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Thermodynamical Approach to a New High Dielectric Capacitor Structure: $W/HfO_2/W$

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The conbination of materials for a high dielectric capacitor structure and its fabrication process were established based on thermodynamic theory. The new capacitor structure, $W/HfO_2/W$, has been obtained by oxidizing the W/Hf/W stacked structure in H_2/H_2O ambients. The leakage current level for this capacitor, $W/HfO_2/W$, was one of the lowest reported so far for other high dielectric films. The dielectric constant for HfO_2 films was about 25.

1. Introduction

In recent years, high dielectric films have become interesting for use as storage capacitor dielectrics in MOS dynamic memories. Tantalum pentoxide(Ta_2O_5) films[1)2)] have been intensively studied among various high dielectric materials. Ta_2O_5 films on Si, however, exhibit very high leakage current,[2)] due to oxygen vacancies in the film, according to the author's interpretation. This will be discussed in this paper based on thermodynamic theory. Using this thermodynamic approach, integration of HfO_2 thin films was studied into a new capacitor-structure, $W/HfO_2/W$. HfO_2 films were chosen because of its relatively high dielectric constant and small free energy of formation. W films were chosen as the electrode material, because W oxides have reletively large free energy.

2. Thermodynamics of dielectric films

The leakage current in transition metal oxide increases monotonically with the oxygen vacancy concentration, C_V. Because the oxide phase is in contact with the metal phase in the phase diagram of metal-oxygen system, the components of these phases dissolve in each other. Therefore, transition metal oxides always include some amount of metal.

The concentration of metal in its oxide phase, C_M is in proportion to C_V with the coordination number. C_M in an oxide, M_XO_Y is ;

$$\Delta G = -RT \ln {}^{a}M_xO_Y / \gamma_M C_M (P_{O_2})^{Y/2X} \quad (1)$$

where ΔG is the free energy of formation, $a_{M_xO_Y}$ is the activity of component M_XO_Y and is approximately 1, γ_M is the activity coefficient of metal in M_XO_Y, P_{O_2} is the chemical potential of oxygen, which is shown by its partial pressure. For choices of low leakage materials and a capacitor structure, various suggestions can be derived from Eq.(1). Small ΔG and large P_{O_2} will result in a low C_M or C_V. The value of ΔG dependes on the choice of the dielectric film material, because ΔG is a specific property of a material. Among various dielectric materials, HfO_2 has the smallest ΔG. In order to keep the electrode material unoxidized, the maximum value of P_{O_2} in a dielectric film is limited by the element used for the upper and lower electrodes of the capacitor structure. This value may be calculated from the oxidation free energy change of the electrode material. For example, in case of Si or W electrodes, the maximum value of P_{O_2} for Si and W at 700 °C are 10^{-36} and 10^{-19} atmosphere, respectively. In a higher P_{O_2} region than the above P_{O_2}, electrode materials change to SiO_2 and WO_3.

HfO_2, which has a small formation energy, was chosen as the dielectric material, and W, whose oxide has large P_{O_2}, was chosen as the

electrode material, based on the above discussion. Figuer 1 shows P_{O_2} diagrams for $Si/Ta_2O_5/Si$ and $W/HfO_2/W$ capacitor structure at 700°C. In a lower $P_{O_2}=10^{-33}$ atmosphere, which is shown in Fig.1, Ta_2O_5 can not exist without oxidation of Si electrode. In other words, Ta_2O_5, having this structure, includes many oxygen vacancies due to reduction of Ta_2O_5 by Si. On the other hand, for the $W/HfO_2/W$ structure, which is the auther's choice, HfO_2 is not only stable but also having low concentration of oxygen vacancy, if it was annealed in an ambient having a near 10^{-19} oxygen partial pressure.

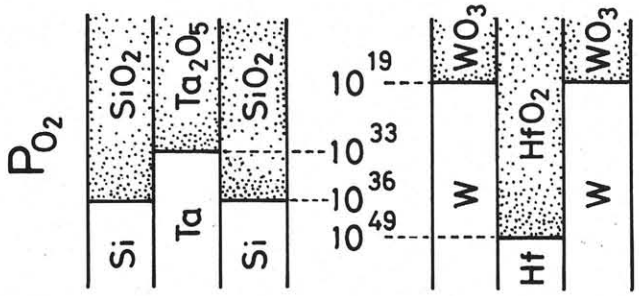


Fig.1 P_{O_2} diagrams for $Si/Ta_2O_5/Si$ and $W/HfO_2/W$ capacitor structures at 700 °C.

The dependence of leakage current on P_{O_2} can be explained based on the relationship between P_{O_2} and C_V calculated by statistical thermodynamics[3] for a hafnium-oxygen-vacancy ternary system. The free energy of a HfO_2 crystal, F_s is ;

$$Fs = -kT \log Zn \qquad (2)$$

where Z_n is determined by ;

$$Zn = K(T)\frac{N!}{(N-Nh)!Nh!}\frac{N!}{(2Nh)!(N-2Nh)!} \cdot \exp(-\frac{Nh}{kT}\omega)\left[q_0(T)\right]^{Nh} \qquad (3)$$

where K(T) is the partition function of the complete crystal, N is the number of oxygen lattice site, N_h is the number of oxygen vacancy, ω is the energy for making one of oxygen vacancy, and $[q_0(T)]^{Nh}$ is the oscilational partition function of the excess N_h atoms. Oxygen in the gas phase and HfO_2 phase is in the equilibrium. When the free energy of oxygen in the gas phase is expressed by F_g, and the number of oxygen atoms by n_{O_2}, the equilibrium relations are;

$$\frac{\partial Fs}{\partial Nh} = -\frac{1}{2}\frac{Fg}{n_{O_2}} \qquad (4)$$

$$P_{O_2} = \exp(\frac{1}{kT}\frac{\partial Fg}{\partial n_{O_2}}) \qquad (5)$$

The vacancy concentration is

$$x = \frac{Nh}{N} \qquad (6)$$

Combining Eqs.(3),(4) and (5),$(P_{O_2})^{1/2}$ is;

$$(P_{O_2})^{-1/2} = \frac{4x^3}{(1-x)(1-2x)^2}q_0(T)\exp(\frac{\omega}{kT}) \qquad (7)$$

In the H_2O-H_2-O_2 system, P_{O_2} is proportinal to P_{H_2O}/P_{H_2} and Eq.(7) is rewriten as ;

$$(P_{H_2}/P_{H_2O})^{1/2} = \frac{Cx^3}{(1-x)(1-2x)^2} \qquad (8)$$

where C is a constant.

Let us assume that trap density in the Poole-Frenkel theory is related to vacancy concentration. When x<<1, P-F current, J_{PF} is ;

$$\log(J_{PF}/E(P_{H_2}/P_{H_2O})^{1/6}) = \frac{-q\phi_T + \beta_{PF}\sqrt{E}}{kT} \qquad (9)$$

It should be noted that Eq.(1), based on chemical thermodynamics and Eq.(2), based on statistical thermodynamics, have the same significance. The HfO_2 and W combination has the smallest J_{PF}, so that this electrode and capacitor material system is the best choice for use as a high dielectric capacitor in VLSI's.

3. Experimental

Figure 2 shows the $W/HfO_2/W$ capacitor process flow. A thin W film (≃50nm), which is the lower electrode, was deposited by the electron-beam-evapolation method. This W film was patterned and etched by a C.D.E.(Chemical Dry Etching) system, using CF_4 and O_2 gases. SiO_2 film, 200nm thick, were deposited on the W and Si surfaces in an RF magnetron sputtering apparatus, in which the SiO_2 target was installed. The capacitor areas were formed by etching in a dilute HF solution. Then, pure Hf film (about 30nm) were fabricated using an E-gun system. Following Hf deposition, W films(70nm), for the upper electrodes, were deposited in the same apparatus without exposing the Hf film to air. With this deposition system, it is possible to clean the surface by magnetron

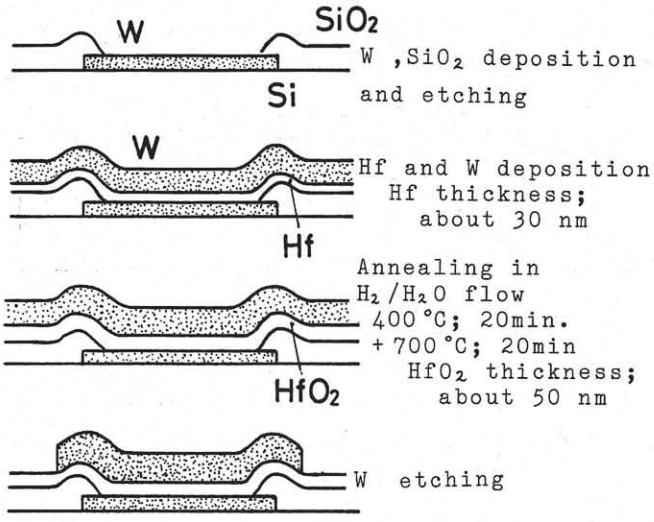


Fig.2 $W/HfO_2/W$ capacitor process flow.

sputtering in pure Ar. In this work, the substrates were cleaned by Ar sputtering before Hf deposition. The deposition chamber in the presently used apparatus had 3×10^{-8} Pa base pressure and 4×10^{-7} Pa during the deposition. The requirement for clean vacuum has not been confirmed for the present work.

The next step is the oxidation of hafnium. Hafnium is a very active element and oxidizes violently. However, oxidation through the W films in the present process is very well controlled. The chemical potential for oxygen, P_{O_2}, in oxidation ambients, were controlled by H_2/H_2O flow. In this process, Hf oxidation is composed of a two step treatment at 450°C and 700°C.

The leakage current, due to oxygen vacancy, of $W/HfO_2/W$ capacitors, is mainly determined by P_{O_2} during the final annealing at 700°C. Hafnium oxide grows in the first step annealing in H_2/H_2O flow. The 2nd step annealing was performed for oxidizing the Hf-oxide film completely and reducing the vacancy concentration. The first step temperature, 450°C, was chosen based on the condition giving a larger oxidation rate and slow alloying rate between W and Hf.

The 2nd step temperature was 700°C, which is the highest temperature possible without silicidation between the Si substrate and the lower electrode, W. The chemical structures of $W/HfO_2/W$ capacitors, which were annealed at 700°C and 800°C, are demonstrated in Fig.3. In the case of 800°C, the silicidation reaction at the interface between W and Si was observed.

At the last step, the upper W electrodes were formed by photolithography and C.D.E.. This process is easy, because the HfO_2 film can not be etched by C.D.E..

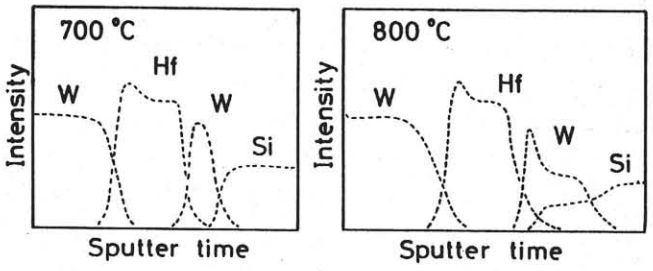
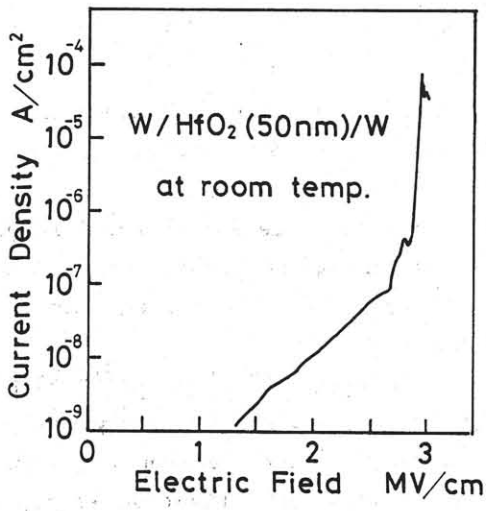


Fig.3 SIMS profiles for $W/HfO_2/W$ structure. Samples annealed at 700 °C and 800 °C.

4. Results and Discussion

The dielectric constant for the HfO_2 film, obtained in this work, was about 25. Therefore a HfO_2 film 50nm thick corresponds to a SiO_2 film as thin as 7.8nm.

Figure 4 shows a typical leakage current characteristic at room temperature(25°C). The capacitor area shown in Fig.4 was $1\times10^{-4}cm^2$ ($100\times100\mu m^2$). The leakage current level for this capacitor was one of the lowest as reported so far for other high dielectric films.[1)4)] This low leakage capacitor could hardly be obtained if the capacitor area as larger than $100\times100\mu m^2$. This can



Fib.4 Current density-electric field characteristic for $W/HfO_2/W$ capacitor.

not be to explained by defect dencity. A large volume change, about 5/3 during Hf oxidation, yields a large stress in the film. It is assumed that an increase in leakage current is caused by this stress.

Figure 5 indicates leakage current dependence on measurement temperature for the sample annealed in $P_{O_2}=10^{-22}$ atmosphere(A) and 10^{-33} atm.(B) ambients at 700°C. Oxygen partial pressures of 10^{-22} and 10^{-33} atm. were given by the H_2/H_2O flow ratio of 10 and $4x10^6$,respectively. In this work, the H_2/H_2O flow rates were controlled by mixing pure H_2 and wet H_2, which was saturated with water at room temperature. Figure 5 clearly indicates that, not only the leakage current level, but also its activation energy, depend on P_{O_2}. The author expects to observe the same leakage current dependence on P_{O_2} in annealing ambients with other transition metal oxides, such as Ta_2O_5.

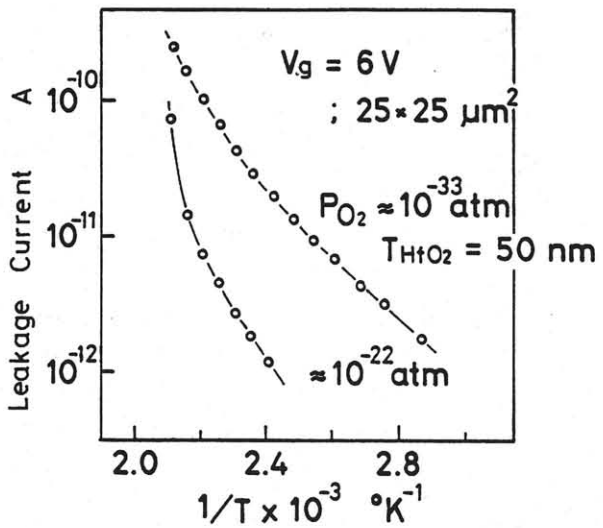


Fig.5 Leakage current characteristics for $W/HfO_2/W$ capacitors.

Table 1 shows the leakage current level at 420°K and annealing ambients which are also shown in Fig.5. Current ratio for samples(A) and (B) are 20. THe value of

$$[(P_{H_2}/P_{H_2O})_A/(P_{H_2}/P_{H_2O})_B]^{1/6}$$ is 8.5.

The current ratio, 20, agrees fairly well with this, 8.5. However, this discussion is not able to explain the change in activation energy for leakage currents by P_{O_2} in Fig.5. It indicates that a discussion on change in ϕ_T due to P_{O_2} in Eq.(9) will be necessary. Then, we can consider

Table 1. Relation between leakage currents at 420°K. and annealing ambients.

Sample	P_{O_2} atm.	P_{H_2}/P_{H_2O}	J_{PF} A
(A)	10^{-33}	4×10^6	2×10^{-11}
(B)	10^{-22}	10	1×10^{-12}

that the change of ϕ_T is caused by the shift from the ideal configurational partition function for the oxygen vacancy in the HfO_2, and the maximum shift corresponds to the occurance of grain boundary.

5. Conclusion

Materials for a high dielectric capacitor structure, $W/HfO_2/W$, were chosen based on thermodynamic theory. The $W/HfO_2/W$ structure was obtained by oxidizing W/Hf/W in H_2/H_2O ambient. The leakage currents for these capacitors were dominated by oxygen vacancy, which depended on the oxygen partial pressures for the annealing ambients. In this optimized process, capacitors were obtained having the leakage current, $1x10^{-9}A/cm^2$ at 1MV/cm. The dielectric constant for the HfO_2 film was about 25. Thus, sufficient capacitance for future DRAM memory cells can be obtained, even in small geometries for them. Thus a new memory capacitor technology for ultra high density DRAM's has been established.

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