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High Quality Ta_2O_5 Films Using Ultra-High Purity Ta Sputtering Target

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High quality and highly reliable Ta_2O_5 films are obtained, using a newly developed, ultra-high purity Ta sputtering target. Leakage current flowing through an extremely thin film of 115 Å thickness is very low and does not increase even after annealing at a temperature of as high as 500°C. This film allows realization of 4-Mbit MOS d-RAM with a conventional planar cell capacitor.

I. INTRODUCTION

Ta_2O_5 film is of special interest because it will enable fabrication of the forthcoming mega-bit class MOS d-RAM's without complicated trench-capacitor technology. The authors reported last year that leakage current in Ta_2O_5 film is drastically reduced by film purification[1]. However, two drawbacks remained unresolved. The leakage current increases with film-thickness decrease, and further increases by annealing. These difficulties have been resolved by development of a Ta sputtering target of increased purity. This report describes the developement of an ultra-high purity Ta target, the leakage properties of high quality Ta_2O_5 films sputtered using this target, and the applicable range of these films in MOS d-RAM's.

II. Ta TARGET PURIFICATION

The electron-beam melting method was previously used to fabricate a high purity Ta target. Although electron-beam melting is a very effective method for metal purification, refractory metals whose melting point is near to or greater than that of Ta are not removed. This is shown in the High Purity column of Table I. Since several refractory metal oxides, such as molybdenum oxide and tungsten oxide, have large electrical conductivity, they can be the cause of Ta_2O_5 leakage current. Therefore, a new method was developed to eliminate refractory metals from the Ta target. This method is described in Fig.1.

TABLE I. IMPURITIES IN Ta SPUTTERING TARGETS (wt.ppm)

Impurities		Target Purity: Ultra-High	High	Conventional
Refractory Metals	Nb	<0.2	50	<30
	Mo	<0.2	2	
	W	0.3	10	
	Zr	<0.2	1	10
Alkaline Metals	Na	<0.02	<0.05	< 1
	K	<0.02	<0.05	< 1
Heavy Metals	Fe	<0.05	<0.1	25
	Ni	<0.02	0.05	<10
	Cr	<0.02	<0.1	<30
Radioactive Element	U	<0.001	<0.001	
Purity		6N	>4N	3N

Main Measurement Methods
Refractory and Heavy Metals: Spark Source Mass Spectrometry
Alkaline Metals: Flameless Atomic Absorption
Radioactive Element: Fluorescence Spectrophotometry

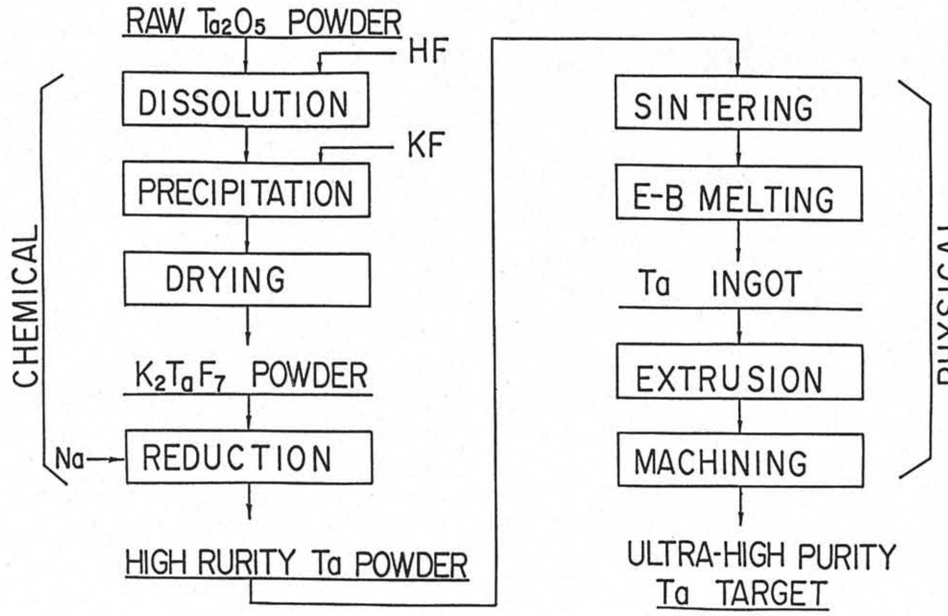

Fig.1 Flow chart of ultra-high purity Ta target fabrication process.

A commercially available 3N(99.9%-pure) raw Ta_2O_5 powder was dissolved in fluoric acid. Potassium fluoride was then added to precipitate potassium tantalum fluoride. The precipitate was filtrated, dried and reduced to Ta by use of sodium[2]. Through the above chemical refinement process, refractory metals and other impurities were removed and high purity Ta powder was obtained. Subsequently, using the physical refinement process described previously[1], a disk-shaped, ultra-high purity Ta target 6 mm thick and 254 mm in diameter was fabricated.

Table I contrasts impurity concentrations of this ultra-high purity target with those of the previously developed high purity and conventional targets. Refractory metal concentrations of the ultra-high purity target have been reduced by 2 orders or more in magnitude. Besides, concentrations of other impurities have been reduced. Target purity was estimated to be 6N.

III. LEAKAGE PROPERTIES OF HIGH QUALITY Ta_2O_5 FILM

The ultra-high purity Ta target was installed in a load lock type DC magnetron sputtering apparatus. High quality Ta_2O_5 films were deposited by reactive sputtering in an Ar-O_2 mixture. The effects of refractory metal elimination were investigated using MOS capacitors with an $Al/Ta_2O_5/p$-Si structure. Ta_2O_5 film was grown on 4-Ωcm (100) p-Si substrates, and Al electrodes were formed by evaporation and photolithography.

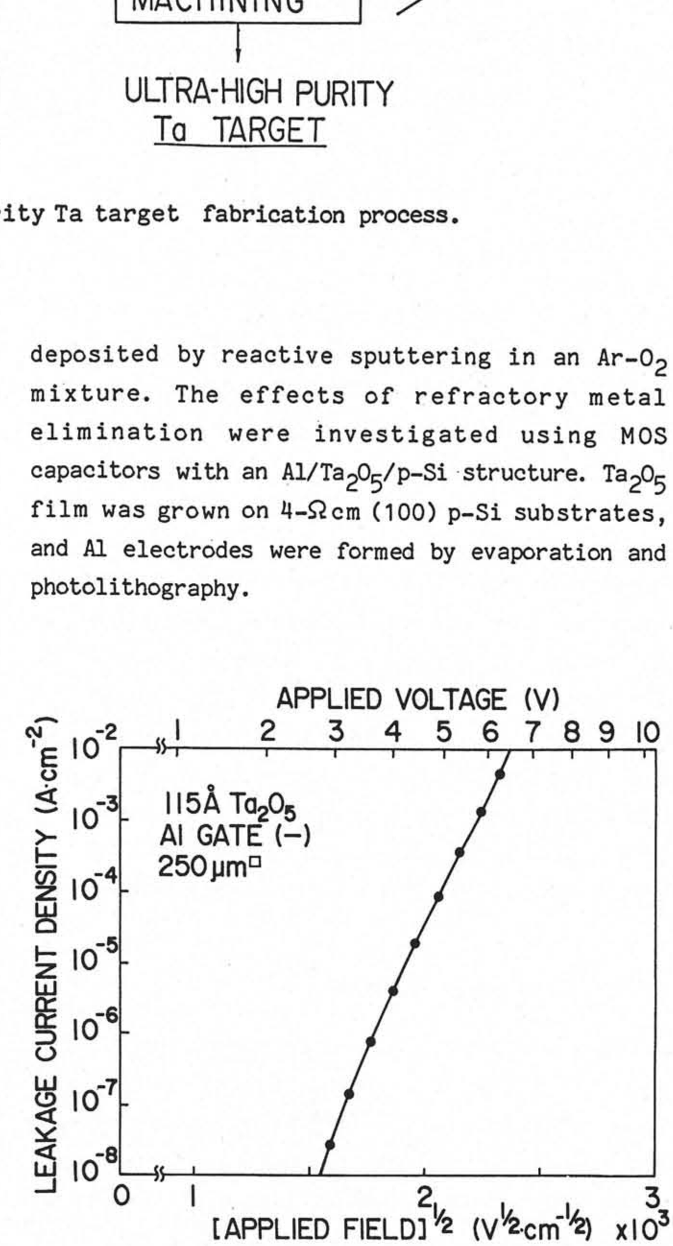

Fig.2 Leakage current of $Al/Ta_2O_5/p$-Si MOS capacitor. The capacitor had received no annealing.

Figure 2 shows the Schottky plot of current flowing through 115-Å-thick Ta_2O_5 film in the MOS capacitor. Although the film was extremely thin, the leakage current was very low. Moreover, its applied field dependence was found to be equal to or better than that of thicker films. In Fig.3, a breakdown strength histogram is shown for capacitors with 115-Å-thick Ta_2O_5 and with a 1-mm-square electrode. The distribution was surprisingly sharp and the breakdown field sufficiently high. Since no defect was found in the experiment, the defect density of the film was estimated to be less than 2 cm^{-2}. These two results indicate that the thin Ta_2O_5 film has high quality and uniformity.

Figure 4 shows the influence of annealing on leakage current. The leakage current decreased after annealing at 500°C, both in O_2 and in Ar, different from the previously reported results. In the previous films, trap levels due to impurities were most likely generated by annealing. The slope of the curve for the present films became smaller by annealing. It may be explained by a change in the conduction mechanism from the normal to the anomalous Poole-Frenkel type[3], meaning that donor levels, such as oxygen vacancies[4], were annealed out by the heat treatment.

All of the above results lead to the conclusion that impurities, including refractory metals, in the sputtering target are the main cause of leakage current increase in Ta_2O_5 film with film-thickness decrease and by annealing.

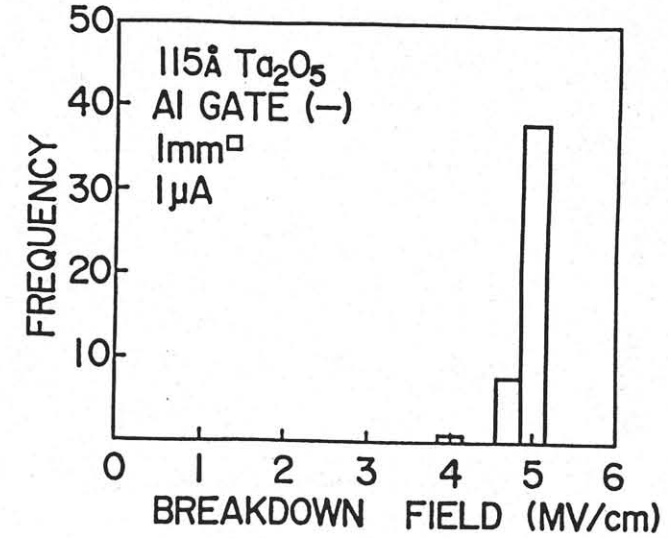

Fig.3 Breakdown distribution for $Al/Ta_2O_5/p$-Si capacitors. The capacitors had received no annealing. Voltage ramp rate was 0.1V/sec.

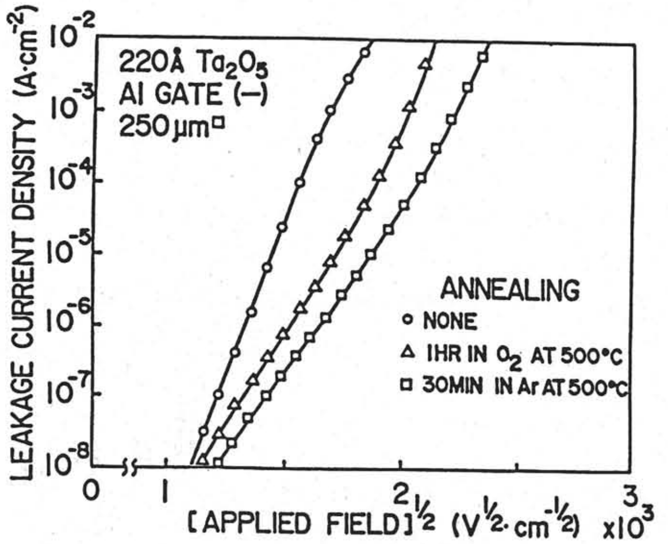

Fig.4 Influence of annealing on leakage current of $Al/Ta_2O_5/p$-Si MOS capacitors. Annealing was performed before Al evaporation.

IV. APPLICABLE RANGE ESTIMATION

To clarify the applicable range of the high quality Ta_2O_5 film developed, when it is used in a conventional planar cell capacitor of MOS d-RAM's, estimates of required capacitor area A and allowable supply voltage V were calculated. First, A is obtained from the equation, $A = C_S t_{OX}/\varepsilon_0 \varepsilon_{OX}$, where C_S is storage cell capacitance, t_{OX} Ta_2O_5 thickness, ε_0 permittivity in vacuum, and ε_{OX} relative dielectric constant of Ta_2O_5. Next, V is obtained from the equation, $V = Jt_{OX}/R\varepsilon_0\varepsilon_{OX}$, where J is leakage current density of the capacitor at supply voltage V, and R storage charge loss rate constant. Assuming C_S is 30 fF[5] and R 3.3 sec^{-1}(10% loss at 30 msec), A and V are obtained as a function of t_{OX}, which is shown in Fig.5. It can be seen in the figure that a 1-Mbit MOS d-RAM can be attained using an approximately 500-Å-thick Ta_2O_5 film, as well as a 4-Mbit MOS d-RAM using a 200-Å-thick film with sufficient supply-voltage margin.

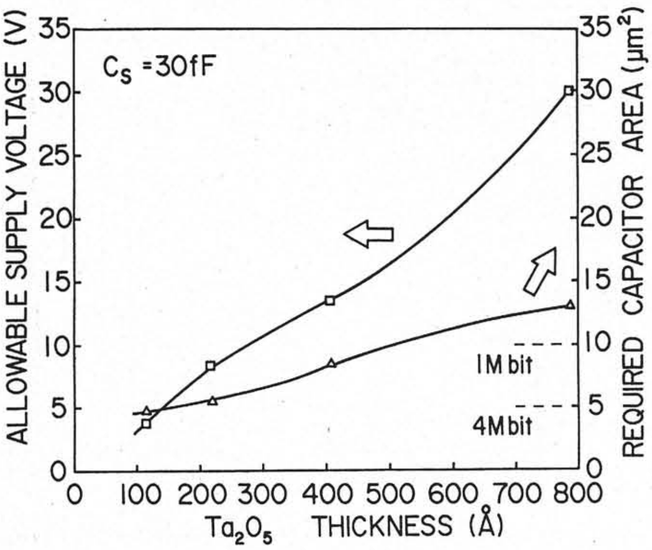

Fig.5 Ta_2O_5 film thickness dependence of allowable supply voltage and required capacitor area for a conventional planer MOS cell capacitor in MOS d-RAM's.

However, devices greater than 4-Mbit are difficult to attain using a conventional MOS capacitor because ε_{OX} decreases with t_{OX} decrease[1]. For this, the MOM(Metal-Oxide-Metal) structure previously proposed[6] will be necessary.

V. SUMMARY

High quality Ta_2O_5 films have been obtained, using a unique ultra-high purity Ta sputtering target. This target has been developed eliminating refractory metal impurities. Leakage current in the high quality Ta_2O_5 film does not increase either with film thickness decrease to 115 Å or by annealing at a temperature of as high as 500°C. MOS d-RAM of up to a 4-Mbit capacity can be attained with a conventional planar cell capacitor by using this film.

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