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K. Le Guen, H el ene Maury, Jean-Michel Andr e, Philippe Jonnard, Aur elie Hardouin, et al.. X-ray spectroscopic application of Cr/Sc periodic multilayers. Applied Physics Letters, 2007, 91, pp.234104. 10.1063/1.2821379 . hal-00575878

HAL Id: hal-00575878

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Submitted on 6 Apr 2012

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Citation: *Appl. Phys. Lett.* **91**, 234104 (2007); doi: 10.1063/1.2821379

View online: <http://dx.doi.org/10.1063/1.2821379>

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X-ray spectroscopic application of Cr/Sc periodic multilayers

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(Received 16 October 2007; accepted 14 November 2007; published online 5 December 2007)

The use of Cr/Sc multilayer interferential mirrors (MIMs) in optical systems such as x-ray microscopes or telescopes have been reported for the water window (between C *K*- and O *K*-absorption edges). However, their possibilities in spectroscopic application have never been described in the literature. The purpose of the paper is to report for the first time on the performances of Cr/Sc MIMs as Bragg dispersive devices for the analysis in wavelength dispersive spectrometry of samples containing N or Sc atoms. The possibility to distinguish the chemical state of the emitting N or Sc atoms is evidenced by using Johan-type and double-crystal spectrometers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2821379]

Multilayers designed to work in the water window, i.e., for photon energy between the oxygen *K*-absorption edge (525 eV) and the carbon *K*-absorption edge (277 eV), have important applications in material science, biology, and medicine. Cr/Sc multilayers made of layers of about 1-nm-thick have proven to be a valuable material combination to implement high-reflectivity mirrors in this part of the soft x-ray range.^{1–4} Up to now, they have been mainly implemented for optical instruments such as Wolter⁵ telescope and x-ray microscope.⁶

Given the very small layer thickness, the reflectivity of such multilayers is critically affected by interdiffusion and interface roughness. The fabrication of such structures with high performances is difficult and their characterization in this spectral region is needed for further improvement. Nevertheless, a reflectivity of 32.1% at 398.6 eV (Sc L-absorption edge), at an angle of 9.2° from normal incidence for Cr/Sc multilayers has been reported, in which a B₄C diffusion barrier was introduced.⁷ The optical performances of other multilayers have been experimentally evaluated in this spectral range, highlighting the fact that Cr/Sc are the optimal devices.⁸

For spectroscopy in the water window, multilayers such as W/Si (Ref. 9) have been tested and, presently, only W/Si or Ni/C multilayers are used in electron microprobes. In this work, we present the first use of Cr/Sc multilayer interferential mirrors (MIMs) as monochromators for x-ray spectroscopy. These MIMs are first characterized at the wavelength of the N *K*α emission (2*p*-1*s* transition) using synchrotron radiation and then tested in two original crystal-based spectrometers. In the IRIS apparatus, a bent Cr/Sc MIM is used to study the x-ray emissions in the water window of different samples containing N or/and Sc atoms: BN, CrN, Sc₅Si₃, and ScN. The Sc *L*α emission, corresponding to the 3*d*-2*p*_{3/2} transition, is close to the N *K*α emission. In the MONOX spectrogoniometer, the N *K*α emission of a BN target is obtained

using two Cr/Sc multilayers inserted in a two-crystal monochromator.

The studied Cr/Sc periodic multilayers are designed to work with a Bragg angle of 45° at the N *K*α x-ray emission (392.4 eV) leading to the aimed period of 2.2 nm. The aimed thickness is 0.8 nm for the Cr layers and 1.4 nm for the Sc layers. The MIMs are made of 200 bilayers. The fabrication process is described in details elsewhere.¹⁰ Briefly, the deposition system is based on magnetron sputtering under constant argon pressure of 0.7 mT, using plasma discharges by radio frequency power. Samples are deposited onto clived samples of polished Si wafers. Typical sample dimensions are 20 × 30 mm² with thickness of 0.75 mm. The thickness uniformity is better than 1% on all samples. The two studied samples are called MP07046 and MP06136.

X-ray reflectivity (XRR) measurements for the MP07046 sample have been performed on the 6.3.2 beamline at the Advanced Light Source (ALS) synchrotron radiation facility. The XRR spectrum of the MP06136 sample has been recorded on the bending magnet for emission absorption and reflectivity (BEAR) beamline at the ELETTRA synchrotron source. In all cases, the degree of *s* polarization of the incident radiation is close to 80%. For each sample, a first measurement in $\theta/2\theta$ mode was performed at a photon energy of 392.4 eV in order to determine the optimal angle of each multilayer. Then a photon energy scan in the vicinity of the N *K*α emission was measured at this optimal angle. In this paper, we report only the photon energy scan measurements, as shown in Fig. 1.

For the MP07046 multilayer at a glancing incidence of 45.3°, the peak reflectivity is centered at 392.4 eV and its maximum is equal to 10.6%. For the MP06136 multilayer at a glancing incidence of 46.5°, the peak reflectivity is centered at 392 eV and its maximum is equal to 12.3%. The spectral full widths at half maximum (FWHMs) of the MP07046 and MP06136 samples are equal to 2.4 and 3.5 eV, respectively. The reflectivity of the ideal Cr/Sc multilayer (no roughness or interdiffusion at interfaces) calculated using the XRV software¹¹ for a degree of *s* polarization of the incident radiation equal to 80% has a maximum

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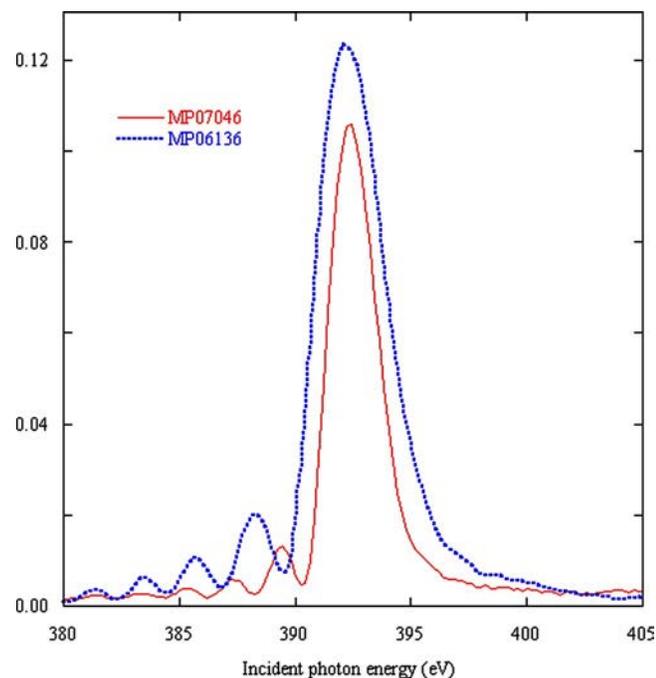


FIG. 1. (Color online) XRR curve of the MP07046 (solid line) and MP06136 (dotted line) samples recorded in the vicinity of the $N K\alpha$ emission for a glancing angle close to 45° .

value equal to 43.6%. The quality of the samples has still to be improved since their reflectivity is less than 30% of the value associated with the perfect structure. In the simulation, we have taken into account a rms roughness height of about 0.55 nm at each interface to reproduce the experimental peak reflectivities.

Furthermore, it was not possible from the analysis of the Cr $3d$ valence states by x-ray emission spectroscopy to evidence the presence of interfacial compounds resulting from the interdiffusion¹² of the Cr and Sc layers. This means that the interfacial imperfection is mainly due to the roughness.

As a first test of application, MP07046 Cr/Sc MIM has been inserted in the bent crystal holder (500 mm radius) of the IRIS x-ray Johann-type spectrometer.¹³ The aim is to obtain the x-ray emission in the water window of different materials containing N or/and Sc atoms: BN, CrN, Sc_5Si_3 , and ScN. This should allow the estimation of the separating power of the dispersive Cr/Sc MIM. The target sample is bombarded by electrons of 3 keV energy. Following the ionization of the atoms present in the sample, characteristic x-rays are emitted, dispersed by the curved crystal following the Bragg law, focused onto the Rowland circle and then detected by an Ar- CH_4 gas-flow counter operated in the Geiger mode.

Figure 2 displays the $N K\alpha$ and $Sc L\alpha$ emission bands originating from BN and Sc_5Si_3 samples, respectively. The BN sample was pressed powder (from GoodFellow) and the Sc_5Si_3 sample was prepared in an arc furnace under argon atmosphere. X-ray diffraction (XRD) measurements has evidenced that Sc_5Si_3 is the major phase in the sample. Both spectra are normalized to their maximum. The two band maxima are separated by about 3 eV. We have superimposed in Fig. 2 the background of the $N K$ domain recorded with a Si target. The experimental conditions are the same with those used for the BN sample. The lower background intensity in the case of BN can be explained by the stronger

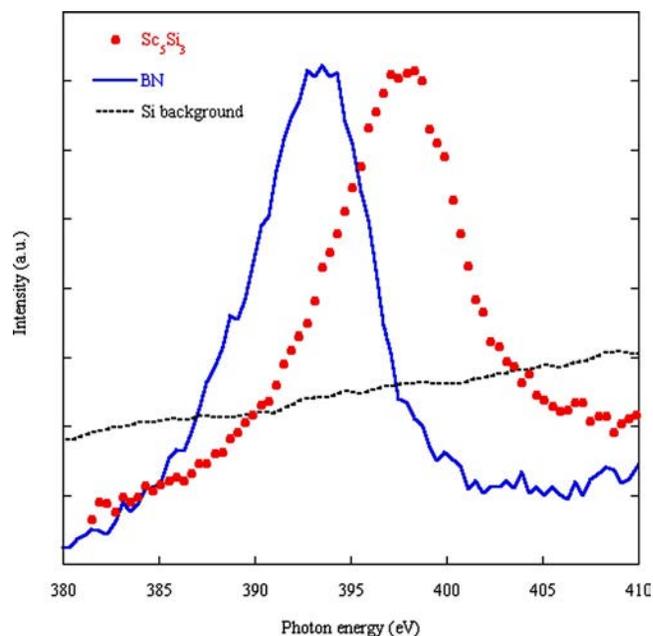


FIG. 2. (Color online) $N K\alpha$ and $Sc L\alpha$ emission bands from BN (solid line) and Sc_5Si_3 (dots), superimposed to the background of the $N K$ domain recorded with a Si target (dotted line).

Bremsstrahlung emitted by the Si target since Si is heavier than BN in terms of atomic number. Small intensity fluctuations exist in the spectrum obtained with Si, which cannot be unambiguously assigned to $N K$ emission from impurity or surface contamination of the Si sample or to anomalous reflection associated with the presence of Sc in the composition of the MIM. If any of them exists, its corresponding intensity is lower than 1% of that of BN. Let us emphasize that in anyway, the anomalous reflection¹⁴ affects the detection limit of N and Sc as trace elements.

In Fig. 3, the $N K\alpha$ emission bands originating from N-containing materials are collected: BN, CrN, and ScN.

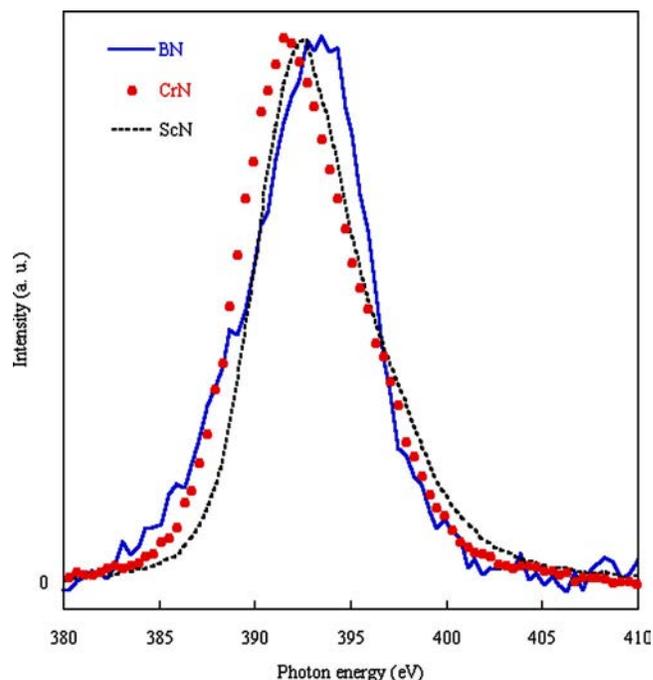


FIG. 3. (Color online) $N K\alpha$ emission bands from N-containing samples: BN (solid line), CrN (dots), and ScN (dotted line).

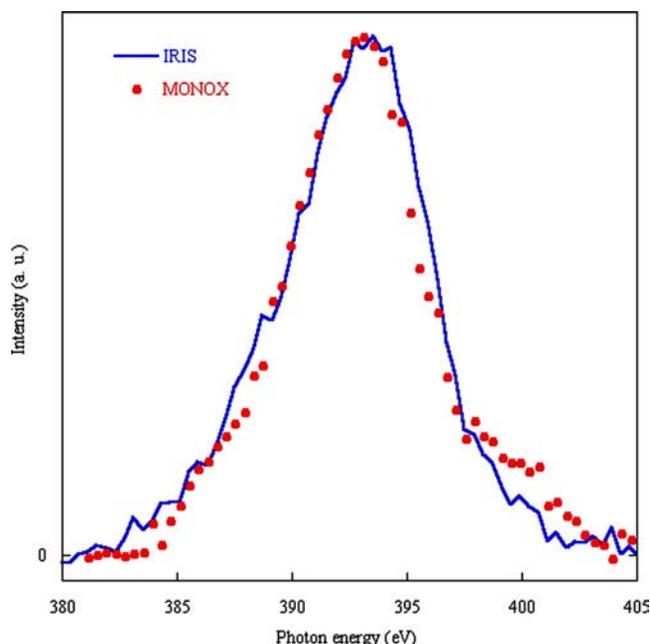


FIG. 4. (Color online) $N K\alpha$ emission from a BN target recorded with MONOX (dots) and IRIS (solid line).

CrN and ScN samples are thin films prepared by magnetron sputtering. Thin films of thickness about 100 nm were deposited using rf reactive sputtering of pure Cr and Sc targets with 20% N_2 in Ar. Their precise stoichiometry is unknown. This comparison evidences that the position and shape of the emission band is sensitive to the chemical environment of the N emitting atoms, despite the broadening introduced by the diffraction pattern of the MIM: compare the about 3 eV width of the XRR curves (Fig. 1) to the about 7 eV width of the $N K\alpha$ emission (FWHM of 6.9, 7.2, and 6.5 eV for BN, CrN, and ScN, respectively). For the ScN sample, one could expect two maxima: one for N and the other for Sc. However, the $N K\alpha$ and $Sc L\alpha$ emissions are bands describing the $N 2p$ and $Sc 3d$ distribution of valence states, respectively. The observation of a single peak for ScN suggests a large $Sc 3d-N 2p$ hybridization. The electronic structure calculations of ScN could answer this question.

As a second application, we have used the MONOX spectrogoniometer.¹⁵ A water-cooled BN target, introduced in the x-ray tube, is bombarded with electrons of 1.5 keV energy. Emitted x-rays are dispersed and detected in an Ar- CH_4 gas-flow counter operated in the Geiger regime. In the present case, the two-crystal monochromator has been equipped with two MP06136 Cr/Sc MIMs. The incident photon energy is scanned by translation and independent rotation of the two dispersive elements. The resulting $N K\alpha$ emission band is shown in Fig. 4 in comparison with the one obtained on IRIS. For the sake of clarity, both spectra are normalized to unity. They give quite similar results (although we expect IRIS to be the more resolutive apparatus) showing that the main contribution to the bandwidth comes from the diffraction pattern of the Cr/Sc MIM.

We have shown that high quality Cr/Sc periodic multilayers can be used as efficient monochromators in the water window range. A peak reflectivity equal to 16.9% is found at

392.4 eV for the MP06032 sample upon a glancing incidence of 45.15° . This reflectivity, 39% of the theoretical value, can probably be improved by changing the deposition process, for example, by sputtering Cr in the dc mode. We have reported the original application of Cr/Sc multilayers for spectroscopic purpose. The use of Cr/Sc MIMs in a curved-crystal or double-crystal spectrometer for the $N K\alpha$ and $Sc L\alpha$ emissions leads to a spectral resolution, good enough to distinguish the chemical state of the emitting N or Sc atoms. The performances of such a monochromator are still lower than the one obtained from a *c*-BN crystal recorded using a spherical grating-based monochromator¹⁶ but better than the one obtained with a W/Si multilayer in a crystal spectrometer.⁹ On the other hand, because of the possible contamination of the surface sample by nitrogen atoms and the anomalous reflection due to the presence of Sc atoms within the MIMs, measurements of N or Sc elements present in samples as dopants or impurities (less than 1%) will not be feasible with the Cr/Sc structures.

We are very thankful to P. Ochin and S. Tusseau-Nenez from CECM-CNRS for the preparation and XRD analysis of the Sc_5Si_3 sample. We also thank S. Nannarone and A. Giglia from the BEAR beamline at Elettra and E. Gullikson and A. Aquila from the 6.3.2 beamline at the ALS for their technical assistance in EUV reflectometry measurements. Dr. R. Benbalagh and Dr. M. Fialin are thanked for helpful discussions. Cr/Sc multilayers have been deposited on the MP800 magnetron sputtering machine implemented in the cleanroom of Institut d'Optique in the framework of CEMOX (Centrale d'Elaboration et de Métrologie des Optiques X).

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