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Iridium layer as oxygen barrier and growth substrate for oriented PZT thin films

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Iridium thin films, grown by RF sputtering method and their behaviour as oxygen diffusion barrier were investigated. The growth of oriented PZT thin films on Ir barrier layer is also discussed. Sheet resistance was measured for $Ir/SiO_2/Si$ samples annealed in O_2 for 15 min. at temperatures up to 750 ^oC. The electrical resistivity of Ir film decreases with increasing annealing temperatures due to a better crystallization. PZT films deposited by RF sputtering method on Ir(111) by means of a 2 nm thick TiO_2 seed layer grow almost perfectly in (111) orientation (98% texture index). Ir layer can be used as a barrier layer in stacked capacitor FRAM's and it also allows the growth of oriented PZT thin films.

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1. Introduction

An ideal memory should have ultimate properties such as random access, fast read and write operation, as well as unlimited usage with non-volatility. None of the existing memories such as DRAM, SRAM and Flash can satisfy the requirements for ideal memory. DRAM and SRAM do not contain non-volatility. On the other hand, Flash neither satisfies fast write operations, nor satisfies the unlimited usage. On the way to pursue ideal memory, ferroelectric RAM (FeRAM), which potentially satisfies all the requirements for ideal memory, was introduced in the last decade but only low density FeRAM, or embedded product with low density FeRAM, is available in limited application [1].

There has been significant progress in ferroelectric memory technology, but the commercial high density FeRAM are still restricted by several challenging problems such as reliability and integration issues. Fabrication of high-density ferroelectric memories requires the growth of ferroelectric materials on the drain contact metal. The structure on top of the drain demands the development of a conductive barrier inhibiting lead and oxygen diffusion down to the contact between capacitor and tranzistor. Chemical elements, which have dense structure (close packing and small lattice constant) and high melting point (low atom mobility) effectively can retard oxygen diffusion. This double criterion is met by five stable elements: Ru, Rh, Re, Os and Ir [2]. Iridium exhibits a very high melting temperature and a very low vapour pressure. Among the noble metals its hardness is second after osmium and is about ten times harder than gold. Against acids it is chemically the most inert metal and even its oxide IrO_2 is electrically conductive. Multilayer structures like IrO_2/Ir, RuO_2/Ru, $RuO_2/Ru/Cr$ are being considered as conductive barrier for integration of PZT capacitors onto CMOS devices for the fabrication of FeRAM [3, 4].

The purpose of the present investigation is to study the growth of oriented PZT thin films onto Ir layer and to evaluate the behaviour of iridium films as oxygen diffusion barrier.

2. Experimental

The substrates used in this experiment were Si wafers coated with a 150 nm silicon dioxide insulating layer and $TiN/W/TiN/Ti/SiO_2/Si$. All films have been deposited in a ULVAC SBR-1102E RF-sputtering system with a single target. The sputtering chamber was pumped with a diffusion pump based system. After the vacuum system was pumped down to 10^{-5} Torr, Ar was admitted to maintain a gas pressure of 5 mTorr. Pre-sputtering of Ir and Ti targets was performed for 5 min. prior to film deposition.

The iridium films were deposited from a metallic target with a 30 W applied power at 12 mTorr Ar pressure on a plane heater at 600 ^oC. A TiO_2 (10 nm)/Ti (2 nm) adhesion structutre was deposited by reactive rf-magnetron sputtering from a metallic Ti target at 10 mTorr O_2 pressure at 600 ^oC. PZT thin films with a thickness of 200 nm were deposited onto $Ir/TiO_2/Ti/SiO_2/Si$ substrate (Fig. 1) at 600 ^oC at 15mTorr O_2 pressure from a single target.

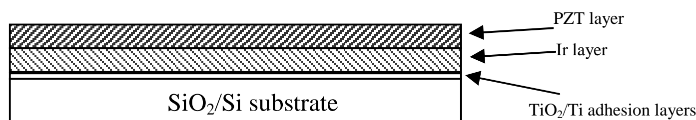

Fig. 1. $PZT/Ir/TiO_2/Ti/SiO_2/Si$ stucture.

The preparation method [5] of PZT target was the usual mixed oxide route. High purity oxides were used. The mixings were carried out in a planetary ball mill, in methanol, using agate vials and balls of 10 mm diameter and a ball/powder weighted ratio of 2/1. After mixing for

3 h, the products were dried and double calcined at 850 ^oC and 900 ^oC respectively with an intermediate milling of 1 h and a final wet milling of 10 h. This processing procedure produced a rather uniform, submicron fine powder. Powders were compacted in a cylindrical die, as discs of 55 mm diameter and about 7 mm thick using uniaxial pressing and a pressure of about 50 MPa. No organic binder was used but a slight wetting, by spraying, using distilled water (about 5% wt). The pressed samples were sintered in covered alumina crucibles at temperatures between 1150-1350 ^oC with a dwell time of 4 h. The sintered samples were then mechanically processed by grinding as discs with 50 mm diameters and 5 mm thick.

For electrical characterization Pt top electrodes (1×1 mm^2) were deposited by sputtering at room temperature through a mechanical mask. The thickness of deposited layers was controlled by a Tencor profilometer. The oxidation resistance of Ir thin films has been tested by means of heat-treatments in oxygen ambient. Samples were annealed in a lamp furnace (RTA) at temperature up to 750 ^oC for 15 min. and in a pure oxygen stream at atmospheric pressure. The standard θ-2θ X-ray diffraction (XRD) was used to study the film structure and orientation and the four-point-probe method was applied for sheet resistance measurements. Auger Electron Spectroscopy has been used for chemical depth profiling of PZT/Ir stacks. The dielectic properties of PZT thin films were measured with a HP4194A impedance analyzer. Polarisation versus electric field hysteresis loops was recorded with a Sower-Tower circuit.

3. Results and discussion

The electrical resistance measurements were made on Ir thin film deposited onto SiO_2/Si substrate in order to evaluate the stability of iridium thin films and reactions that may occur in the bottom electrode during ferroelectric film deposition (severe oxidation atmosphere at high temperature).

A 200 nm thick Ir thin film deposited onto SiO_2/Si substrate was annealed in O_2 atmosphere for 15 min. at temperatures up to 750 ^oC. Table 1 shows the behaviour of electrical resistivity of iridium thin film deposited on SiO_2/Si substrate annealed at different temperatures in O_2. Electrical resistivity of iridium bulk is 5.1 μΩ·cm and is twelve times lower than electrical resistivity of IrO_2 which is 60 μΩ·cm.

Table 1. Electrical resistivity of Ir layer versus annealing temperature in O_2 atmosphere.

Atmosphere	O_2			
Temperature ^0C	500	575	650	750
Resistivity (μΩ·cm)	9.8	9.7	9.4	8.6

The electrical resistivity of annealed iridium thin film decreases with increasing annealing temperature even on top of Ir layer is formed a tiny oxide scale. It is supposed that the microstructure of iridium thin film improves during annealing.

In order to confirm the reduction of electrical resistivity of Ir layer annealed in O_2 atmosphere, we annealed the film in N_2 atmosphere. Annealing in N_2 yielded to a lower sheet resistance (Table 2).

Table 2. Electrical resistivity of Ir layer versus annealing temperature in N_2 atmosphere.

Atmosphere	N_2			
Temperature ^0C	500	575	650	750
Resistivity (μΩ·cm)	9.8	9.7	8.9	8.2

XRD measurements were made on Ir thin film deposited onto TiN/W/TiN/Ti/SiO_2/Si substrate in order to evaluate the barrier role of Ir layer against oxygen diffusion during ferroelectric film deposition (severe oxidation atmosphere at high temperature).

XRD patterns of 200 nm Ir deposited on a metallic TiN/W/TiN/Ti/SiO_2/Si substrate after annealing at different temperature revealed that oxidation of W layer sets in between 600 and 650 ^oC. The first peaks of WO_3 are visible after annealing at 650 ^oC (Fig. 2). Iridium layer can be effective as barrier layer against oxygen diffusion up to 650 ^oC. The oxygen reaches tungsten most probably through the grain boundaries.

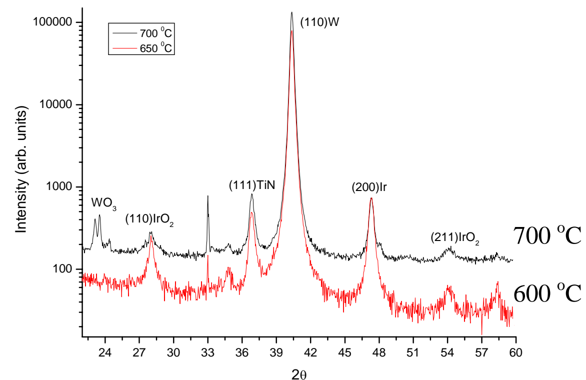

Fig. 2. XRD patterns of 200 nm Ir deposited on W/TiN/Ti/SiO_2/Si after annealing at different temperature in O_2 atmosphere.

Nucleation and texture, are mainly governed by underlying substrate and the interface properties. It is of interest to obtain a defined texture of Ir thin film in order to achieve a homogeneous texture of the PZT thin film.

The XRD profiles of the crystallized PZT thin films deposited on Pt/TiO_2/Ti/SiO_2/Si substrate without and with TiO_2 seed layer are shown in Fig. 3 and 4 respectively. All the patterns show the perovskite structure.

As Ir can be grown with a high degree of (111) texture, a (111) orientation of PZT is expected to be favoured. However, different orientation can be obtained on Ir(111) (Fig. 3). It was shown in ref. [6] that a crystalline, few nanometer thick of TiO_2 layer represents a

very efficient seed layer for the nucleation of PZT(111) deposited on Pt(111)/TiO_2/Ti/SiO_2/Si substrate. PZT grown on Ir(111) by means of 2nm thick TiO_2 (Fig. 4) grow almost perfectly in (111) orientation (98% texture index) in analogy to Pt(111).

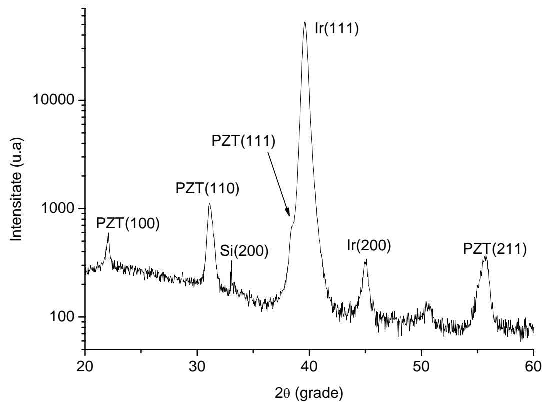

Fig. 3. XRD spectra of random PZT thin film deposited on Ir/TiO_2/Ti/SiO_2/Si substrate

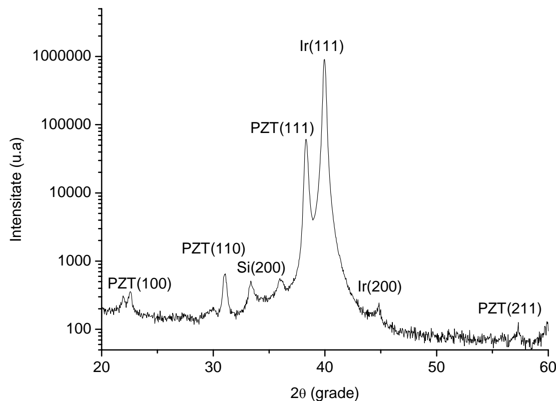

Fig. 4. XRD spectra of highly oriented (111) PZT thin film deposited on TiO_2/Ti/SiO_2/Si substrate.

The dielectric constant was calculated from capacitance measurements at 100 Hz-1MHz. The values were around 720 and dielectric loss 0.03.

Polarization-electric field hysteresis loops have been measured with a Sawyer-Tower circuit. Fig. 5 shows the square shaped and well saturated hysteresis loop. The remnant polarization is about 22 $\mu C/cm^2$ and the coercive field 48 kV/cm.

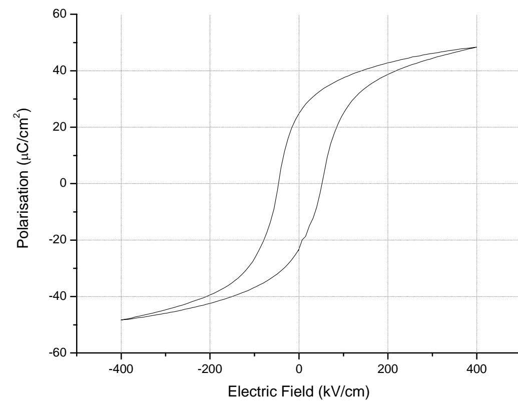

Fig. 5. P -E hysteresys loop of a Pt/PZT/Ir/TiO_2/Ti/SiO_2/Si capacitor.

4. Conclusions

The growth of oriented Ir thin films and their barrier properties were investigated. Iridium layer can be effective as barrier layer against oxygen diffusion up to 650 ^oC and it can be used for applications in stacked capacitors FeRAM. PZT grown on Ir(111) by means of 2 nm thick TiO_2 seed layer grow almost perfectly in (111) orientation (98% texture index). The remnant polarization of the films is well above the minimum requirements for a non-volatile memory device.

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