearly seen that the thickness of the titanium silicate thin films is affected by the value of the applied bias voltage. While it remains almost unchanged for $|V_S|$ values of up to $\sim$40 V, it decreases significantly at higher bias voltages. At $V_S = -108$ V, the thick-

ness is found to be ~10% lower compared to the films deposited at low biasing values. This decrease strongly suggests the occurrence of resputtering during the growth of the titanium silicate films under high substrate biasing.[38] Indeed, when a high bias voltage is applied, the ions bombarding the substrate can acquire enough energy to sputter off the films.[31,32,34,39–41] Figure 9 suggests that the bias voltage threshold for which the resputtering becomes appreciable is around $V_S \sim -40$ V for the titanium silicate films. This threshold is consistent with the values reported for TiN, ZrO_2, and CdO films for which resputtering typically appears when the negative bias voltage reaches roughly 40–60 V.[39–41] Finally, it is noteworthy that the occurrence of resputtering of the titanium silicate films during their growth strongly suggests that the observed increase of the [Ti]/[Si] ratio for $|V_S|$ values higher than 40 V (see Fig. 7) is caused by the preferential sputtering of the Si atoms of the films.

C. Discussion

The structural characterizations of the titanium silicate films provided interesting insights to better understand the effect of the substrate bias voltage on their electrical properties. First, the improvement of the electrical properties of the films observed as $|V_S|$ is increased from 0 to 20 V (see Figs. 1–3) correlates well with the film densification revealed by XRR in the same bias voltage range [Fig. 8(b)]. Indeed, the increase of the films density is naturally accompanied with a decrease of the density of pores and/or microvoids in the films, thereby reducing the absorption of moisture and other gaseous contaminants in the films. Thus, the film densification caused by a bias voltage of about −15 V is believed to be at the origin of the improved electrical properties of the films (dispersion, dielectric losses, leakage currents, and breakdown fields). Second, by increasing the bias voltage beyond 40 V, the titanium silicate films are shown to become more Ti rich (as a result of a preferential resputtering of Si atoms from the surface of the growing film), thereby explaining the measured enhancement of their dielectric constant. Moreover, at $|V_S| > 40$ V, the increasing energetic Ar ion bombardment causes either some Ar ion incorporation into the growing films (as confirmed earlier by our RBS measurements) and/or the creation of some oxygen vacancies in the films (as a result of preferential oxygen sputtering which is well known to occur for oxides[40,42]). The presence of such Ar impurities and, more importantly, O vacancies is a highly plausible explanation for the noticeable degradation of the leakage current densities of the films deposited with high biasing voltages (see Fig. 3). (Oxygen vacancies have been previously shown to deteriorate markedly the electrical properties of titanium silicate thin films.[16]) In fact, O vacancies (even at doping levels) can drastically affect the electrical properties of insulating oxides. As a consequence, it is not astonishing to have O vacancies of which content is low enough to be detected by either XPS or RBS (a reason why such discussion cannot be invoked earlier in the article) but high enough to affect drastically the leakage current of the titanium silicate films.

In sum, the best electrical properties are obtained for substrate biasing conditions that improve significantly the films density while keeping the level of ion bombardment induced damages (resputtering, oxygen vacancies, defects, etc.) the lowest possible. The present work points up a V_S of about −15 V as the optimal biasing voltage for high-*k* titanium silicate films exhibiting a combination of excellent electrical properties.

IV. CONCLUSION

The effect of the substrate bias voltage on the structural and electrical properties of sputtered high-*k* titanium silicate thin films grown at room temperature has been investigated. It is shown that substrate biasing can be advantageously used to improve the electrical properties of the films. In the present work, we were thus able to demonstrate that the dielectric losses and the leakage current of the films can be markedly improved by applying an optimal bias voltage of ~−15 V during their growth. Under this optimal substrate biasing condition, titanium silicate films combining a dielectric constant of ~17, a leakage current as low as 5×10^{-9} A/cm^2 at 1 MV/cm, and a dissipation factor <0.01 were obtained. This highly attractive combination of electrical properties is correlated with the film densification that results from a soft-hammering effect occurring at moderate ion-bombardment conditions ($V_S \sim -15$ V). On the other hand, higher biasing voltages are not beneficial anymore and tend to provoke Ti enrichment of the films (due to preferential resputtering of Si atoms) and creation structural defects. In this energetic ion-bombardment regime, the dielectric constant increases (due to Ti enrichment of the films) but the leakage currents particularly degrade. This work highlights the importance of the optimization of ion-bombardment conditions (through substrate biasing) to grow titanium silicate films with optimal electrical properties. The key point is to take advantage of the ion bombardment to densify "gently" the films while favoring surface mobility without reaching the resputtering threshold. Finally, our results demonstrate the possibility of growing high-quality dielectric thin films at room temperature, opening thereby a new prospect for back-end advanced MIM capacitor applications.

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[1]Semiconductor Industry Association, *The International Technology Roadmap for Semiconductors (ITRS)*, 2005 ed. (International SEMATECH, Austin, TX, 2005).
[2]G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **89**, 5243 (2001).
[3]H. Wong and H. Iwai, Microelectron. Eng. **83**, 1867 (2006).
[4]J. J. Chambers and G. N. Parsons, J. Appl. Phys. **90**, 918 (2001).
[5]G. D. Wilk, R. M. Wallace, and J. M. Anthony, J. Appl. Phys. **87**, 484 (2000).

[6]A. Paskaleva, A. J. Bauer, M. Lemberger, and S. Zurcher, J. Appl. Phys. **95**, 5583 (2004).
[7]S. Regnery, R. Thomas, P. Ehrhart, and R. Waser, J. Appl. Phys. **97**, 073521 (2005).
[8]X. F. Yu, C. X. Zhu, H. Hu, A. Chin, M. F. Li, B. J. Cho, D. L. Kwong, P. D. Foo, and M. B. Yu, IEEE Electron Device Lett. **24**, 63 (2003).
[9]S. J. Kim, B. J. Cho, M. F. Li, X. F. Yu, C. X. Zhu, A. Chin, and D. L. Kwong, IEEE Electron Device Lett. **24**, 387 (2003).
[10]S. Y. Lee, H. Kim, P. C. McIntyre, K. C. Saraswat, and J. S. Byun, Appl. Phys. Lett. **82**, 2874 (2003).
[11]C. Durand, C. Vallee, V. Loup, O. Salicio, C. Dubourdieu, S. Blonkowski, M. Bonvalot, P. Holliger, and O. Joubert, J. Vac. Sci. Technol. A **22**, 655 (2004).
[12]S. B. Chen, C. H. Lai, A. Chin, J. C. Hsieh, and J. Liu, IEEE Electron Device Lett. **23**, 185 (2002).
[13]S. Blonkowski, M. Regache, and A. Halimaoui, J. Appl. Phys. **90**, 1501 (2001).
[14]M. Y. Yang, D. S. Yu, and A. Chin, J. Electrochem. Soc. **151**, F162 (2004).
[15]D. K. Sarkar, E. Desbiens, and M. A. El Khakani, Appl. Phys. Lett. **80**, 294 (2002).
[16]D. Brassard, D. K. Sarkar, M. A. El Khakani, and L. Ouellet, J. Vac. Sci. Technol. A **22**, 851 (2004).
[17]D. Brassard and M. A. El Khakani, J. Appl. Phys. **98**, 054912 (2005).
[18]D. Brassard, D. K. Sarkar, L. Ouellet, and M. A. El Khakani, J. Vac. Sci. Technol. A **24**, 600 (2006).
[19]D. Brassard, L. Ouellet, and M. A. El Khakani, IEEE Electron Device Lett. **28**, 261 (2007).
[20]D. K. Sarkar, D. Brassard, M. A. El Khakani, and L. Ouellet, Thin Solid Films **515**, 4788 (2007).
[21]T. Kamada, M. Kitagawa, M. Shibuya, and T. Hirao, Jpn. J. Appl. Phys., Part 1 **30**, 3594 (1991).
[22]T. Busani, R. A. B. Devine, X. K. Yu, and H. W. Seo, J. Vac. Sci. Technol. A **24**, 369 (2006).
[23]R. C. Smith, N. Hoilien, C. Dykstra, S. A. Campbell, J. T. Roberts, and W. L. Gladfelter, Chem. Vap. Deposition **9**, 79 (2003).
[24]S. Larouche, H. Szymanowski, J. E. Klemberg-Sapieha, L. Martinu, and S. C. Gujrathi, J. Vac. Sci. Technol. A **22**, 1200 (2004).
[25]X. T. Gao and I. E. Wachs, Catal. Today **51**, 233 (1999).
[26]A. Ennaoui, B. R. Sankapal, V. Skryshevsky, and M. C. Lux-Steiner, Solar Energy Mater. Solar Cells **90**, 1533 (2006).
[27]X. R. Wang, H. Masumoto, Y. Someno, and T. Hirai, Thin Solid Films **338**, 105 (1999).
[28]P. H. Giauque, H. B. Cherry, and M. A. Nicolet, Microelectron. Eng. **55**, 183 (2001).
[29]K. L. Choy, Prog. Mater. Sci. **48**, 57 (2003).
[30]S. M. Rossnagel, J. Vac. Sci. Technol. A **21**, S74 (2003).
[31]J. A. Thornton, J. Vac. Sci. Technol. A **4**, 3059 (1986).
[32]J. L. Vossen, J. Vac. Sci. Technol. **8**, S12 (1971).
[33]R. Messier, A. P. Giri, and R. A. Roy, J. Vac. Sci. Technol. A **2**, 500 (1984).
[34]J. H. Kim and K. W. Chung, J. Appl. Phys. **83**, 5831 (1998).
[35]B. Gallas, A. Brunet-Bruneau, S. Fisson, G. Vuye, and J. Rivory, J. Appl. Phys. **92**, 1922 (2002).
[36]A. Gibaud and S. Hazra, Curr. Sci. **78**, 1467 (2000).
[37]RBS measurements directly yield the film thickness in atoms/cm^2. This thickness can also be independently determined by taking into account the films composition, their physical thickness (in nm) and the density (in g/cm^3) provided by XRR analysis. (It is to be recalled here that these thicknesses correspond to the films deposited with the same deposition time of 90 min.)
[38]The amount of material sputtered from the target during the deposition of the titanium silicate films is independent of the bias voltage applied on the substrate (as confirmed by using an unbiased microbalance). Thus, the observed variation of the thickness shown in Fig. 9 is not caused by a change in the flux of the incoming sputtered species, but rather indicates some material loss (through resputtering) from the growing films submitted to high bias voltages.
[39]P. M. Babu, G. V. Rao, P. S. Reddy, and S. Uthanna, J. Mater. Sci.: Mater. Electron. **15**, 389 (2004).
[40]J. E. Greene, R. E. Klinger, L. B. Welsh, and F. R. Szofran, J. Vac. Sci. Technol. **14**, 177 (1977).
[41]N. Jiang, H. J. Zhang, S. N. Bao, Y. G. Shen, and Z. F. Zhou, Physica B (Amsterdam) **352**, 118 (2004).
[42]M. M. Yang, T. M. Reith, and C. J. Lin, J. Vac. Sci. Technol. A **8**, 3925 (1990).