Journal of Electron Spectroscopy and Related Phenomena 185 (2012) 470–474

Contents lists available at SciVerse ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Effects of epitaxial films of nanometric thickness on the X-ray photoelectron diffraction intensities from substrates

A. Atrei*

Dipartimento di Chimica, Università di Siena, 53100 Siena, Italy

ARTICLE INFO

Article history:
Received 3 August 2012
Received in revised form
13 September 2012
Accepted 24 September 2012
Available online 2 October 2012

Keywords:
Photoelectron diffraction
Multiple scattering
Surface structure
Thin films
Nickel oxide
Silver

ABSTRACT

The effects on the X-ray photoelectron diffraction intensities from the substrate produced by epitaxial NiO(0 0 1) films of various thickness deposited on Ag(0 0 1) were investigated. The variations in the Ag XPD curves induced by the NiO films can be explained in terms of multiple scattering of the electrons emitted by the substrate atoms along the close-packed rows of the overlayer. Intensity minima in the XPD curves from the substrate in correspondence to intensity maxima in the XPD curves from the overlayer are observed when the thin film is commensurate with the substrate. For films of suitable thickness, the analysis of XPD curves from the substrate allows one to get information about the structure of the film and of the film–substrate interface.

1. Introduction

The intensity enhancement of electrons along close packed atomic rows in crystalline solids, due to forward scattering of the probe electrons, is at the basis of several techniques for the structural characterization of epitaxial thin films. Among these experimental techniques we can cite angle scanned X-ray Photoelectron Diffraction (XPD) [1,2], Auger Electron Diffraction (AED) [3], Incoherent Medium Energy Electron Diffraction (IMEED) [4], Primary-beam Diffraction Modulated Electron Emission (PDMEE) [5] and Directional Elastic Peak Electron Spectroscopy (DEPES) [6]. In all these methods the spatial distributions of the emitted (or scattered) electrons present maxima along atomic rows in the crystal due to forward scattering (or focusing) of the electrons. Hence, these techniques have been extensively used for structural characterization of the surface region of solids, in particular in the case of epitaxial thin and ultrathin films [3,7,8]. Quantitative structural parameters can be derived by fitting the experimental intensity curves of the electrons as a function of the emission direction with those calculated for trial structural models employing single scattering or multiple scattering approaches [1,2,9,10].

When considering chemical selective techniques such as XPD or AED applied to the study of thin films, usually the spatial distributions of electrons emitted from atomic species in the overlayer are monitored. On the other hand, the spatial distribution the electrons emitted by substrate atoms is expected to be modulated by the structure of the overlayer. In principle from the analysis of the diffraction pattern of the substrate covered by a thin film it should be possible to derive information about the registry with respect to the substrate, the interlayer spacing at the film substrate interface etc. Indeed, a method based on the analysis of the substrate emission was proposed to determine the structure of adsorbed layers [11].

In the present work, the effects on the XPD intensities of the substrate produced by epitaxial NiO(0 0 1) films deposited on Ag(0 0 1) were investigated. The variations in the Ag XPD curves induced by the NiO films can be explained in terms of multiple scattering of the electrons emitted by the substrate atoms along the close-packed rows of the overlayer. For films of suitable thickness, the analysis of the XPD curves from the substrate allows one to get information about the structure of the film, in particular to determine whether the film grows in a pseudomorphic mode.

2. Experimental details

Experiments were carried out in an ultra-high vacuum chamber equipped with ion gun, X-ray source and hemispherical electron energy analyser and other facilities for sample preparation and characterization. The angle between the analyser axis and the X-ray source was 55° and the semicone angle of acceptance of the

---

* Fax: +39 0577 234233.
E-mail address: andrea.atrei@unisi.it

0368-2048/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elspec.2012.09.009

analyser was 4°. Non-monochromatized Al Kα radiation was used for X-ray photoelectron spectroscopy (XPS) and XPD measurements. XPS and XPD measurements were performed in the fixed analyser transmission mode with a pass energy of 44 eV. The sample was mounted on a manipulator which permits polar rotation (around the manipulator axis) and azimuthal rotation (around the normal to the sample surface). The XPD curves were acquired by monitoring the intensity of the $Ni2p_{3/2}$ and $Ag3d_{5/2}$ peaks as a function of the polar emission angle in non equivalent azimuthal directions. The polar XPD curves were measured in a range from −20° to 70° with a step of 0.5° along the appropriate azimuthal dirctions. For the azimuthal XPD curves a step of 1° was used. The background was estimated by measuring simultaneously the intensity at a given peak maximum and the intensity at kinetic energies 5–10 eV higher than the peak. The maximum value of the amplitude of the intensity modulation in each XPD curve was estimated by the value (in percent) of $(I_{\max} - I_{\min})/I_{\max}$ where $I_{\min}$ and $I_{\max}$ are the minimum and maximum intensity in the XPD curve. The maximum value of the amplitude provides an information about the degree of order of a surface and is of the order of 30–50% for surfaces of single crystals and for relatively thick films.

NiO films were prepared by evaporation of nickel in the presence of O_2 at a pressure in the 10^{-6} mbar range. The thicknesses of the NiO films were determined from the areas of the Ni 2p and Ag $3d_{5/2}$ XPS peaks. The thickness of the film is expressed in monolayer (ML), considering that 1 ML of NiO(0 0 1) has a thickness of 2.1 Å. Details about sample preparation and characterization are reported elsewhere [12,13]. The cleanliness and order of the surface before and after XPD measurements was checked by XPS and LEED. By means of these techniques we did not observe any change in the surface after a set of XPD measurements which lasted about 1–2 h. When a variation in the O1s peak shape was observed either the sample was annealed to ca. 400–500 K to remove the contamination or a new film was prepared.

The CdS films on Ag(1 1 1) were prepared by means of Electrochemical Atomic Layer Epitaxy (ECALE) as described in ref. [14]. The thickness of the CdS(0 0 0 1) film was ca. 10 layers of Cd and S.

3. Results and discussion

$Ag3d_{5/2}$ azimuthal XPD curves measured at a polar angle of 45° for the clean Ag(0 0 1) surface and after deposition of NiO films of various thickness are shown in Fig. 1. For the clean surface, the most intense peak (located at $\phi = 0°$) corresponds to forward scattering of the $Ag3d_{5/2}$ photoelectrons along one of the ⟨1 1 0⟩ directions of the fcc lattice. After deposition of 2 ML of NiO, only a decrease of the anisotropy of the XPD curves is observed. Upon increasing the thickness of the film, the intensity at $\phi = 0°$ decreases further and becomes a minimum in the curves above ca. 10 ML. Features located at $\phi = -8°$ $\phi = 8°$ appear after deposition of 7 ML of NiO and become the strongest peaks at higher coverages. The distance between these peaks corresponds to the full width half maximum of the forward scattering peak at $\phi = 0°$ of the clean surface. The observed intensity variations of the substrate diffraction features can be qualitatively interpreted in terms of multiple scattering of photoelectrons along atomic rows of the film [3,15]. At energies of the photoelectrons above a few hundred eV, the atomic scattering cross section for the emitted electrons is peaked at small scattering angles. This forward scattering can be referred to as forward focusing since the scatter atom acts as a focusing lens for the photoelectrons [3]. In this energy regime, the direct emitted wave and the scattered wave in the forward direction (i.e. scattering angle equal or close to zero) are always in phase since the phase shift appearing in the path difference can be considered negligible [3]. The forward scattering is responsible for the main features in the XPD curves which correspond to close-packed rows in the crystal. If only single scattering events are considered the intensity of each process sums up resulting in the forward scattering peaks observed in the diffraction patterns from single crystals. In single scattering cluster calculations, the intensity of the forward scattering peaks is limited by the elastic mean free path of the photoelectrons or by the size of the cluster used to model the crystal. When multiple scattering is taken into account after a number of elastic scattering events (which depends on the type of scatters and on the kinetic energy of the photoelectrons) a destructive interference can occur between the scattered and non-scattered waves. Due to these multiple scattering processes, a reduction of the photoelectron intensity from the substrate is observed along the close packed rows of the overlayer. This defocusing effect which effectively weakens the forward scattering peak intensity from emitters further below the surface was evidenced for the first time in the calculations by Xu et al. [15] and investigated experimentally [16,17]. Multiple scattering limits the intensity of the forward scattering peaks with an increase of surface sensitivity of XPD technique. The interplay of forward scattering focusing and multiple scattering defocusing along the close-packed atomic rows results in an angle dependence of the attenuation lengths for photoemission measurements carried out on single crystal surfaces [18].

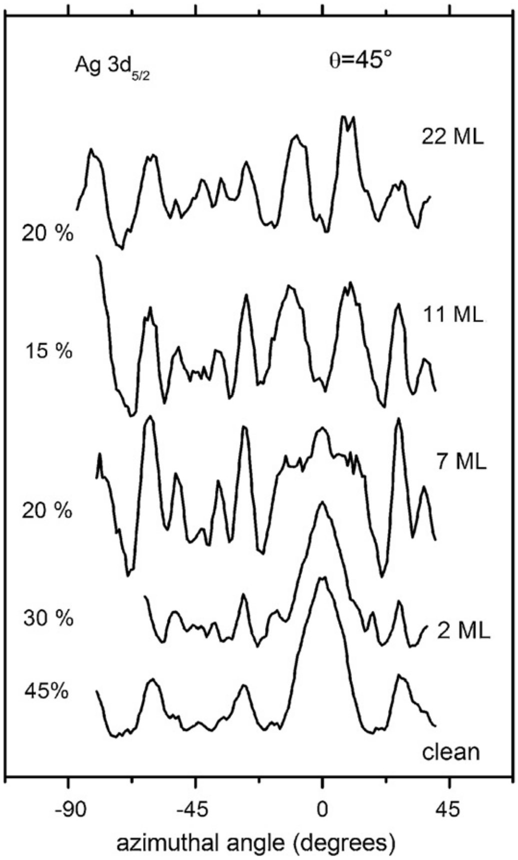

Fig. 1. $Ag3d_{5/2}$ azimuthal curves measured at a polar angle of 45° for the clean Ag(0 0 1) surface and for NiO films of various thickness deposited on Ag(0 0 1). $\phi = 0°$ corresponds to the [0 1 1] direction. The maximum value of the intensity anisotropy defined as $(I_{\max} - I_{\min})/I_{\max}$ %, where $I_{\min}$ and $I_{\max}$ are the minimum and maximum intensity, respectively, in each XPD curve is reported.

In the present case, for relatively thick NiO films, multiple scattering along the ⟨1 1 0⟩ directions of the oxide films produces a reduction of Ag3d intensity as shown in Fig. 1. In Fig. 2a, the $Ni2p_{3/2}$ (top curve) and the $Ag3d_{5/2}$ (middle curve) azimuthal XPD curves measured at $\theta = 45°$ for a thick NiO oxide film and for the clean Ag(1 0 0) surface (bottom curve) are shown. The main maximum