Essay

My Footprints on the Field of Practical Surface Analysis

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(Accepted: September 11, 2006)

When I was asked by Prof. Shimizu to join VAMAS project in 1985, my work on the practical surface analysis started. Then I organized interlaboratory studies with the help of many colleagues. The objective of the first interlaboratory study was to investigate the reliability of relative sensitivity factors using Au-Cu alloys and Ni-Co alloys. To analyze the experimental data, we had to treat spectral data in a computer. Therefore, we started to develop software which could convert the data file structure to a common one. This software was called Common Data Processing System (COMPRO). Then, we tried to find calibration procedures for energy and intensity scales to construct spectral databases. We carried out interlaboratory study, and proposed the usefulness of a spectrometer function for the energy scale calibration. To calibrate intensity scale, we used Cu spectra taken on absolute CMA manufactured by Prof. Goto. At present, COMPRO has data processing algorithms and databases, and can be downloaded from the home page of Surface Analysis Society of Japan (SASJ). We also prepared GaAs/AlAs reference material for depth profiling, which is now available from SASJ. For the practical analysis, it was important to set the analytical condition without beam damage. To investigate the beam damage in XPS, we carried out interlaboratory study using three kinds of organic materials, and proposed that poly(vinyl chloride) and nitrocellulose + cellulose acetate would be good specimens for the indicators of x-ray source flux. ISO TC201 was established in 1991, and SASJ was founded in 1995. These societies enhance the unification of surface analysts, and will lead to the establishment of practical surface analysis.

I would like to express my sincere thanks to my colleagues. Without their cooperation, I could not have left any footprint on the field of practical surface analysis.

1. Introduction

My first research on surface science started from the measurements of surface self diffusion coefficients of metals. In this research, we investigated the effect of oxygen pressures on the surface self-diffusion coefficients of Fe [1] and Ag [2], and proposed the relationship between surface self-diffusion coefficients and metal surface structures. However, at that time, we had no apparatus to determine surface compositions of metals, so we installed AES with a sample heating stage in the laboratory. Then we investigated the surface segregation of S, P and O on the surface of Fe single crystal at high temperatures, and proposed the order of surface activities of impurities in Fe [3]. In this experiment, we converted peak intensities to concentrations using relative sensitivity factors. Though I had doubts about the applicability of relative sensitivity factors to materials at high temperatures, we had no other way to determine surface compositions at that time. We continued the investigation of the surface composition change of metals at high temperatures, and found the surface precipitation of graphite on low carbon steel [4], TiC on 321 stainless steel [5] and BN on stainless steel doped with B and N [6]. The precipitation behavior of TiC was applied to the adhesion between ceramics and metals [7,8], and that of BN was applied to the improvement of the property of vacuum chamber [9, 10].

Besides the research on surface composition change of metals, we measured diffusion coefficients of metals along grain boundaries of thin films, and found that the diffusion coefficients of metals in metallic thin films were very large [11]. So we proposed the application of this phenomenon to a getter material of vacuum pump [12,13]. During these research works, my main concern was the surface composition change of materials at high temperatures, and I always used relative sensitivity factors for the quantification.

In 1985, Prof. Shimizu asked me to join VAMAS program. This was my first step in the field of practical surface analysis.

2. Relative Sensitivity Factors

At that time, my principal interest was the reliability of relative sensitivity factors, which were widely used in the field of practical surface analysis, and I believed it was the main mission to give a guideline for using relative sensitivity factors to determine surface compositions. Therefore, we proposed the project on the reliability of relative sensitivity factors for AES in VAMAS TWA2, and this was approved as a VAMAS No.17 project. In this project we carried out interlaboratory study using Au-Cu alloys with the collaboration of 18 institutes. In this study, we could say that the error of the surface concentration calculated with pure Au and pure Cu as the reference materials lied between about 3 % and 10 %, and that with the relative sensitivity factors lied between about 7 % and 20 % [14,15]. We also carried out interlaboratory study on relative sensitivity factors for XPS using Au-Cu alloys (VAMAS No.25 project), and 19 institutes participated in this study. The coefficient of variations of measured surface concentration by XPS lied between 2 % and 6 %, if pure Au and Cu were used as reference materials [16].

3. Sharing Spectral Data

After Au-Cu alloy study, interlaboratory study on quantitative analysis of Co-Ni alloys (VAMAS No.20 project) started [17]. In the case of Co-Ni alloy, however, some of the peaks of Co and those of Ni overlapped. Therefore, we had to treat spectral data in digital form to calculate surface concentration. To achieve this objective, we started the VAMAS No.30 project, the objective of which was to develop the software to process spectral data in a computer [18]. We called this software Common Data Processing System (COMPRO). To treat spectral data taken on different machines in digital form, the spectral data format must be common. Therefore, we installed the routine into COMPRO to convert data file format to the standard one (VAMAS No.29 project) [19]. This standard format is now ISO 14976. By incorporating the standard data format conversion routine, COMPRO could display the spectra taken on different machines simultaneously.

To share spectral data, a practical and simple procedure for calibrating the energy scale had been necessary. So, we carried out interlaboratory study on AES energy scale calibration using Ni with the collaboration of 11 institutes [20]. In this study, the spectrometer offset function was introduced to calibrate the energy scale by referencing to the peak energies of Au, Ag and Cu [21]. By calibrating the energy scale using the spectrometer offset function, the scatter in the peak positions of Ni M_3VV and L_3VV were decreased remarkably. The standard deviations for Ni M_3VV and L_3VV peaks were found to be decreased from 1.9 eV to 0.21 eV and from 1.36 eV to 0.49 eV, respectively. These results showed that the calibration procedure with a spectrometer offset function was very effective and could be suitable as a possible standard calibration method. This calibration procedure was a seed of ISO 15472, 17973 and 17974.

It was also important to calibrate the intensity scale. Therefore, we manufactured the ‘standard' channel electron multiplier, which was compatible with Faraday cup [22]. Prof. Goto manufactured the ‘absolute' CMA and obtained ‘standard' spectra of Cu [23]. We carried out interlaboratory study on the energy dependence of sensitivity in AES with the cooperation of 29 institutes using ‘standard' spectra of Cu [24]. The intensity calibration procedure using ‘standard' spectra was incorporated into COMPRO [25,26].

4. Sputtering

In the practical surface analysis, it is quite common to carry out the sputtering to get depth files. We prepared the GaAs/AlAs multi-layered material [27] and obtained the relation between the interface resolution and ion energy. The relationship between interface resolution (Δz) and ion energy (E) was obtained as $\Delta z = \Delta z_0 + kE$, where Δz_0~1.6 nm, k ~ 1.5 (nm/keV) [28]. The GaAs/AlAs multilayered material is now registered as a reference material (NIMC CRM 5201-a) for depth profiling in ISO 14606, and available from http://sasj.gr.jp.

Prof. Hofmann proposed MRI model, and we applied his model to the GaAs/AlAs multi-layered material using COMPRO. We could get a simulated depth profile using the MRI model in COMPRO, and estimate roughness and mixing factors [29].

5. Beam Damage

It was important to set the analytical condition without beam damage. We checked the stability of MgO, Al_2O_3 and SiO_2 during AES [30]. The main factor affecting the change of surface compositions was found to be the electron beam current density. The stability of ceramics was related to their free energies of formation, and we proposed the analytical conditions to minimize the dissociation during AES experiment. We also investigated SiO_2 case more closely, and proposed a theoretical model for electron stimulated desorption and gas adsorption on the solid surface [31].

In XPS, it is often observed that x-ray flux causes changes in the surface structure and chemistry in the surface region of organic materials. We conducted an interlaboratory study on the degradation of polymers as VAMAS A5 project [32]. 40 laboratories participated in this study. From this experiment, it was concluded that the rate constant of the degradation for poly(vinyl chloride) and nitrocellulose + cellulose acetate could be obtained from the peak intensity changes of Cl 2p and N 1s photoelectrons respectively, and these polymers would be good specimens for the indicators of x-ray source flux.

6. COMPRO

COMPRO originally had been designed to treat spectral data taken on different machines in a computer. When the spectral data structure was converted to a common format, COMPRO could assess the data processing procedures proposed by scientists, calibrate a spectrum, and construct spectral databases [33]. So, we constructed spectral database by the volunteer work of Surface Analysis Society of Japan (SASJ), and it was retrieved by InterNet [34,35]. COMPRO has been upgraded many times [36,37], and the latest version is 8.1. From version 4, COMPRO can be downloaded from the home page of Surface Analysis Society of Japan (http://www.sasj.jp). By using COMPRO, one can convert the format of spectral and depth profile data to ISO format, and attach calibration information of energy and intensity scales to spectral data. At present, COMPRO has data processing algorithms such as zooming, deconvolution, differentiation, smoothing, background subtraction, peak fitting, quantification, qualification, film thickness measurement and so on. COMPRO also has databases for physical properties of elements, standard spectra, reference spectra and AES absolute spectra measured by Prof. Goto. Reference spectra database has been constructed by the volunteer work of SASJ members. Their contribution is very much appreciated. The help menu of COMPRO shows the recent information of ISO standards determined by ISO TC201.

7. Surface Analysis Society of Japan

We founded the Surface Analysis Society of Japan (SASJ) in 1995. SASJ promotes national and international collaborative researches, holds symposia and publishes related documents in order to improve the authenticity and the standardization of surface analysis techniques. SASJ has been a bed for the interlaboratory studies of VAMAS, and promotes construction of database for surface analysis. Members can improve their skill and knowledge at regular meetings. Journal of Surface Analysis is published regularly from the society, and the series of International Symposia on Practical Surface Analysis are held.

8. ISO TC201

ISO TC201 was established in 1991 by the proposal of Japanese Industrial Standards Committee (JISC). The scope of the committee is the standardization in the field of surface chemical analysis. At present 10 member bodies participate as P-member, and 20 member bodies participate as O-member. TC201 has 9 subcommittees and 1 working group. The first chair of TC201 was Dr. Powell, and then succeeded by Prof. Shimizu. At present I am working as a chair. TC201 has published 27 standards, and I believe TC201 is one of the most successful technical committees of ISO. Surface analysis becomes matured, and is widely used in many industrial fields. Therefore, it becomes important to publish standard procedures to guarantee the surface analysis results.

Acknowledgment

Since I was asked to join VAMAS project by Prof. Shimizu in 1985, 20 years have passed. During this period, I met many nice friends, and they brought me to the nice field of practical surface analysis.

In this special issue, many prominent surface analysts presented papers. I would like to express my sincere thanks to all of them. The all overseas contributors to this issue visited Japan many times, and kindly presented nice lectures at the meetings of SASJ. By their help, the unification of surface analysts has improved very much. Prof. Grant gave us nice lectures at teaching courses, and has educated many young surface analysts in Japan. Prof. Hofmann stayed in Japan for 3 years, and introduced Japanese activities to the world. Dr. Kover participated in PSA many times, and informed us of the importance of the basic electron spectroscopy. Prof. Mathieu has shown the splendid research works on the application of surface analysis. He opened the gate to the new field, and has extended the SASJ activity. Dr. Powell has shown us the best way to proceed since the beginning of SASJ activity. He also contributed very much to the establishment of ISO TC201. Without his effort, the activity of ISO TC201 would have fallen. Dr. Seah informed us of the importance of metrology, and helped us very much in VAMAS activity. He has established the world of standard metrology, and brought us to there. Prof. Tougaard informed us of the basic electron transport phenomena, and guided us to nano-structure analysis.

Dr. Fujita was my coworker in the institute. He has deep insight, and has extracted many basic principles for practical surface analysis from experiments. Prof. Fukuda knows basis of electron spectroscopy very well and always encourages me by his warm character. Prof. Shimizu is a real leader of surface analysis society. He has educated many scientists and engineers in this filed, and his students now occupy the leading positions. Without his guide, we could not have done any work. Dr. Tosa was my coworker for a long time. He works in the field of surface finishing, and has discovered useful materials and processes. Dr. Yoshitake was also my coworker for a long time. She has summarized a number of interlaboratory studies, and found many useful guides in practical surface analysis. I very much owe the accomplishment of VAMAS works to her.

Finally, I would like to express my sincere thanks to the members of SASJ led by Dr. Tanuma who contributed very much to the establishment of SASJ. He is now President of SASJ. Also I very much appreciate Dr. Fujita's effort to publish this special issue.

That's one small step for a man, one giant leap for mankind. (Neil A. Armstrong)

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