AIP | Review of Scientific Instruments

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Citation: Rev. Sci. Instrum. **84**, 015102 (2013); doi: 10.1063/1.4773002
View online: http://dx.doi.org/10.1063/1.4773002
View Table of Contents: http://rsi.aip.org/resource/1/RSINAK/v84/i1
Published by the American Institute of Physics.

Reactive sputter magnetron reactor for preparation of thin films and simultaneous *in situ* structural study by X-ray diffraction

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(Received 3 August 2012; accepted 6 December 2012; published online 2 January 2013)

The purpose of the designed reactor is (i) to obtain polycrystalline and/or amorphous thin films by controlled deposition induced by a reactive sputtering magnetron and (ii) to perform a parallel *in situ* structural study of the deposited thin films by X-ray diffraction, in real time, during the whole growth process. The designed reactor allows for the control and precise variation of the relevant processing parameters, namely, magnetron target-to-sample distance, dc magnetron voltage, and nature of the gas mixture, gas pressure and temperature of the substrate. On the other hand, the chamber can be used in different X-ray diffraction scanning modes, namely, θ-2θ scanning, fixed α-2θ scanning, and also low angle techniques such as grazing incidence small angle X-ray scattering and X-ray reflectivity. The chamber was mounted on a standard four-circle diffractometer located in a synchrotron beam line and first used for a preliminary X-ray diffraction analysis of AlN thin films during their growth on the surface of a (100) silicon wafer. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4773002]

I. INTRODUCTION

Non-reactive and reactive sputter magnetrons are widely used in basic research and industrial processing for the growing of thin films that contain a number of elements or compounds with nano or micrometer thicknesses.[1] In non-reactive sputtering magnetron technique, the physical process consists of the sputtering of metallic or non-metallic elements promoted by non-reactive ions such as Ar. The sputtered elements projected from the magnetron target to different substrate surfaces can be pure materials (Al, C, Ti, etc.), or a mixture of several of them such as Al/Ti, Cr/Ni, etc. In the reactive sputter magnetrons (RSM) technique instead, the same process as that described above is developed but through ions of reactive elements such as nitrogen, oxygen, etc., that are combined with the sputtered elements giving rise to the formation of different compounds (AlN, TiO_2, TiN, etc.) on the substrate surface. The plasma ions taking part in the sputtering process are generated in different types of discharges such as dc, pulsed dc or RF.

The overall nature of the deposited compounds then depends on the specific elements composing the magnetron target and on the type of ions generated in the plasma. However, the detailed properties of the resulting thin films such as compound stoichiometry, atomic (monocrystalline, polycrystalline, or amorphous) structure, mass density, degree of adhesion to the substrate, film thickness, etc., depend on many other processing parameters, such as type of the (dc or RF discharge) plasma source, power delivered to plasma, concentration ratios between the different filling gases,[2] operating pressure, magnetron target-substrate distance,[3] substrate temperature, and nature of the structure of the substrate surface.

The literature reports a number of investigations using different techniques that provide useful information about the structure and physical properties of thin films produced by different procedures. Among the variety of structural analysis techniques, X-ray diffraction (XRD) is one of the most reliable and commonly applied,[4] but, generally, the reported XRD measurements are performed on films after their removal from the reactor. Nevertheless, in order to characterize the mechanisms involved in film growth, the precise features and modifications of its structure—along the whole growth process—should be known. In order to do that, a possible procedure could be a serial study of different films by stopping the deposition process after different time periods. However, in this case, each film is not subjected to exactly the same conditions of cooling and oxidation after its contact with atmosphere, which can at least partially modify the structural evolution during the continuous growth process.[2]

In the literature, some reactor chambers for *in situ* studies of thin films growing by means of the RSM technique were previously reported.[5,6] A simple experimental set up[5] allows for X-ray diffraction studies using the energy dispersive technique (at fixed angle and varying photon energy). A much more sophisticated chamber equipped with two small magnetrons was also developed.[6] This chamber allows for *in situ*

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measurements during multilayer growth. In this case, the reactor chamber was designed to allow for thin film serial studies using symmetric Bragg-Brentano X-ray diffraction, vertical grazing incidence diffraction and reflectivity, in plane grazing incidence/exit diffraction and crystal truncation rod scattering.

In previous works of some of the authors of this paper, a chamber—designed and installed in a synchrotron beam line[7]—allowed to record a series of XRD patterns for *in situ* structural analyses of surface modifications of austenitic stainless steels subjected to ion-nitriding.[4,8] The use of this setup allowed to achieve the structural characterization *in situ* of different austenitic stainless steels. In particular, the development of a new phase named as expanded austenite in the early periods of ion-nitriding was clearly established.[7]

Our purpose was to build up a RSM chamber with a single magnetron for *in situ* studies of thin films—during their growth—by X-ray (non-dispersive) diffraction using a parallel synchrotron X-ray beam. Our reactor chamber has a design simpler than that reported in Ref. 6 and can be used for out-of-plane nearly symmetrical (θ-2θ) and grazing incidence X-ray diffraction. By adding a vacuum path downstream, grazing incidence small-angle scattering and X-ray reflectivity measurements can also be performed.

In this paper, we are reporting the design details of the reactor chamber and presenting the results of its first use for the preparation and structural characterization of polycrystalline AlN thin films.

II. CHAMBER FEATURES

The reactor chamber was designed in order to contain a magnetron for promoting the growth of thin films of different compounds by sputtering of pure elements in atmospheres of either non-reactive or reactive gases. The operating conditions of the reactor were chosen to be versatile enough for fast and easy changes of the processing parameters during deposition process itself, allowing for the investigation of their influence on the kinetic and on the features of the film growth process.[4] At the same time, the chamber was designed to allow for a continuous analysis of the film structure by XRD during the deposition process itself, so as nearly transparent windows for the entrance and exit of the incoming and diffracted X-ray beams, respectively, were properly placed in the reactor chamber.

The design was based on a cylindrical body of AISI316 stainless steel of 184 mm inner diameter, 3 mm wall thickness, and 128 mm long. Two diametrically opposed vacuum ports were open in the wall of the cylinder, one of them to locate the sputter magnetron and the opposite one for placing the sample holder. These main components of the reactor can be seen on top and on bottom of Fig. 1(a). In the upper part of the scheme, we can see the lateral view of the head of the magnetron, with the downward surface being the target to be sputtered. On the substrate placed below—with its upward surface exposed to the sputtered material—the thin film progressively grows. As shown in Figure 1(a), a thermocouple introduced from the bottom and making physical contact with

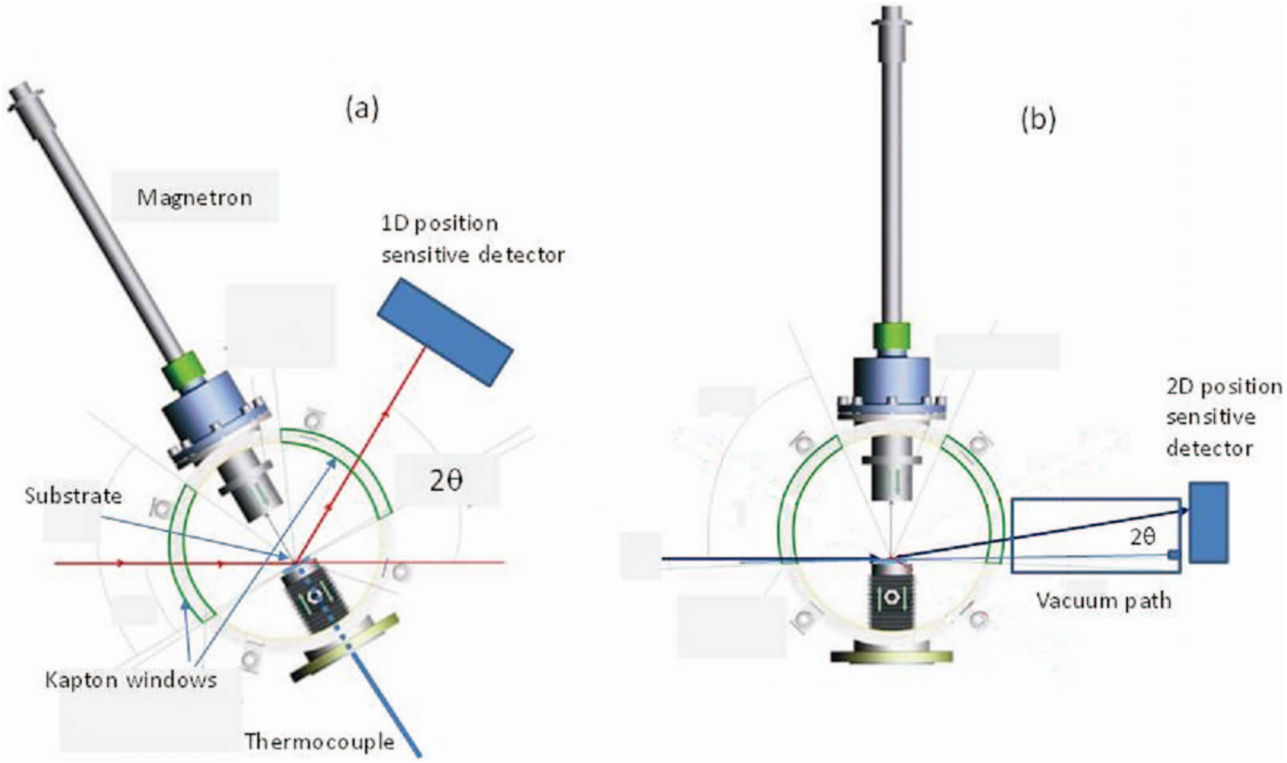

FIG. 1. (a) Reactor chamber for nearly symmetrical θ-2θ geometry. (b) Reactor chamber with the proper orientation for grazing incidence X-ray diffraction, X-ray reflectivity, and grazing incidence small-angle X-ray scattering (GISAXS). The place where the vacuum path to be added for GISAXS measurements is needed is schematically indicated.

the external side of the sample support, allows for a precise sample temperature monitoring.

The commercial magnetron itself (US Inc. Mak 1.3 in.) consists of a long rod that allows for (i) proper electrical connections of its head to power supply and (ii) circulation of cooling water to keep the target cool during its operation. The common central axis of the magnetron rod and sample substrate is centered with respect to the chamber volume and aligned perpendicularly to the axis for θ and 2θ rotations, θ being the Bragg angle between the incident X-ray beam and the reflecting crystallographic planes. The magnetron rod is vacuum sealed and can be longitudinally displaced in order to vary as desired the magnetron target-to-substrate distance, d. The sample holder is placed on a screwed rod that can be longitudinally displaced, with its upper face in contact with the sample support. The sample support is inserted in the chamber through a flexible and vacuum tight bellow, which leaves the screwed rod outside the internal volume at atmospheric pressure. Samples can then be displaced up and down by the action of a motor located outside the chamber. This system can externally and continuously control the position of the sample surface inside the chamber during the reactor operation. Notice that the sample surface should be maintained coincidentally with the line axis of θ-2θ rotations. In addition, this configuration allows for an easy insertion of a thermocouple close to the substrate that precisely records the sample temperature during the whole deposition process while the plasma discharge takes place.

Two 70 μm thick Kapton® films were used to cover the incidence and exit windows, being total transmission factor for both films 94.2%. Our first goal was to use the chamber for the growth of AlN thin films through the sputtering of pure aluminum under a mixture of nitrogen and argon gas atmosphere. For a photon energy $E = 8$ keV—used in the XRD experiments performed at the XRD2 National Synchrotron Light Laboratory (LNLS) beam line—the peaks corresponding to the main Bragg reflections expected for polycrystalline AlN thin films lie within the $33^o < 2\theta < 60^o$ angular range. Then we have two 8 mm wide open windows along the lateral wall of the chamber, allowing the entrance and the exit of the X-ray beam over the angular range mentioned above, using either the classical θ-2θ scanning mode or the 2θ scanning with a constant incidence angle, α.

The maximum distance between target and substrate is $d_{max} = 60$ mm. Since the sample during the first transient stages of sputtering discharge must be covered by inserting a moving shutter, the minimum target-to-sample distance is kept larger than $d_{min} = 25$ mm. Notice that the maximum θ and 2θ angles depend on the distance, d, between the magnetron target and the substrate sample.

For grazing incidence XRD (GIXRD) experiments, the chamber is fixed by the diffractometer in such a way to keep the incidence angle, α, close to zero. For this geometry, the 2θ detector angle can vary from zero up to a maximum angle that depends on the target-to-sample distance. With d at its maximum value ($d = 60$ mm), the maximum 2θ angle that can be reached is 63^o. Above $2\theta = 63^o$ the sputter magnetron hinders the diffracted beam.

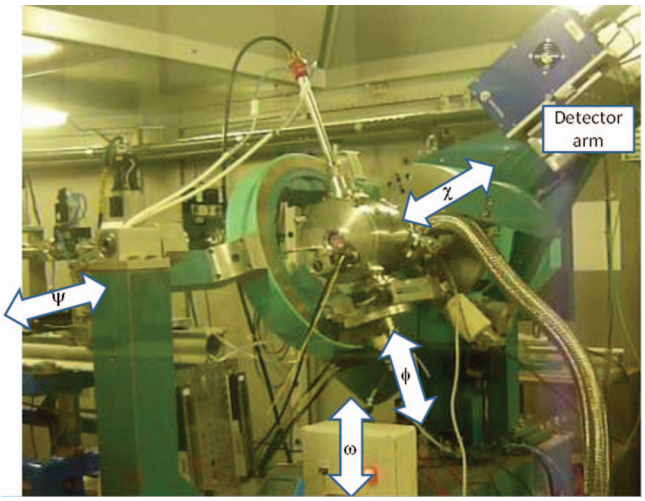

FIG. 2. Picture of the 5021 (4+2) Huber diffractometer on which the reactor chamber is placed. The four axes for sample rotations are indicated. The reactor chamber is mounted on the ϕ rotation axis.

For the θ-2θ XRD scanning mode, the substrate surface for θ and 2θ angles close to zero is nearly horizontal. The magnetron axis becomes progressively more inclined as both θ and 2θ increase, the 2θ angle for $d = 60$ mm reaching its maximum values equal to 63^o. This maximum 2θ value is obviously lower for shorter d distances.

Since the film deposition by the RSM process uses high purity gas mixtures and should be performed under low pressure, the chamber is properly sealed to work at pressures lower than 10^{-4} Pa.

Because of the required high quality of XRD patterns and high temporal resolution for an efficient real time recording, a high intensity and well-collimated X-ray beam with small cross section should be used. Those requirements were well satisfied using the XRD2 beam line of National Synchrotron Light Laboratory, at Campinas, Brazil. In Fig. 2, can be seen the vacuum chamber placed in the Huber diffractometer.

The chamber design has been developed to allow for grazing incidence XRD, grazing incidence small angle scattering (GISAXS), and X-ray reflectivity (XRR) experiments. The GISAXS method allows for the characterization of eventual nanosized heterogeneities inside the thin films[8] and the XRR procedure yields useful information about sample thickness and surface roughness. In order to allow for the use of these techniques, a vacuum path and a second position sensitive detector are added, as schematically shown in Figure 1(b). The vacuum path is needed in order to suppress the parasitic scattering intensity produced by air.

III. FIRST USE

The first use of the reactor chamber was a XRD study of the kinetics of growth of polycrystalline AlN thin films deposited on a (100) Si single crystal substrate.[3] The magnetron target was pure aluminum. The substrate-to-target distance was $d = 30$ mm, the dc voltage was set equal to 300 V, with a mixture of nitrogen and argon as reacting gases

and pressures ranging from 620 Pa to 820 Pa, and a nitrogen to argon content ratio ranging from 1:3 up to 14:11.

We have used 8.000 keV ($\lambda = 1.549$ Å) photon beam with a narrow cross-section emerging from the synchrotron source. The XRD intensity as a function of the scattering angle 2θ was recorded by a Pilatus 2D position sensitive detector used in a 1D detection mode. The detector was placed at 470 mm from the sample substrate thus allowing for simultaneous data collection by 487 pixels over an angular interval of 10°. Two series of XRD measurements were carried out keeping invariant in both of them the incidence α angle.

Figure 3(a) displays a sequence of XRD patterns recorded for an incidence angle α kept constant and equal to 2° during the whole 2θ detector scan from $2\theta = 32.5°$ up to $2\theta = 37.5°$. These patterns correspond to the profiles of the $(10\bar{1}0)$ and (0002) Bragg peaks of AlN polycrystals located close to $2\theta = 33.3°$ and 36.3°, respectively. The first XRD pattern of this series corresponding to only 3 minutes of deposition time already shows the presence of clear Bragg peaks indicating the existence of a polycrystalline structure from the very beginning of the sputtering process. The last pattern of Figure 3(a) corresponds to 33 minutes of processing.

Figure 3(b) shows a sequence of XRD patterns taken under similar conditions as those of Fig. 3(a) but for longer growth processing periods, starting this time from 36 min up to 54 min. In order to investigate eventual structural changes by varying selected processing parameters, we have modified, just after 30 minutes of growth, the nitrogen to argon concentration ratio and the total pressure from 1:3 and 620 Pa to 14:11 and 820 Pa, respectively.[3] After these parameter changes, the $(10\bar{1}0)$ peak at $2\theta = 33.3°$ shows continuous growth at nearly same rate as before the parameter changes, while the growth rate of the (0002) Bragg peak, at $2\theta = 36.3°$, is drastically reduced. A qualitative conclusion from these results is that the mentioned changes in processing parameters strongly alter the initial texture or preferred orientations of the individual crystals in the polycrystalline thin film.

Finally, Figure 3(c) displays the whole sequence of XRD patterns for a constant and small grazing incidence angle, $\alpha = 2.0°$, over a wide 2θ angles interval from $2\theta = 27.85°$ up to $2\theta = 63.11°$ and processing time periods from $t = 3$ min up to $t = 54$ min. These GIXRD peak profiles yield useful information about the kinetics of growth of the polycrystalline AlN thin film deposited by the reactive sputtering magnetron process.[1] Notice that in the case of rather thick films, the GIXRD experiments would only probe a thin layer close to the film surface. Thus, a properly controlled variation of the incidence angle can be applied to vary the penetration depth of the X-ray beam, this effect allowing for an in-depth profile analysis of the crystallographic structure. On the other hand, the systematic determination of the XRD intensity for many different incidence angles and substrate orientations can be applied to quantitatively characterize the crystalline texture or preferred orientations of the individual crystals of the deposited thin films and their variations during the growth process. Figure 4 corresponds to an animation in which it is possible to see the reaction chamber and Pilatus detector in a

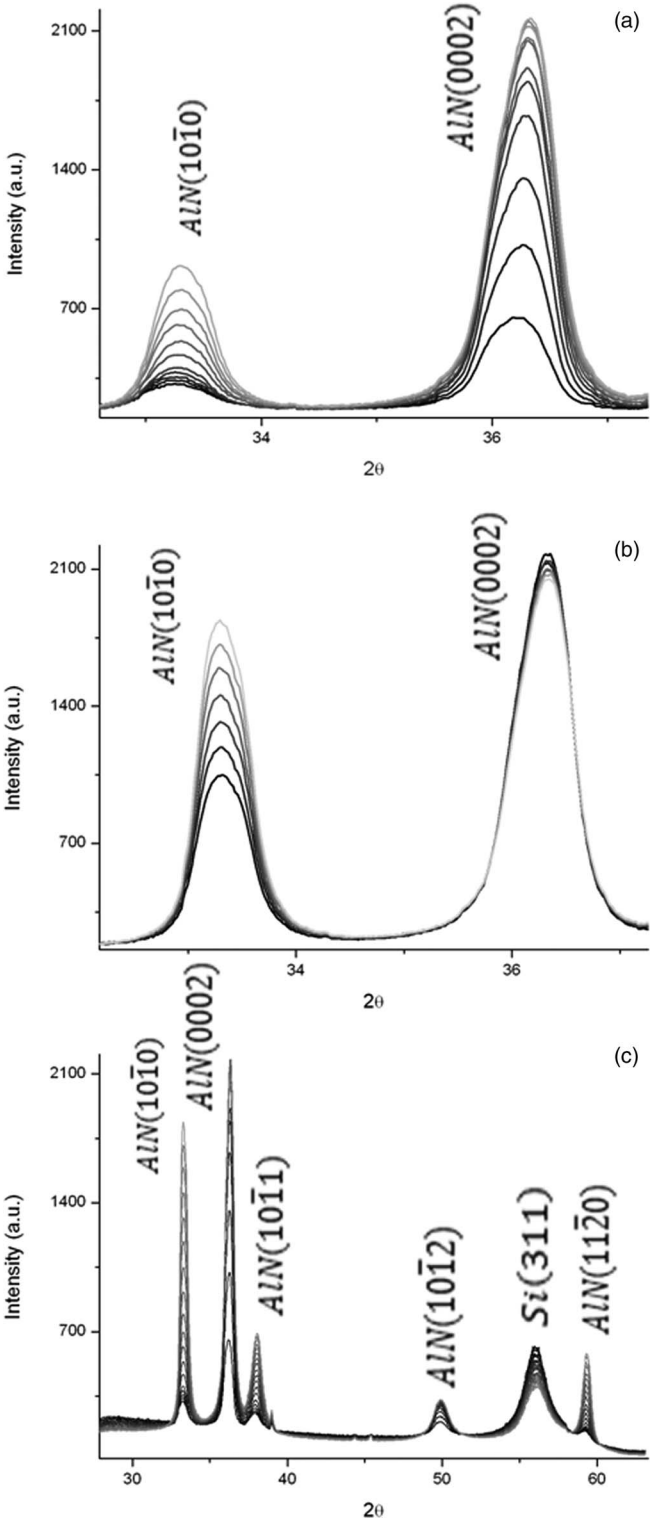

FIG. 3. (a) Series of XRD patterns for a fixed incidence angle, $\alpha = 2°$ corresponding only to the $(10\bar{1}0)$ and (0002) Bragg peaks recorded during the AlN thin film growth. The first spectrum corresponds to a deposition time $t = 3$ min and the last one to $t = 33$ min. (b) XRD pattern sequence following that displayed in (a) for deposition times from $t = 36$ min up to $t = 54$ min. The parameters related to gas composition and pressure were changed at $t = 30$ min as indicated in the text. (c) Complete sequence of XRD patterns for an incidence angle kept equal to 2° within a large 2θ interval along deposition times starting from $t = 3$ min up to $t = 54$ min. The sequence of curves indicates a monotonously increasing intensity for increasing time periods. The time period elapsed between two successive patterns is 3 min.

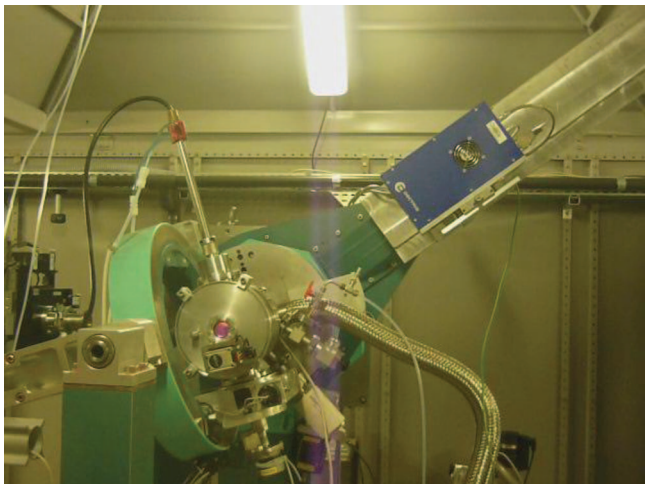

FIG. 4. Animation of reaction chamber during simultaneous AlN thin film deposition and X-ray diffraction (enhanced online) [URL: http://dx.doi.org/10.1063/1.4773002.1].

synchronized rotation during an experiment of AlN film deposition.

IV. CONCLUSION

We have designed and constructed a reactor chamber for *in situ* XRD studies of thin film growth induced by reactive magnetron sputtering. This chamber was placed on a standard four-axes Huber diffractometer, installed in the XRD2 beam line of the LNLS and used by first time for a preliminary study of the process of growth of AlN thin films deposited on a (100) Si substrate.

The reactor chamber allows for the controlled setting and variation of all processing parameters relevant for film growth such as target-to-sample distance, type of magnetron discharge, composition of the reactive gases, pressure of the gas mixture, temperature of the thin film, and nature of the substrate surface.

The chamber was mainly designed for XRD measurements using the classical θ-2θ scanning procedure or, alternatively, the 2θ scanning procedure keeping constant the incidence α angle. Moreover, by adding a long vacuum path along the direction of the incident X-ray beam and using a second position sensitive detector, GISAXS or X-ray reflectivity measurements can be simultaneously performed.

ACKNOWLEDGMENTS

Research work performed with Grant No. BID-PICT 2008-0374 from the Agencia Nacional de Promoción Científica y Tecnológica (ANPCyT), Argentina, and under the Scientific Project XRD2-8090 and Research Proposal XRD2-13427 of Laboratório Nacional de Luz Síncrotron, Campinas, Brazil.

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