Journal of Electron Spectroscopy and Related Phenomena 181 (2010) 150–153

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

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

Atomic-layer-resolved analysis of surface magnetism by diffraction spectroscopy

Fumihiko Matsui[a,*], Tomohiro Matsushita[b], Hiroshi Daimon[a]

[a] Materials Science, Nara Institute of Science and Technology (NAIST), Takayama 8916-5, Ikoma, Nara 630-0192, Japan
[b] Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Koto 1-1-1, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

ARTICLE INFO

Article history:
Available online 4 March 2010

Keywords:
Surface magnetism
Auger electron diffraction
X-ray absorption spectroscopy
Magnetic circular dichroism
Subsurface

PACS:
61.05.js
61.05.cj
81.70.Jb
79.60.Dp
75.70.−i

ABSTRACT

X-ray absorption near edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) measurements by Auger-electron-yield detection are powerful analysis tools for the electronic and magnetic structures of surfaces, but all the information from atoms within the electron mean-free-path range is summed into the obtained spectrum. In order to investigate the electronic and magnetic structures of each atomic layer at subsurface, we have proposed a new method, diffraction spectroscopy, which is the combination of X-ray absorption spectroscopy and Auger electron diffraction (AED). From a series of measured thickness dependent AED patterns, we deduced a set of atomic-layer-specific AED patterns arithmetically. Based on these AED patterns, we succeeded in disentangling obtained XANES and XMCD spectra into those from different atomic layers.

1. Introduction

The spin reorientation transitions (SRTs) of the magnetic epitaxial film from in-plane to perpendicular direction are the key phenomena for the high-density magnetic recordings. A Ni ultra thin film on a Cu(0 0 1) surface exhibits both SRT and reversal SRT [1–3]. SRT occurs when a subtle balance of magnetic moments at surface and subsurface breaks. Therefore it is critical to understand nanosize magnetic phenomena from an atomic level point of view.

Previously, we have reported the atomic-layer resolved characterization of subsurface by a new method, *Auger electron diffraction spectroscopy*, which is a combination of two existing techniques: X-ray absorption spectroscopy and Auger electron diffraction (AED) [4,5]. Forward focusing peaks (FFPs) appear at the local interatomic directions from emitter to scatterer atoms [6–10]. By analyzing AED patterns, the surrounding atomic configuration around the Auger electron emitter atom is obtained. On the other hand, X-ray absorption near edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) measurements by Auger-electron-yield detection are powerful analysis tools for the electronic and magnetic structures of surfaces. Taking advantage of the FFP as an excellent element and site-selective probe [11], we have succeeded in separating surface and subsurface XANES and XMCD spectra of Ni film epitaxially grown on Cu(0 0 1) surface [5]. Surface and interior core-level shifts and magnetic moments around the SRT are determined for each atomic layer.

However, the shifts obtained previously were more or less underestimated values. At the thin film regions, the information from each atomic layer is well separated, while at the thicker film regions, the signals from deeper layers mix with that of shallower layers. The maximum probing depth is limited by the length of the Auger electron mean free path. It is roughly 10 atomic layers (monolayers: MLs) in the present case. Signals from deeper layers are damped by multiple scattering and become as a part of background intensity. In the previous study, we denoted the background subtracted FFP intensity in [1 0 0], [1 0 1], and [0 0 1] as the signals from the first, second, and third layers, to avoid inclusion of extra ambiguity by making further assumptions [5].

Here we introduce an alternative approach for atomic-layer-resolved electronic structure analysis. AED patterns from various thicknesses have been measured. These AED patterns are the linear combination of AED patterns from each atomic layer. Layer-specific AED patterns can be calculated by solving arithmetic equations. From a series of measured thickness dependent AED patterns, we deduced atomic-layer-specific AED patterns and succeeded in disentangling XANES spectra into those from different atomic layers.

* Corresponding author.
E-mail address: matui@ms.naist.jp (F. Matsui).

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doi:10.1016/j.elspec.2010.02.015

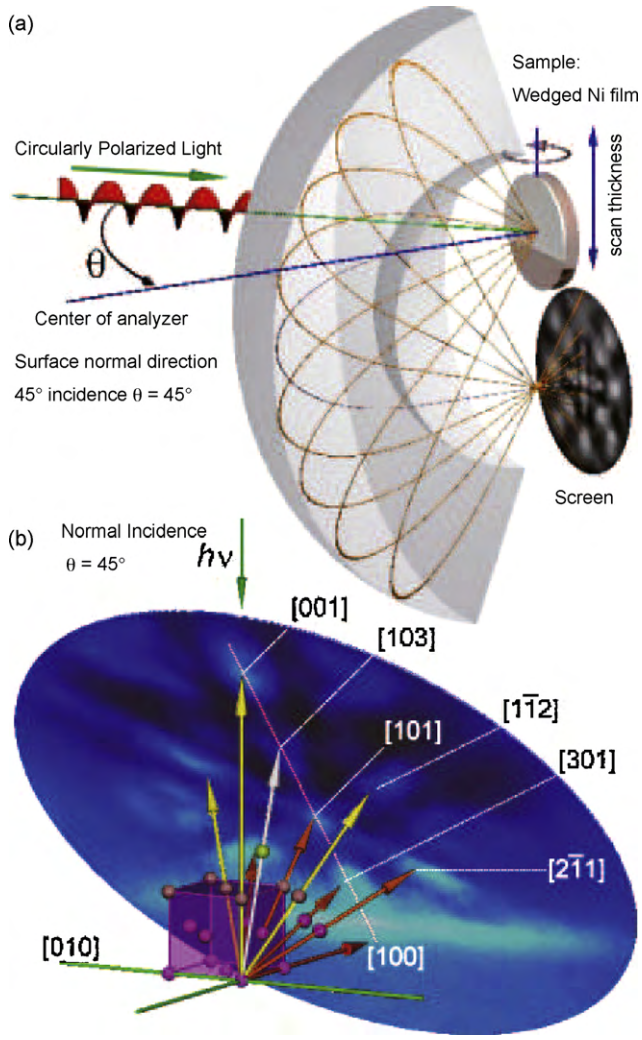

Fig. 1. (a) Schematic diagram of display-type spherical mirror analyzer. By scanning a wedged Ni film sample, the Ni LMM Auger electron diffraction (AED) patterns of different Ni film thicknesses are projected onto the fluorescent screen sequentially. (b) Crystal orientation and screen.

2. Experimental

The experiments were carried out at the circularly-polarized soft X-ray beamline BL25SU of SPring-8, Japan [12]. The AED patterns were measured by a two-dimensional display-type spherical mirror analyzer (DIANA) [13–15]. Fig. 1(a) is a schematic diagram of DIANA and measurement set up. Light was incident from the direction 45° inclined from the center of the analyzer. Photoelectrons emitted from the sample are energy-analyzed and angular distribution of emitted electron intensity is projected onto the fluorescent screen with the emission angle preserved. Acceptance angle of the analyzer is ±60°.

As described elsewhere [5], we prepared Ni wedged films on Cu(0 0 1) surface to study thickness dependence of atomic and magnetic structures. A wedged Ni thin film of 5 mm in length was deposited on the clean Cu(0 0 1) surface at room temperature. By scanning the position of wedged Ni film, the Ni LMM AED snapshots from various film thicknesses were measured in a short time.

Photon energy used for the excitation was 853.0 eV. Pass energy of analyzer was set to 846.0 eV. In the case of normal incident geometry shown in Fig. 1(b), the emission angle (θ_{out}) dependence from 0° to 90° respective to the surface normal was measured simultaneously. Note that pronounced FFPs appear along the direction of atoms surrounding an excited atom in the AED pattern. For example, FFP at the [1 0 1] direction coincides with the direction of scatterer atom seen from the emitter atom located at one layer below. FFP at [0 0 1] direction coincides with that of scatterer atom seen from the emitter atom located at two layers below.

3. Results and discussion

AED pattern $\mathbb{P}_i$ from film with the thickness of i MLs is composed of the contribution from each k-th atomic layer $\mathbb{L}_k$. $\mathbb{P}_i$ and $\mathbb{L}_k$ are two-dimensional intensity distribution data: $\mathbb{P}_i = c_{i1}\mathbb{L}_1 + c_{i2}\mathbb{L}_2 + \cdots$. Here we assumed that $\mathbb{L}_k$ is common for any thickness. We analyze n different AED patterns. **P** and **L** are n-dimensional AED pattern vectors consisting of $\mathbb{P}_i$ and $\mathbb{L}_k$, respectively.

$$\mathbf{P} = \mathtt{C}\mathbf{L} \tag{1}$$

$$\mathbf{L} = \mathtt{C}^{-1}\mathbf{P} \tag{2}$$

A coefficient matrix C denotes a distribution of Ni atoms in depth direction at various film thicknesses. Parameter c_{ij} is a scalar value and is unity (zero) when j-th atomic layer of i-ML-thick film is occupied completely with Ni (Cu) atom. A set of AED patterns **L** from first to n-th atomic layer can be calculated by solving Eq. (2).

For example, a coefficient matrix and its inverse matrix for a 4-ML film with abrupt interface are expressed as Eq. (3). Thus, atomic-layer-specific AED patterns, $\mathbb{L}_1$, $\mathbb{L}_2$, $\mathbb{L}_3$, and $\mathbb{L}_4$ are equivalent to $\mathbb{P}_1$, $\mathbb{P}_2 - \mathbb{P}_1$, $\mathbb{P}_3 - \mathbb{P}_2$, and $\mathbb{P}_4 - \mathbb{P}_3$, respectively.

$$\mathtt{C} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 0 \\ 1 & 1 & 1 & 1 \end{pmatrix}, \quad \mathtt{C}^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & 0 & -1 & 1 \end{pmatrix} \tag{3}$$

Actual atomic-layer-specific AED patterns are calculated by using an appropriate distribution matrix C taking the interlayer atomic exchange at interface into account. To determine n^2 matrix elements, we analyzed a series of 60 AED patterns with various fractional thicknesses. AED pattern $\mathbb{P}_x$ at the fractional thickness x is also expressed by the linear combination of $\mathbb{L}_k$, e.g. $\mathbb{P}_x = \sum_{k=1}^{n} c_k(x)\mathbb{L}_k$. We used a vector $\mathbf{N}_x$ and a matrix M. Scalar components N_{xj} and M_{kj} are the inner products of two AED patterns: $N_{xj} \equiv \mathbb{P}_x\mathbb{L}_j$ and $M_{kj} \equiv \mathbb{L}_k\mathbb{L}_j$, respectively. All the products for a pair of corresponding pixels are summed. $\mathbf{N}_x$ is the projected norm vector of $\mathbb{P}_x$ to **L**. M is the orthogonalization matrix for vectors **L**. As shown in Eq. (4), the vector $\mathbf{N}_x$ is the product of vector $\mathbf{C}(x)$ and matrix M. Thus coefficient functions $c_k(x)$ are obtained by solving Eq. (5).

$$N_{xj} \equiv \mathbb{P}_x\mathbb{L}_j (j = 1, 2, \ldots, n) = \sum_{k=1}^{n} c_k(x)\mathbb{L}_k\mathbb{L}_j = \sum_{k=1}^{n} c_k(x)M_{kj} \tag{4}$$

$$\mathbf{C}_x = \mathtt{M}^{-1}\mathbf{N}_x \tag{5}$$

We started with trial values of $c_{ij} = 1$ for the case of $j \le i$ and $c_{ij} = 0$ for $j > i$. This assumption corresponds to epitaxial growth with abrupt interface. From the expectation that the input parameters c_{ik} $(i = 1, 2, \ldots, n)$ and the output functions $c_k(x)$ $(0 \le x \le n)$ are continuous, coefficient matrix C can be determined self-consistently within an error of ±5%. As a result, we have obtained layer-specific AED patterns and Ni atom occupation ratio at each atomic layer at the same time as shown in Fig. 2. Interlayer mixing of Ni and Cu at the interface was evaluated quantitatively. The present result indicating the Cu atom ejection at the interface agrees quite well with the X-ray diffraction investigation of the interlayer atom exchange at Ni/Cu interface by Meyerheim et al. [16].

Auger electron yield is proportional to the number of core-holes created by photon absorption. Two-dimensional emission-angle-resolved XANES spectra are obtained by measuring AED patterns