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Mo Gate MOS Devices Stability Using High Purity Sputtering Target

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A Mo sputtering target with purity of 99.999 % has been developed and the stability of Mo gate MOS devices fabricated using this high purity target has been examined. No mobile charges are observed even in MOS capacitors annealed at 1000°C in nitrogen. Breakdown strength of MOS capacitors with a very thin gate oxide 60 Å thick is held at 12 MV/cm after 1000°C annealing. Long-term instability is also improved by using this high purity Mo target.

1. Introduction

In recent years, refractory metals and refractory metal silicides have been widely investigated for use as gate electrodes in VLSIs because of their low resistivity. However, the purity of the sputtering targets used for deposition of the refractory metal films is as low as 3N (99.9%). Thus, degradation of MOS device characteristics due to impurities in the sputtering targets has been recognized as one of the most critical problems affecting progress in refractory metal gate technology.[1)] Threshold voltage shift caused by alkaline metals such as sodium and potassium has been pointed out from the beginning of refractory metal gate development.[2)] Recently, it has been clarified that large quantities of such radioactive elements as uranium and thorium are contained in deposited Mo (molybdenum) films.[3)] These radioactive elements are known to cause soft errors in MOS RAMs.[4)] Further, it has been suggested that heavy metals such as iron and copper generate surface states in silicide gate devices.[5)] It is assumed that these instabilities will become a more serious problem with increased LSI integration density.

To overcome these MOS device instabilities caused by impurities in sputtering targets, we have developed a Mo target with a purity of 5N. The instabilities of fabricated Mo gate MOS devices using high purity Mo targets have been examined. It was found that mobile charge instability, breakdown strength, and long-term instability of MOS capacitors were greatly improved by the use of this newly developed high purity Mo target.

2. High purity Mo target development

The high purity Mo target is fabricated as follows: Commercially available 99.9 %-pure raw Mo powder containing 10 ppm potassium, 1.4 ppm sodium, 0.7 ppm uranium, 58 ppm iron, and other impurities is dissolved in distilled nitric acid and heated to form molybdic acid, followed by washing in pure water. Then it is dried and reduced to Mo by high temperature heating in hydrogen. In order to prevent the evaporation of molybdenum oxide, a two stage reduction method that consists of heating at 600-700°C as the first stage and heating at 1000-1100°C as the second stage is employed. This high purity Mo is sintered, and the sintered compact is further purified by electron-beam melting in a high vacuum. The resulting ingot is hot-extruded and machined into a disk-shaped high purity Mo target 12 mm thick and 254 mm in diameter. Through these refining processes, each impurity concentration in the Mo is decreased by about two to three orders of magnitude.

A comparison of main impurity concentrations in a conventional target and in the newly developed high purity Mo target is shown in Table 1. In a conventional target, impurity concentrations are from one ppm to several dozen ppm and the purity is only 3N. For the high purity target, concentrations of alkaline metals, radioactive metal (uranium), and heavy metals are reduced to 0.01ppm, 0.001ppm, and less than 1ppm, respectively. The purity of the new target is 5N or higher.

Table 1. Impurities in Mo Sputtering Targets.

(ppm)

Impuritiy		High Purity Target	Conventional Target
Alkaline Metals	Na	<0.01	10
	K	<0.03	10
Radioactive Element	U	<0.001	0.7
Heavy Metals	Fe	<0.01	50
	Ni	<0.05	15
	Cr	<0.01	25
Purity		5N	3N

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

3. Mo gate MOS device stability

Both conventional and high purity targets were installed in a DC magnetron sputtering apparatus where special care was taken to exclude such contaminants as oxygen and alkaline metals from the apparatus environment. Mo film was deposited onto a thermally oxidized silicon wafer by using a two step deposition method developed to prevent Mo penetration into the SiO_2.[6] Fabricated MOS capacitors were used to examine MOS instabilities.

3.1 Impurities in deposited Mo films

The films described above were examined to determine impurity content. Most impurities were greatly reduced by the use of the high purity target. For example, concentrations of uranium in Mo films deposited by conventional and high purity targets were measured and found to be 0.28ppm and below 0.001ppm, respectively. Alpha fluxes from Mo films can be estimated using the emisitivity of natural uranium.[7] For an assumed Mo film thickness of 3000 Å, alpha fluxes were calculated to be 1.2×10^{-2} alpha/cm^{2}h for the conventional target and 4.2×10^{-5} alpha/cm^{2}h for the high purity target. Soft error rate is known to be proportional to alpha flux over a wide range, although the rate differs according to device structure or circuit design. So, the soft error rate due to radioactive impurities in the Mo film is estimated to decrease by more than two orders of magnitude using the high purity target. This is practically negligible even in MOS dRAMs with integration densities of 1Mb or higher.

3.2 Mobile charges

Comparisons of mobile charge densities in MOS capacitors fabricated using conventional and high purity Mo targets are shown in Table 2. To avoid contamination during the lithography process, Mo film patterns with a circular shape were deposited using a quartz plate mask. When the MOS capacitors were not annealed, mobile charges were less than the detectable limit of TVS (Triangular Voltage Sweep) measurement, regardless of which target was used for fabrication. After annealing at 1000°C in nitrogen, mobile chages of about 5×10^{10} cm^{-2} were obserbed in capacitors fabricated using the conventional Mo target. For the high purity target, however, no mobile charge was detected.

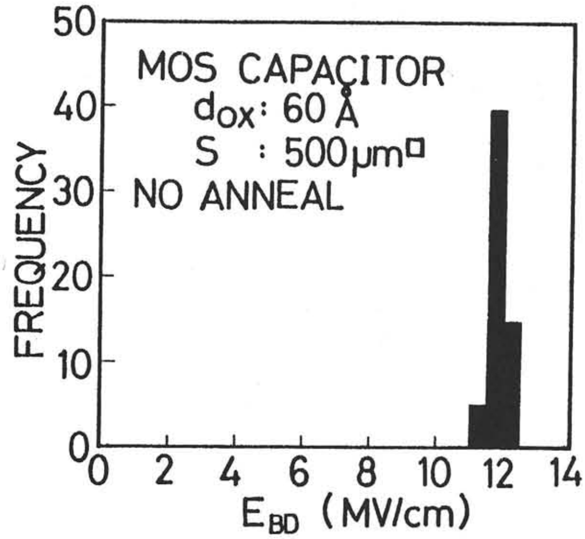
Table 2. Mobile Charge Densities in Mo Gate MOS Capacitors.

	High Purity Target	Conventional Target
No Anneal	Undetected	Undetected
N_2 1000°C Anneal	Undetected	5×10^{10}cm^{-2}

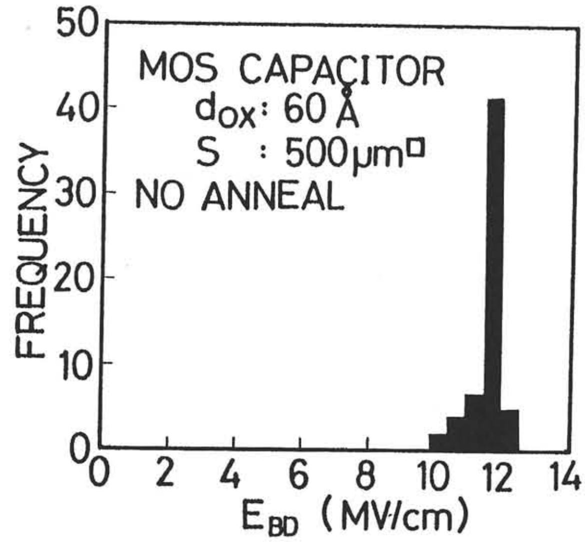
(Detectable Limit: 3×10^9 cm^{-2})

3.3 Breakdown strength

It is well known that breakdown strength of a Mo gate MOS capacitor is reduced by annealing at about 1000 °C. This reduction depends largely on gate area and gate oxide thickness, and is not significant when gate area is as small as 500 µm□ and oxide thickness is more than 100 Å. Therefore, we evaluated breakdown strength for capacitors with a very thin gate oxide of 60 Å. Examples of histograms of the breakdown strength are shown in Figs.1 and 2. When the MOS capacitors are not annealed, breakdown strengths are around 12 MV/cm regardless of target purity. When the capacitors are annealed, however, distributions of breakdown strength clearly differ according to target purity. For the conventional target, breakdown strength is greatly reduced in more than half of the capacitors. These results lead to the conclusion that impurities in the sputtering target are one of the main causes of reduced breakdown strength.

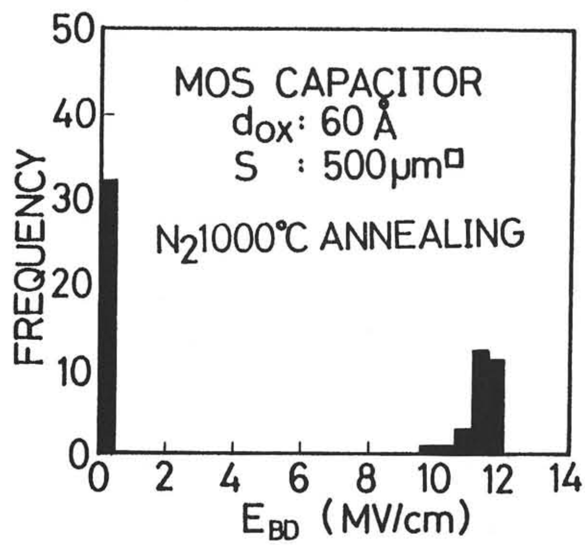


(a) Conventional Target

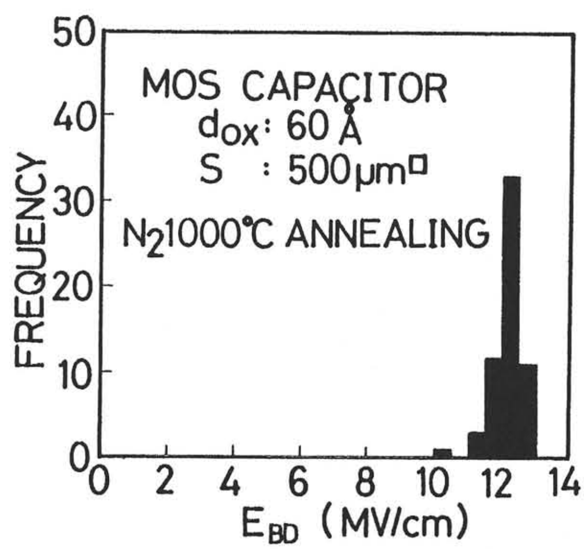


(b) High Purity Target

Fig.1 Breakdown strengths of unannealed Mo gate MOS capacitors.



(a) Conventional Target



(b) High Purity Target

Fig.2 Breakdown strengths of Mo gate MOS capacitors after 1000 °C annealing in N_2.

4. Reliability

The main causes of long-term instability in Mo gate MOS devices, i.e., negative V_{FB} shift and surface state generation, were also examined. MOS capacitors with a gate oxide thickness of 200 Å were fabricated by conventional photolithography and chemical etching. All samples were annealed at 1000 °C in nitrogen, followed by forming gas annealing at 450 °C. Table 3 shows V_{FB} shift after positive bias-temperature (B-T) stress aging in which the stress bias was +5 V, and the temperature was 250 °C. When aging time is 100 hours, a V_{FB} shift of 0.18 V is observed for capacitors fabricated using the conventional target. However, using the high purity Mo target, V_{FB} shift is suppressed to within 0.05 V. This small shift is considered to be caused by contamination during the photolithography process. Figure 3 shows the surface states of MOS capacitors before and after B-T stress aging. To clarify the behavior of surface state generation, strong stress bias and longer aging time were utilized. For capacitors before B-T stress aging, surface state densities N_{SS} are near the measurement limit of 1×10^{10} $cm^{-2}eV^{-1}$. N_{SS} for Mo gate MOS capaciters after B-T stress is about 10^{11} $cm^{-2}eV^{-1}$. Thus, surface state generation caused by B-T stress aging decreased greatly and approached that of a Si gate.

Table 3. V_{FB} Shift Caused by B-T Stress Aging of Mo Gate MOS Capacitors.

(250 °C, +5 V)

	High Purity Target	Conventional Target
1 hour	0.01 V	0.12 V
100 hours	0.05 V	0.18 V

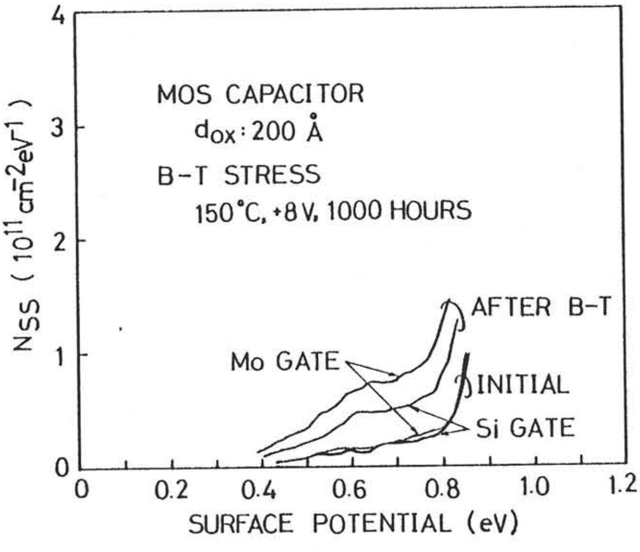


Fig.3 Surface states of Mo gate MOS capacitors before and after B-T stress aging.

5. Summary

A Mo target with a purity of 5N has been developed and Mo gate MOS device stability using the target has been examined. Using this high purity target, mobile charges were reduced to less than the detectable limit and reduction of breakdown strength was eliminated. Long-term instability was also improved.

Acknowledgement

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