ESF Exploratory Workshop on

"Atomistic modeling of growth, structure and electrical properties of high-k gate dielectrics "

March 17th – 18th, 2003
IBM Zurich Research Laboratory
Rüschlikon (Zurich), Switzerland

Organizers:
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SCIENTIFIC REPORT

ESF PESC EXPLORATORY WORKSHOP
Growth, structure and electrical
properties of high-k gate dielectrics:
atomistic modeling vs experiment

Rüschlikon (Zürich), Switzerland
17-18 March 2003

1. Executive Summary

In view of continuously improving the speed and circuit density of silicon integrated circuits (ICs), the semiconductor industry has since its early days adhered to an aggressive reduction of the critical dimensions of the complementary metal-oxide-semiconductor (CMOS) transistor. Transistor scaling brings along the need to reduce gate oxide thickness. Conventional, thermally grown (nitrided) SiO_2 can soon no longer be used because direct tunneling leads to excessive gate leakage. To this end, the worldwide silicon IC industry has embarked on a large-scale research effort to develop a high-k alternative for SiO_2.

Both physical and and chemical vapor deposition - based techniques are currently under investigation for the growth of high-k metal oxide gate dielectrics on silicon wafers on an industrial scale. However, the development of reliable deposition methods is time consuming and the number of candidate compounds to be screened is large. In addition, physical and chemical analysis of the layers demands the utmost of today's state-of-the-art characterization techniques. In conclusion, the development, within the time window available, of a high-k dielectric of sufficient quality to replace the mature SiO_2-based materials of today, represents a formidable challenge for growth, characterization, and device characterization experts.

Meanwhile, today's state-of-the-art theoretical methods can play a large role in avoiding the elaborate experimental efforts needed for screening large numbers of candidate materials. Theoretical approaches can speed up the selection of suitable gate dielectrics and growth methods by limiting the experimental input needed. Due to the tremendous increases in the power of computers during the last decades, along with improvements in theoretical methods, considerable progress has been made in the development of powerful *ab initio* methods, capable of accurately predicting electronic properties without the need for any experimental input.

The principal objective of the ESF PESC Workshop on "*Growth, structure and electrical properties of high-k gate dielectrics: atomistic modeling vs experiment*" was to achieve an effective cross-fertilization between research performed in the simulation, characterization, and layer growth communities. In the interactive workshop format, theoreticians can be exposed to the growth results of experimentalists, giving them the chance to assess their methods and gather ideas for new systems to study. Likewise, growth and characterization experts can learn about the capabilities and limitations of theoretical techniques for predicting both atomistic structure and electronic properties.

The workshop took place in Rüschlikon (Zürich) at IBM's Zurich Research Laboratory on 17-18 March, 2003. Both IBM and the European Commission – IST program contributed additional financial backing, to cover infrastructure costs and travel for participants from outside Europe. The 2-day workshop program consisted of 14 invited talks (30 minutes presentation + 15 minutes discussion), divided over 5 sessions (High-k interface issues for CMOS devices; MBE growth of high-k oxides on silicon; Oxide-semiconductor band offsets: theory vs experiment; High-k film growth, structure and properties: modeling vs experiment; First principles calculation of electrical properties.)

From the feedback received from many participants during and after the meeting, the main factor for the workshop's success was found to be the high quality of the invited speakers. Their presentations were well structured, and the time schedule was very well adhered to. Most presentations were followed by a lively discussion of high scientific level, helped by the relaxed, collegial atmosphere and the relatively small size of the audience.

There was excellent attendance from participants in EU projects funded under the 5th framework program (INVEST and HIKE). For these projects, the workshop provided an excellent forum for networking, as well as for dissemination of their results in the international scientific community. The success of the workshop certainly confirmed Europe's well-recognized strength in the area of *ab initio* modeling for the simulation of advanced materials.

2. Scientific content of the event

Ritala (Helsinki) started out with an overview of the issues in ALCVD growth of high-k layers on silicon, pointing out that modeling is especially needed for understanding the most efficient surface reaction schemes and for designing precursors to obtain optimal decomposition behavior. The theme of *ab initio* modeling of CVD grown films was discussed in great detail by **Elliott** (Cork), who simulated spinodal decomposition in high-*k* zirconium and hafnium silicate layers. Even though the phenomena in question occur in amorphous layers, modeling based on crystalline systems has proved quite useful to gain insight in experimentally observed trends in crystallization behavior as a function of M/Si ratio (M= Hf, Zr). The theme of phase separation during high-temperature treatment of amorphous high-k layers received further attention in the talk of **Stemmer** (Santa Barbara). Her results indicate that phase separation in Hf-silicate and Zr-silicate systems with different composition has different pathways, but resulting microstructures look similar at the atomic scale for large undercoolings. Stemmer further pointed out the need to further develop atomic scale characterization techniques to accurately measure composition (e.g. HRTEM-EELS (electron energy loss spectroscopy)). Using EELS and XANES (X-ray absorption near edge structure), a processing window was found to exist for ZrO_2/Si films between interfacial SiO_2 growth and silicide formation, which is likely promoted by oxygen deficiency of the films. Furthermore, excess oxygen in low temperature CVD process was found to cause silicate formation in Y_2O_3/Si system.

The talk of **Heyns** (Leuven) put the experimental and theoretical for amorphous oxides on silicon systems in technological perspective, pointing out that while 0.86 nm EOT has been demonstrated with Hf/Al based layers on RTO (rapid thermally oxidized) and NH_3 treated starting surfaces, using a TiN gate dielectric, serious problems remain with charge trapping. Detailed studies show that electron trapping occurs for positive bias (substrate injection), while charge extraction for negative bias by de-trapping is quite efficient and occurs at all voltages. A defect band, spatially located close to the interfacial SiO_2 layer, and most likely associated with the presence of oxygen vacancies in the films, is believed to be responsible for the observed charge trapping behavior.

The important issue of band offsets between the high-k dielectric and silicon was introduced from the theoretical angle by **Fiorentini** (Cagliari), who presented computational results for ZrO_2, HfO_2 and CeO_2, as well as La and Lu sesquioxides (M_2O_3). **Chambers** (PNNL) covered the same topic from the experimental side (X-ray photoelectron spectroscopy (XPS)) Using high photoelectron kinetic energies, determination of band offsets and band bending at buried interfaces 40 - 60Å below the surface is possible. Crystalline $SrTiO_3$/Si and $BaTiO_3$/Si band offsets were found to be well behaved (no dependence on oxide thickness; conduction band and valence band offsets accurately predicted by semi-empirical theory (*e.g.,* Robertson and Chen). Rather different observations were made for amorphous oxide/Si ($LaAlO_3$/Si) band offsets (large thickness dependence, thermal history dependence). In conclusion, $LaAlO_3$/Si was found to have a large (> ~1 eV) conduction band and valence band offset after 400°C anneal in UHV, making this compound a quite interesting candidate high-k gate dielectric.

In his talk "*Lessons from SiO_2 – the mother of all interfaces*", **Pantelides** (Vanderbilt) provided an excellent historical perspective on the role of *ab initio* modeling for understanding defect processes in SiO_2. Issues such as the effect of atomistic structure of the interface on its electrical behavior, and defect generation mechanisms were covered also by other speakers, including Foerst, Foster, and McKee.

One of the highlights of the workshop was a fresh perspective on the issue of band offsets, provided by **McKee** (Oak Ridge). As the founder of the "COS" (crystalline oxides on silicon) field, he focused on recent experimental results on epitaxial BaSrO layers grown on Si(100) with different interfacial alkaline earth silicide layers. He concluded the interface phase acts as a "coulomb buffer" for charge in the interface states between Si and the epitaxial oxide. Systematic trends were studied, varying the alkaline earth metal M in the interfacial silicide layer (M = Be, Mg, Sr, Ba), as well as the Ba/Sr ratio, and hence the dielectric constant, of the epitaxial BaSrO layer grown on top. Excellent agreement between bond distances, calculated *ab initio*, and experimentally observed band offsets was observed. McKee's workshop contribution represented the first presentation of his work, which is due to be published in *Science* in the coming months.

McKee's presentation set the stage for theme of epitaxial oxides, as possibly disruptive alternatives to amorphous high-k systems. **Foerst** (Vienna and Clausthal) reported *ab initio* results on the structure and electronic properties of the interfacial template layers for growth of epitaxial perovskite-structure oxides on silicon (100). The question whether the desired interface contains ¼ or ½ monolayer of alkaline earth metal fuelled a lively debate between MBE growers, theoreticians and HRTEM characterization experts. **Foster** (Helsinki) discussed *ab initio* calculations of defect energetics in ZrO_2 and HfO_2 (defect generation, charge transfer, defect reaction, diffusion). His main conclusions are that O_2 readily dissociates and diffuses as O^- through the lattice. Exposure of these oxides to N_2, will lead to incorporation of molecular rather than atomic species. An atomic nitrogen source or NH_3 are needed to achieve effective nitridation of the layers. H in the films forms immediately OH, either in the form of interstitial OH groups or as complexes with lattice oxygen.

Finally, three talks reported results of thin film growth studies by MBE. **Dimoulas** (Athens) presented an overview of the results achieved so far in the framework of the European project "INVEST". **Fompeyrine** (Zurich) presented a number of examples from the study of complex oxides, showing how the richness of their structure and phase equilibria can explain the large effect of terminating layer and interfacial energies on growth modes. From the grower's point of view, these two aspects imply that atomic level control is needed during the growth, and that issues of thermodynamic equilibrium at the interface have to constantly be kept in mind to avoid the formation of undesirable phases. **Osten** (Hannover) presented very detailed results on the Pr_2O_3/Si system, pointing out the role of interfacial energy minimization in orientation selection. On Si(100), crystalline Pr_2O_3 grows as (110)-domains with two orthogonal in-plane orientations. Meanwhile, on Si (111), high quality epitaxial growth of hexagonal phase (La_2O_3 type) Pr_2O_3 was observed; these films can be overgrown epitaxially with high quality Si (111). Pr_2O_3 has a band gap of 3.5 eV with symmetric band offsets to Si. Together with the localized and flat *f* states in the conduction band this results in ultra-low leakage currents. No significant hysteresis is observed in C-V measurements. However, interfacial oxide growth is observed in air for uncapped layers. Furthermore, it was found that the oxygen content at the interface determines the relative magnitude of

the conduction and valence band offsets. In layers annealed in vacuum (at 1075 K), stoichiometric Pr_2O_3 is formed at the Si/ Pr_2O_3 interface. For this structure, the band offset is nonsymmetric (increased valence band offset, decreased conduction band offset), resulting in a higher leakage current (10^{-8} A/cm² for standard layer; 10^{-2} A/cm² for vacuum annealed layer). Meanwhile, in the as deposited films, the interface is oxygen rich and PrO_2 forms locally at the interface with Si. The associated interface dipole results in symmetrical band offsets between Si and the Pr_2O_3 dielectric. In this work, the values for the band offsets obtained experimentally from electrical measurements and XPS were backed up with *ab initio* electronic structure calculations, showing the dependence of the interfacial dipole on oxygen content.

3. Final Workshop Program

Monday morning, March 17th, 2003

9.00 – 9.05	Gerd Norga, IBM Zurich Research Laboratory Welcome
9.05 – 9.15	Jim Greer, National Microelectronics Research Centre, Cork, Ireland, ESF Delegate "Overview of the European Science Foundation"
9.15-9.30	Paul Seidler, IBM Zurich Research Laboratory, Switzerland "Research activities in IBM ZRL's Science and Technology Department"

Session I – High-k interface issues for CMOS devices *Chair: Peter Bloechl*

9.30 – 10.15	Socrates Pantelides, Vanderbilt University, Nashville, USA "Lessons from Si-SiO_2 -The mother of all interfaces"
10.15 – 10.45	Coffee Break
10.45- 11.30	Marc Heyns, IMEC, Leuven, Belgium "Issues and achievements in scaling Hf-based high-k gate stacks to sub-1nm EOT"
11.30 – 12.15	Rodney McKee, Oak Ridge National Laboratory, USA "MOS capacitor physics for crystalline oxides on semiconductors"

12.15 – 13.00 Clemens Foerst, Vienna Technical University, Austria
"Interfacing high-k oxides with silicon: solutions from *ab-initio* simulations"

13.00 – 14.00 Lunch

Monday afternoon, March 17th , 2003

Session II – MBE growth of high-k oxides on silicon Chair: J. Dabrowski

14.00 – 14.45 Joerg Osten, University of Hannover, Germany
"Towards understanding epitaxial growth of alternative high-k dielectrics on Si(001): application to praseodymium oxide"

14.45 – 15.30 Athanasios Dimoulas, National Center for Scientific Research "Demokritos", Athens, Greece
"Molecular beam epitaxy of metal oxide/semiconductor structures for advanced CMOS"

15.30 – 16.00 Coffee break

Session III – Oxide-semiconductor band offsets: theory vs experiment Chair: J. Robertson

16.00 – 16.45 Scott Chambers, Pacific Northwest National Laboratory, Richmond, USA
"Band offset investigations of novel oxide/Si heterojunctions by high energy resolution X-ray photoemission spectroscopy"

16.45 – 17.30 Vincenzo Fiorentini, INFM and Università di Cagliari, Italy
"Interface offsets and dielectric properties of X/Si (001) [X=zirconia, hafnia, yttria, ceria]"

Evening Program

17.30 – 18.30 Reception at IBM ZRL

18.30 Departure of shuttle bus in front of main entrance IBM ZRL to Seehotel Meierhof

20.00 Dinner at Restaurant "*Crazy Cow*", Horgen

Tuesday morning, March 18th, 2003

Session IV – High-k film growth, structure and properties: modeling vs experiment
Chair: Marco Fanciulli

9.30-10.15 Mikko Ritala, Universty of Helsinki, Finland
"Reaction mechanisms in Atomic Layer Deposition"

10.15 – 10.45 Coffee break

10.45 – 11.30 Susanne Stemmer, University of California, Santa Barbara, USA
"Structure and stability of alternative high-k gate dielectrics"

11.30 – 12.15 Simon Elliot, National Microelectronics Research Centre
"Atomic Layer Deposition and phase segregation: simulating high-k dielectric films from First Principles"

12.15 – 13.00 Jean Fompeyrine, IBM Zurich Research Laboratory, Switzerland
"Complex oxides: Interface control for IT applications

13.00 – 14.00 Lunch

Tuesday afternoon, March 18th, 2003

Session V - First principles calculations of electrical properties
Chair: Jean-Pierre Locquet

14.00 – 14.45 Adam Foster, Helsinki University of Technology, Finland
"Defect processes in high-k oxides"

14.45 – 15.30 Wanda Andreoni, IBM Zurich Research Laboratory, Switzerland
"The dielectric constant of high-k oxides: underlying mechanisms and doping effects" (cancelled)

15.30 – 16.00 Coffee Break

16.00 – 17.00 Workshop wrap-up.

4. Assessment of the results, contribution to the future direction of the field

Apart from the base funding from the ESF, the workhop also received financial assistance funding from two co-sponsors, IBM Zurich Research Laboratory and the European Commission – IST program through the project "INVEST". For IBM Zurich Research Laboratory the workshop was an excellent opportunity to highlight the activities of its "Advanced Functional Materials" research group, which has been in the field of MBE-grown epitaxial high-k gate dielectrics active since 5 years. For the IST project "INVEST", the ESF workshop was a key dissemination action, and was reported as such to the European Commission.

Emerging from the discussions at the workshop, especially in light of McKee's and Foerst's results, was the realization that *ab initio* methods can play a large role in the development of novel crystalline silicon-epitaxial oxide interfaces. From the talk of Pantelides it became clear that SiO_2 remains a "magic" interface – a precious gift of nature, as has often been said. To capture the full complexity of its disordered structure with theoretical methods that are intrinsically more suited to handle crystalline systems, remains an elusive goal. The fact that powerful *ab initio* methods came of age at a time when SiO_2 technology was already mature, further explains why basic understanding has tended to lag behind the relentless technological progress in the Si/SiO_2 system. For the novel crystalline oxide-silicon interfaces, powerful theoretical techniques can no doubt play a larger role than they did for SiO_2, since these systems will have to largely be designed "from scratch" and taken to technological implementation during the next 5 – 10 years.

The issue of structure and stoichiometry of the Sr interfacial layer, essential for the commensurate growth of epitaxial perovskites on silicon, remains the subject of intensive debate among theoreticians and experimentalists. This topic received particular attention at the workshop because several presentations focused on it from different angles. It has

certainly been one of the workshop's merits that a forum was created where results were debated at a high scientific level, in an atmosphere that was at times animated, but always constructive. The workshop proved very timely, as demonstrated by the fact that a number of people presented very recent work (unpublished or submitted for publication only days before the workshop date). As a result, many scientific contacts were established, which are likely to impact future research directions and/or foster further scientific exchange.

After consultation with the participants, the organizers decided to make available all workshop presentations in CD-ROM format to the workshop attendants as well as to the sponsors (ESF, the INVEST consortium and IBM).

5. Statistical information on the participants

The workshop attracted a total of 35 participants from 11 European countries and 4 from the USA. Growers, modeling experts and characterization people were roughly equally represented both in the presentations and among the participants. (Of the 35 participants, 13 were growth specialists, 11 modeling experts/theoreticians, and 11 characterization people. Of the 14 scheduled presentations, 6 were principally focused on modeling work[1], 3 on characterization results, and 5 on growth experiments.)

The convenors made a special effort to encourage the participation of young scientists; this effort was quite successful since of the people who finally attended the workshop, roughly one third falls in the ≤ 35 years age bracket.

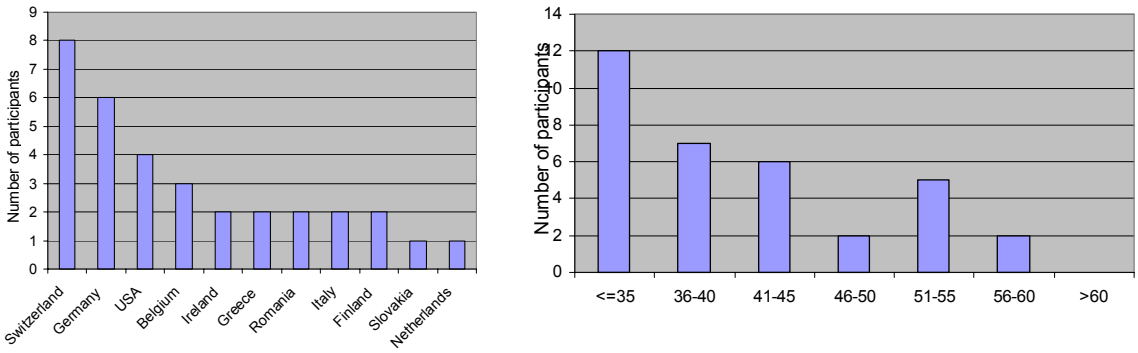

Figure 1: Geographical and age distribution of the workshop participants.

[1] One presentation in the area of modeling has to be cancelled due to illness of the speaker.

6. Final list of participants

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1	Afanase'ev	Valerie	Dr	Afd. Halfgeleiderfysica, Celestijnenlaan 200D, B-3001 Heverlee, Belgium	Valeri.Afanasiev@fys.kuleuven.ac.be
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