Spectrochimica Acta Part B 114 (2015) 34–37

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Research Note

Total reflection X-ray photoelectron spectroscopy as a semiconductor lubricant elemental analysis method

Abbas Alshehabi *, Nobuharu Sasaki, Jun Kawai

Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

ARTICLE INFO

Article history:
Received 10 May 2015
Accepted 21 September 2015
Available online 28 September 2015

Keyword:
XPS
TRXPS
Fluorocarbon
Hard disk
Storage media

ABSTRACT

Photoelectron spectra from a typical hard disk storage media device (HDD) were measured at total reflection and non-total reflection at unburnished, acetone-cleaned, and argon-sputtered conditions. F, O, N, and C usually making the upper layer of a typical hard disk medium were detected. Enhancement of the photoelectron emission of the fluorocarbon lubricant was observed at total reflection. Pt and Co were only found by non-total X-ray photoelectron spectroscopy (XPS) because they are constituents of a deeper region than the top and interface regions. Argon-sputtered, ultrasonic acetone-cleaned, and unburnished top layers were compared at total and non-total reflection conditions. Total reflection X-ray photoelectron spectroscopy (TRXPS) is demonstrated to be a powerful tool for storage media lubrication layer chemical state analysis, reliable for industrial quality control application , and reproducible.

1. Introduction

Total reflection X-ray photoelectron spectroscopy (TRXPS) exhibits enhanced features and higher sensitivity at nanometer scale than conventional X-ray photoelectron spectroscopy (XPS) [1–3]. It is conducted by irradiating the sample at below the critical angle and penetrates shallow depths (<2 nm) and thus incorporates total reflection and with photoelectron emission [1]. Both X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are used for surface analysis for structure analysis and finding foreign particles. Because AES only detects Auger electrons, it has a low peak-to-background ratio. Besides, analyzing a sample by AES using a shallow detection angle is difficult because sensitivity decreases as the detection angle is lowered in AES. These disadvantages are overcome by TRXPS. TRXPS has little found application in industry because of uncertainty and spectra irreproducibility at small angles due to surface irregularities [4–11]. Mehta et al. used TRXPS to investigate the surface chemical state of Si wafers and carbon containing overlayers on Au [3]. The method has been proved feasible characterizing different types of multilayers [8–10] and complimentary metal oxide semiconductor (CMOS) gate dielectrics [12–18]. However, samples analyzed by TRXPS have always been synthesized in laboratory and were not commercially available samples [3,12–16]. Recently, materials like storage media devices; hard disk and DVD's, and functional materials have been developed with a special processing in 1–2 nm region from the surface. The International Technology Roadmap for Semiconductors (ITRS) addressed in 2013 elemental analysis at device dimensions and measurements for beyond complimentary metal oxide semiconductor (CMOS) and emerging materials and devices (<12 nm) as one of the semiconductor future challenges in the industry [19]. It addresses (1) capability to distinguish between the particle and the substrate signal, (2) information on chemical state and bonding especially of organics, and (3) small volume technique adapted to the scales of technology generations through non-destructive analysis techniques as yield enhancement difficult challenges for the semiconductor industry from 2013 to beyond 2020. A new method to characterize hard disk storage media device (HDD) top surface and surface functional materials is essential in this regard [19]. Alshehabi et al. demonstrated for the first time a real application by analysis of hard disk storage media device (HDD) lubricant surface by TRXPS [2]. They demonstrated that XPS element spectra of hard disk storage media device (Western Digital Model: WDAC33100-76H) top layer is enhanced and more prominent in TRXPS than XPS and showed that TRXPS is applicable in industrial elemental analysis. However, the reproducibility of spectra and the accuracy in application to HDD samples are to be confirmed, and lubricant-wear effects on XPS need to be evaluated.

Chemical and morphological heterogeneity is known to affect reliability and reproducibility of any surface method. In the case of low Z thin films, like in fluorocarbon lubricant layer on HDD surfaces, evaluation becomes more complicated [20–24]. Because the probability of an incident electron being scattered varies as the square of the atomic number of the atom, and inversely as the incident kinetic energy and hence greater depth of penetration happens for low Z materials, it is difficult to conduct surface analysis. In such a case, the back scattered electrons area in the sample is also increasing.

Fig. 1 shows (a) the experiment setup and (b) hard disk storage media device (HDD) profile. When applying low detection angle like

* Corresponding author.
E-mail address: abbas.jaafar@gmail.com (A. Alshehabi).

http://dx.doi.org/10.1016/j.sab.2015.09.016
0584-8547/

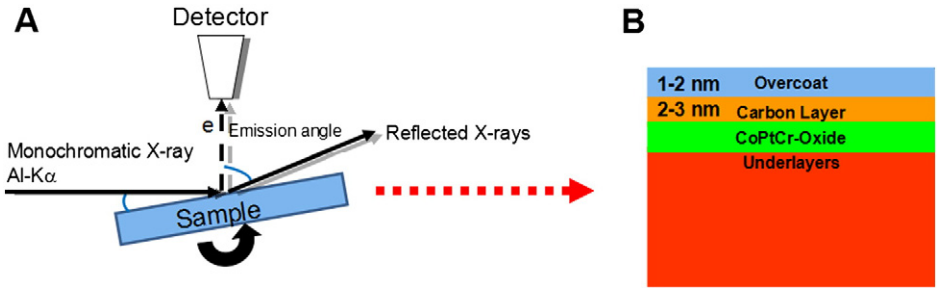

Fig. 1. (A) Total reflection X-ray photoelectron spectroscopy (TRXPS) experiment setup, and (B) hard disk storage media device (HDD) top layer depth profile.

in TRXPS, the sample must have an extremely flat and homogeneous surface with a broad area of few square millimeters. It is difficult to analyze the sample if the surface lacks uniformity, inhomogeneous, or it has a small area. In this paper, we produce XPS data from a different HDD sample (Hitachi Model: HTS541660JT00) [25] before treatment (intact surface layer of 2 nm) and after ultrasound-and-acetone burnishment (partly removal of surface layer <2 nm) at total and non-total reflection. To confirm reproducibility, we conduct X-ray photoelectron spectroscopy (XPS) at total reflection and non-total reflection conditions on the same hard disk sample (Hitachi Model: HTS541660JT00), after argon sputtering on a different top layer spot (complete removal of the surface layer). It shows that top layer treatment did not affect TRXPS feasibility to HDD top layer analysis, and confirmed reproducibility of XPS data at small angles in the range of total reflection for HDD top layer analysis.

2. Experiment

TRXPS measurements were performed with a commercially available (JEOL TRXPS Spectrometer JPS 9010 TRX) using monochromatized Al-Kα ($h\nu = 1486.6$ eV) radiation with a SiO_2 $(10\bar{1}0)$ ($2d = 0.6686$ nm) monochromator. The X-ray beam size was restricted to 5 mm×10 mm. The pass energy was 50 eV for the wide scan measurement, 30 eV for the narrow scan and the base pressure of the vacuum chamber was 10^{-6}Pa. The spectra were obtained with an electron spectrometer consisting of a concentric hemispherical micro-channel plate-type analyzer with a 10 cm long central orbital radius. The spectrometer was calibrated by reference to the Au *4f* photoelectron peak. The X-ray tube input was 12 kV and 30 mA, and the intensity counting rate of the spectrometer was 13500 cps with 5 channels per second. The sample was tilted manually by a micrometer screw. Measurements were carried out at 1.5° and 10.0° to the surface for acetone-cleaned (partly removal of surface layer <2 nm) and non-burnished surfaces (intact surface layer of 2 nm). The acetone-cleaned hard disk top surface was also exposed to 120 min ultrasonic before measurement.

Another area of the same hard disk sample (Hitachi Model: HTS541660JT00) has produced the same spectra after treatment with argon ion sputtering (complete removal of the surface layer). The sample was etched by argon ions + 300 for 15 s before measurement. Measurements after argon sputtering were conducted at total reflection (1.5°) and non-total reflection (4°, 10°, and 30°).

3. Results and discussion

Fig. 2. shows XPS wide scan spectra of a typical disk media at total reflection 1.5° and at non-total reflection, 10.0°, for both the burnished and the non-burnished conditions. It shows a series photoelectron intensity peaks. Prominent among them are the C 1s, O 1s ,and F 1s. Auger peaks [F (KLL), O (KLL), and C (KLL)] are also seen. Since they are main elements in a typical hard disk media; F, C, Co, Pt, and N are observable. Apart with Pt, N, and Co peaks, C and O are attributed to the contribution from ambient. At TRXPS (1.5°), only the top surface elements; F, C, O, and N are observable. With the relative zero at ±0.4 eV, the TRXPS wide scan shows the top lubrication layer is composed of hydrocarbon (probably environmental contamination), with the spectra showing a C 1s peak at 285.0 eV (binding energy) as well as the fluorocarbon over-layer, with a peak at 293.3 eV (20). O 1s implies that the surface of the fluorocarbon also contains adsorbed oxygen. N 1s, usually making the interface between the lubrication layer and deeper ones, is also observable with slightly higher photoelectron yield in TRXPS than in ordinary XPS. F 2s is only seen in TRXPS. Although the intensity of fluorine had a small decrease after cleaning, XPS spectra were the same in both and after cleaning. The least background and best sensitivity was obtained at total reflection at 1.5°, which only diagnosed the top layer elements. The fluorocarbon photoelectron intensity, at 1.5° and 10.0° at both surface conditions, is demonstrated by the C 1s spectra in Fig. 3. Only the fluorocarbon layer intensity increased at total reflection. The C-C peak was mainly constant because it is not originated from the layer. Since the C-C peak remains approximately constant with angle, C and O is assigned to contamination. The angular deviation

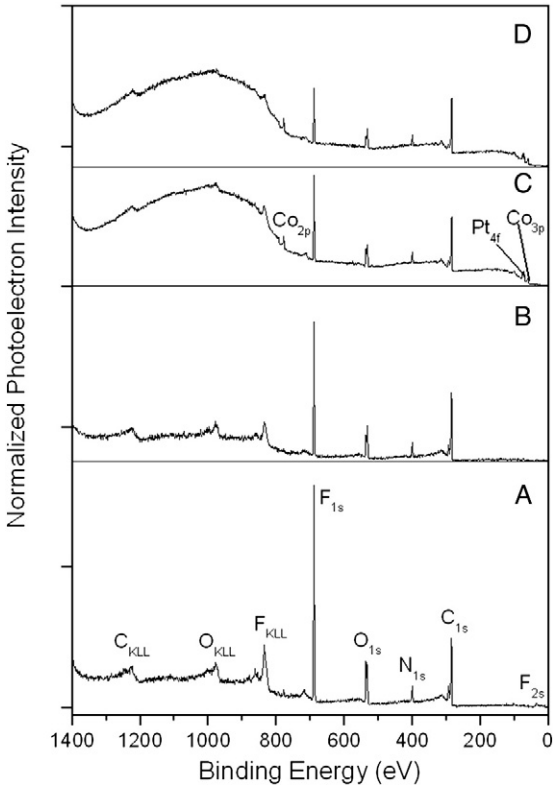

Fig. 2. XPS wide scan of a typical hard disk media, (A) non-treated at total reflection (1.5°), (B) acetone-cleaned at total reflection (1.5°), (C) non-treated at non-total reflection (10°), and (D) acetone-cleaned at non-total reflection (10°) conditions. Normalized to C 1s.