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A Comparison of SiO₂-Based Alloys as High Permittivity Gate Oxides

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1. Introduction

As the industry is viewing the end of Si scaling, several alternative routes to high performance CMOS logic devices are being considered. In this paper, we address the issue of alternative high permittivity dielectrics to replace SiO₂ or Si-O-N dielectrics.

It is not yet clear when the alternative dielectrics will be required, i.e., the date or technology generation, as demonstrated by the current debate [1-4]. However, we assume that alternatives will be required for equivalent oxide thicknesses of 1.0 nm, or below, and this value is therefore the focus of our developmental effort.

Our project initially focused upon identifying candidate dielectric materials, considering factors such as the required process conditions; reactivity with Si and gate metal candidates under these process conditions; crystalline structure; dielectric properties; band gaps, alignment and leakage. On the basis of these considerations, a set of candidate materials were selected. In this paper, we will describe progress to date on the development of the La₂O₃-SiO₂ and HfO₂-SiO₂ dielectric systems.

The paper is divided into two sections: the first deals with thermodynamic stability, and the second gives limited examples of properties that have been achieved.

2. Thermodynamic Stability and Reactivity.

The process conditions which the SiO₂ gate dielectric currently endures, both during the front end processing, as well as during the subsequent backend processing of contacts and connects, may be described as 'severe'. In particular, although the time at elevated temperature is usually short (several seconds), the standard process route includes a diffusion anneal typically exceeding 1000° C under reducing conditions. SiO₂ is extremely resistant to reduction, reaction, and crystallization, accounting for its excellent performance and scalability. In considering alternative dielectric systems, particularly as a direct replacement for Si, attention must be paid to these issues of thermodynamic and structural and kinetic stability [5].

The apparent crystallization temperatures for the La system are higher than those for Hf. These temperatures are dependent on film thickness and the time at elevated temperature, as shown also in Figure 1. It can be observed that the amorphous alloy with the initial composition La₂SiO₅ resists crystallization until about 60 secs at 1000° C (Figure 1). It must be noted, however, that composition of these layers may change upon heat treatment, in particular, through uptake of Si from the substrate. On the

other hand, the thin film amorphous alloy with the initial composition HfSiO₄ shows similar crystallinity after 60secs at only 800° C, and is well crystallized after 120 seconds. At higher temperatures, the crystallization is significantly more rapid. The results emphasize that achieving the backend temperatures of >1000° C will be difficult for the Hf system, without moving to the compositions more rich in SiO₂ [6].

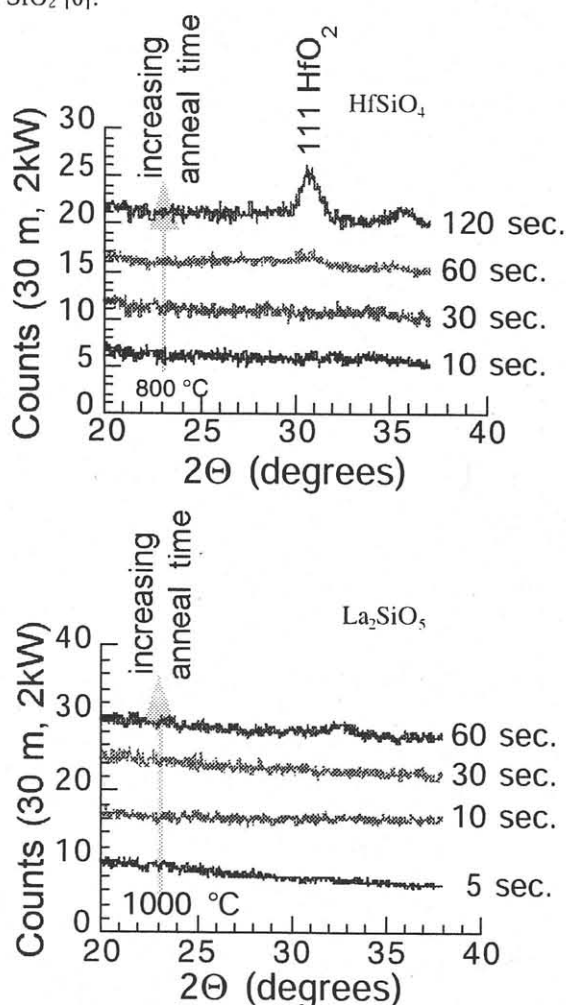


Figure 1. X-ray diffraction patterns for HfSiO₄ and La₂SiO₅. Anneals performed at temperatures indicated in the lower left corner of plots.

It is worth noting that the crystalline phase in the case of the HfO₂-SiO₂ correspond to HfO₂. This implies that phase segregation is occurring, which is consistent with the phase diagrams for the system. The line compound HfSiO₄ melts incongruently, and there is a large-two phase sub-

liquidus region in the system. This is consistent with the expectation that an amorphous alloy in the $\text{HfO}_2\text{-SiO}_2$ system will initially phase segregate to form crystalline HfO_2 and an SiO_2 -rich alloy. The hafnon (i.e., HfSiO_4) crystalline phase occurs only after extended high temperature anneals due to the requirement for solid state diffusion. These same observations are also pertinent for the $\text{ZrO}_2\text{-SiO}_2$ system, which behaves in analogous fashion.

There are some interesting implications which follow from the above observations. The $\text{HfO}_2\text{-SiO}_2$ and $\text{La}_2\text{O}_3\text{-SiO}_2$ systems are rather different from each other with respect to their phase behavior. Consequently, it is expected that a deposited amorphous alloy with the composition La_2SiO_5 will remain single phase upon annealing over a wide temperature range. In contrast, an amorphous alloy like HfSiO_4 clearly phase segregates into nano or micro-regions of HfO_2 surrounded by an amorphous SiO_2 -rich matrix. In related fashion, low energy deposition of HfO_2 onto SiO_2 shouldn't initially result in reaction, such reaction would only occur after crystallization of HfO_2 . Alternatively, deposition of La_2O_3 onto SiO_2 will result in an La-Si-O alloy provided even modest heat treatments (i.e., 800°C for 30 seconds). These observations have recently been confirmed by medium energy ion scattering spectroscopy (MEIS) by the Rutgers group [7].

An important cautionary note should be made, viz that the process atmosphere must be controlled. For high oxygen partial pressures, oxygen diffuses through the dielectric predominantly forming SiO_2 at the Si interface. At very low partial pressures, the oxides tend to reduce, which strongly increases the reactivity with Si. The La oxide system appears to be more problematic in this respect than the Hf system. Detailed process windows, however, must still be established.

3. Summary of Properties.

The properties that can be achieved for capacitors

based upon the $\text{HfO}_2\text{-SiO}_2$ and $\text{La}_2\text{O}_3\text{-SiO}_2$ systems are strongly dependent upon the backend process conditions. Figure 2 shows the C-V and I-V curves for an annealed capacitor with the approximate composition La_2SiO_5 . This particular capacitor has an equivalent oxide thickness of ~ 1.4 nm. These types of result are somewhat encouraging, but implications cannot be drawn until transistors are evaluated.

4. Conclusions

The $\text{HfO}_2\text{-SiO}_2$ and $\text{La}_2\text{O}_3\text{-SiO}_2$ systems have been selected for more detailed study. This research has commenced in our laboratory by an investigation of the phase stability and reactivity of the systems as a function of possible process conditions.

Acknowledgments

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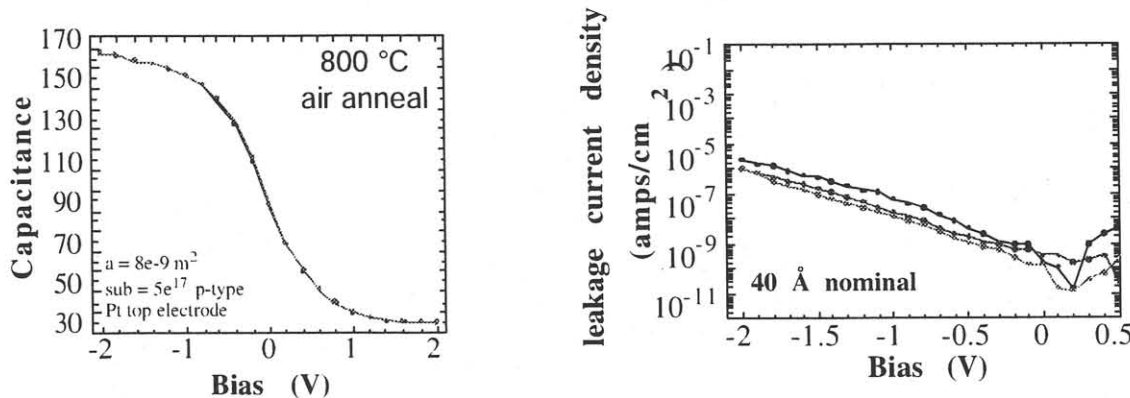


Figure 2. Representative C-V and J-V curves for an amorphous alloy with the composition La_2SiO_5 , deposited by MBE, and annealed in air at 800°C .