Report on experiment MA328 (BM32)
ESRF may 16th – 22th, 2007

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Purpose of the experiment

The epitaxy of crystalline oxides on Si has given rise to growing interest in the last few years, due to their potential in replacing SiO_2 as gate oxide in C-MOS devices. INL studies the molecular beam epitaxy of various high-k oxides on silicon. Our studies have demonstrated that besides their possible use as C-MOS high-k gate oxides, these materials could also be used as crystalline buffers for further growth of III-V semiconductors, due to the peculiarities of the III-V/oxide heterointerfaces.

In this context, a detailed understanding of the crystal structure and orientation of ultrathin (a few nanometers) oxide layers grown on Si is required. For this purpose, the use of synchrotron radiation is indispensable. Various studies have been carried out at INL in the timespace between the submission of the proposal and the experiment at ESRF. These studies have incited us to focus our efforts on γ-Al_2O_3/Si(001), Gd_2O_3/Si(001), Gd_2O_3/Al_2O_3/Si(001) systems. Gd_2O_3 is an high-k oxide, that could find applications in C-MOS systems. Al_2O_3 has a moderate dielectric constant of 11, but is thermodynamically stable against Si and can be used as stable interface for further growth of oxides on Si. In the end, we have also performed preliminary experiments on InP quantum dots grown on $SrTiO_3$ substrates.

A summary of the main results obtained at ESRF is presented in the following. It is to be noted that further work is needed to fully understand and interpret these results. Complementary experiments and modeling will be carried out in the next weeks and months, the results of which is obviously not presented in the present report.

Al_2O_3/Si(001)

One of the major issues of the growth of oxides on Si is the control of the Si-oxide interface. Si is highly reactive with respect to oxygen, and the growth of oxides on Si, or the thermal treatments carried out during C-MOS processes, are liable to lead to the formation of SiO_2 or silicate interfacial layers that strongly spoil the structural and electrical properties of the oxides. Al_2O_3 is stable against Si, and could therefore be used as buffer layer for further growth of oxides on Si. Our studies have shown that the two first monolayers of Al_2O_3 grown on Si(001) are coherently strained and (001)-oriented on Si(001)[1]. We plan to use this ultralow thickness buffer for further growth of higher-k oxides (Gd_2O_3, $LaAlO_3$, $SrTiO_3$) on Si. The purpose of the experiment was to collect information on the crystal structure of this ultrathin Al_2O_3 buffers. The sample consists in a two ML thick γ-Al_2O_3 layer grown on Si(001), and capped with a 3 nm thick amorphous Si layer to avoid any reaction of Al_2O_3 with air.

An in-plane h-scan recorded along the [400]Si axis of Si is shown in Fig.1. The reciprocal space has been graduated by taking [400]Si as a reference.

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[1] C. Merckling, M. El-Kazzi, G. Delhaye, M. Gendry, G. Saint-Girons, G. Hollinger, L. Largeau, and G. Patriarche, Appl. Phys. Lett. **89**, 232907 (2006)

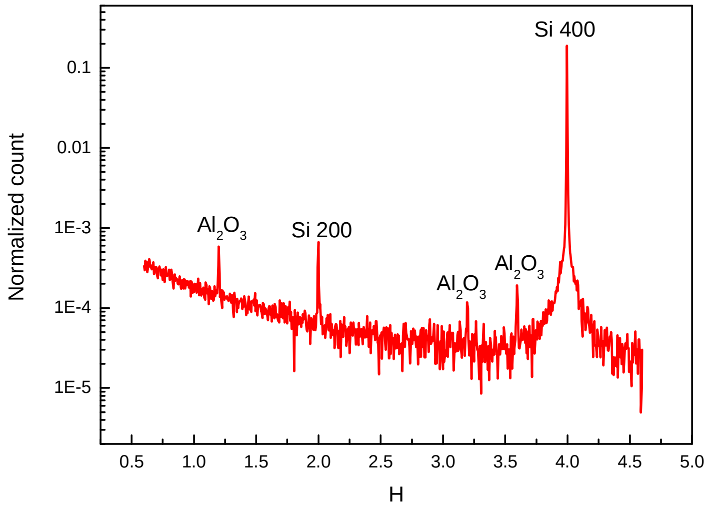

Fig.1 *: h-scan recorded along the [400]Si axis. 3 peaks corresponding to the diffraction of γ-Al_2O_3 can be seen at h = 1.2, h = 3.2 and h = 3.8. The peak centered at h = 2 corresponds to the forbidden 200 reflexion of Si.*

The spectrum present peaks corresponding to the diffraction of γ-Al_2O_3, centered at h = 1.2, h = 3.2 and h = 3.6. The low FWHM of the peaks attest of the excellent crystalline quality of the Al_2O_3 layer. Similar peaks have been detected along the main crystallographic axis of Si, as well as along the [1.2/3.2/3.6 k 0] directions of the reciprocal space. This shows that Al_2O_3 presents a 4-fold symmetric superstructure having a lattice parameter 5 times larger than the one of Si. In previous experimental and theoretical studies carried out on this material, a reorganization of the Al-vacancies in the lacunar γ-Al_2O_3 spinel structure was already suspected to lead to the formation of such superstructures[2]. Atomistic models of the crystallographic conformation Al_2O_3/Si(001) will be built up on the basis of our results (in collaboration with IEMN-Lille), and their diffraction will be simulated and compared to the results presented here. This should allow getting more information on the conformation of the interfacial Al_2O_3 layer. However, a complete understanding of the complex structure of the layer would require further experiments at ESRF : the 3 nm thick cap layer deposited on the sample (in order to prevent unavoidable reactions of the Al_2O_3 layer with here) imposes quite large incidence angles, detrimental for the sensitivity of the experiment. In-situ experiment at ESRF could allow getting much higher sensitivity for the measurement, and could also allow monitoring in-situ the evolution of the Al_2O_3 morphology during growth.

<u>Gd_2O_3/Si(001)</u>

Gd_2O_3 presents a bixbyite structure, with a lattice parameter of 10.813 Å, which is close to be twice as the one of Si. The connection between Gd_2O_3 and Si takes place via an O-atomic plane of the oxide. The conformation of the latter is therefore determinant for the in- and out-of plane crystallographic orientation of the oxide lattice with respect to the Si one.

We have performed an extensive study of the crystallographic properties of a 7 nm thick Gd_2O_3 layer grown on Si(001) using in-plane diffraction. This study has evidenced that :

-Gd_2O_3 is (110) oriented on the Si(001) surface. (out of plane : [110]Gd_2O_3//[001]Si).
-The growth of Gd_2O_3 is bidomain : two equivalent orthogonal in-plane orientations of Gd_2O_3 are possible
-These in-plane orientations are defined by [110]Gd_2O_3//[110]Si

The in-plane orientation of Gd_2O_3/Si(001) is sketched in Fig.2 :

[2] P. Boulenc and I. Devos, Microelec. Rel. **47**, 709, (2007).

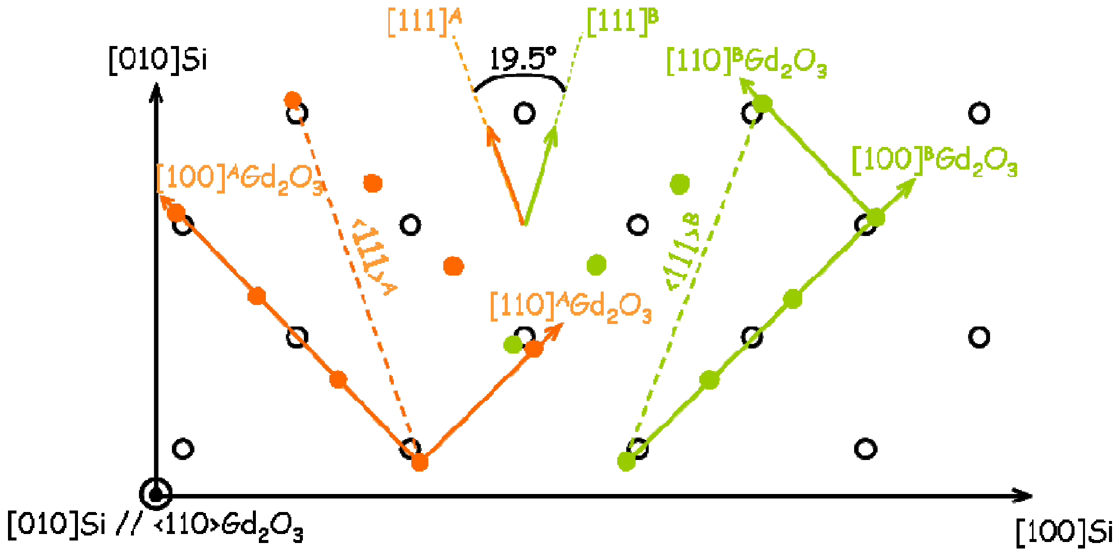

Fig.2 : *In plane orientation of Gd_2O_3/Si(001), as deduced from our experiments. Two Gd_2O_3 domains (A and B) coexist, twisted of 90° with respect to each other*

An (h k 0) scan of the reciprocal space recorded around the 222 reflexions of both domains of Gd_2O_3 is shown in Fig.3, as well a zoom on one of the 222 reflexions are plotted in Fig.3.

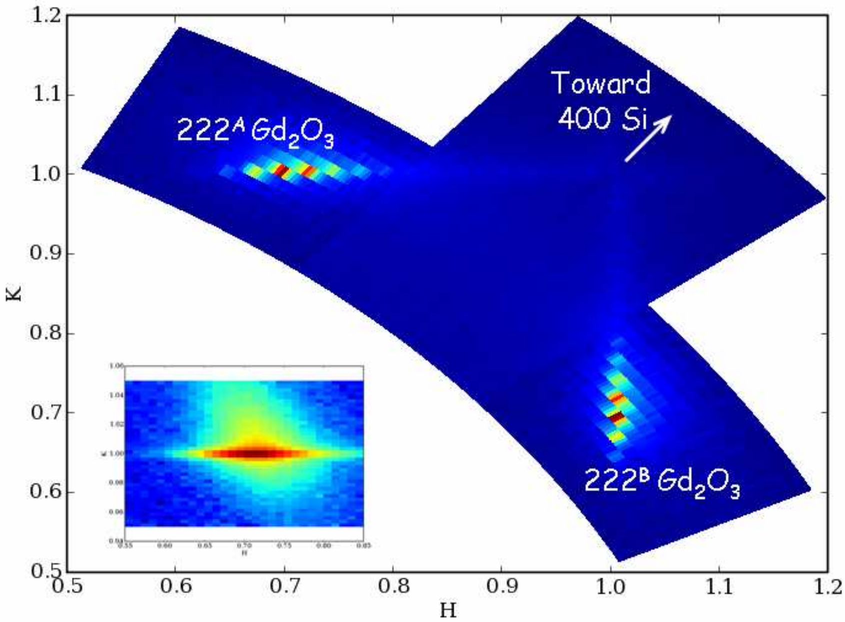

Fig.3 : *(h,k,0) scan of the reciprocal space around the 222 reflexions of Gd_2O_3. Inset : Zoom on a 222 spot.*

The 222 reflexions corresponding to domains A and B are of equivalent intensity, indicating that both domains cover an equivalent surface of the Si substate. The anisotropic elongation of the spots is a remarkable feature. It is the result of the anisotropic strain of Gd_2O_3/Si(001) : the lattice mismatch between Gd_2O_3 and Si is -0.44% along the in-plane <110> directions of Gd_2O_3, but exceeds 5.6% along the in-plane <100>Gd_2O_3 directions assuming a 3x2 epitaxial relationship. A detailed analysis of the shape of the reflexion spots will be carried out in order to deepen the understanding of the relaxation process in this unusual anisotropically strained system. Further experiments carried out on thinner pseudomorphic Gd_2O_3 layers should also be carried out.

Gd_2O_3/Si(001) 6°off

Experiments were also carried out an a Gd_2O_3 sample similar to the one described above, but grown on an Si(001) 6°off substrate. An (h k 0) scan of the reciprocal space taken around the 222 reflexion of Gd_2O_3 is shown in Fig.4.

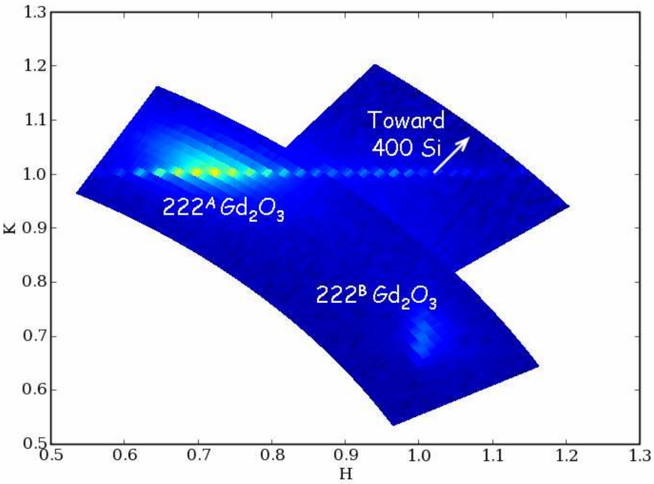

Fig4 *: (h,k,0) scan of the reciprocal space around the 222 reflexion of Gd_2O_3.*

The mapping is similar to the one obtained in the case where Gd_2O_3 is grown on nominal Si(001) substrates, except that in the present case, the growth of Gd_2O_3 is almost single domain : the intensity of the 222^B reflexion of Gd_2O_3 is very weak in Fig.4. This indicates that the bidomain growth is related to the anisotropy of the nominal Si reconstruction : the formation of double steps at high temperature of 6°off Si substrates restores the isotropy of the Si 2x1 reconstruction, leading to a single domain growth. The fact that the 222^B reflexion is not totally absent in Fig.4 indicate that the thermal treatment carried out on the Si substrate before the growth of Gd_2O_3 was not efficient enough to form double steps over the entire substrate surface.

Gd_2O_3/Al_2O_3/Si(001)

A reciprocal space mapping recorded on a sample for which 7 nm of Gd_2O_3 were grown on a 2ML thick Al_2O_3 buffer deposited on Si(001) is shown in Fig. 5. This type of structure could be used as crystalline gate oxide stacks in C-MOS systems : Al_2O_3 ensures the thermal stability versus Si, and the high dielectric constant of Gd_2O_3 ensures improved performances as compared to standard SiO_2 gate stacks.

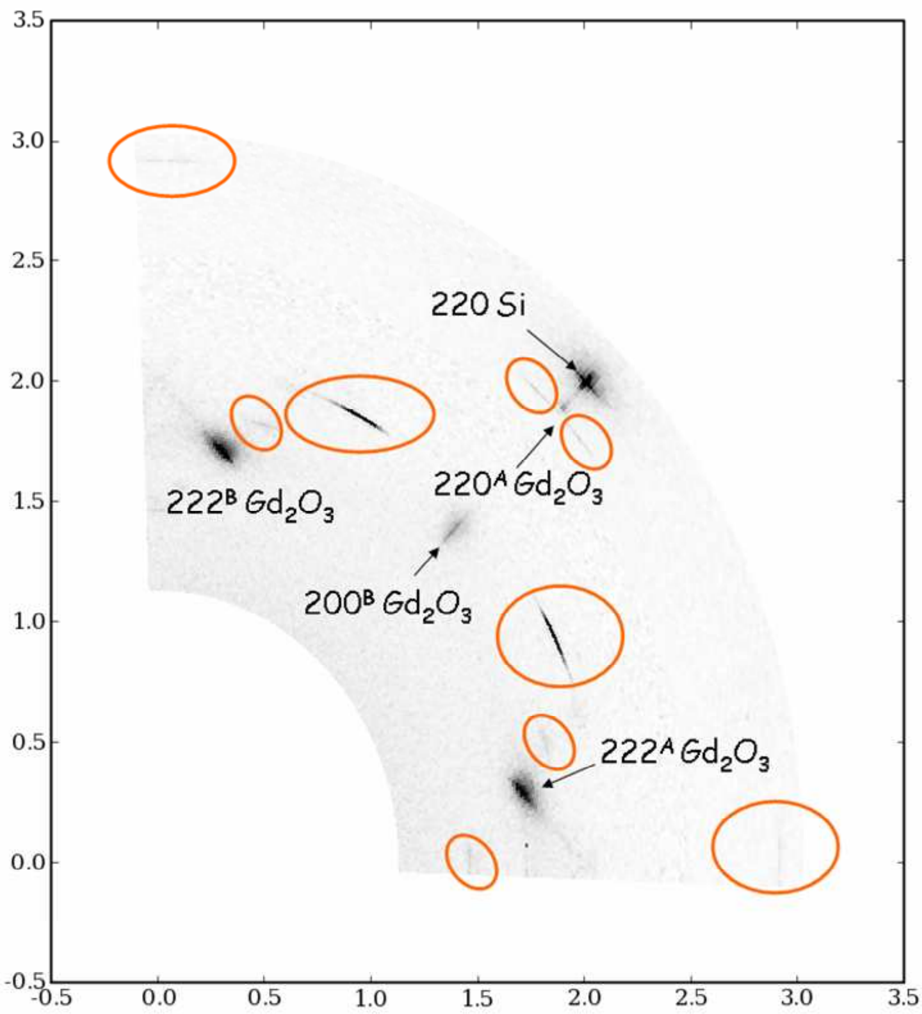

Fig. 5 *: Reciprocal space map of the sample*

This mapping indicates that Gd_2O_3 is single crystalline and bidomain on Al_2O_3/Si(001). Additional spots (circled in Fig.5) have been detected, the origin of which is not clearly understood yet and requires further analysis.

InP/$SrTiO_3$

The sample consists in InP quantum dots grown on a $SrTiO_3$ (STO) substrate. The purpose of the study of this system is to achieve monolithic integration of InP quantum dots based emitters on Si. In fact, $SrTiO_3$ crystalline buffers can be grown on Si[3]. Preliminary TEM studies have shown that the InP QDs are fully relaxed on STO, and that they do not contain any dislocation related to the relaxation process (Fig. 6).

[3] G. Delhaye, C. Merckling, M. El-Kazzi, G. Saint-Girons, M. Gendry, Y. Robach, G. Hollinger, L. Largeau, and G. Patriarche , J. Appl. Phys. **100**, 124109 (2006)

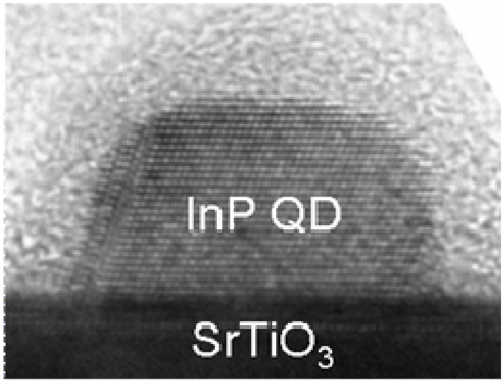

Fig.6 *: TEM cross sectional view of an InP quantum dot grown on STO*

These peculiarities are assumed to be related to particular properties of the InP/STO heterointerface. The purpose of the experiment was to determine the epitaxial relationship between InP and STO. Our results have shown that :

-InP is (111) oriented on the STO(001) surface. (out of plane : [111]InP//[001]STO).

-The in-plane orientation of the InP lattice is defined by <110>InP//<100>STO

This leads to typical in-plane omega scans similar to the one presented in Fig.7 :

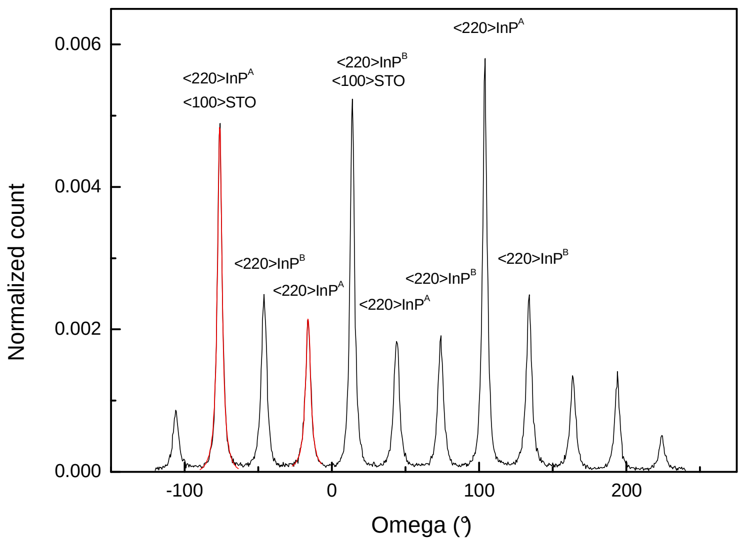

Fig.7 *: Omega-scan of the <110> reflexions of InP*

Further information concerning the density of QDs obeying the different orientations will be extracted from the spectrum presented in Fig.7. Moreover, the angular width of the peaks (of the order of 2°), gives an indication concerning the "twist" of the InP QDs around the equilibrium positions.

Our studies have shown that the InP growth temperature has an important impact on the degree of orientation of the QDs. Further studies at synchrotron are required to analyze and understand the crystallographic properties of the InP/STO heterointerface.