Fabrication of rutile TiO_2 thin films by low-temperature, bias-assisted cathodic arc deposition and their dielectric properties

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The use of rutile-type titanium dioxide (TiO_2) thin films as advanced gate dielectrics has been hampered by thermodynamic instability during the high deposition or annealing temperature of 800 °C. In this work, we demonstrate that rutile-type TiO_2 thin films can be produced on *p*-type Si (100) at lower substrate temperature by means of bias-assisted cathodic arc deposition. The influence of the substrate bias on the microstructural and dielectric characteristics of the TiO_2 thin films is investigated in detail. Our results show that by applying a suitable bias to the Si substrate, as-deposited rutile-type TiO_2 thin films can be obtained at 450 °C. The permittivity of the materials increases significantly from 21 up to 76. The interfacial and electrical properties of TiO_2/Si (100) are also improved. The effects and mechanism of the bias on the microstructural and dielectric characteristics are described.

I. INTRODUCTION

The high integrated circuit density and performance demanded by the microelectronics industry requires thin gate dielectric layers. The use of SiO_2-based thin films as the gate oxide dielectric is quickly reaching a limitation due to the rapid increase in the tunneling current causing unsustainably large energy consumption and worsened device reliability.[1–3] One solution being extensively explored is to increase the capacitance by replacing SiO_2-based dielectrics with higher permittivity ones.[4] Among various high-*k* materials, titanium dioxide (TiO_2) is a possible substitute for silicon dioxide as storage capacitors in dynamic random-access memory (DRAM) and gate oxides in field effect transistors (FET) because its rutile phase has a high-dielectric constant of approximately 80 and good thermal stability on Si.[5,6] Another polymorph of TiO_2 is the anatase phase which is a metastable state at temperatures below 600 °C and whose dielectric constant is about 30, smaller than that of the rutile phase. It can be transformed to the rutile phase during deposition or postannealing at temperatures higher than 800 °C.[7] However, it is difficult to control the interfacial layer between TiO_2 and Si as an interfacial layer can easily be formed during high-temperature deposition or postannealing, thereby canceling the benefits of the high-dielectric constant.[8] This issue is also one of the serious challenges in the use of metal-oxide films as high-*k* gate dielectrics because even a very thin interlayer of low-*k* material can decrease the capacitance of the stack so much that the electrical property of the device degrades.[9] Therefore, it is necessary to control the crystallization temperature and to obtain rutile-type TiO_2 thin films at low substrate temperatures to suppress the formation of the interfacial layer.[10] Recently, it is believed that the application of a sample bias during fabrication is an effective way to increase both the ionization density and the energy of incoming particles from the gas phase onto the surfaces, so it is beneficial to improve the microstructure of the thin films.[11]

In this work, TiO_2 thin films were prepared on *p*-type Si (100) wafers at low substrate temperature by bias-assisted cathodic arc deposition. The influence of the substrate bias on the microstructural and dielectric characteristics of the thin films was investigated. Our results show that by using a higher substrate bias, as-deposited rutile-type TiO_2 thin films can be obtained at 450 °C, and the electrical properties of Au/TiO_2/Si metal-oxide-semiconductor (MOS) structure were obviously improved. Our study suggests that substrate bias assistance can effectively control the crystallization and interface of the TiO_2/Si structure. The underlying mechanism and

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effects of the substrate bias on the thin film are also discussed in this paper.

II. EXPERIMENTAL DETAILS

TiO_2 thin films were fabricated on *p*-type, 100 mm Si (100) wafers with resistivity of 4–7 Ω·cm using a bias-assisted magnetic filtered cathodic arc system. The experimental apparatus used in this study mainly included a magnetic duct and cathodic arc plasma source as shown in Fig. 1. A curved magnetic duct was inserted between the plasma source and main chamber to remove macro-particles produced in the cathodic arc plasma.[12] The cathode used in our experiments was a 99.9% pure Ti rod with a diameter of 1 cm, and oxygen gas was bled into the arcing region as shown in Fig. 1. The arc was ignited within the pulse duration of about 100 μs and repetition rate of 60 Hz. The degree of the titanium discharge was controlled by the main arc current between the cathode and anode. The cathodic arc plasma composed of titanium and oxygen was guided into the vacuum chamber by an electromagnetic field applied to the curved duct. The duct was biased to −20 V to build up a lateral electric field while the external solenoid coils wrapped around the duct produced the axial magnetic field with the magnitude of 100 G. The substrate temperature controlled by a heating assembly mounted below the stainless steel substrate holder was measured by a chromel-alumel thermocouple attached to the backside of the Si substrate. The vacuum chamber was pumped down using a turbomolecular pump to a base pressure below 1×10^{-7} Torr. Prior to film deposition, the samples positioned about 15 cm away from the exit of the plasma stream were cleaned by 99.99% pure argon plasma for 2 min using a sample bias of −1 kV to avoid contamination of the thin film. After pre-sputtering, the chamber was re-evacuated to a base pressure of 1×10^{-7} Torr.

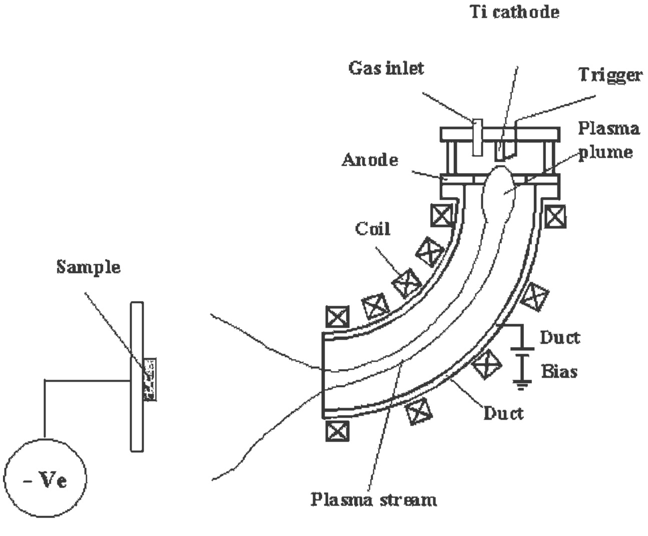

FIG. 1. Schematic diagram of the bias-assisted magnetic filtered cathodic arc system.

The composition of the thin films was determined by Rutherford backscattering spectrometry (RBS) using a 2 MeV $^4He^{++}$ beam and a backscattering angle of 170°. Microstructural analyses were carried out using a Perkin Elmer Fourier transform infrared (FTIR) spectrometer and Philip X-ray diffractometer (Eindhoven, The Netherlands) in a θ-2θ configuration and Cu K_α radiation. The thickness and interfacial microstructure of the TiO_2 thin films on Si (100) were evaluated by cross-sectional high-resolution transmission electron microscopy (Philips CM20 FEG-TEM). The surface morphology was evaluated by contact mode atomic force microscopy (AFM) performed using a Nanoscope III manufactured by Digital Instruments (US) over a scanned area of 5 μm^2. The electrical characteristics of the $Au/TiO_2/Si$ MOS capacitor with an electrode area of 7.85×10^{-5} cm^2 fabricated by evaporation were measured using an HP4284A precision inductance-capacitance-resistance (LCR) meter and HP4140B pA Meter/direct current (dc) source, respectively (Hewlett-Packard, US).

III. RESULTS AND DISCUSSION

The elemental composition of thin film influences the structural and electrical properties and RBS was used to characterize our materials.[13] Figures 2(a), 2(b), and 2(c) display the RBS spectra that show both the experimental and fitted results acquired from different substrate biasing samples. The results indicate that stoichiometric TiO_2 thin films were formed and that the composition of the thin films produced under different substrate biases was basically uniform throughout the thickness. These good results are in part due to the effective elimination of Ti macro-particles formed in the cathodic arc using the curved magnetic filter. The process efficacy can be evaluated according to the simulation results of the titanium contents in the layer.[12] It can clearly be observed from the RBS spectra that the thicknesses of the thin films produced under different conditions are different; that is, the growth rate decreases as the substrate bias increases. This is in agreement with the results acquired from the as-deposited TiO_2 thin films measured by a Seimitzu Surfcom 480A profiler (Japan) as shown in Fig. 3.

Figure 4 shows the x-ray diffractometer (XRD) results of the samples deposited at 450 °C under different substrate biases. The unbiased thin film exhibits no diffraction peaks signifying an amorphous phase. When a bias of −200 V is applied to the substrate, diffraction peaks at 25.28°, 37.80°, and 55.06° emerge corresponding respectively to the (101), (004), and (211) planes of the anatase TiO_2 phase.[14] The results indicate crystallization of the TiO_2 thin films and formation of the anatase phase. Besides, the diffraction peak at 27.45° corresponding to

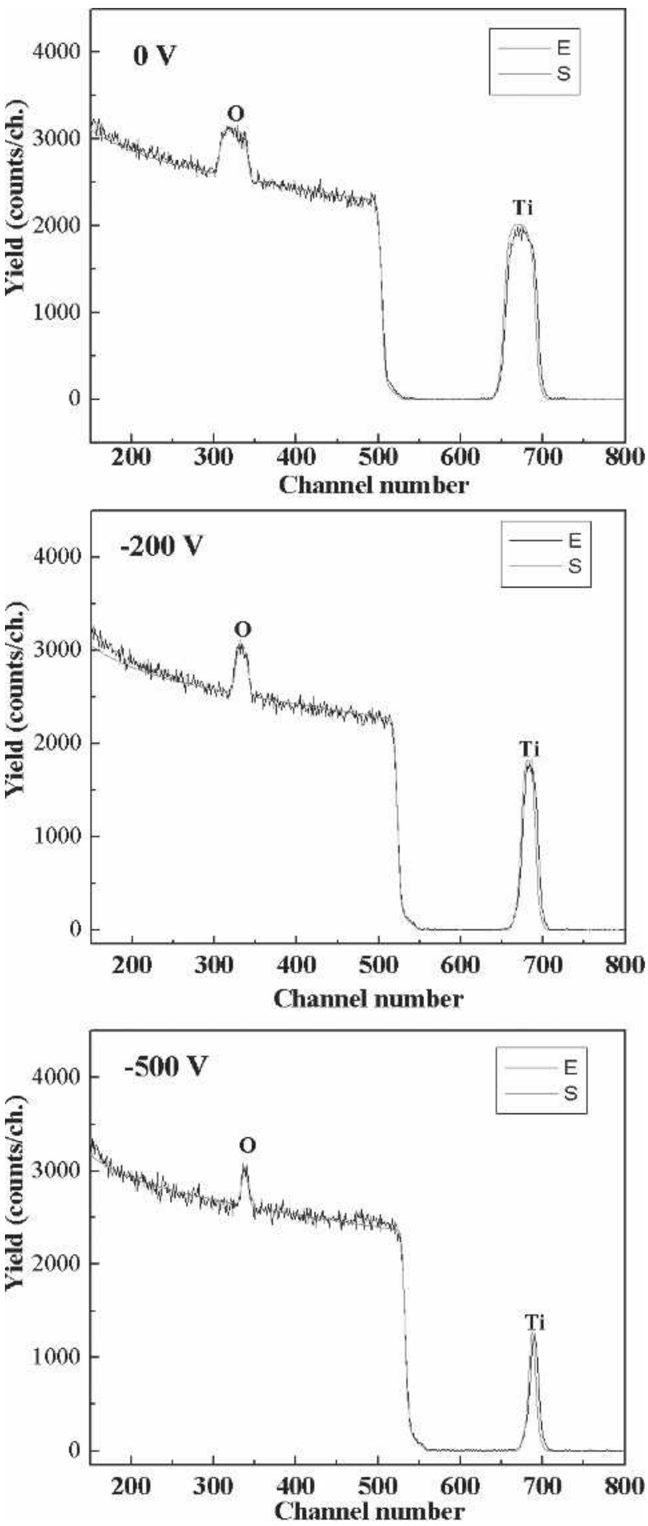

FIG. 2. Experimental and fitted RBS spectra acquired from the TiO_2 deposited under different biasing conditions at 450 °C.

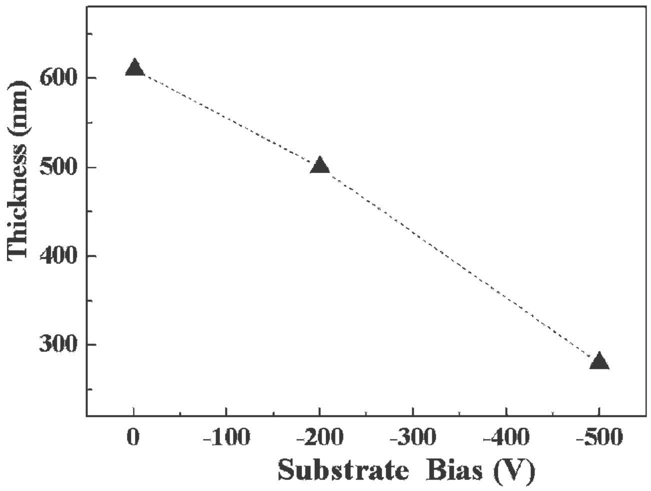

FIG. 3. Thickness of TiO_2 thin films as a function of the substrate bias.

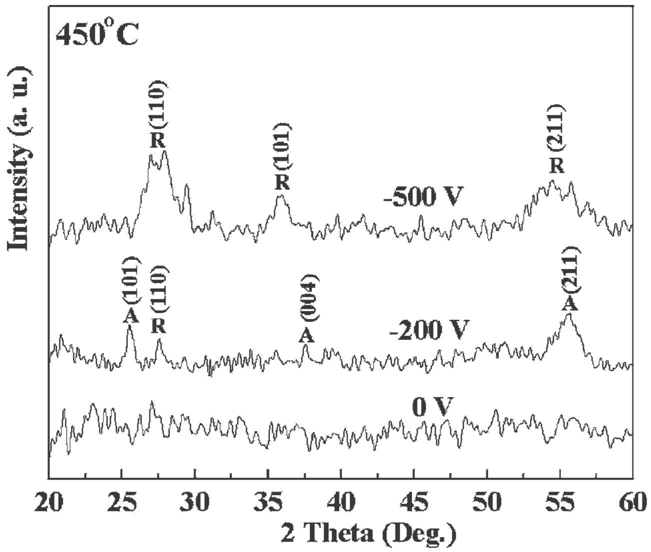

FIG. 4. XRD spectra of TiO_2 thin films prepared under different biasing conditions at 450 °C.

(110) planes of rutile TiO_2 phase also appears.[15] As the substrate bias further increases to −500 V, the diffraction peaks at 27.45°, 36.08°, and 54.32° appear corresponding respectively to the (110), (101), and (211) planes of the rutile TiO_2 phase, and no other diffraction peaks are detected.[15] This suggests that rutile-type TiO_2 thin films can be formed on the silicon substrate at low temperatures by using the proper biasing assistance. The overall biasing effects on the crystallization of the TiO_2 thin films can be attributed to the interactions between the positive ions accelerated from the plasma and the atoms on the surface. A higher substrate bias increases the number of positive ions with high energy. Diffusion of the incident particles and relaxation of the surface are also expected to be enhanced by the collisions between the impacting ions and substrate atoms.[16]

Further studies of the substrate bias on the interfacial microstructure between the TiO_2 thin films and Si substrate were carried out using Fourier transform infrared (FTIR) spectroscopy. The Si–O vibrational mode is

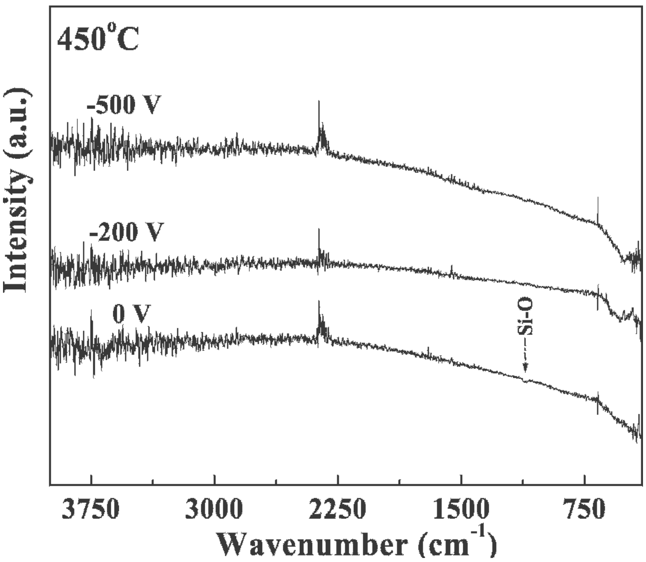

FIG. 5. FTIR spectra of TiO$_2$ thin films prepared under different biasing conditions at 450 °C.

very sensitive and easy to detect in the FTIR spectra.[17] Figure 5 shows the FTIR spectra of the TiO$_2$/Si thin films deposited at 450 °C under different biases from 0 V to −500 V. The thin films without biasing exhibit an absorption peak located near 1060 cm^{-1} corresponding to the Si–O vibrational mode, implying the formation of some SiO$_x$ at the interface.[18] Besides, the peak of Ti–O vibrational modes located at 430 cm^{-1} is on the verge of the mid-infrared range between 4000 and 400 cm^{-1}, it cannot be unequivocally identified.[19] As the substrate bias increases, the intensity of the Si–O absorption peak obviously weakens. In particular, at a substrate bias of −500 V, the Si–O absorption peaks almost disappears, indicating that at higher substrate biasing, the interfacial structure of the TiO$_2$/Si thin films can be optimized. Ono et al. suggested that the formation of the interfacial layer depended on neither the thickness of oxide films nor the annealing atmosphere, but rather the deposition or annealing temperature.[20] In our experiments, the substrate bias does not affect the deposition temperature but aids to generate energetic ions that participate in the growth of the thin films through sputtering, atomic mixing, densification, enhanced migration of adatoms, and field-enhanced diffusion via charging.[21] Therefore, our results suggest that by using a negative substrate bias, the interfacial layer with low permittivity is reduced, thereby boding well for the dielectric properties of the thin films.

To further verify the effects of the substrate bias on the microstructure of TiO$_2$/Si, high-resolution transmission electron microscopy (HRTEM) was conducted and the results acquired under different biases are displayed in Figs. 6(a), 6(b), and 6(c). The cross-sectional transmission electron microscopy (TEM) images confirm that the TiO$_2$ thin film prepared without biasing has an amorphous phase whereas the bias-assisted samples are polycrystalline, and the results are in good agreement with the XRD results. Moreover, the interfacial microstructure of the thin film deposited at high bias assistance is obviously improved. The sample without biasing shows a 2-nm-thick interfacial layer, which mainly consists of SiO$_x$ and is easy to detect by FTIR spectroscopy. When a substrate bias is introduced, a visible interlayer can be observed in the −200 V sample, and the thickness increases slightly, which may be because mixed phases emerge in the thin film and the Ti–Si–O interlayer can be easily formed. When the substrate bias further increases to −500 V, the thickness of the interfacial layer diminishes apparently. This can be attributed to the formation of a pure rutile-phase TiO$_2$ thin film under high substrate bias assistance. It can block the diffusion of oxygen into the interfacial area and suppress the formation of the

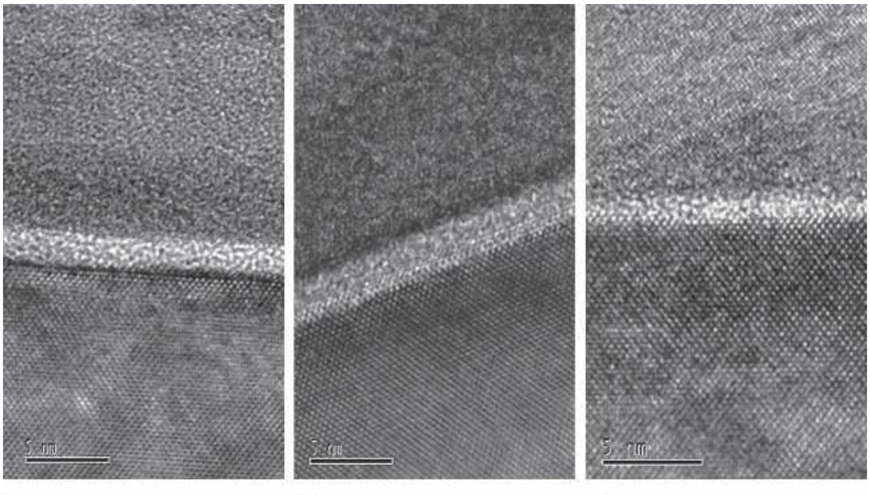

FIG. 6. HRTEM images of TiO$_2$ thin films prepared at 450 °C under different biasing conditions: (a) 0 V, (b) −200 V, and (c) −500 V.

Ti–Si–O interlayer. The results are in agreement with the FTIR results. Based on these data, it can be concluded that negative bias assistance is beneficial to the fabrication of rutile-type TiO_2 thin films at lower temperature and the interfacial structure can also be improved.

The surface morphology and roughness of the thin films were assessed by AFM in the contact mode, and the results of representative samples prepared under different conditions are displayed in Fig. 7. Amorphous particles on the thin films without biasing are clearly seen in Fig. 7(a). Regular surface features are observed on the samples fabricated by substrate biasing as seen in Figs. 7(b) and 7(c). In addition, as the thin film crystallizes and the mean size of the grains increases, the surface of the crystallized thin film becomes rougher, as shown in Fig. 7. It further corroborates that better crystallization can be achieved at low substrate temperature under a negative substrate bias.

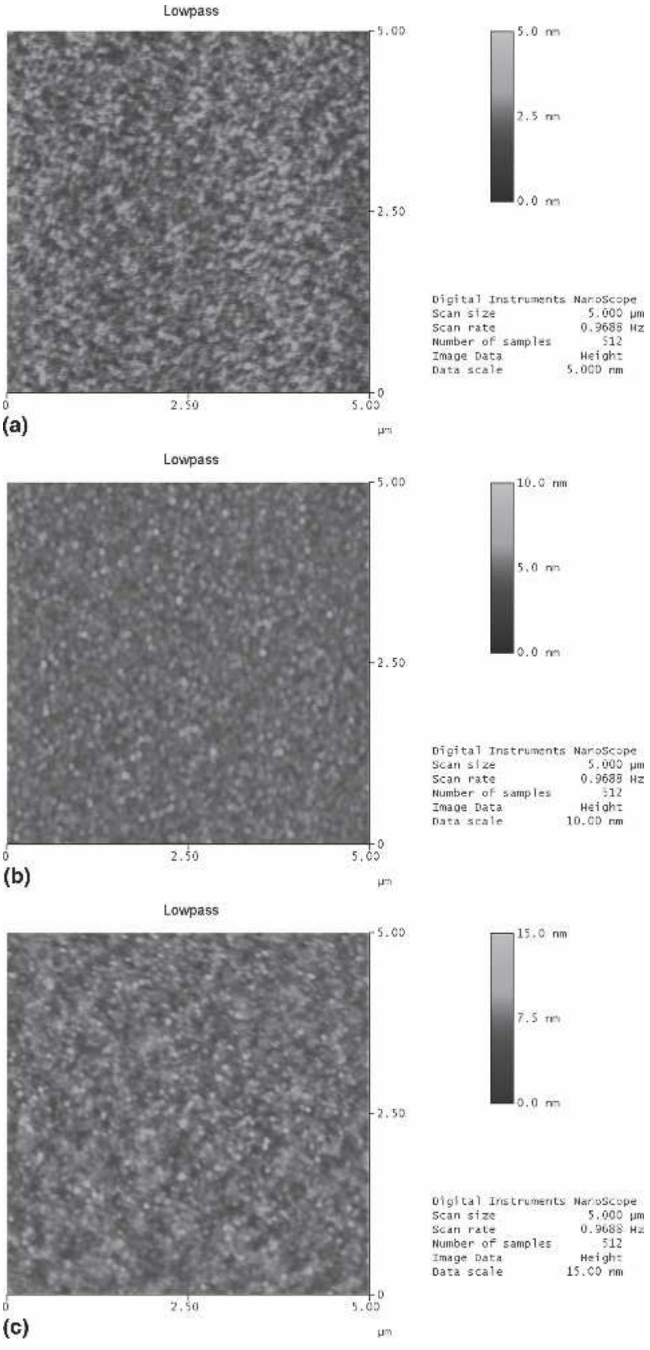

FIG. 7. AFM images of TiO_2 thin films prepared at 450 °C under: (a) 0 V, (b) −200 V, and (c) −500 V substrate bias.

The dielectric performance of the thin films is of interest because rutile-type TiO_2 thin films with higher permittivity are suitable for new-generation thin film capacitors.[22] Therefore, the dielectric properties of the thin films deposited at low substrate temperature under different biases were measured by *C-V* and *I-V* tests. The permittivity of the dielectric thin films can be calculated according to the *C-V* curve. Figures 8(a), 8(b), and 8(c) display the *C-V* curves of the as-deposited Au/TiO_2/Si MOS structure undert different substrate biases from 0 V to −500 V. The permittivity of the thin films as a function of the substrate bias is also shown in Fig. 8(d). It can be seen that as the substrate bias increases, the saturated capacitance value is enhanced, which corresponds to the improvement of the ability to save electrical charges in the Au/TiO_2/Si MOS structure. It also means a larger permittivity. That is, the relative dielectric constant k of the as-deposited rutile-type TiO_2/Si sample at a substrate bias of −500 V can reach about 76, while that of the amorphous and anatase phase reaches 21 and 34, respectively, as shown in Fig. 8(d). This high-dielectric constant is believed to originate from the formation of the rutile phase at a higher substrate bias assistance as confirmed by the XRD results.[8] Meanwhile, it can be seen that the flatband in the *C-V* curves shifts toward the negative voltage direction as the substrate bias increases and the flatband voltage V_{fb} extracted from the *C-V* curve of the as-deposited TiO_2 at a bias of −500 V is close to zero. This V_{fb} value indicates that the MOS structure of the TiO_2 gate dielectric layer has a few trapping charges, which can result from the formation of excellent microstructural TiO_2 gate dielectric thin films.[23] Therefore, the use of a suitable substrate bias can be beneficial to enhance the dielectric properties of the as-deposited TiO_2 thin films.

Figure 9 shows the forward-and-reverse *J*-V curves of the Au/TiO_2/Si structure under different substrate biasing conditions. The leakage current densities are 10^{-3}A/cm^2 of 0 V bias, 10^{-5}A/cm^2 of −200 V bias, and 10^{-6}A/cm^2 of −500 V bias, respectively, at the saturated electric field. This implies that the leakage current density of the thin films decreases as the substrate bias increases. It can be attributed to that the microstructural and interfacial characteristics of the thin films are improved as the substrate bias is introduced. Furthermore, when a negative test voltage is applied to the Au electrode, the leakage

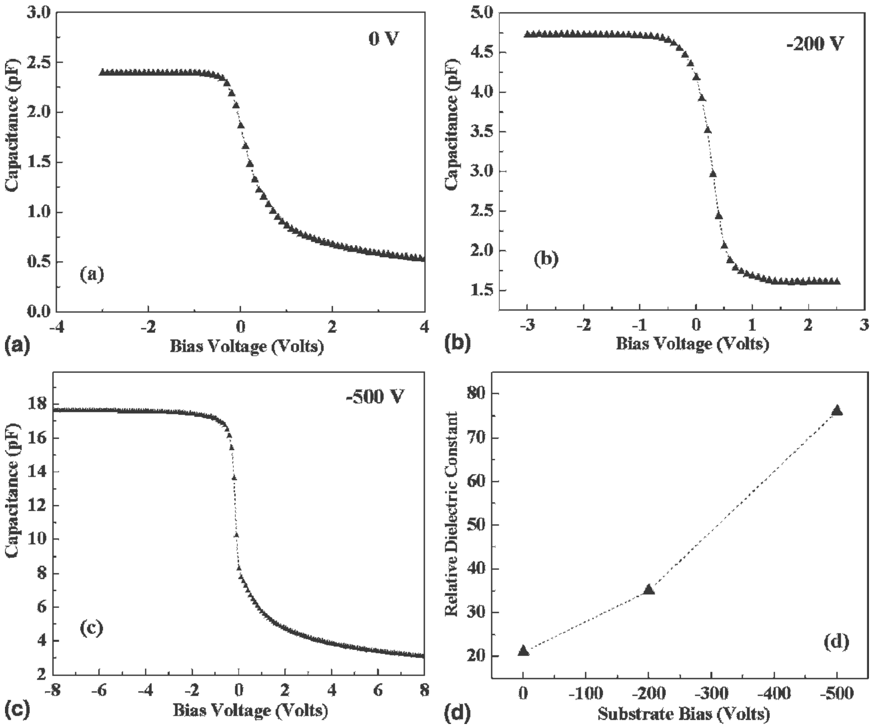

FIG. 8. *C-V* curves of the as-deposited Au/TiO_2/Si MOS structure at 450 °C under different substrate biases measured at a frequency of 1 MHz: (a) 0 V, (b) −200 V, and (c) −500 V, respectively. The relative dielectric constant ϵ_r of TiO_2 thin films prepared at 450 °C as function of substrate biases is shown (d).

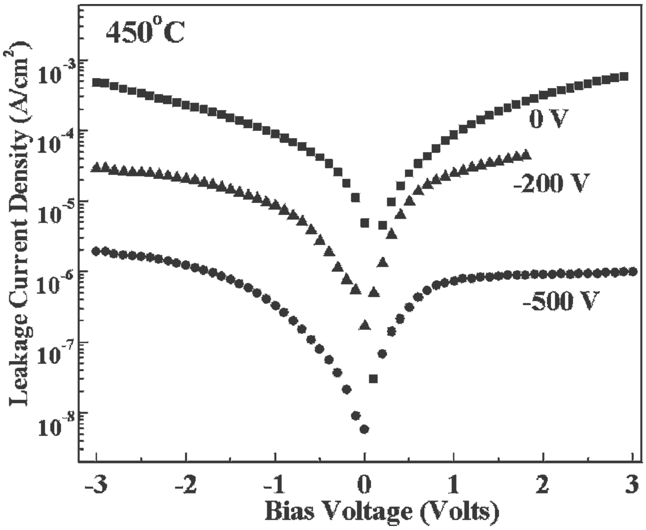

FIG. 9. Forward-and-reverse *J-V* curve of TiO_2 thin films prepared at 450 °C under different substrate biases.

current density is slightly higher than that measured under a positive voltage. It may be due to the difference in the work function ($\Delta W_{\text{Au}-p\text{-Si}}$) between the Au electrode and *p*-type Si substrate and has been reported by Wolf et al.[24] Our results therefore suggest that it is possible to obtain the as-deposited rutile-type TiO_2 thin films with high dielectric properties at low substrate temperature by using a different degree of substrate biasing. Because of the simplicity of this method, it can be readily applied to the synthesis of other dielectric materials.

IV. CONCLUSION

TiO_2 thin films as alternative gate dielectrics deposited by a bias-assisted hybrid cathodic arc system have been demonstrated. By applying the proper substrate bias assistance, as-deposited rutile-type TiO_2 thin films have been obtained at 450 °C. The permittivity of the materials increases significantly from 21 up to 76 due to the formation of rutile phase induced by higher biasing. Besides, the interfacial and electric properties of TiO_2/Si (100) are also improved. Our results suggest a means to fabricate as-deposited rutile-type TiO_2 thin films with optimized interfacial and dielectric properties at low temperature using substrate biasing.

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