Fabrication and Electrical Properties of Titanium Oxide by Thermally Oxidizing Titanium on Silicon*

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Abstract: Polycrystalline titanium oxide films are fabricated on silicon by thermally oxidizing titanium. The current-voltage and capacitance-voltage characteristics of the $Ag/TiO_x/Si/Ag$ capacitors are measured. The thickness of the titanium oxide films arranges from 150nm to 250nm, and their dielectric constants are within 40~ 87. As the oxidation time is shortened, the fixed charges of the titanium oxide films become less and the leakage current characteristics become better.

Key words: high k materials; thermally oxidation; DC magnetron sputtering

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1 Introduction

The sustained growth in VLSI technology is fueled by the continued shrinking of transistors to ever smaller dimensions. But the scaling MOSFETs down to sub-100nm face the challenges when SiO_2 is used as gate dielectric. The thickness of gate oxide in sub-100nm MOSFETs is projected to be mere 1.5nm[1]. Thus the electrons can tunnel through the gate oxide easily, which increases the static power. The boron penetrates through the thinner oxide, which results in a higher concentration of boron in the channel region. Then, a change in channel doping causes a drift in threshold voltage in an unacceptable way. The alternative solution is to use high k dielectric materials with higher dielectric constant for thicker thickness of gate dielectric with the same electric field. The alternative gate oxides have been studied for over 40 years. Such subject is drawing more attention to study presently[2].

A variety of metal oxides, including Al_2O_3, Y_2O_3, Gd_2O_3, Ta_2O_5, La_2O_3, HfO_2, ZrO_2, and TiO_x, have been suggested as high-k replacements for silicon dioxide. Among them titanium oxide has been studied extensively for application to optical and microelectronic technologies[3~9]. Titanium reacts with oxygen easily, and titanium oxide can be fabricated by various thin-film deposition techniques such as evaporation, ion beam techniques, chemical vapor deposition techniques, sol-gel method, reac-

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tive DC, or RF diode or magnetron sputtering. DC magnetron sputtering has been known for a long time for the deposition of compound films from elemental targets. But there is little research on the preparation for titanium oxide by directly thermally oxidizing titanium on silicon.

In our previous work[10], we studied the impact of the high k dielectric on the whole MOSFETs. In this paper, the fabrication of titanium oxide films on silicon and their electrical properties are being studied.

2 Experiment

A planar magnetron sputtering apparatus was used in this study. A water-cooled titanium target (99.99% of purity) of 64mm in diameter was positioned at the center of the lid of the stainless steel vacuum chamber above the substrate holder. The space of target-substrate was 40mm. The background pressure in the process chamber was 3×10^{-3}Pa. The depositions were carried out in pure Ar 99.99% at pressure ranging from 15 to 17Pa with substrates kept at ground potential. A constant current supply was used to keep the target current at 200mA for all titanium oxide films' depositions, which result in target voltages between 250 and 300V. The substrates used here are n and p conductivity types with a resistivity of 5~ 10Ω·cm and 4~ 7Ω·cm ⟨100⟩ silicon wafers, respectively. Prior to growth, the substrates were ultrasonically cleaned in each of acetone and ethanol, then washed by deionized water. The substrate temperature is room temperature. The target was presputtered in an argon atmosphere for 10min to remove surface oxides on the target. The oxidation of the titanium was done in the chamber. The high-pure oxygen gas was used at atmospheric pressure.

The thickness of titanium films is about 120~ 140nm. The titanium oxide films were formed of thicknesses from 150~ 250nm. And the silver was deposited on the titanium oxide films as top electrode. The electrode area is $100\mu m\times100\mu m$. The silver back contact covering the whole sample was deposited on the back.

3 Results and discussion

Amorphous films will exhibit isotropic electrical properties and will not suffer from grain boundaries. It also can be easily deposited by manufacturable techniques[2]. Very encouraging results were obtained, as both high permittivities and low leakage currents were obtained by Van Dover on TiO_x films to create and to maintain an amorphous film for capacitor applications[9].

The titanium oxide thin-films grown here are polycrystalline which were indicated by XRD measurements, and some factors may affect the growth of the films, such as substrate temperature, the distance between the target and the substrate, and the oxidization time and temperature.

Atomic force microscopy (AFM) is sometimes used to study the surface topography of thin films, here it was used to observe the atomic-scale surface structure of materials like titanium oxide films.

In Fig. 1, the AFM image shows that the root-mean-square roughness of the titanium oxide film is around 2.3nm, which is similar to the results from other researchers. The titanium was deposited on silicon at room temperature and was oxidized at 700℃ for an hour. There were mounds, which can

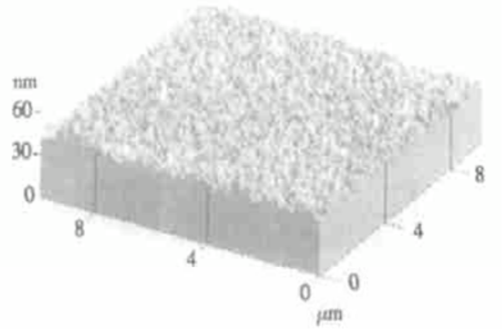

Fig. 1 Atomic force micrograph of titanium oxide The titanium was deposited on silicon at room temperature and oxidized at 700℃ for an hour. The root-mean-square roughness of the titanium oxide film is 2.3nm.

affect the electrical properties of the $Ag/TiO_x/Si$ capacitor, on the surface of TiO_x. Surface may be a factor for the mobility reduction, in fact, the rougher the surface, the more enhanced is the diffuse scattering. The roughness of surface also may dominate the leakage current[11].

The high frequency (1MHz) capacitance-voltage characteristics of the films were also measured. The results in Fig. 2 show that interface state intensity and fixed charge are larger. The values of dielectric constants were higher than 40. The difference of work function for silver and silicon was 0.75. After the titanium was oxidized for 2h, the flat voltage was − 0.199V, but when the oxidation time was 1h, the flat voltage became 0.23V. The result indicates the fixed charges became less.

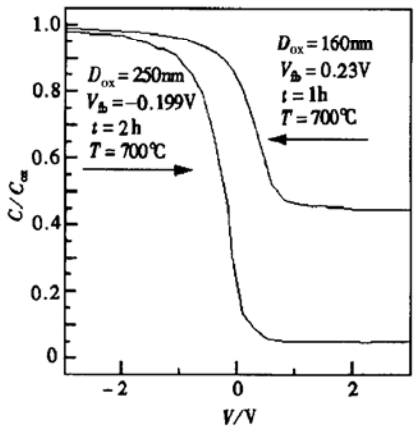

Fig. 2　Capacitances-voltage plots for Ag/TiO_x/p-Si capacitors at 1MHz　D_{ox}: oxide thickness, V_{fb}: flat-band voltage, C_{ox}: oxide capacitance, t: oxidation time, T: oxidation temperature

When a fresh titanium surface is exposed to an oxygen atmosphere, oxygen is absorbed in the titanium and, with passage of time, lower oxides of titanium are expected to form in the first instance. As time progresses further, oxygen has to pass through this initial oxide layer in order to reach the titanium oxide-titanium interface and form fresh oxide. As it passes through the lower oxide, some of the oxygen is expected to be absorbed by the oxide, which is converted into a higher oxide and the remainder is expected to reach the titanium oxide-titanium interface[12].

According to a four-layer model[13], it is possible to estimate the thickness of the titanium dioxide layer (the first layer adjacent to the oxygen atmosphere) upon thermal oxidation in our films. Based on oxygen mass balance and Fick's diffusion law, the change in the layer thickness (h) of titanium dioxide, at time t, can be formulated as

$$\frac{dh}{dt} = \frac{AD^{1/2}}{t^{1/2}2(1-W)}$$

where D is the effective oxygen diffusion coefficient, W is the mass fraction of oxygen, and A is the surface area exposed to oxygen.

So the thickness h can be estimated by:

$$h = \frac{A(Dt)^{1/2}}{(1-W)}$$

This equation is a parabolic expression representing the growth of the titanium dioxide layer upon oxidation. Following a substituting of the appropriate values ($A = 1cm^2$, $W = 0.36$, D which is estimated to be the order of $10^{-12}cm^2/s$ at 700℃, and $t = 1800s$) into this equation, the calculated h is 662.9nm (which is considerably thicker than the sputtered Ti film). According to the calculation above, the Ti film should be completely converted to a near-stoichiometric titanium dioxide at 700℃, within 0.5h under 10^5Pa ambient oxygen pressure. But the films were non-stoichiometric and associated with the formation of a sufficient quantity of oxygen vacancies. If the oxidation time is too long, the non-stoichiometric titanium oxide films may occur[14]. When titanium was oxidized on n-type silicon, the result shown in Fig. 3 is similar. The flat voltage changed from − 0.7V to 0.3V. The fixed charges become less. The titanium film was converted to a near-stoichiometric titanium dioxide at 700℃ by using less oxidation time.

The current-voltage characteristics were also measured. The results are shown in Fig. 4 and Fig. 5. Though the titanium oxide film shown in Fig. 4 is thicker than the titanium oxide film shown in Fig. 5, its leakage current characteristic is worse than that of the film in Fig. 5, which was mainly caused by the long oxidation time.

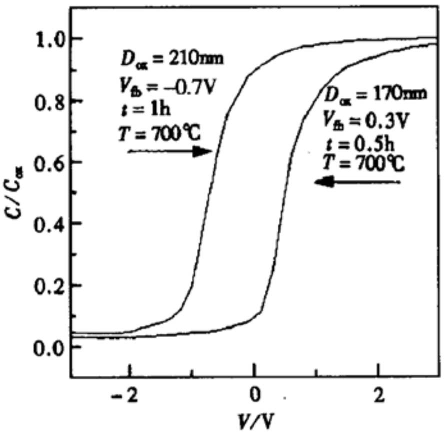

Fig. 3 Capacitances-voltage plots for Ag/TiO$_x$/n-Si capacitors at 1MHz D_{ox}: oxide thickness, V_{fb}: flat-band voltage, C_{ox}: oxide capacitance, t: oxidation time, T: oxidation temperature

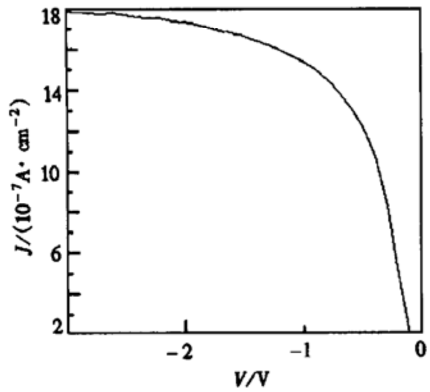

Fig. 4 J-V curve for the Ag/TiO$_x$/p-Si The titanium oxide film thickness is 250nm, the oxidation time is 2h at 700℃.

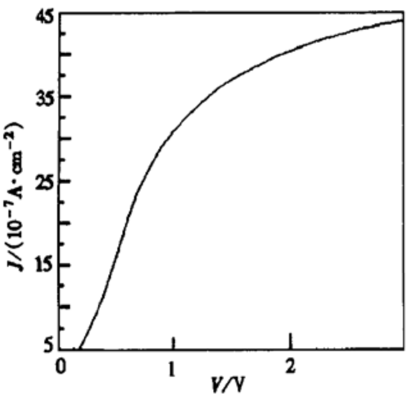

Fig. 5 J-V curve for the Ag/TiO$_x$/n-Si The titanium oxide film thickness is 170nm, and the oxidation time is 0.5h at 700℃.

4 Conclusion

The titanium oxide films were fabricated by oxidizing titanium deposited on silicon. XRD measurements show that these films were polycrystalline. The thickness of the titanium oxide films arranges from 150nm to 250nm. The current-voltage and capacitance-voltage characteristics of Ag/TiO$_x$/Si/Ag capacitors were also measured. The results show the dielectric constants of titanium oxide films are about 40~ 87. A four-layer model was used to explain the diffusion of oxygen in titanium films. As the oxidation time is shortened, the titanium film was converted into a near-stoichiometric titanium dioxide, the fixed charges of the titanium oxide films become less, and the leakage current characteristic becomes better.

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硅上后热氧化钛膜制备氧化钛及其电学特性*

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摘要: 采用在硅上磁控溅射金属钛膜再热氧化的工艺制备了多晶氧化钛薄膜. 测量了 $Ag/TiO_x/Si/Ag$ 电容器的 *I*-*V* 和 *C*-*V* 特性. 结果表明, 氧化钛薄膜的厚度为 150~ 250nm, 其介电常数是 40~ 87. 随着氧化时间的缩短, 氧化钛薄膜中的固定电荷减少, 漏电特性得到改善.

关键词: 高 *k* 材料; 热氧化; 直流磁控溅射

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