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Report:

In the framework of fundamental surface science studies of heterogeneous catalysis, ultrathin oxide layers on metallic substrates are widely used as substrates for metallic cluster growth. They mimic the effect of dispersed supports used in actual catalyst while remaining thin enough to be free of charge effects towards several characterization tools.[1,2] Among them, alumina layers have attracted great interest due to their easy way of preparation that allows one to grow crystalline layers with a well-defined thickness of the order of a few Å.[3] Despite the high number of studies performed, the atomic structure of the TAF as well as the origin of the epitaxial relationship with the substrate is still an open question. An atomic structural model has only been proposed for Al_2O_3/NiAl(110).[4] The atomic arrangement has been described as specific of the NiAl(110) substrate,[4] in particular for the interface plane, where the pentagon-heptagon organization of Al atoms would be due to preferred chemical short-range order favoring Al-Ni neighbors. However, a similar organization has recently been observed for alumina grown on Cu-9at%Al(111),[5] for which the Al atoms of the substrate should play a minor role, and also on Ni(111).[6] In the latter case, the misfit observed between the alumina structure and the substrate indicates a weak coupling between Al and Ni atoms.[7] Rutherford backscattering spectrometry channeling experiments have also evidenced that the substrate remains unaffected by the aluminum layer.[6] In order to elucidate the origin of the atomic structure of alumina films on metal substrates, we have studied by grazing incidence X-ray diffraction (GIXD) the ultrathin alumina film grown on Ni(111).

GIXD experiments were performed on the ID3 beamline at the European Synchrotron Radiation Facility (ESRF) storage ring. The Ni sample was a disk of 9 mm diameter, with one side polished and oriented along the (111) direction with an accuracy of 0.1°, as checked with X-rays. The sample was prepared and aligned inside an ultrahigh vacuum chamber (base pressure in the low 10^{-10} mbar) coupled to a six-circle diffractometer of "z-axis" type. Sample cleaning was achieved by cycles sputtering with 2 kV Ar^+ ions for 30 min, followed by annealing during 5 min at 1000 K under UHV. Neither carbon nor oxygen contamination could be detected by Auger electron spectroscopy at the end of the preparation. A 2.5 monolayer thick Al film, corresponding to an atomic density of $4.6 \ 10^{15}$ atoms/cm^2, was deposited on clean Ni(111) at room temperature and annealed at 700 K for 15 min. During the annealing, as shown in our previous works, a thin epitaxial Ni$_3$Al(111) film formed.[8,9] The sample was then oxidized at room temperature during 16 min under $1.6 \ 10^{-6}$ mbar oxygen and further annealed at 1000 K.

For GIXD measurements, monochromatic X-rays with a photon energy of 20 keV were selected by using a Si(111) monochromator. The incidence angle was kept constant at the critical angle (0.17°) of the substrate to reduce beam penetration depth and bulk diffuse scattering. For the alumina layer, we have measured, by performing standard rocking scans, 105 in-plane structure factors, corresponding to a set of 65 non-equivalent

reflections (see Fig. 1), and 168 out-of-plane structure factors along 9 non-equivalent rods (see Fig. 2). For the Ni substrate, we have measured 76 out-of-plane structure factors along 4 non-equivalent crystal truncation rods (CTR). Voigt curves were used for integrating the profile of the rocking scans and deriving the diffracted intensity. The standard instrumental correction was applied to the structure factors for taking into account the geometry of the diffractometer and the sample dimensions. The experimental uncertainties take into account both statistical uncertainties and systematic errors due, for example, to misalignment. These systematic errors have been estimated in the range of 5% using the fluctuations of equivalent reflection structure factors.

We have been able to unambiguously determine the three-dimensional structure of the film, which consists of a substrate/Al_{16}/O_{24}/Al_{24}/O_{28} stacking within a (18.23 Å × 10.53 Å) R0° unit cell (see Fig. 3). From the different Al coordinations (3/4/5) in the layer and from the precise determination of the Al-O interatomic distances, we conclude that the film structure presents some similarities with the η-phase of bulk alumina which also has a high surface/bulk ratio. The precise comparison between these two structures allows us to explain that the perfect $\sqrt{3}$ ratio between the two sides of the mesh of the film is governed by the stacking of the two central planes, combining oxygen close-packed atoms below Al atoms in tetrahedral or pyramidal positions. Moreover, Al atoms at the interface plane of the ultrathin film adopt a quasi-trihedral configuration, which confirms that, in the alumina η-phase, Al atoms with such a coordination are located near the surface of the nanocrystals. The atomic structure is also very near to the one first proposed by Kresse et al. for alumina films on NiAl(110).[4] This strongly suggests that this atomic model, within small variations, can be extended to ultrathin alumina film on numerous other metal substrates and may be quasi-intrinsic to a free-standing layer rather than governed by the interactions between the film and the substrate. Since there is neither registry between the film and the substrate nor induced Ni relaxations, this system appears to be a prototypical free standing oxide layer.

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Concerning the growth of Au nanoparticles on this film, it seems that the structure suffer some disordering upon deposition of Au atoms, due to contamination (the vacuum was not very good during Au evaporation). No GISAXS signal indicating nanoparticle growth has been obtained
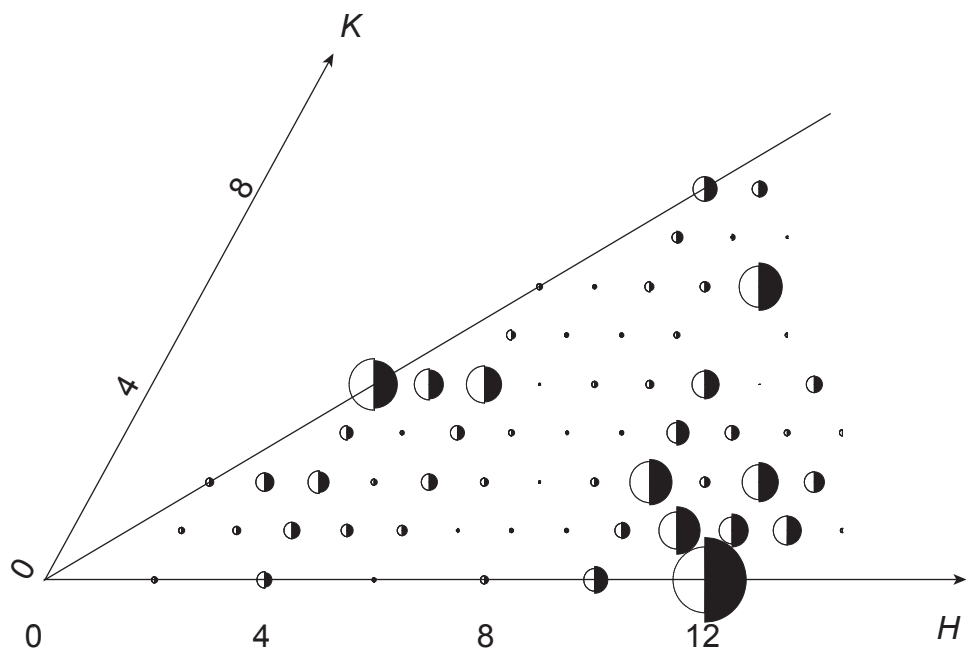
Fig. 1. Comparison between experimental (black semicircles) and theoretical (white semicircles) in-plane structure factors for the set of non-equivalent reflections (the radii of the circles are proportional to the value of the structure factors). The theoretical structure factors are the result of the best fit using a model with 92 atoms ($Al_{40}O_{52}$) in the primitive unit cell (18.23 Å × 10.53 Å).
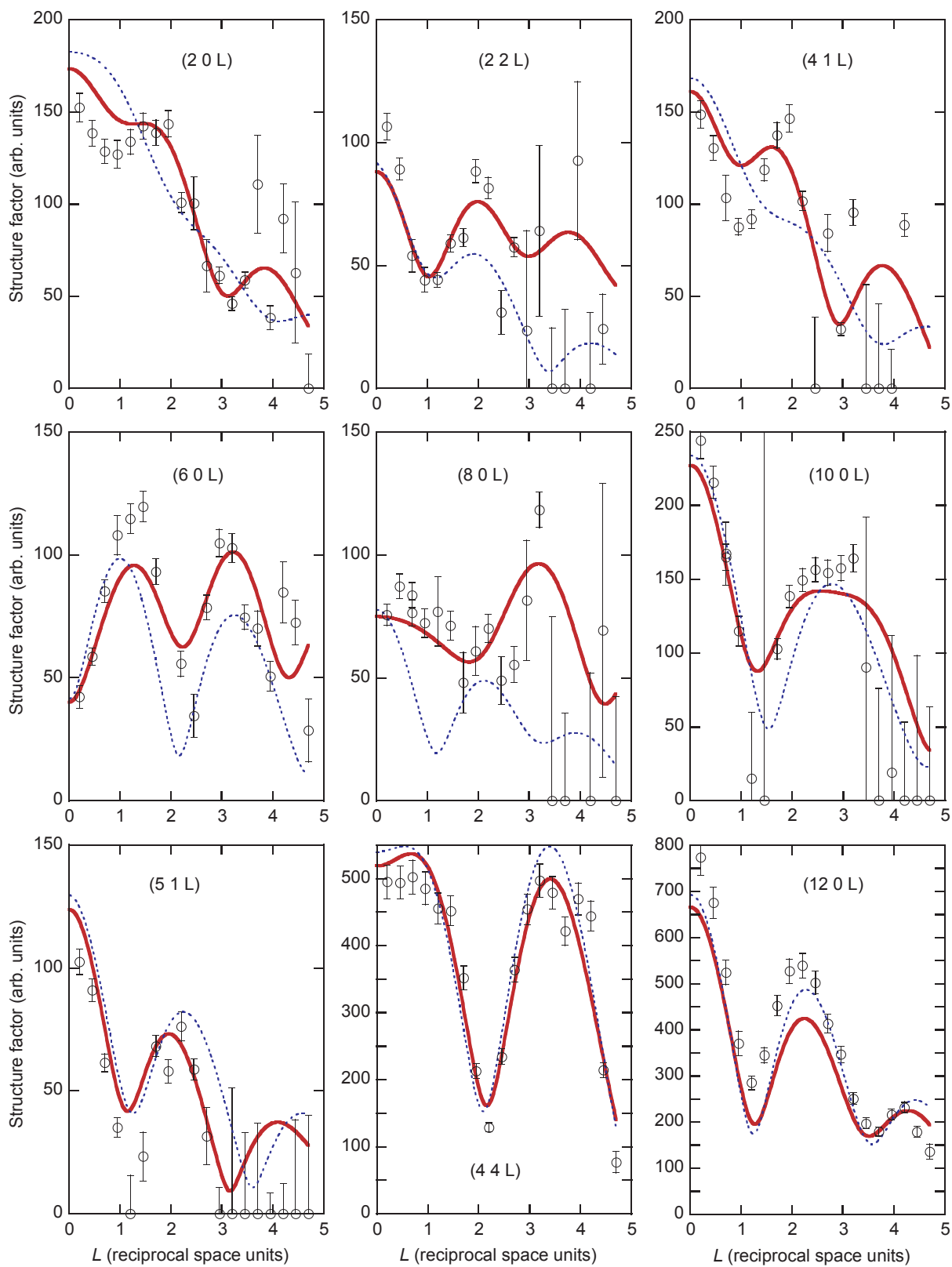
Fig. 2: Comparison between experimental (dots) and simulated (lines) structure factors along various CTRs. $L = 1$ corresponds to $2\pi/(6.104\text{Å})$. The number of free parameters considered for the out-of-plane relaxations are respectively 3 (blue dotted line), and 22 (red continuous line).
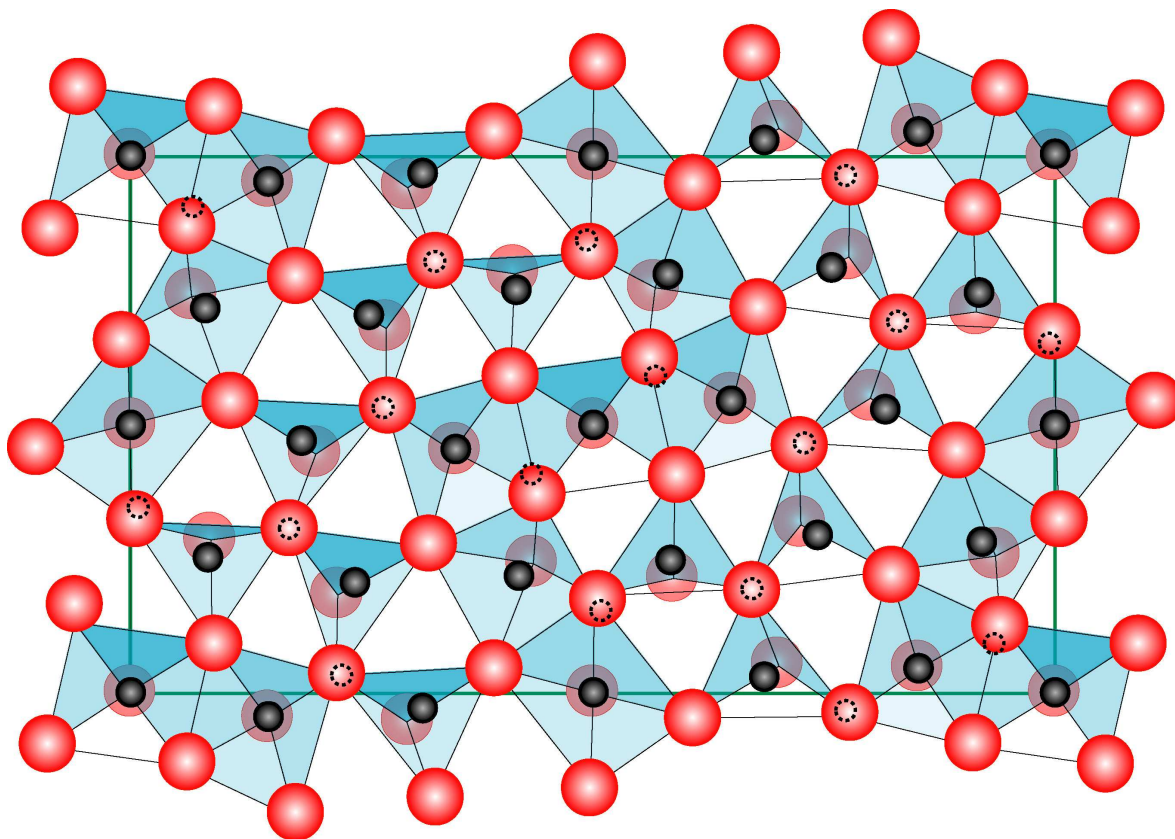
Fig. 3. In-plane view of the $Al_{40}O_{52}$ model structure giving the best fit of the experimental data. Red dots: O atoms. Black dots: Al atoms. Interface Al atoms masked by O surface atoms are represented by a dotted circle. Pyramids and tetraedra showing the coordination of the Al surface atoms are also drawn (blue polyhedra).

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