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An extended anomalous fine structure of X-ray quasi-Bragg diffuse scattering from multilayers

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Abstract

An X-ray quasi-Bragg diffuse scattering anomalous fine structure technique was probed near the absorption Ni K-edge to study the interfacial structure of the Ni/C multilayer deposited by the laser ablation. Like other combinations of the EXAFS and diffraction techniques, this method has a spatial selectivity and was shown qualitatively to provide atomic structural information from the mixed interfacial layers. The possibilities and advantages of this technique are discussed.

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Keywords: Multilayers; X-ray diffuse scattering; EXAFS-spectroscopy

1. Introduction

The recent vigorous advancement of physics and chemistry of the thin films, multilayers, magnetic and semiconductor superlattices was caused by their unique properties principally differing from those of bulk materials. There is no doubt that these unique properties are immediately associated with the surface and interface structures. Of special interest is the chemical or atomic arrangement of interfaces. Thus, the development of X-ray structural methods allowing one to obtain this information is a very real problem. At present, there are two X-ray structural techniques that can provide the direct atomic structural information from interfacial layers.

EXAFS spectroscopy of the atoms-markers [1]: The principle of this method is that at the stage of multilayer growth, the atoms-markers having the same chemical properties as the constituting atoms are embedded at a required depth, then the usual fluorescent EXAFS technique can be used. Nevertheless, this technique has its own evident limitation.

X-ray standing waves [2]: Owing to the fact that the yields of secondary processes are proportional to the standing wave intensity, one can perform localized probes of the atomic structure. The main problem of this technique is the drastic modification of the diffraction (the extinction depth and so on) as the photon energy moves through the

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absorption edge. To some degree, this problem can be overcome with the use of special substrates that can generate the standing waves [3] so that the diffraction from the studied thin films can be excluded from consideration. Nevertheless, from the technical standpoint, the last method is not universal. Besides, due to the fact that the standing wave size is comparable to the multilayer period, the ratio between the interfacial and bulk signals is not large, which also restricts this method.

The diffraction Anomalous Fine Structure (DAFS) technique is widely used currently [4]. This method is based on the fact that the energy-dependence of the diffraction intensity near the absorption edge provides a local chemical environment information just as the EXAFS spectrum. In spite of a more complicated data treatment compared to the standard EXAFS spectroscopy, this method has a very important advantage: this is the spatial selection. Unlike EXAFS spectra which are contributed from all specimen atoms, DAFS spectra provide information on the atoms involved in diffraction.

Like the diffraction, the off-specular resonant diffuse scattering has the spatial selectivity also due to the fact that only the "roughness atoms" localized at the interfacial layers $2\sigma = 2\sqrt{\sigma_{\text{rough}}^2 + \sigma_{\text{mix}}^2}$ thick, where σ_{rough} is the roughness dispersion and $2\sigma_{\text{mix}}$ is the thickness of the mixed layers, are involved in this scattering. Thus, the Diffuse Scattering Anomalous Fine Structure (DSAFS) spectra contain information on the local chemical environment of the "roughness atoms". The main purpose of this work was to test the DSAFS technique.

The resonant quasi-Bragg diffuse scattering [5,6] was used in this study for two reasons. Firstly, this scattering is caused by the interfacial imperfections coherently repeated from one layer to another (interfacial cross-correlation). Thus, when the incident angle differs greatly from the Bragg angle, this scattering has a clear kinematic nature. It simplifies the data treatment considerably. The second reason is the high intensity of this scattering, which allows one to obtain the experimental data for a reasonable time.

The Ni/C multilayer deposited by the laser ablation technique was chosen as a test sample due to the fact that this system was previously studied by us in details [1,7–9]. The presence of strong intermixing between the metal and carbon layers was revealed by EXAFS spectroscopy and X-ray diffraction in low- and high-angle ranges. At a thickness smaller than about 2 nm, the metal layers are saturated by carbon and are present in the carbide glass-like phase instead of the metal one. The interfacial regions have the highest carbon concentration. This strong intermixing is specific to the laser ablation technique and is explained by the ballistic effect due to high-energy atom (ion) bombardment of the growing layer.

2. Experimental

The Ni/C multilayer was deposited by the laser ablation technique on the flat silica wafer with a surface roughness of 0.4 nm. The number of bilayers was 30. The other parameters were obtained from the usual reflectivity scans: the multilayer period, Λ, was 4 nm, and the Ni-rich layer comprised approximately 0.4 of this period or 1.6 nm. The effective roughness parameter, σ, was found to be equal to 0.3 nm. According to our previous studies [9] this value is determined by the presence of intermixed layers, whereas the true roughness dispersion, σ_{rough}, is smaller ($\sim$0.1–0.2 nm).

The measurements were performed using SR of the VEPP-3 storage ring of the Siberian SR Centre at Budker INP, which operates at 2 GeV and with a maximum stored current of 165 mA. The diffractometer of the "anomalous scattering" station [10] with a primary channel-cut single-crystal Si(1 1 1) monochromator and the scintillation detector based on an FEU-130 photomultiplier with a NaI(Tl) scintillator were used. The experimental setup is shown in Fig. 1.

The energy scan through the Ni K-edge was performed in such a manner that the diffuse scattering intensity was always measured at the same point in q-space. The standard fluorescent EXAFS spectrum was obtained concurrently with the basic measurements.

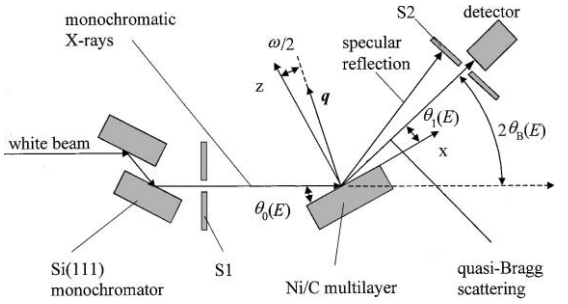

Fig. 1. The experimental setup: θ_0, θ_1 and θ_B are the incident, scattered and Bragg angles, respectively; E is the photon energy; S1, the primary slit (100 μm) providing an energy resolution of about 1 eV; S2, the secondary slit ($\sim$2 mm) were used to select quasi-Bragg diffuse scattering. The energy scan was performed in such a manner that the diffuse scattering intensity was always measured at the same point in q-space. Though θ_0, θ_1 and θ_B are changed during this scan, the momentum transfer, q and off-specular angle, $\omega = \theta_0 - \theta_1$ (0.2°) were kept constant.

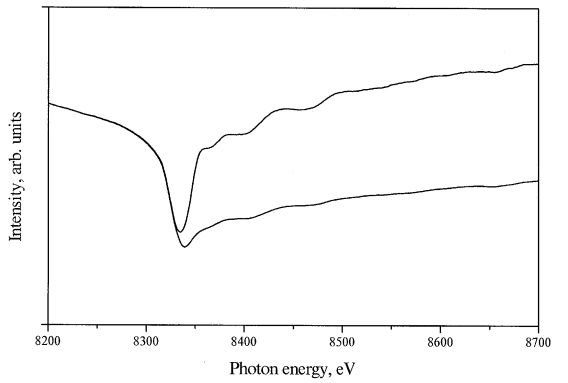

Fig. 2. The DSAFS spectra obtained: the experimental (lower curve) and corrected data (upper curve).

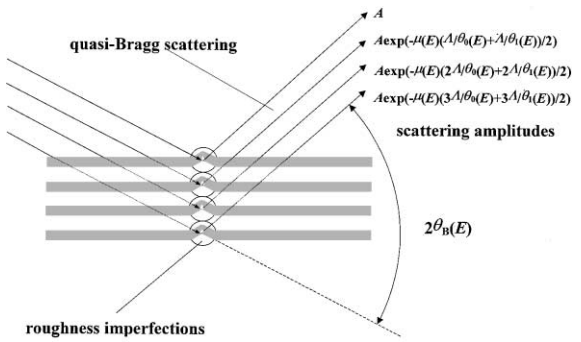

Fig. 3. The shield effect due to strong absorption: $\mu(E)$ is a bulk absorption attenuation coefficient obtained from the fluorescent EXAFS measurements. The roughness cross-correlation was assumed to be complete.

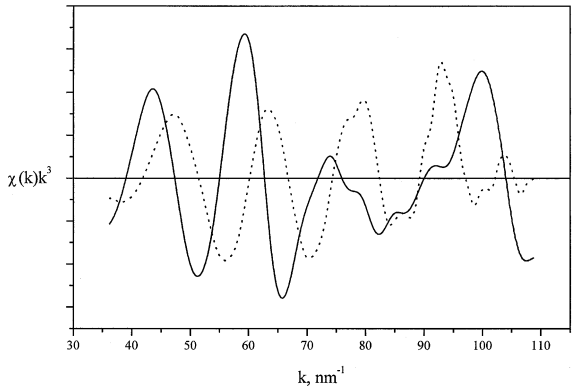

Fig. 4. The dependence of $\chi(k)k^3$ obtained from the DSAFS spectrum (solid curve) and standard fluorescent EXAFS (points).

3. Results and discussion

The DSAFS spectrum obtained (Fig. 2) was corrected with regard to the wave extinction due to strong absorption (Fig. 3). Ignoring the quadratic in the anomalous dispersion correction terms (their contribution does not exceed a few percent), the corrected experimental data were used to obtain the oscillation part of the imaginary anomalous dispersion scattering amplitude, $\chi(k)$ (Fig. 4) by means of the Kramers–Kronig dispersion relations. Further data treatment was performed using the standard methods [11].

The resulting Fourier transforms of k^3-weighted DSAFS and usual fluorescent EXAFS are shown in Fig. 5. The coordination shell positions, that may be observed using the bulk EXAFS data [1] are depicted as well. The main difference, which is seen at a single glance, is the splitting of the Ni–Ni(I) shell. The origin of this splitting can be explained by the $\chi(k)$ behavior (Fig. 4). It is well known that the presence, in any shell, of two types of neighboring atoms at approximately same distances in approximately equal amounts cause the modulation of the fine structure oscillation. In other words, the oscillation amplitude alternately decreases and increases, which is seen from Fig. 4.

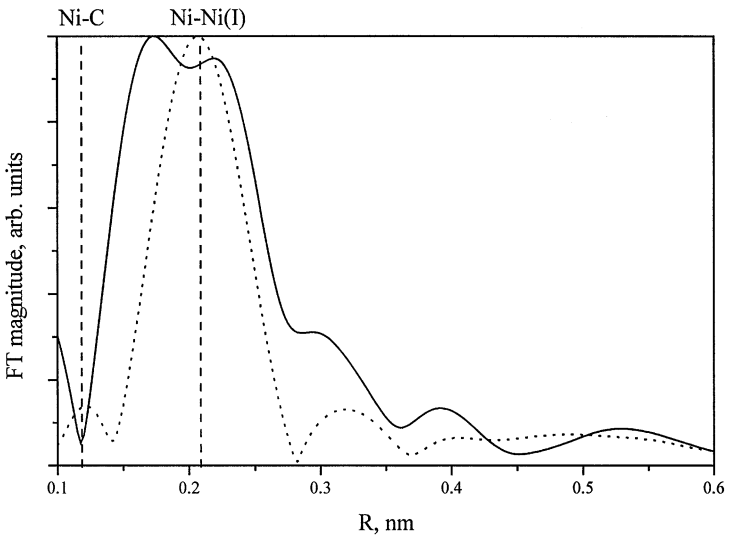

Fig. 5. The resulting Fourier transforms of k^3-weighted DSAFS (solid curve) and standard fluorescent EXAFS (points).

Although both curves are shown in Fig. 2 in the same scale, the amplitude of DSAFS oscillation is much smaller compared to the EXAFS one and this is not a surprise. Indeed, the structural imperfections in the interfacial layers are at their maximum.

Thus, the results are in a good qualitative agreement with our assumption that the DSAFS spectrum provides the structural information on the interfacial layers. As has already been mentioned, the thickness of the studied interfacial layers is determined by the mixed layer thickness in our case and is about 0.6 nm.

The structural method used in this work can be developed further. For example, using the linear SR polarization and the corresponding experimental geometry of DSAFS measurements, one can obtain the local chemical surrounding not only in the lateral plane, but also normal to it. Another possibility is the use of the diffuse scattering discrimination in the direction normal to the specular diffraction plane [12]. This allows one to study the local structure at the roughness imperfections with different spatial ranges. In principal, this method can be used for the single interface or surface, but one should bear in mind that the diffuse scattering intensity is proportional to N^2, where N is the bilayer number. Thus, the diffuse scattering intensity falls off drastically in this case. One more application is DSAFS studies based on the superlattice satellite reflections in a high-angle range. The interfacial stress studies are of interest in this case.

4. Conclusion

The DSAFS method was shown to provide information on the local atomic structure and its disruptions at the interfacial layers of thickness 2σ in the multilayers.

Acknowledgements

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