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Formation and stability of a ruthenium-oxide thin film made of the O_2/Ar gas-mixture sputtering

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Abstract

To obtain high remnant polarization and good crystalinity of ferroelectric thin films in non-volatile memory devices, the high temperature treatment in oxygen ambient is inevitable. Severe problems that occur in this process are oxygen diffusion into substrate, oxidation of electrode and buffer layer, degradation of microstructure and so on. We made ruthenium dioxide thin film by reactive sputtering with oxygen and argon mixture atmosphere. Comparing quantitatively the core-level spectra of Ru and RuO_2 obtained by x-ray photoelectron spectroscopy(XPS), we found that chemical state of RuO_2 is very stable and of good resistance to oxygen diffusion and oxidation of adjacent layers. It opens the use of RuO_2 thin film as a multifunctional layer of good conducting electrode and resistive barrier for the diffusion and the oxidation. We also suggest a correct understanding of Ru 3*d* core-level spectrum for RuO_2 based on the scheme of final state screening and charge transfer satellites.

1. Introduction

Recently, the necessity of the Gbit scale non-volatile memory devices have required extensive researches on high dielectric materials, such as lead zirconium titanate($PbZr_xTi_{1-x}O_3$, PZT) and barium strontium titanate ($Ba_{1-x}Sr_xTiO_3$, BST), and their conducting electrodes. Among the electrodes are widely investigated platinum, ruthenium, and their oxide films due to their catalytic, electric and reactive versatilities [1-6].

PZT and BST have been used as key elements in the high density memory devices because they have ferroelectic property with high remnant polarization [5-8]. To store an information in the ferroelectric layer an appropriate bias voltage should be applied in between two conducting electrodes. On the other hand, one side of the electrodes is in contact with very large scale integrated(VLSI) circuits made of single crystal semiconductor wafer and successive fabrication processes.

When one combines two heterogeneous material in parallel, the structural mismatch and chemical discordance between those materials may cause severe stress and mechanical instability at the interface. Platinum and platinum oxides are in this category when they contact with Si and SiO_2 based VLSI circuits. The buffer layer such as tantalum, titanium or other compounds should be introduced in order not to make structural collapse and improve adhesion property [4-7].

Microstructure and crystalinity of PZT and BST ferroelectric materials are also very important to reduce the leakage current and the fatigue property - reduction of remnant polarization. It is known that the substrate should be maintained with high temperature when the dielectric thin film is grown in oxygen or oxygen/argon-mixture ambient by rf-magnetron sputtering [6-9]. However the high temperature treatment of the dielectric thin

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films in oxygen ambient oxidizes the buffer layer and weakens the adhesion property due to oxygen indiffusion into the buffer layer and the semiconductor substrate [7,9,10]. This results in the degradation of the remnant polarization.

Ruthenium and ruthenium dioxide(RuO_2) are found to have strong resistance for oxidation itself and oxygen indiffusion through it during high temperature treatment [6-11]. Especially, the ruthenium dioxide is of a thermally and mechanically stable conductor even after high temperature annealing in oxygen atmosphere. Therefore the ruthenium dioxide thin film in ferroelectric memory devices can be introduced as a multifunctional layer of both the conducting electrode and the diffusion barrier for oxygen.

In this work, we have investigated the oxide formation of the ruthenium metal and the oxidation states of the ruthenium dioxides using x-ray photoelectron spectroscopy (XPS). We focused on the changes of binding energy position and line shapes for Ru 3*d* and O 1*s* core-levels. Determining the binding energy positions as well as the change of line shapes of core-levels by numerical curve fitting analysis we suggest a correct understanding of the oxidation state of ruthenium dioxide surface.

2. Experiments

We prepared four samples of ruthenium-oxide related thinfilms including pure ruthenium as a reference. They were clean ruthenium, 10^4L O_2/Ru, RuO_2 thinfilm(O_2/Ar mixture sputtering), and powder RuO_2. Each sample was prepared as the following. Ruthenium thinfilm was deposited by rf-magnetron sputtering of 5 mTorr argon onto silicon single-crystal wafer at room temperature. On this ruthenium thinfilm surface after cleaning of Ar sputtering in ultra high vacuum(UHV) chamber, 10^4 Langmuir exposure of oxygen gas was performed. When the exposure of oxygen molecule was executed, the ruthenium substrate had been maintained at the temperature 600℃. We performed three more trials of oxygen gas exposure less than 10^4 Langmuir and found that the core-level spectrum of Ru 3*d* looked not very different from those of 10^4 L O_2/Ru surface and of pure ruthenium surface either.

For the RuO_2 thin film(O_2/Ar mixture sputtering) on Si substrate, RuO_2 ceramic target was used in deposition process by the reactive sputtering of O_2/Ar=1/1 gas mixture [7-10]. This *ex situ* grown RuO_2 thin film was transfered to UHV chamber for the XPS measurement. Powder RuO_2 was purchased from Nilaco corporation, Japan and attached to the sample holder by dropping small amount of ethanol and drying. Other characteristics of samples were reported elsewhere [10,12].

We preformed XPS measurements manufactured by VG Microtech with the triple-channel electron analyser CLAM2. The Mg K α line($h\nu$=1253.6 eV) was used as an excitation source and the analyzer pass energy was fixed at 10 eV. This setting gives the line width of Pt $4f_{7/2}$ core-level of clean platinum metal about 1.4 eV full-width at half maximum(FWHM) which includes both the intrinsic lifetime width and the instrumental broadening. The base pressure was maintained under 1×10^{-10} Torr.

We have made the measurement without any further treatment in UHV for the *ex situ* prepared samples; RuO_2 thinfilm(O_2/Ar mixture sputtering) and powder RuO_2. We obtained Ru 3*d* core-level spectra and O 1*s* core-level spectra. The binding energies are referenced by the Pt $4f_{7/2}$ core-level(71.2 eV).

For the powder RuO_2, there was a charging shift due to poor adhesion to the sample holder with the amount less than 0.3 eV. The peak position of Ru 3*d* of the powder RuO_2 was referenced to that of RuO_2 thin film made of O_2/Ar mixture sputtering. The binding energy of Ru $3d_{5/2}$ for the pure ruthenium film was 280.1 eV by referencing Pt $4f_{7/2}$ core-level.

3. Results and Discussion

Fig. 1 shows(from bottom to top) Ru 3*d* core-levels for clean ruthenium thin-film on silicon substrate, 10^4 Langmuir exposure of oxygen molecules on a ruthenium

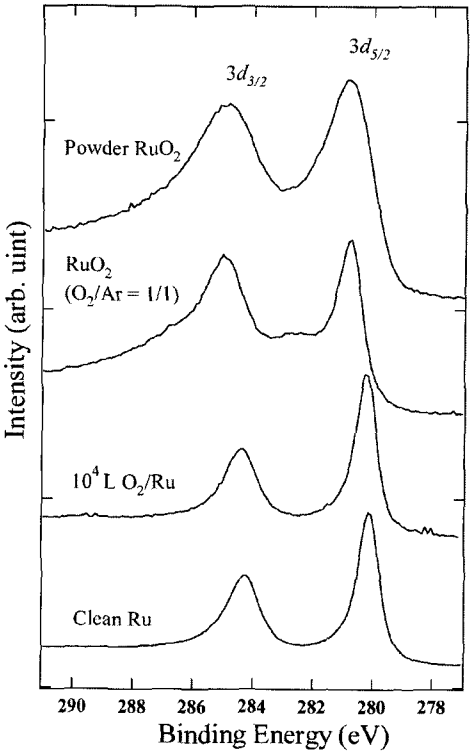

Fig. 1. From bottom to top : XPS spectra of Ru 3*d* core-level for clean ruthenium metal thin film on silicon substrate, 10^4 Langmuir exposure of oxygen molecules on high temperature Ru surface, RuO_2 thin film made of O_2/Ar mixture sputtering, and powder RuO_2.

Table 1. Characteristic parameters of the main peak of Ru $3d_{5/2}$ core-levels for ruthenium and ruthenium dioxides thin films(Reference of Pt $4f_{7/2}$: BE = 71.2 eV and FWHM = 1.4 eV).

	Binding Energy (eV)	Line Width (FWHM in eV)
Clean Ru	280.1	0.90
10^4L O_2/Ru	280.1	0.90
RuO_2(O_2/Ar=1/1)	280.8	1.01
Powder RuO_2	280.8	1.74

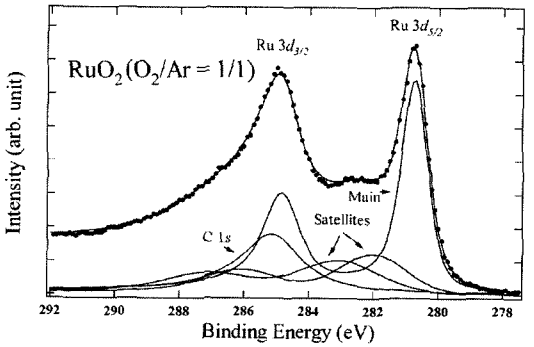

Fig. 2. Results of the curve fitting analysis of Ru 3*d* spectrum for RuO_2 thin film made of O_2/Ar mixture sputtering : Dots are raw data and solid lines are of fitting curves. Characteristic parameters are listed in Table 1.

surface at high temperature, RuO_2 thin film made of O_2/Ar mixture sputtering, and powder RuO_2. In order to clarify quantitatively the oxidation procedure of ruthenium and the chemical states of the ruthenium dioxide, we applied curve fitting analysis as shown in Fig. 2. The numerical results for the Ru $3d_{5/2}$ main peak are listed in Table 1.

All samples except powder RuO_2 have not shown any charging effect. It is natural in considering that Ru and RuO_2 are good conductors at room temperature. The charging effect for the powder RuO_2 is mainly originated from poor adhesion of the powder sample onto the holder. This can be known from the fact that the line width of Ru $3d_{5/2}$ of powder RuO_2 is unusually wide ($\simeq$ 1.7 eV) compared with that of others (< 1.0 eV) as shown in Fig. 1. The reason is that the local granules of powder RuO_2 are poorly connected each other and charged differently as the photoejected electrons are escaped from the surface.

We note that the peak position and the line width of Ru 3*d* for Ru thinfilm treated by 10^4 Langmuir exposure of oxygen molecules at high temperature ($\simeq$ 600℃) are changed little comparing with that of clean ruthenium metal. This means, as we mentioned already, that the oxidation of ruthenium metal is very hard to be formed [7,11,13]. On the other hand, we found clear difference of Ru 3*d* spectrum for RuO_2 thin film made of O_2/Ar mixture sputtering from that of clean Ru metal as shown in Fig. 1.

Considering the amount of binding energy shift and line width change as listed in Table 1, we suggest that

the peak of Ru 3*d* for RuO_2 thin film is constituted of only one chemical state of the ruthenium oxide different from that of pure ruthenium metal. If there were the pure ruthenium component the lower binding-energy slope of the spectrum should not fit well as it did in Fig. 2. Some literatures insisted that the Ru 3*d* spectrum was constituted of ruthenium metal and ruthenium oxides without applying quantitatively line shape analysis [11,14]. The behavior of shoulder structure of Ru 3*d* at higher binding energy is consistent well with our suggestion that it can be attributed to the final state effect due to the charge transfer and/or the hybridization between ruthenium and oxygen in their valence bands [15,16].

We applied two satellite peaks to obtain the characteristics of the main peak at lower binding energy in Fig. 2. This situation is different from the oxide states of platinum that we have reported recently [17]. Although we have found two notable states of different platinum oxides from platinum metal, it seems not the case for ruthenium metal and ruthenium oxides. Cox et al. [18] strongly rejected the possibility of the transition of ruthenium dioxide to other metallic Ru or volatile RuO_3 and RuO_4 based on the experiments of ultraviolet photoelectron spectroscopy(UPS) and electron energy loss spectroscopy(EELS). Therefore we suggest that the Ru 3*d* core-level spectrum of ruthenium dioxide have to be understood based on the scheme of final state screening and charge transfer satellites [15,16].

The oxygen 1*s* core-levels are shown in Fig. 3 as the same order as in the Fig. 1. We ascribe the peak at 532.2 eV to physiorbed or hydroxyil adsorbent on surface. One thing we have to note is the peak at 529.4 eV which is grown as the phase of ruthenium oxide increases. This state not shown in O 1*s* for ruthenium clean metal is mainly originated from the O 1*s* state of ruthenium dioxide. Under the assumption of the same amount of the physiorbed or hydroxyil adsorbents on the surfaces, we compared quantitatively the amount of the oxidation state of the samples. Considering the intensity ratios of the lower binding component of O 1*s* to the higher one for both 10^4L O_2/Ru and RuO_2

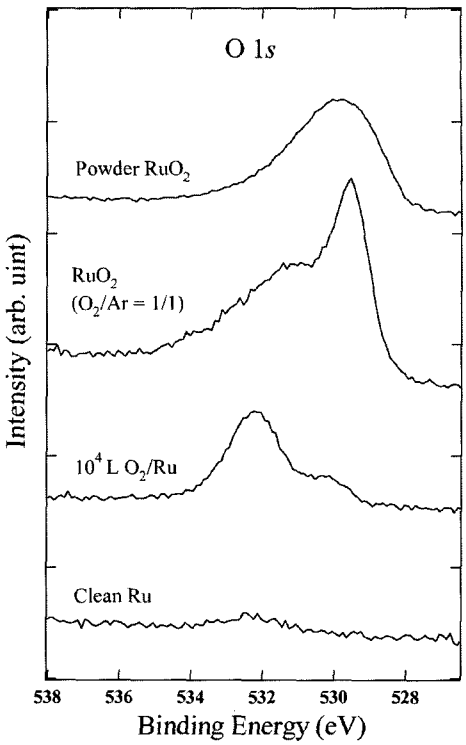

Fig. 3. XPS spectra of O 1*s* : (From bottom to top) Clean ruthenium metal thin film on silicon substrate, 10^4 Langmuir exposure of oxygen molecules on high temperature Ru surface, RuO_2 thin film made of O_2/Ar mixture sputtering, and powder RuO_2.

as listed in Table 2, we estimated that the amount of ruthenium oxide state on the surface of 10^4L O_2/Ru was at most about 15%. The kinetic energy of photoexcited electron for O 1*s* is about 720 eV which is smaller than that for Ru 3*d* about 970 eV. Since the higher the kinetic energy of electron in solid is the longer the inelastic mean free path in this energy range [19,20],

Table 2. Relative intensities of O 1*s* states for 10^4L O_2/Ru and RuO_2(O_2/Ar=1/1).

	Binding Energy(eV)	Relative Intensity
10^4L O_2/Ru	532.2	1.00
	529.4	0.29
RuO_2 (O_2/Ar=1/1)	532.2	1.00
	529.4	1.97

the surface contribution is more enhanced in O 1s core-level spectrum than in Ru 3*d* one. This means that the oxidation state of ruthenium oxide made of 10^4 Langmuir exposure of oxygen molecules on high temperature Ru surface might be formed on the utter most surface of the sample.

4. Conclusion

We have investigated the oxide formation of the ruthenium metal and the oxidation states of the ruthenium dioxides using x-ray photoelectron spectroscopy(XPS). We focused on the changes of binding energy position and line shapes for Ru 3*d* and O 1*s* core-levels. The numerical analysis gave quantitatively the binding energy positions, the intensity variations and the change of line shape of core-levels for various samples we prepared. We found that chemical state of RuO_2 was very stable and of good resistance to oxygen diffusion and oxidation of adjacent layers. It opens the use of RuO_2 thin film as a multifunctional layer of good conducting electrode and resistive barrier for the diffusion and the oxidation. We also suggest a correct understanding of Ru 3*d* core-level spectrum for RuO_2 based on the scheme of final state screening and charge transfer satellites.

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