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Behavior of Substrate-Originating Si Atoms during Chemical Vapor Deposition and Subsequent Active Oxygen Annealing of Tantalum Pentoxide Film

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The behavior of substrate-originating Si atoms during CVD and subsequent active oxygen annealing of Ta_2O_5 films was comprehensively investigated by XPS analysis. Elemental Si atoms incorporated near the film/substrate interface, when annealed in active oxygen ambients, migrated toward the film surface and changed into oxidized Si there. As a result, the Ta_2O_5 films showed remarkably low leakage current. However, excessive active oxygen annealing resulted in the encroachment of a large amount of elemental Si atoms from the substrate, with the result that the leakage current increased again. It is concluded that the leakage current reduction induced by active oxygen annealing results from a certain cooperative action in which active oxygen diffuses into the Ta_2O_5/Si interface and Si atoms migrate outward toward the film surface.

1. INTRODUCTION

Chemical vapor deposited Ta_2O_5 films are one of the most promising capacitor dielectric candidates for 64Mb DRAMs and following 256Mb devices because they provide a high dielectric constant ($\epsilon_r \approx 25$) and excellent step coverage. However, CVD Ta_2O_5 films had long suffered from leakage current. At the 19th conference on SSDM[1)] in 1987, one of the authors demonstrated that Ta_2O_5 films with much lower leakage current could be obtained using photo-CVD followed by subsequent annealing at low temperature in an active oxygen ambient produced by UV photolysis of O_2 (UV/O_2 annealing). Since then, similar leakage current reductions achieved with various modified active oxygen annealing processes (Table 1) have been reported for photo-CVD and LPCVD Ta_2O_5 films by several investigators.[2-6)]

In a recent paper,[7)] the authors indicated that, besides active oxygen, Si atoms migrating from the substrate to the film surface during annealing play an important role in leakage current reduction. However, all investigators do not necessarily agree on the role played by Si. (It should be noted that the other investigators in Table 1 used Si-containing substrates without exception.)

A comprehensive discussion based on the results of XPS analysis is presented here concerning the behavior of Si atoms observed in Ta_2O_5 films during various active-oxygen and non-active-oxygen annealing processes. A variety of Ta_2O_5 films grown with photo-CVD and LPCVD using different Ta precursors are discussed.

2. EXPERIMENTAL

Ta_2O_5 films chemically vapor-deposited on n-type Si(100) substrates to a thickness of 40 nm were used as samples. The Ta_2O_5 films, unless otherwise specified, were identical to those electrically characterized in Ref. 7, which had been grown by photo-CVD using $TaCl_5$(6N) and O_2, followed by one of the following annealing processes at 400°C and 1 atm: A) UV/O_2, B) UV/O_3, C) O_2 or D) UV/N_2. Here "UV" means irradiation into the annealing chamber from a low pressure Hg lamp and "O_3" indicates oxygen gas containing 5 mol% ozone. The A) and B) processes involve active oxygen annealing. Photo-CVD and LPCVD Ta_2O_5 films grown using $Ta(OC_2H_5)_5$ and $H_3Ta(C_5H_5)_2$ were also investigated. The films were deposited at a substrate temperature of 300°C during photo-CVD and 400°C during LPCVD.

In order to analyze the bonding state and the concentration of elements present at the film surface, the X-ray photoelectron emission spectra for Si 2p, Ta 4f, C 1s, O 1s and Cl 2p were carefully measured with a VG Scientific ESCALAB-MK II spectrometer. A Si wafer and a themal SiO_2 film, measured as standard samples, exhibited a single Si 2p peak at 99.3 eV and 103.2 eV, respectively. A depth profiling analysis of the films was carried out by repeated stepwise-etching using a 5%HF solution and subsequent surface analysis by XPS. Since ion bombardment etching in a high vacuum preferentially removes oxygen from the Ta_2O_5 films, the use of wet etching is essential for depth profiling.

Table 1 Various active oxygen annealing processes for CVD Ta_2O_5 films.

Investigators	*Annealing process*	*Growth process*	*Precursors*	*Substrate*
Tarui *et al.*[1)]	UV/O_2	photo-CVD	$TaCl_5+O_2$	Si
Yamagishi *et al.*[2)]	UV/O_2	photo-CVD	$TaCl_5+O_2$	WSi_2
Shinriki *et al.*[3)]	UV/O_3	LPCVD	$Ta(OC_2H_5)_5+O_2$	poly Si
Isobe *et al.*[4)]	O_3	LPCVD	$Ta(OC_2H_5)_5+O_2$	Si
Tabuchi *et al.*[5)]	UV/O_2	LPCVD	$Ta(N(CH_3)_2)_5+O_2$	Si
Park *et al.*[6)]	plasma−N_2O	LPCVD	$Ta(OC_2H_5)_5+O_2$	Si

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Table 2 Si concentration at surface of about 40-nm-thick photo-CVD and LPCVD Ta_2O_5 films using various Ta precursors and O_2. The data for both the as-grown and 60 min-UV/O_2 annealed films are listed as the Si/Ta atomic ratios.

Ta *precursor*	Si/Ta *atomic ratio at the* Ta_2O_5 *film surface*			
	Photo-CVD		*LPCVD (thermal)*	
	as-grown	*UV/O_2*	*as-grown*	*UV/O_2*
$TaCl_5$	0.016	0.047	0.046	0.103
$Ta(OC_2H_5)_5$	0.005	0.060	0.025	0.054
$H_3Ta(C_5H_5)_2$	0.008	0.025	-	-

3. RESULTS AND DISCUSSION

Figure 1 shows typical Si 2p photoelectron emission spectra recorded from the surface of Ta_2O_5 films, before and after 60 min UV/O_2 annealing. These films were deposited with LPCVD using $Ta(OC_2H_5)_5$ and O_2. It can be seen from this figure that a detectable amount of Si was incorporated in the as-grown film surface and that Si incorporation was markedly facilitated by UV/O_2 annealing. The detected Si was in the oxidized state since it had a binding energy more than 2 eV higher than that of elemental Si. The Si concentration was then quantified for photo-CVD and LPCVD Ta_2O_5 films formed with O_2 and various Ta precursors. The Si concentarations for both the as-grown and 60 min-UV/O_2 annealed films are given as the Si/Ta atomic ratios in Table 2. In this experiment, elemental Si was not observed at all. The most important observation that can be made from Table 2 is that the striking enhancement of the Si concentration due to active oxygen annealing (UV/O_2) is a common phenomenon for Ta_2O_5 films chemically deposited on Si substrates regardless of the Ta precursor and whether the process was photo-CVD or LPCVD. The table also indicates that Si incorporation in the as-grown film surface for LPCVD was several times greater than for photo-CVD. This may have been due to the relatively higher growth temperature of LPCVD. The following discussion will concentrate on the photo-CVD Ta_2O_5 films using $TaCl_5$ and O_2, as their leakage current properties were described in detail in our previous works.[1,7]

Figure 2 shows how the concentration of Si at the film surface changed as a function of the annealing time for different processes. In this experiment as well, only oxidized Si was observed. We can see that the Si concentration increased quickly with both UV/O_2 and UV/O_3 annealing and then saturated, while the Si accumulation rates for O_2 and UV/N_2 annealing were actually zero or extremely small. In addition, UV/O_3 annealing with relatively more active oxygen showed a higher Si accumulation rate than UV/O_2 annealing. These results indicate that active oxygen helps Si atoms to migrate to the film surface. Obviously, Si migration cannot be explained only by the thermal outer diffusion of Si. In a previous paper,[7] the authors pointed out that Si migration during active oxygen annealing contributes significantly to leakage current reduction. It should be noted that Fig. 2 supports that view.

In order to analyze the in-depth distribution and chemical state of Si, depth profiling using a wet etching technique was carried out for various Ta_2O_5 films having a thickness of about 40 nm. Oxidized Si and also elemental Si were observed in the films. In Fig. 3, the concentrations of (a) oxidized and (b) elemental Si in as-grown and UV/N_2(60 min), UV/O_2(60 min) and UV/O_3(30 min) annealed films are plotted as a function of the normalized depth from the film surface. The UV/O_2 and UV/O_3 films exhibited an extremely low leakage current, as shown in the inset in Fig. 3(b). Oxidized Si shows a "U" shape distribution having a high concentration near the surface and the film/substrate interface, while elemental Si shows a "diffusion" shape distribution in which the Si concentration decreases exponentially toward the surface. It should also be emphasized that elemental Si is significantly distributed over a wide region ranging (about 25 nm) from the interface to the film center and that a pure Ta_2O_5 region containing neither oxidized nor elemental Si is present in the center of the films. When the films were annealed in the active oxygen ambients, a decrease in elemental Si and an increase in oxidized Si occurred simultaneously near the film/substrate interface and near the surface, respectively. This means that a portion of the elemental Si present near the interface migrated toward the surface and changed into oxidized species as a result of reacting with active oxygen. On the other hand, in the case of UV/N_2 annealing, although elemental Si near the interface similarly decreased in concentration, the distribution of oxidized Si near the surface remained fixed. Hence, Si migration to the surface did not occur during UV/N_2 annealing.

In a previous paper,[7] the authers demonstrated that, as UV/O_3 annealing time was inceased, leakage current rapidly decreased, reached a minimum after 30 min, and then eventually began to increase. Figure 4 shows depth profiling for Ta_2O_5 films subjected to UV/O_3 annealing for a long duration of 180 min. The most notable difference between the results for 30 min and 180 min annealing was in the distribution of elemental Si. As can be seen from Fig. 2(b), 180 min UV/O_3 annealing gave rise to an elemental Si distribution with a higher concentration over the entire region of the film, even compared with the as-grown film. Since there seems to be less possibility for the generation of elemental Si due to a "reduction" of oxidized Si in an active oxygen ambient, there is no doubt that this increase in elemental Si was induced by the encroachment of Si atoms from the substrate. Eventually, the increase in elemental Si resulted in a recurrence of leakage current in the Ta_2O_5 film inasmuch as elemental Si easily becomes an origin of leakage current.

4. CONCLUSION

The behavior of substrate-originating Si atoms during CVD and subsequent annealing of Ta_2O_5 films was investigated in detail. It was found that in the as-grown Ta_2O_5 films, substantial amounts of elemental and oxidized Si were incorporated in the region near the film/substrate interface. When subsequently annealed in active oxygen ambients, a portion of the elemental Si migrated toward the film surface and changed into oxidized Si there through a reaction with active oxygen, while the concentration of elemental Si in the film decreased. As a result of this process, the leakage current through the films was markedly reduced, as reported previously. However, excessive active oxygen annealing resulted in the encroachment of a large amount of elemental Si atoms from the substrate, with the result that the leakage current increased again. Considering the results of both the previous and present studies, it is concluded that the leakage current reduction induced by active oxygen annealing results from a certain cooperative action in which active oxygen diffuses into the Ta_2O_5/Si interface and Si atoms migrate outward toward the film surface. This understanding is expected to be useful in establishing the next generation of DRAM cell fabrication technology using CVD Ta_2O_5 dielectrics.

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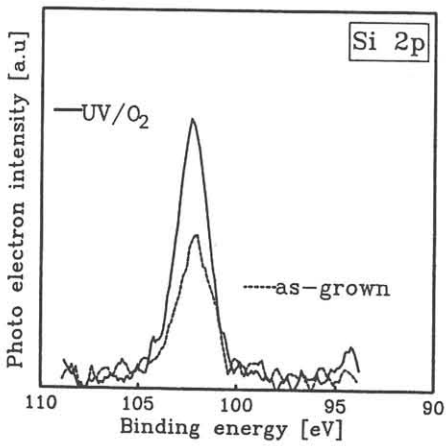

Fig. 1 Typical Si 2p photoelectron emission spectra recorded from the surface of 40-nm-thick Ta_2O_5 films, before and after 60 min UV/O_2 annealing. These films were deposited with LPCVD using $Ta(OC_2H_5)_5$ and O_2.

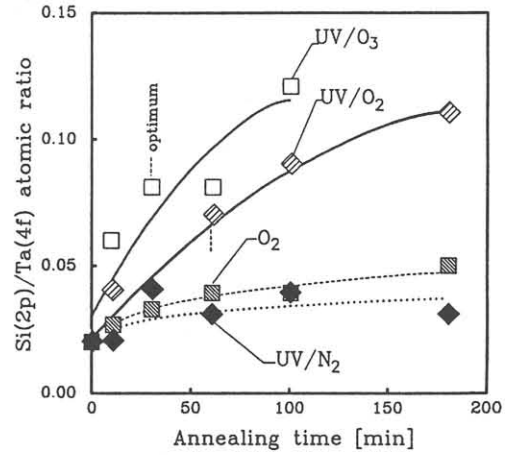

Fig. 2 The concentration of Si atoms accumulated at the film surface as a function of annealing time for various annealing processes.

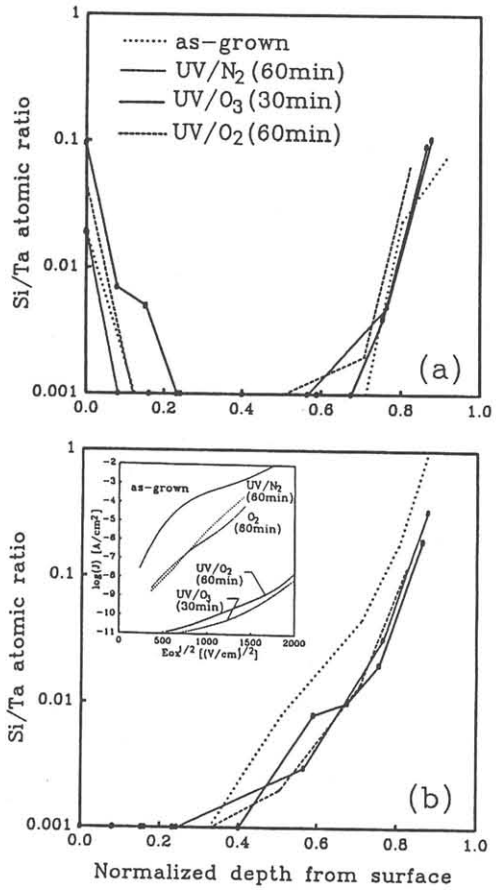

Fig. 3 Depth profilings for (a) oxidized Si and (b) elemental Si in as-grown and 60 min UV/N_2, 60 min UV/O_2 and 30 min UV/O_3 annealed Ta_2O_5 films. The insert in (b) shows the leakage current characteristics of the same films obtained by XPS analysis.[7]

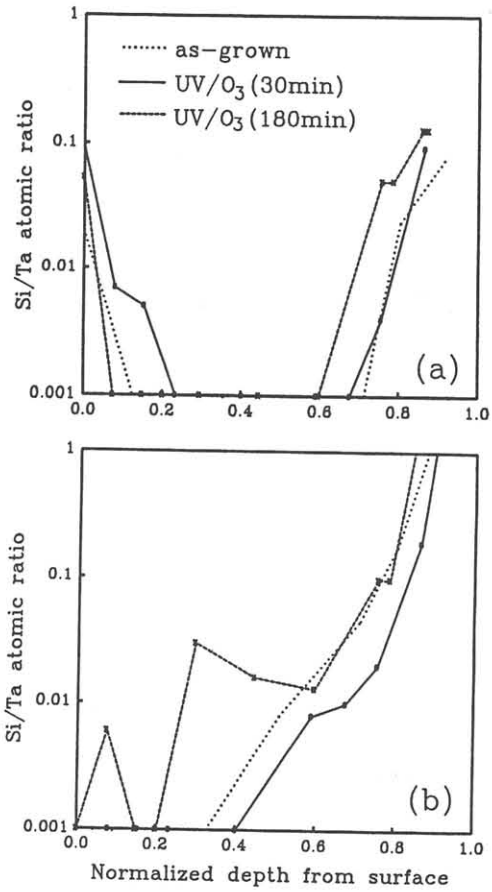

Fig. 4 Depth profilings for (a) oxidized Si and (b) elemental Si in 180 min UV/O_3 annealed Ta_2O_5 film in comparison with those in as-grown and 30 min UV/O_3 annealed Ta_2O_5 films.