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Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

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- 1st March for experiments carried out up until June of the previous year;
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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Interface between epitaxial $Ce_{0.54}Al_{0.46}O_X$ thin film and Si	**Experiment number**: SI-1382
Beamline: ID1	**Date of experiment**: from: 8/11/2006 to: 14/11/2006	**Date of report**: July 4, 2007
Shifts: 18	**Local contact(s)**: Oier Bikondoa	*Received at ESRF:*

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Report:

Interfacing oxides with Si is very challenging and important technological problem. Defect-free dielectric oxide, namely SiO_2 is used as gates in MOSFET transistors. Now SiO_2 is at its fundamental limits (thin SiO_2 layers start tunneling electrical current); further transistor scaling requires its substitution by other oxides with high dielectric constant (high-*k*). The challenge is that all presently known high-*k* dielectrics have large concentration interfacial defects.[1] These defects scatter charge carriers in transistor channel thus impairing operation of FET. Moreover, the high-*k* oxides react with Si during fabrication, and the byproducts of such reactions precipitate at the interface as detrimental low-*k* layers.[2]

We have recently discovered a new class of oxides that form stable self-restoring epitaxial interfaces with silicon without any interfacial layers.[3] These compounds might become technologically very important in the nearest future. Yet, nothing is known on the mechanism of formation of these unique interfaces, origins of their stability and mechanisms of self-reconstruction. Nothing is known about the atomic arrangement and other structural characteristics of the interface.

Our goal during this experimental run was to perform an initial evaluation of the new high-*k* oxide/Si interface. The roughness of the interface was examined with X-ray reflectivity and its atomic structure was examined with surface x-ray diffraction.

1. Materials and methods

The chemical composition of the oxide used in this study corresponded to the formula $7Ce_2O_3{\cdot}6Al_2O_3{\cdot}1SiO_2$. It was fabricated from $7CeO_2{\cdot}6Al_2O_3$ precursor by pulsed laser deposition (PLD) and subsequent rapid thermal annealing at 1030ºC. The films were formed on p-type Si(001) and Si(111)

substrates. The thickness of the films was 48±3 nm. Prior to the synchrotron experiments the films were annealed in two different ambients: pure N_2 atmosphere and (97% N_2 + 3%H_2) "forming gas" mixture.

2. Crystal structure of the films and their epitaxial relation with silicon

The crystal structure of the $7Ce_2O_3 \cdot 6Al_2O_3 \cdot 1SiO_2$ films was determined by combining data from the present experimental run with data taken previously at ID-15B (combinatorial high-energy XRD) and data taken by conventional XRD. Surprisingly, epitaxial films of identical chemical composition had different crystal structures, depending on the orientation of the silicon substrate. The films formed on Si(111) had a hexagonal unit cell with lattice parameters $c = \sqrt{2} \cdot a$. For these films we found a = 7.075 Å and c = 10.006 Å. The orientation of this hexagonal epitaxial phase with respect to the substrate was Hex-I(001)‖Si(111). The X-ray diffraction spectrum implies the $P\bar{6}c2$ space group. The same oxide formed on Si(001) has a hexagonal apatite crystal structure with c/a = 0.756: a = 9.55 Å and c = 7.22 Å. The apatite films are mosaic-like coatings consisting of four epitaxial domains. The domains maintain an Apatite(140)‖Si(001) orientation. The $\hat{c}$-direction of the apatite unit cell lines up along the Si$<110>$ direction or rotated by 90° and 180º with respect to this direction.

3. Interfacial and surface roughness of the films

X-ray reflectivity shows that films annealed in pure N_2 had interfacial roughness of approximately 0.45 nm and a surface roughness of about 0.8 nm. Surprisingly, films annealed in forming gas were much smoother; they exhibit an interfacial roughness below 0.2 nm. Films annealed in pure N_2 had an additional interfacial layer approximately 1.3 nm-thick with slightly smaller density. Forming gas specimens had the same chemical composition from the bottom to the top of the films. The synchrotron x-ray diffraction data were later confirmed by transmission electron microscopy.

4. Atomic arrangements at the oxide/Si interface

To establish the atomic arrangement at the heteroepitaxial Apatite/Si(001) and Hex-I/Si(111) interfaces the following crystal truncation rods (CTRs) were measured. For Si(001) substrate: Si(31L), Si(11L) and (20L) rods together with seven apatite rods with different indexes. For Si(111) substrate Si(22L) rod together with three rods from the Hex-I film. Fitting of the data is hampered by the lack of definitive information on atomic positions in the bulk of the new structures. The preliminary results are as follows. Neither Si(001) nor Si(111) surfaces show interfacial reconstructions. For the N_2–annealed films the oxide/Si interface is relatively rough, with randomly distributed protrusions of Si atoms into the film. Si lattice remains well-ordered: Si atom positions in the interfacial region are similar to their positions in the bulk of the lattice.
In contrast, from the oxide side the interface is ***very*** disordered. In the 1.3 nm thick interfacial region the atomic positions are distributed in very wide range of coordinates. It appears that at the oxide/Si interface there is only one commensurate direction, namely Si(110)‖Apatite(001). Other directions are incommensurate and have a disordered or amorphous-like character.

In summary, our first investigations of the properties of apatite/Si interfaces provide encouraging results. Interfacial roughness can be controlled by the annealing ambient. Structurally, disordered or amorphous-like interface is beneficial for transistor performance because it eliminates strain effects and may provide a 'homovalent' charge-free interface.[4] From a structural point of view heteroepitaxial apatites on Si(001) may become ideal gate structures for semiconductor applications.

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[1] Muller, D. A. A sound barrier for silicon? Nature Materials **4**, 645-647 (2005).
[2] Wallace, R. M. & Wilk, G. High-*k* gate dielectric materials. Mat. Res. Bull. **27**, 192-197 (2002).
[3] Kukuruznyak, D.A., Reichert, H., Ohmori, K. Ahmet, P., Chikyow, T. Pliant ionic oxides on silicon for semiconductor devices. submitted to Nature Materials, June 2007.
[4] Misra, V., Lucovsky, & Parsons, G. Issues in high-*k* gate stack interfaces. Mat. Res. Bull. **27**, 212-216 (2002).