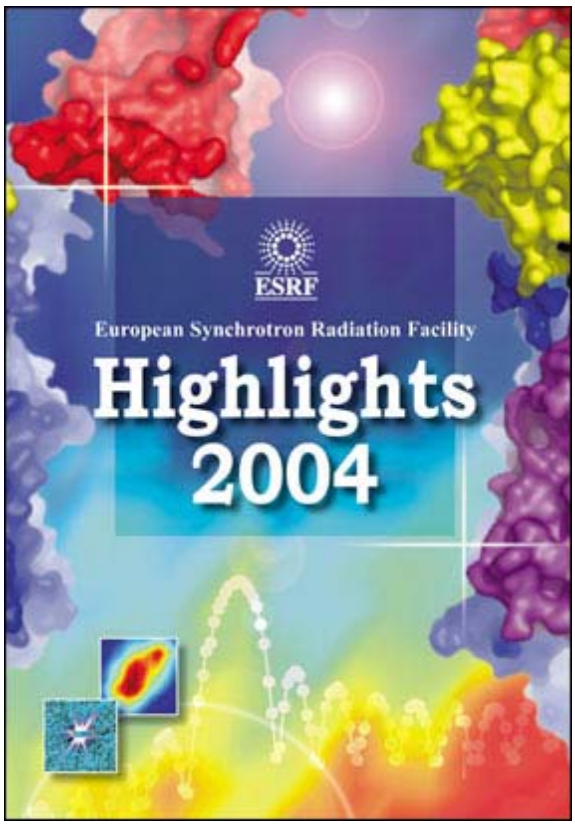
ESRF Highlights 2004



Credits

Acknowledgements and Publishing Information

We gratefully acknowledge the help of:

C. Argoud, R. Barrett, J. Baruchel, N. Brookes, T. Bouvet, D. Cornuejols, P. Elleaume, A. Freund, A. Kaprolat, Å. Kvick, S. Larsen, G. Leonard, R. Mason, T. Metzger, C. Riekel, M. Rodriguez Castellano, R. Rüffer, F. Sette, W.G. Stirling, S. McSweeney, K. Witte, J. Zegenhagen, and all the users and staff that have contributed to this edition of the Highlights.

Thank you.

Editor
G. Admans

Layout
Pixel Project

Printing
Imprimerie du Pont de Claix

HTML Version by Pixel Project and ESRF Webmaster

Available in printed format or PDF (28 mb), by request from:
Communication Unit
ESRF
BP220 • 38043 Grenoble • France
Tel. (33) 4 76 88 20 56 • Fax. (33) 4 76 88 24 18
http://www.esrf.fr

Surface and Interface Science

Introduction

While investigations relating to surfaces and interfaces are performed at a number of beamlines around the ESRF storage ring, the three beamlines ID01, ID03, and ID32 of the surface and interface science (SIS) group are highly specialised in this area of research. Resolving structural properties is the predominant goal, because the structure determines many other properties of a material. The X-ray tools are diffraction in grazing incidence geometry at all three beamlines and X-ray standing waves (XSW) at ID32. Work at ID03 and ID32 is mostly concentrated on the picometer scale, i.e. the precise atomic structure, whereas investigations at ID01 are more focused on the nanoscale. However, chemical composition as well as electronic and magnetic properties of surfaces and interfaces are also within the reach of the capabilities of the three beamlines. The method of choice is anomalous scattering at ID01, photoelectron- and fluorescence spectroscopy at ID32, and magnetic scattering at ID03.

At the tenth anniversary of the start of user operations in 1994, ID03 could look back at ten years of successful user experiments. ID32 will also celebrate its tenth anniversary of user mode this year, while ID01 will have to wait for another five years until 2010. Some exciting results obtained during the last year are presented in the following pages. They should give a taste of the diversity of scientific applications and the rapid evolution of novel techniques in the SIS group.

An example of "pushing back the limits" is given by the work of S. Ferrer et al. showing that hydrogen atoms adsorbed on a metal single crystal can be "seen" by surface X-ray diffraction (SXRD) at **ID03**. Subsequently, they followed the reaction of the Ni(111) surface when exposed to high H_2 pressure under real, catalytic conditions.

The contribution by H.L. Meyerheim *et al.* aids our understanding of the magnetic anisotropy in layered structures, which are used in recording devices and are thus of crucial importance. In the system Ni on W(110), the spin orientation can be changed by a single layer of Fe, while it is reoriented again by the deposition of an additional, single monolayer of Ni. At **ID03** the group found that the spin reorientation is not magneto-elastically driven, because the structural changes are much too small.

X. Torrelles *et al.* used crystal truncation rod measurements to determine the atomic structure of the vicinal "terraced" $SrTiO_3$ (106) surface under UHV conditions at **ID03**. They find an extraordinary order of the surface on the long-range, established by "charge undulations" of neighbouring terraces of opposite electrical polarity, while the surface is disordered on the short range.

Unravelling structural changes at electrode surfaces in contact with aqueous electrolytes is important for the understanding of processes such as corrosion, crystal growth, metal plating, and semiconductor processing. A.H. Ayyad *et al.* applied grazing incidence diffraction at **ID32** to study *in situ* the surface reconstruction before and after homoepitaxial growth of Au on Au (111) from electrolytes. They find an unexpectedly strong compression of the surface layer at certain Au-electrode potentials.

A layer of aluminium oxide on the NiAl(110) surface was investigated using X-ray diffraction by A. Stierle *et al.* at **ID32**. The sample was prepared in their home-lab in Stuttgart and shipped to the ESRF inside the UHV chamber, which was then mounted on the diffractometer. The complexity of the structure of the ultra-thin Al_2O_3 layer, which this experiment revealed, sheds light on the atomic mechanisms acting in corrosion protection or catalysis.

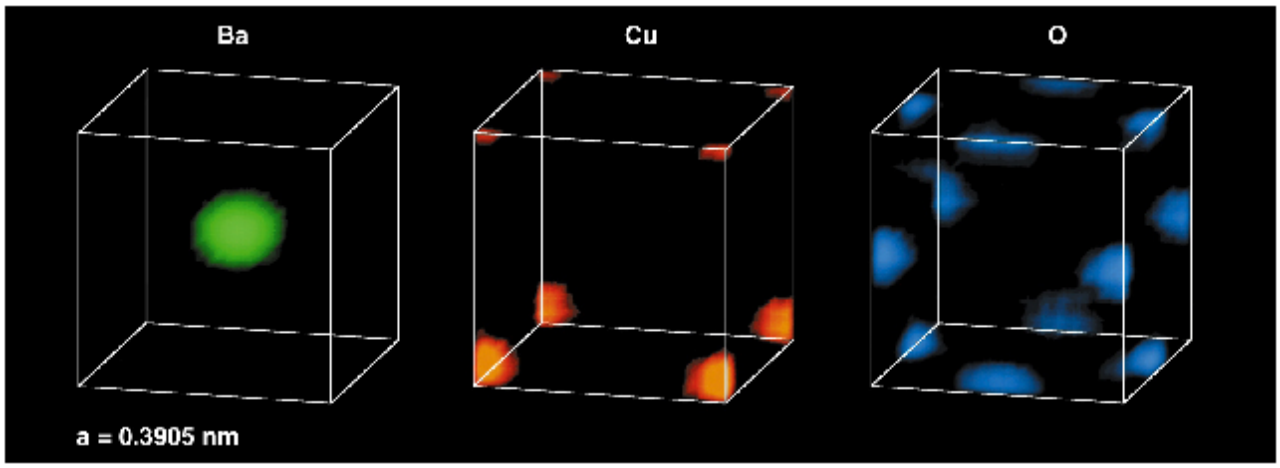


Fig. 85: Element specific X-ray standing wave imaging: Image of three elements of a monolayer of the superconductor $YBa_2Cu_3O_{7-\delta}$ on $SrTiO_3(001)$ (projected into the cubic $SrTiO_3$ unit cell). Measurements done at ID32.

At **ID01**, S. Hazra *et al.* investigated the relationship between the surface morphology, modified by ion-bombardment, and the crystalline interface below, using depth-resolved grazing-incidence diffraction. With increasing dose of the Ar^+ ions they found that the buried subsurface layer is eventually rendered completely amorphous, but retaining a ripple structure that is well replicated at the surface. These results illuminate the ion-solid interaction processes responsible for the formation of nanostructures on metal and semiconductor surfaces.

T.U. Schülli *et al.* employed anomalous diffraction at **ID01**. They analysed the (111) superstructure reflections at two complementary energies to study the near surface structure of an EuSe/PbSe epitaxial multilayer. The scattering factor of the thicker PbSe layer, dominating the diffraction pattern at other energies, was suppressed at the Pb MV edge such that the corresponding (111) Bragg intensity of this compound almost vanished. This study convincingly demonstrates the sensitivity of anomalous diffraction to strain and interdiffusion in heteroepitaxial systems with very small lattice mismatch.

Tien-Lin Lee *et al.* combined XSW with photoemission at **ID32** for investigating the room temperature structure of the Ge(111):Sn-$\sqrt{3}$x$\sqrt{3}$ surface. The existence of two components in the Sn core level photoemission spectra had given rise to extensive discussions. The work of Lee et al. establishes a link between the chemical state of Sn and the structure. The result supports molecular dynamics simulations that predict a very rapid oscillation of the Sn atoms between two vertical positions.

Finally, we want to briefly comment on the future of the SIS beamlines. ID01 is enjoying successful routine operation and for ID32 a rigorous refurbishment process is almost finished that has dramatically enhanced its potential and attractiveness to users. ID03 has been the world-wide undisputed benchmark beamline for surface X-ray diffraction over the years. A refurbishment is now pending. Furthermore, both scientists at ID03, S. Ferrer and O. Robach, left the ESRF at about the same time. This was an opportunity to review the scientific direction of the SIS group in general. To poll the interest and needs of the SIS user community, a round table discussion and a workshop on surface and interface science was organised in 2004, centred around three issues: 1) surface X-ray diffraction (on ideal and real surfaces) 2) further development of X-ray Standing Wave (XSW) methods for surface and interface structural characterisation (also in combination with XPS) and 3) the possibility of developing hard X-ray photoelectron spectroscopy (HAXPES) at the ESRF. The unanimous opinion of the users and thus the conclusion of the workshop was that no major change in the program of ID01 should be envisaged and the ongoing refurbishment of ID32 should be completed, further enhancing the spectroscopic capabilities of the beamline. The SIS community expressed very strong interest in keeping ID03 as the leading beamline for surface X-ray diffraction. This view was adopted by the ESRF management and a refurbishment of ID03 will be carried out during the next two to three years.

T. Metzger / J. Zegenhagen

Ion Beam Induced Ripple Structure of Crystalline Layers in Si Wafers

The formation of a ripple-like pattern with a spatial periodicity varying from nm to mm on obliquely ion-bombarded solid surfaces has become a topic of intense research because of its potential as templates for the fabrication of nanoscale structured materials [1]. The ion-induced ripples are produced by interplay between a roughening process caused by the ion beam erosion (sputtering) of a surface and a smoothening process caused by thermal or ion-induced surface diffusion [2]. The ion-beam modified ripple structure on a semi-conducting surface such as silicon wafer has been studied in recent years mainly using microscopy, which provides images of the top surface morphology. In order to understand the ripple formation mechanism the amorphous-crystalline interface and the structure below have also been studied.

Si(001) wafer surfaces were bombarded with $^{40}Ar^{+}$ beam of varying energy and dose at fixed incidence angle (60°) to form the rippled surfaces, which were characterised by atomic force microscopy (AFM) at the Saha Institute of Nuclear Physics [2]. The near surface structural studies were performed by depth-resolved X-ray grazing-incidence diffraction (GID) at the **ID01** beamline using a wave length λ = 1.55 Å. Typical GID curves for a sample show the presence of satellite peaks on both sides of the main (220) Bragg peak (Figure 96). The appearance of satellite peaks confirms the existence of lateral undulation of the buried crystalline part of the sample. The separation between the satellite-peaks is inversely proportional to the subsurface crystalline ripple wavelength, which agrees well with the ripple-like structure on the top surface observed through AFM measurements. At a certain value of *incident angle* the shape of the curve changes from a narrow to a broad one, indicating the onset of defect formation.

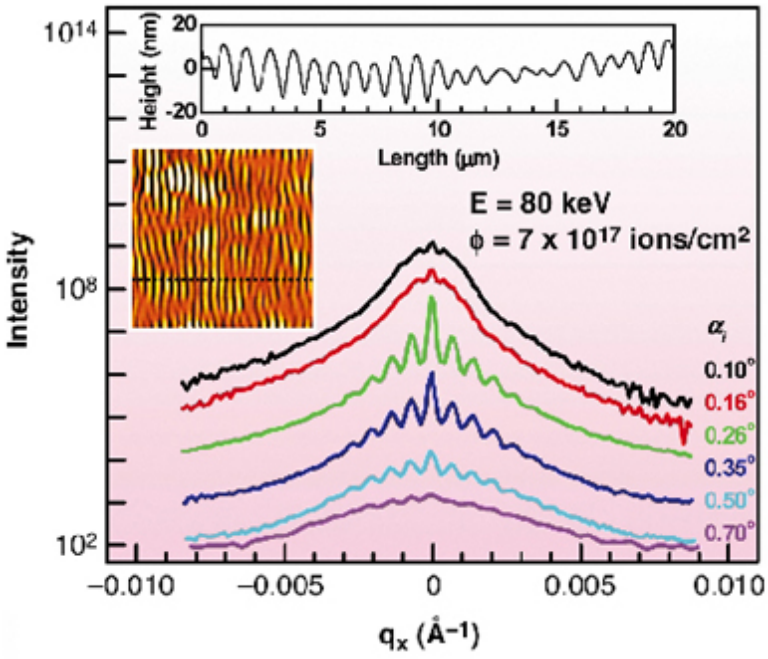


Fig. 96: Transverse GID curves perpendicular to the ripple structure around (220) Bragg peak of a ion-beam modified Si(001) wafer. Insets: AFM image (20 μm x 20 μm) and corresponding height profile.

The Bragg intensity as a function of the incidence angle ai (Vineyard profiles) for samples bombarded with different dose are shown in Figure 97. The plateau below $\alpha_{c,\,Si}$ at about 0.23° (instead of a single peak at $\alpha_i = \alpha_{c,\,Si}$) seen here, corresponds to materials of low density, gradually decreasing towards the top. Since the measurements are on an in-plane Bragg peak, intensities at all incident

angles stem from crystalline material. Note that the onset angle, the shape and height of the plateau are a function of the implantation dose. For low doses there are two distinct critical angles; the appearance of a peak at 0.05° is attributed to the existence of a partially crystalline top layer with much lower density compared to crystalline silicon. For increasing dose the intensity of the plateau-region decreases. In the case where the dose was $7x10^{17}$ ions/cm^2, the plateau-region almost disappears and the shape of the α_i scan curve turns into a Vineyard profile expected for a sample with a non-scattering (amorphous) top layer. The reconstructed depth profile obtained from the simulation of the Vineyard profile (dotted lines in Figure 97) shows that the material density of the subsurface layer is very low (about 15% of the crystalline Si bulk density); at the same time the rippled, modulated crystalline part underneath is damaged and has a reduced density. The partially crystalline top layer at low dose, transforms to a completely amorphous layer for high doses and the surface morphology was found to be conformal with the underlying crystalline ripples.

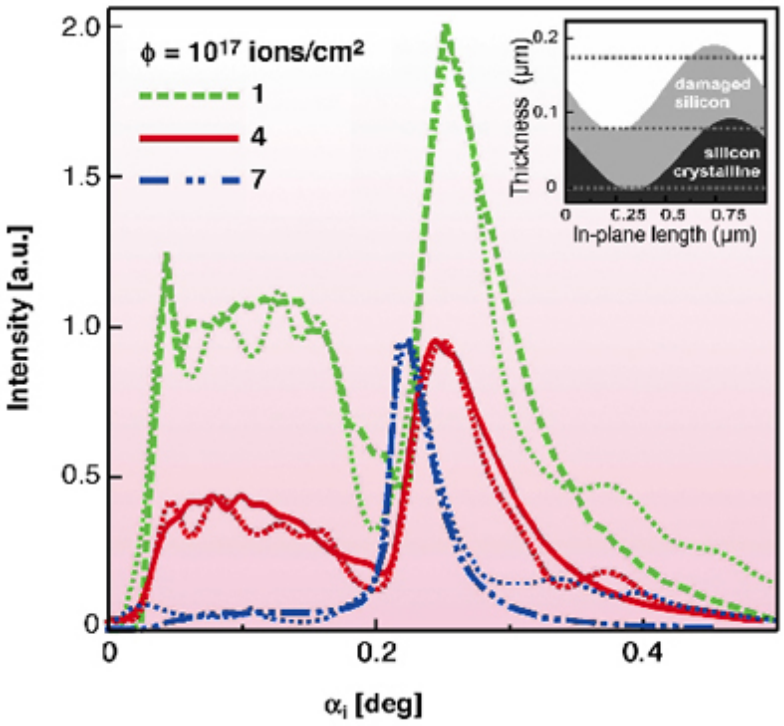


Fig. 97: Experimental and simulated (dotted) α_i scans measured at (220) Bragg peak for samples irradiated with different dose Φ at E = 80 keV. Inset: Schematic Cross-section of the sample used for the simulations.

In conclusion, by a combination of GID and AFM measurements we have characterised the relation between the formation of ripple-like structure at the surface and the crystalline material in the subsurface region of the silicon wafer due to ion bombardment. The wavelength of the buried crystalline ripple structure is well replicated at the top surface as observed by AFM measurements.

References

[1] U. Valbusa, C. Boragno, and F.B. de Mongeot, *J. Phys.: Condens. Matter* **14**, 8153 (2002).
[2] T.K. Chini, M.K. Sanyal, and S.R. Bhattacharyya, *Phys. Rev. B* **66**, 153404 (2002).

Principal Publication and Authors

S. Hazra (a), T.K. Chini (a), M.K. Sanyal (a), J. Grenzer (b) and U. Pietsch (b), Phys. Rev. B 70, 121307 (2004), and H. Metzger (c).
(a) Saha Institute of Nuclear Physics, Kolkata (India)
(b) Institut fur Physik, Potsdam (Germany)
(c) ESRF