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Nano structural properties of Al₂O₃/SiO₂/Si in Integrated electronic Systems

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Abstract: In ultra thin silicon oxide, increasing leakage currents and gate oxide degradation impose a practical limit for ultra thin oxide to be a scaleable gate dielectric in the next CMOS (complimentary metal-oxide-generations. To counter the tunneling, alternative dielectrics with higher permittivity than silicon)semiconductor oxide may be used, as their equivalent oxide thickness may be smaller, in proportion to the permittivity ratio. These issues have led to a search for other possible substitutes for SiO₂ with higher dielectric constants and higher electrical quality.

 Al_2O_3 is one of the superior candidates in consideration of the high dielectric constant. It exhibits several properties superior to those of conventional thermal O_2 oxides (SiO₂), the more important being suppression of boron penetration from the poly-Si gate. It has excellent protective action against diffusion and corrosion.

The pure ultra thin aluminum oxide onto silicon oxide films have therefore been grown and studied on Si(111) in furnaces and studied by AES, SAM and AFM techniques. One result shows that the Al_2O_3 film growth is self limiting, but differing from the self limiting growth of oxide under isothermal conditions, which both have half Sigmoid-like behavior. In general, the present work deals with the physical and chemical properties of Al_2O_3 film surfaces and interfaces of silicon and how these systems interact with e.g. adsorbing oxygen atoms.

Keywords: Thin film, Nanostructure, Al₂O₃ and surface sensitive technique.

Introduction:

The development of microelectronics has entered the nanometric range due to the continuous shrinking of electronics device dimensions. The oxide of silicon is a uniquely critical material within silicon semiconductor technology, in that it is a major component for MOS and MIS (I: Insulator) devices. It has therefore become crucially important to study the properties and behavior of ultra thin oxides (UTO) as well as aluminum oxide on Si. This vital role of very thin dielectrics has been the motivation for characterizing and modeling of the oxidation of silicon and aluminum in the thin and ultrathin film regimes. Progress in this area will probably be based both on firm experimental results and on some modeling of steps to bridge over lacking experimental details. There are important concerns about growing the amorphous and thinnest possible aluminum oxide layers, to optimal control of the process, to stop it at a given thickness of film and to understand the dynamics of the process steps and the resulting chemical structure. The efforts concern oxidizing them followed or paralleled by various ways to achieve films growth. In the dry thermal oxidation process with Si the growth rate of the initial parts of the reaction is currently modeled with additional terms [1- 5], besides the usual linear - parabolic dependence on time. Several phenomenological models have been proposed to account for this faster initial growth. Reviews of the models can be found elsewhere [5 and references therein]. Among them, Massoud et al. [6, 7] added an exponential term to the Deal- Grove model [8] to improve it.

Thermal oxidation is the most common, and also the simplest way, to produce silicon dioxide layers. However, due to limitations in the present processing set- ups, these methods do not produce aluminum oxides less than 3 nm thick. A self-limiting growth phase is discovered. It follows a Boltzmann-like (sigmoidal) thickness vs time behavior. In our forthcoming paper, this mechanism will be explained within a model where both diffusion and reaction occur in discrete cells and with Si, Al and O₂ treated as moving and reacting species for the very thin films.

Experimental Procedures and details

The silicon samples in 3 cm x1 cm size were introduced in the furnace after a rinse with ethanol in an ultrasonic bath. A quartz furnace connected to a gas flow system has been used for the growth of oxide layers. The silicon samples are preheated in air to 1020° C for 10 minutes at a pressure of one atmosphere to remove the native oxide layer. Following this step, dry oxygen has been allowed into the furnace at one atmosphere pressure and evaporated aluminum wire (which is kept with thallium holder, allow passing current through Al wire), has then been allowed into the quartz furnace. The temperature range was between 500- 900°C for different exposure times.

The quartz tube exhaust was connected to a water container through a hose1. A huge peak of oxygen is part of the Al_2O_3 growth as shown in Fig. 1 under this conditions. In addition to that, Ar which is necessary to remove native oxide is used which is the other reason for cleaning in Al_2O_3 nanostructures.

The oxidized samples were then immediately transferred to a Auger Electron Spectrometer and SAM in order to evaluate the film uniformity, interface structure and film thickness. The figures indicate that the region between the oxide, aluminum and the silicon substrate is not very sharp. Oxygen, aluminum intensities gradually increases from the bulk stoichiometric SiO_2 and nearly vanishes at the interface (see figure 2).



Figure 1- Auger spectra of oxygen at 500 ^oC in Si(111) (Oxygen exposing time: 5, 15, 20 and 30 min).



Figure 2- SAM spectrum of aluminum oxide film on silicon dioxide (substrate is Si(111)).



Figure 3 - A self limiting growth of film. The film thickness has been found with using intensity ratio of silicon, oxygen and aluminum and their mean free path through the film and substrate as addressed in [2].

AFM and AES techniques are analytical and surface sensitive techniques for measuring Al_2O_3 thickness and film morphology on films, respectively. The thickness of the Al_2O_3 layers as a function of growth time are shown in figure 3.

It is clear that the initial growth is the linear growth kinetics with oxidation time and an initially enhanced growth rate. These results, shown in figure 3, are different from the reported data in [9 - 15].

In parallel to the AES experiments, AFM has been used to study how the aluminum and oxygen atoms are rearranged on the silicon oxide onto Si(111), (see figure 4). The substrates are kept at a temperature of 500° C. After the first, short exposure, 20 minutes oxygen and evaporated Al atoms on the film surface indicating a change of the surface reconstruction. The following larger exposures, 60 minutes oxygen and evaporated Al, change the structure of the entire spectrum (figure 5).



Figure 4 - AFM image of aluminum oxide on silicon dioxide film which has been grown on Si(111) substrate at 500^oC, and 20 minutes oxygen and evaporated Al.



Figure 5 - AFM image of aluminum oxide on silicon dioxide film which has been grown on Si(111) substrate at 500^oC and 60 minutes oxygen and evaporated Al.

Discussion

There are some reasons why atoms on the film surface are scattered on the silicon substrate and after exposing more oxygen atoms could come close together to produce a film. In fact, as the reacted volume occupies more of the sample, atomic oxygen has an increasingly more difficult transport from a cell to the other cell (like in the diffusion limit) and the O₂ recombination probability to form Al - O - Si bonds, which also prevents atomic oxygen to fill up the (larger) volume. The transport (ballistic or sub diffusion) is apparently enhanced with oxygen exposure, and even if the recombination rate is also likely to be enhanced, the balance apparently is favoring a higher Al - O with higher exposures, for comparable thickness of aluminum oxide film.

One can conclude that there are significant qualitative differences for exposing oxygen and evaporated Al time, which have been still more details and will be discussed in the next future. The spectral region around the main Si lines is also affected by these exposures, and the atomic rearrangement on the silicon surfaces have been changed after the highest doses employed (not shown here).

These figures clearly show that the process gave rise to unwanted Si- O bonds, instead of desirable Al- O- Si bonds. Thus, we have to find how these bonds should be removed; otherwise the question of whether the Al-Si bonds are as suggested by the authors of ref [14 -15] cannot be answered on the basis of our experiments.

Conclusion:

The important issues which are threatening the use of ultra thin (<1-2 nm) oxides of the silicon, are: quantum- mechanical tunneling of carriers through the thin gate oxide, from source to drain, and from drain to the body of the MOSFET channel and this gate oxide degradation imposes practical limits on ultrathin silicon oxide as a gate dielectric of future CMOS device.

As stated above, Al_2O_3 is discussed in detail and it is suggested that it could be a good gate dielectric to

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replace silicon oxide. Some issues such as reports about a low electrical quality at the aluminum oxide / silicon dioxide/ silicon interfaces and unsaturated bonds in the Al_2O_3 limit it to be introduced as a good gate dielectric, meaning we have to study their interfaces with some other techniques such as Tunneling Electron Microscopy (TEM) technique.

We presently believe that the isothermal, self limiting aluminum oxide which leads to films less than three .nm thick is a sub diffusion process.

In summary, much of the progress in nanotechnology has been achieved in the electronic industry to find a suitable gate dielectric in future CMOS components. So successful is in that now research is following the initiatives of industry and research funding seems to be totally directed by the trend presented in the present work. With these findings it is strongly suggested that the uniform amorphous aluminum oxide films grown at 500^oC should be tested as obvious candidates for replacing SiO₂ in the next generation of CMOS components in CPU chips.

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