Work function dependence of Schottky barrier height and leakage mechanism in thin film capacitors using perovskite dielectrics

氏　　　　名	金　兌映
学 位 の 種 類	博士（学術）
学 位 記 番 号	博甲第 1050 号
学位授与の日付	平成２０年９月２６日
学位授与の要件	課程博士(学位規則第４条第１項)
学位授与の題目	Work function dependence of Schottky barrier height and leakage mechanism in thin film capacitors using perovskite dielectrics （ペロブスカイト誘電体薄膜キャパシタにおけるショットキー障壁高さの仕事関数依存性とリーク電流機構）
論文審査委員（主査）	森本　章治（理工研究域・教授）
論文審査委員（副査）	久米田　稔（理工研究域・教授），黒堀　利夫（人間社会研究域・教授）， 高橋　光信（理工研究域・教授），猪熊　孝夫（理工研究域・准教授）

Doctoral dissertation abstract

Work function dependence of Schottky barrier height and leakage mechanism in thin film capacitors using Perovskite dielectrics

Abstract

The leakage mechanism of metal-insulator-metal(MIM) thin film capacitor using Perovskite dielectrics and bottom noble metal electrodes has been investigated. The leakage behavior through the interface at the top electrode/STO films depends on the surface of the STO films. On the other hand, the leakage current through the interface at the STO/bottom electrodes shows typical interface-limited leakage behavior. The microstructures of bottom electrodes are altered by crystalline orientation, under-layer, and deposition temperature. This microstructure variation leads to a change about 0.16 eV on the work function of metal electrodes measured by PESA. A plot of Schottky barrier heights as a function of work function shows a good linear relationship. It suggests that high work function of the metal electrode is effective in increasing Schottky barrier heights in the dielectric/metal interface, leading effective reduction of the leakage current in MIM capacitors. The tuned microstructure of an electrode appears to be an essential factor in the performance of excellent MIM thin film capacitors.

1. Introduction

The silicon-based metal-oxide-semiconductor devices for the device scaling following Moore's law are being reached in the fundamental limits, and thus demand for replacing silicon dioxide is driving strong interest in high dielectric constant materials (high *K*). The high *K* materials have been widely investigated for an alternative gate oxide and a capacitor. However, the large leakage current problem is still regarded as great obstacle in these applications. Leakage current behavior is one of the major factors to determine the reliability, and it is known that the MIM capacitor is reasonable structure. Especially, much attention has been paid to MIM capacitor which consists of Perovskite-type dielectrics and noble metal electrode. In spite of these efforts, leakage problem remains unsolved. It is known that the leakage current is not only governed by the bulk ferro- or dielectric films(bulk-limited) but also by the Schottky junction between films and metal electrodes(interface-limited). Here I wish to point out the important of barrier formation to reduce leakage current efficiently so that the metal electrode with high work function will be great help in reducing the leakage current. Based on this idea, I have been focused on the interface phenomena, and investigated the effect of enhanced work function on the Schottky barrier formation of MIM capacitor using $SrTiO_3$ (STO) dielectrics and noble metal electrode. I have obtained an interesting result and wish to report it herein.

2. Film preparation and characterization

The films were prepared by PLD method. The PLD technique is widely used for either various metal films or oxide compounds such as high-temperature superconductors, ferroelectrics, multiferroics, and electro-optics. The one of the most advantages features of PLD technique is the ability to reproduce the target composition with relative ease under the appropriate conditions. It is an efficient method to produce the layer by layer growth for thin films in the atomic range. The X-ray diffraction(XRD) was used for crystalline structure analysis, and atomic force micro spectroscopy(AFM) was used for microstructure observation of film surface. The work function was measured by photoelectron spectroscopy in the air(PESA) based on an electron counting mechanism by an open counter.

3. Consideration of leakage mechanism and work function

The consideration of leakage mechanism seems to be worthwhile subject in order to investigate how to control the leakage current. The available leakage mechanisms are following: Schottky emission, Ohmic contact, Fowler-Nordheim tunneling, Poole Frenkel emission, and Space-charge-limited current. Likewise, the work function is also essential factors. The work function is fundamental physical quantity, and it is known that the work function is depends on the material types. However, the work function is strongly affected by surface condition because the work function can be unified as summarize of surface term Δf and bulk term ϕ_B as following:

$$\phi_m = \Delta\varphi + \phi_B \quad . \qquad (1)$$

It indicates the work function can be controlled by surface modification, and it will be useful for Schottky barrier formation.

4. Leakage mechanism in thin film capacitor using Perovskite dielectrics

The dielectric constants for amorphous STO film deposited below 300°C are around 20 as shown in Fig. 1. In the I-V characterization, the current direction is defined from the top electrode(positive) to the bottom electrode(negative) as shown in Fig. 2. The leakage current through the interface at the STO / bottom electrode shows typical interface-limited leakage behavior. The interface-limited leakage behavior is also detected on the contact of top electrode/STO films prepared at 300 °C and 550 °C. Whereas the STO films has very rough surface at the deposition temperature of 450 °C which is about halfway temperature from amorphous to crystallized phase. This rough surface originated from meta-stable phase of STO films leads to bulk-limited leakage behavior on the contact of top electrode/STO films. In the leakage behavior of MIM capacitors using STO films, the interface phenomena are predominant component to control the leakage current.

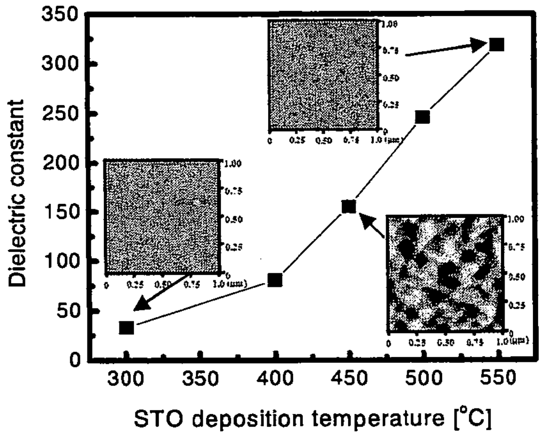

Figure 1. The dielectric constant of STO films at various deposition temperature

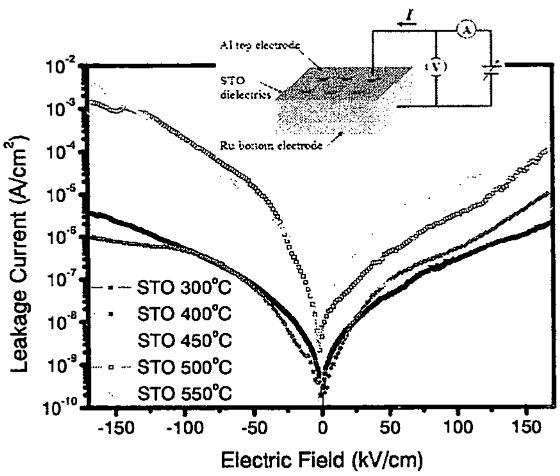

Figure 2. The leakage current density as a function of electric field of STO films

5. Effect of microstructure of bottom electrodes on the work function

The work function of the (111)-oriented Pt electrode is approximately 4.93 eV whereas the work function of the (100)-oriented Pt electrode is 4.78 eV. This difference of work function depending on the crystal orientation can be explained the electron density distribution on the metal surface due to smoothing effect. The work function of Pt/Ru bilayer electrode increases from 4.75 to 4.90 eV according to the thickness of the Pt top layer decreases. The work function of Ru top layer electrodes also increases from 4.87 to 4.97 eV according to the under-layer. It supports the assumption that the work function is related with microstructure on the surface. The work functions are plotted against roughness of surface as shown in Fig. 3. It shows the strong linear relationship against roughness of electrodes. In other words, the work function decreases at electrodes with rough surface. It can be explained by smoothing effect which is a tendency to smooth out the surface as shown in the previous chapter. The smoothing effect leads the electron flow from the hills to the valleys and forms the positive potential barrier to the vacuum as shown inset in Fig. 3. It suggests that the work function can be enhanced by

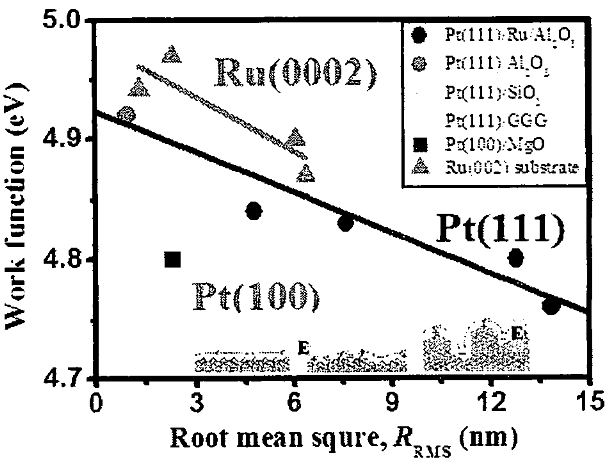

Figure 3. The work function as a function of roughness on the metal surface. Inset shows the smoothing effect

modification of microstructure such as crystalline orientation or surface roughness. The enhanced work function by tuned microstructure of electrodes is expected to form high Schottky barrier on the contact of bottom electrode and dielectrics. This relationship will be investigated at next chapter.

6. Schottky barrier enhancement by tuned work function

The variation of Schottky barrier heights as a function of work function on the metal electrode surface shows a strong linear relation among the same crystal orientation of metal both Pt and Ru electrodes as shown in Fig. 4. It suggests that the Schottky barrier enhancement is might be dominated by enlargement of work function on metal electrode. In other words, the leakage current of dielectric thin films with metal electrodes may be controlled by tuning of the roughness on the metal electrode. The tuned microstructure of electrodes appears to be an essential factor in the performance of excellent MIM thin film capacitors.

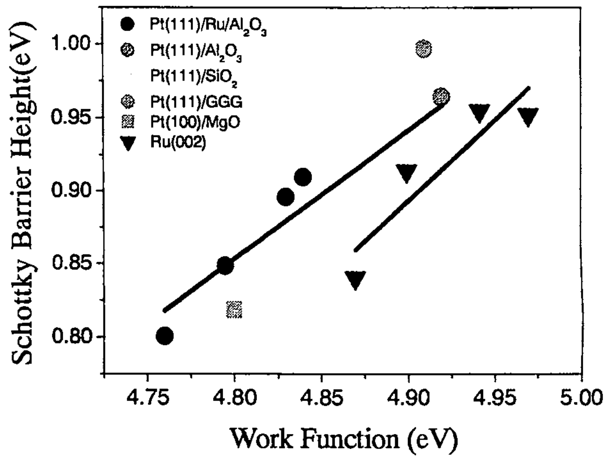

Figure 4. The Schottky barrier heights as a function of work function of the metal surface.

7. Leakage behavior affected by top and bottom interface

Figure 5 shows AFM images of Ru electrodes according to the deposition temperature. The amorphous STO film surface relates to the surface of Ru bottom electrode as shown in the inset of Fig. 5. This surface variation of amorphous STO films leads to the leakage current variation as shown in Fig. 6. The leakage current curves affected by both top and bottom electrodes resemble each other. It indicates that the leakage current is also affected by morphology of STO films.

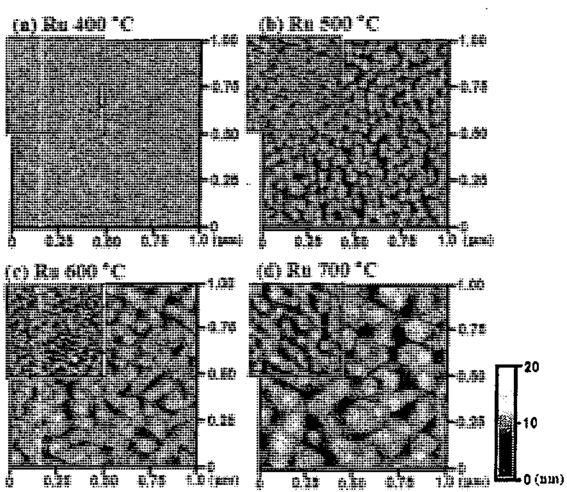

Figure 5. AFM images for Ru electrodes deposited at various temperature. Inset shows the amorphous STO films on these Ru electrodes

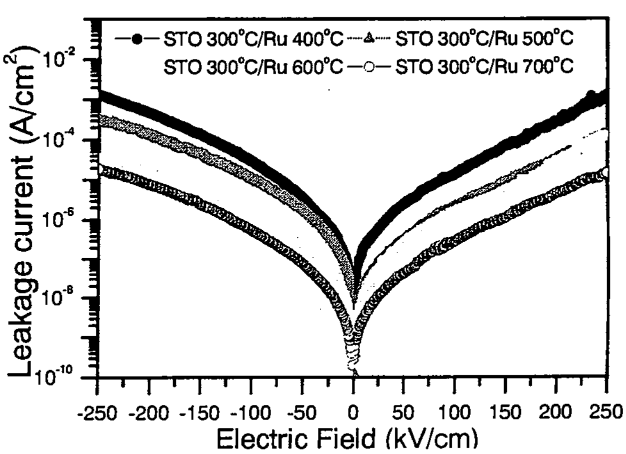

Figure 6. I-V curves for amorphous STO films. Leakage current at negative bias shows current originated by interface of Al top electrode and STO films

8. Summary

The effect of work function by microstructure of electrode on the leakage behavior has been investigated on the MIM thin film capacitors. The STO films deposited on the Pt and Ru metal electrodes show a typical interface-limited leakage behavior on the contact of STO films/bottom electrodes. On the contrary, the rough surface originated from meta-stable phase of STO films leads a bulk-limited leakage behavior on the contact of top electrode/STO films. The leakage current density can be suppressed by Schottky barrier height formation. The Schottky barrier can be formed by enhancement of work function on the bottom electrodes. Moreover, the work function can be increased by modification of microstructure such as crystalline orientation or surface roughness. In other words, the leakage current on the MIM capacitor can be controlled by tuning of roughness on the metal electrode. The tuned microstructure of electrodes appears to be an essential factor in the performance of excellent MIM thin film capacitors.

学位論文審査結果の要旨

当該学位論文に対して、平成 20 年 7 月 29 日に第 1 回論文審査委員会を開催し、同年 8 月 1 日に行われた口頭発表後に第 2 回論文審査委員会を開催し討議した結果、以下の通り判定した。なお、口頭発表における質疑応答を持って最終試験にかえるものとした。

益々微細化し高密度化する次世代 DRAM 用キャパシタやチップキャパシタなどでは、そのリーク電流低減が大きな課題となっている。本研究は、次世代キャパシタで重要となるペロブスカイト型誘電体薄膜を用いて、金属／誘電体界面のショットキー障壁高さ、金属の仕事関数、界面粗さが密接な関係にあることを明らかにし、リーク電流低減の指針を与えている。主な成果は以下の通りである。

上部金属／誘電体／下部金属（MIM）キャパシタ作製のため、Pt や Ru などの貴金属薄膜及びペロブスカイト型誘電体の代表格である $SrTiO_3$ 誘電体薄膜のパルスレーザアブレーション堆積を行った。得られた Pt や Ru など下部電極表面を原子間力顕微鏡で観察し、金属結晶の方位、電極構造、電極堆積温度により、微視的な金属表面粗さを制御可能であることを示した。さらに、その表面粗さが大気中光電子分光法で測定した下部電極の仕事関数、MIM キャパシタの電流－電圧特性から測定したショットキー障壁高さ、そしてリーク電流特性に大きな影響を与えることを見いだした。

本研究は、MIM キャパシタのリーク電流は、誘電体／電極界面の微視的な粗さ制御により制御可能であることを示したもので、博士（学術）の学位を受けるに値するものと判定する。