Results in Physics 6 (2016) 263–264

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Microarticle

Frozen O_2 layer revealed by neutron reflectometry

A. Steffen [a,*], A. Glavic [c], O. Holderer [a], H. Frielinghaus [a], H. Ambaye [d], S. Pütter [a], T. Brückel [a,b]

[a] Forschungszentrum Jülich GmbH, JCNS Outstation at MLZ, Lichtenbergstr. 1, 85747 Garching, Germany
[b] Forschungszentrum Jülich GmbH, JCNS-2, Leo-Brandt-Str., 52425 Jülich, Germany
[c] Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villingen PSI, Switzerland
[d] Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ARTICLE INFO

Article history:
Received 1 March 2016
Accepted 23 May 2016
Available online 27 May 2016

Keywords:
Thin films
Surface oxygen layer
Neutron reflectometry

ABSTRACT

A 63 Å thick film originating from frozen air on a solid substrate has been investigated via neutron reflectometry. The experiment shows that neutron reflectometry allows performing chemical surface analysis by quantifying the composition of this frozen layer and identifies the film to be frozen oxygen.

Introduction

The interaction of oxygen with a flat surface is a widely studied subject. Neutron reflectometry enables to investigate the density profile with a resolution in the nm range, perpendicular to the interface. While surface oxidation of metals [1] and H-containing films [2] or the oxygen wetting process of graphite [3] was studied in detail, the influence of a magnetic substrate onto the element-specific separation of air is less investigated. We analyze a thin layer on a flat substrate at 5 K, which can be identified as frozen oxygen from air by combined refinement of specular X-ray (XRR) and polarized neutron reflectometry (PNR) utilizing magnetic contrast variation.

Method

A thin layer deposited on a substrate has been measured. The substrate consists of a $La_{2/3}Sr_{1/3}MnO_3$ layer on top of a $SrTiO_3$ crystal, cooled down to 5 K in dry atmosphere with a closed cycle refrigerator (CCR). The oxygen layer was deposited by introducing a small air leakage leading to condensation and finally freezing of air at the surface for analysis with PNR employing magnetic contrast variation. This experiment represents a situation of imperfect vacuum seals of the CCR.

While room temperature XRR measurements provide the structure of the substrate layer along z (perpendicular to the surface), the low temperature PNR allows one to distinguish between different candidates by their nuclear scattering length density (NSLD) as well as their magnetic behavior. The main candidates of the introduced gas composition are N_2 (NSLD: 4.15×10^{-6} Å^{-2} for solid nitrogen, Inorganic Crystal Structure Database, FIZ Karlsruhe) and O_2 (3.29×10^{-6} Å^{-2} for solid oxygen). Details about the reflectometry technique are described elsewhere [4,5].

Neutron scattering experiments were performed on the Magnetism Reflectometer instrument (beamline 4A) at the Spallation Neutron Source (SNS) at ORNL [6]. For combined X-ray and neutron fitting, GenX [7] utilizing the Parratt formalism [4] was used.

Results and discussion

The reflectometry data with corresponding three different fittings are shown in Fig. 1a; the nuclear and magnetic scattering length density (NSLD and MSLD) profile perpendicular to the surface is given in Fig. 1b–d for these cases. Frozen H_2O (NSLD: -0.52×10^{-6} Å^{-2}) was excluded due to the positive SLD required by the fit. The background pressure and hence leakage rate during the experiment was constant, therefore the measurement averages over 200 min of film growth at large Q values.

Initially the NSLDs of pure bulk O_2 and N_2 were used for data modeling; these table values are indicated with vertical lines in Fig. 1b and c. The fitting algorithm then resulted in the NSLD and MSLD profiles in Fig. 1b and c. For comparison, a sample without any additional surface layer and with identical MSLD profile for the LSMO part obtained by fit 1b is shown in Fig. 1d.

Only a 63 Å thick layer of O_2 on top of the substrate (SLD profile in 1b) describes the measured data correctly. This is a plausible

* Corresponding author.

http://dx.doi.org/10.1016/j.rinp.2016.05.010
2211-3797/

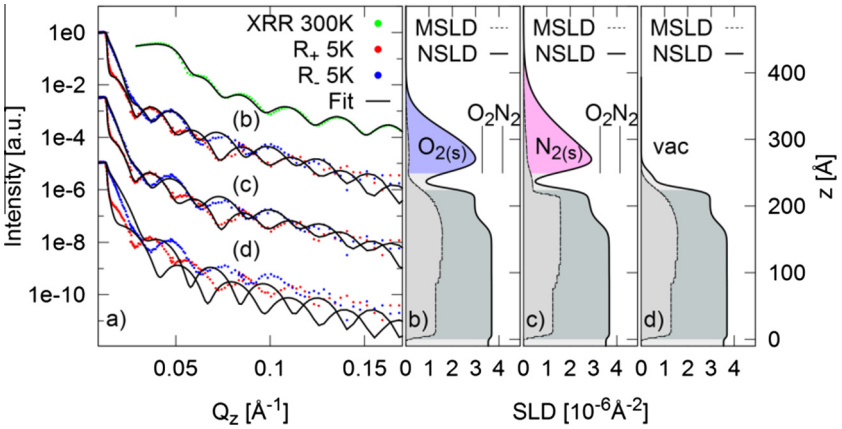

Fig. 1. (a) X-ray (XRR, green) and polarized neutron (R_+, red, and R_-, blue) Reflectometry data as a function of scattering vector $Q = k_i - k_f$ for the sample. The subfigures (b–d) refer to the used SLD models. The reflectivities are shifted in vertical direction for clarity. The solid curves are reflectivities calculated from the SLD models. (b–d) SLD profiles (proportional to density profile) along the z direction; vertical lines indicate values for bulk SLD of O_2 and N_2. (b) $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) with solid oxygen film (Figure of Merit (FOM): 0.88e−01), (c) LSMO with solid nitrogen (FOM: 0.86e−01), (d) model from (b) with vacuum instead of oxygen (FOM: 2.11e−01). Note that the bulk SLD value for nitrogen of 4.15 * 10^{-6} Å^{-2} is reached nowhere within the model. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

scenario since the origin of the layer is a small amount of air condensed at the surface at 5 K in a field of 1.2 T, a pressure below 10^{-4} mbar and on top of a ferromagnetic substrate within the 4 h of the experiment. O_2 has a higher boiling point than N_2 (36 K vs. 31 K for 10^{-4} mbar to 32 K vs. 27 K for 10^{-6} mbar) and condenses first on the cooled down surface.

The most likely alternative, a nitrogen layer, is shown in Fig. 1c. This layer required an unphysically large roughness value, which in fact distorts the SLD profile in a way, that it resembles the solid oxygen SLD. Additionally, the positive magnetic SLD, necessary to fit the data, seems highly unlikely for the diamagnetic N_2, in contrast to antiferromagnetic O_2.

The fit parameters obtained from fits in Fig. 1b were then used to visualize the need for this frozen gas layer via substituting the oxygen layer with vacuum (Fig. 1d). While the corresponding simulation in Fig. 1a describes R_- ("spin-down reflectivity") to some degree, R_+ ("spin-up reflectivity") fails to describe one oscillation period, indicating the presence of additional material on the surface, which is not visible in the 300 K XRR measurement.

In conclusion, we could successfully model and explain a surface layer forming on a substrate at low temperatures in imperfect vacuum conditions. Including such a surface layer to describe other PNR experiments is therefore warranted.

Acknowledgement

The Neutron experiments were carried out on Beam line 4A at ORNL's Spallation Neutron Source which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

References

[1] Lee W-Y, Scherer G, Guarnieri CR. J Electrochem Soc 1979;126:1533.
[2] Mongstad T, Platzer-Björkman C, Mæhlen JP, Hauback BC, Karazhanov SZh, Cousin F. Appl Phys Lett 2012;100:191604.
[3] Krim J, Coulomb JP, Bouzidi J. Phys Rev Lett 1987;58:583.
[4] Parratt LG. Phys Rev 1954;95:359.
[5] Lauter V, Lauter HJC, Glavic A, Toperverg BP. Reference module in materials science and materials engineering. Elsevier; 2016.
[6] Lauter V, Ambaye H, Goyette R, Hal Lee WT, Parizzi A. Phys B 2009;404:2543–6.
[7] Björck M, Andersson G. J Appl Cryst 2007;40:1174.