〈기술해설〉

Application of Electron Spectroscopies for Thin Film Analysis

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Abstract — A number of different thin-film analytical method using electron spectroscopies are reviewed and evaluated. Results from various kinds of films (e.g. superconductive, electron-emissive, amorphous, rare-earth containing, etc.) are given for illustration. The existing quantification problems from this technology and some approaches for solving them are also discussed.

1. Introduction

The understanding and interpretation of the characteristics of thin solid films and their modification for a particular purpose require detailed characterization. Thin film analysis can be characterized by their capability for providing information from a millimeter to nanometer scale of the spatial distribution of physical or chemical properties. In the strict sense, the sampled volume is in the cubic micrometer range or less.

Many surface analysis methods have been used for thin film analysis because the film can be "sliced" into numerous "very thin" surfaces by ion sputtering. Only in this way can the three-dimensional analysis (elemental and/or structural), but not information coming from the bulk, be realized. Surface analysis also gives information about the electronic density of states (DOS) which is useful for the study of fundamental processes to explain physical and chemical behaviour of the thin film. Unfortunately, no single method in surface analysis can provide sufficient information on materials characterization, and it is usually hampered by its inherent uncertainties. Therefore, to choose two or more methods depending on requirment seems necessary. This is what we usually called *multi-method synergism*.

Some features of surface analysis in the last 40 years include: (1) the lowering of the detection limit, (2) to improving the capability of elemental imaging on a submicron scale with lateral resolution down to single atom, and (3) having sophisticated methods of data acquisition, processing and computer graphics with minicomputer as a powerful tool.

Electron spectroscopies which are using electrons as information carrier in thin film analysis provide some improtant advantages as follows [1]:

(1) The inelastic mean free path of the electrons with a conventionally used primary energy E_p is in the sub-nanometer range. The energy and momentum of an electron are therefore characteristics of elementary excitations near the surface.

(2) Electrons can be easily generated, accelerated, deflected and/or focused into beams.

(3) Electrons can be efficiently detected and counted as well as directly converted to electric signals.

(4) Electrons cause no contamination to a vacuum chamber. They disappear after being used for analysis.

In this paper some of the analytical methods regarding electron spectrometers are reviewed. The detailed description of principles and experimental procedures have been omitted because many monographs on this topic can be easily found. Applica-

tions mainly deriving from our own experiences are given for illustration.

2. Auger Electron Spectroscopy

Auger Electron Spectroscopy (AES) and its derivative, the Scanning Auger Microprobe (SAM), are widely used for thin film analysis. They are using Auger electron emission which is accompanied with a radiationless process in bringing an electron-excited atom to a lower energy state with the characteristic energy as a "finger print" of the atom. An electron beam with energy E_p is used as the primary source and an electron energy analyzer is used to pick up Auger electrons from measuring

Fig. 1. AES survey of a used cathode of TV picture tube. (a) dark region, (b) normal region.

the number of secondary electrons within a proper energy range. If the primary electron beam is focused into a very sharp spot (about 1 micron diameter) on the sample surface, then elemental maps (usually called the *Auger map*) referred to the surface distribution of certain constituents can be obtained by scanning the beam and using the analyzer as a special programmed energy filter.

AES and SAM are very useful for analyzing the surface of thin films. For instance, it is well known that the operating life of a picture tube depends upon the electron emission coming from the uppermost layer of an oxide-coated cathod. The Ba-Sr-Ca oxide coated cathode of a tube in failure after life test usually presents dark spots on the surface and has been interpreted as the exhaust of Ba atoms on the surface due to the sustained evaporation during operation. To obtain a direct and sufficient proof, AES/SAM have been used to investigate the "dark region"[2]. The result of an AES survey is shown in Fig. 1. It shows that in this dark region Ca has an anomalous segregation on the oxide film surface but not the depletion of Ba as usually expected. At some points in this region, Ca/Ba is 8 times greater than usual. Since the work function of Ca is larger than Ba, then the electron emission decreases. An Auger map of Ca obtained from SAM shows that on the cathode surface there are many Ca islands, the coverage of which can be greater than 50%.
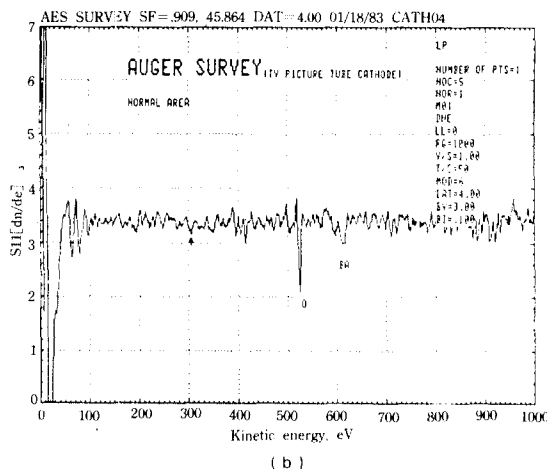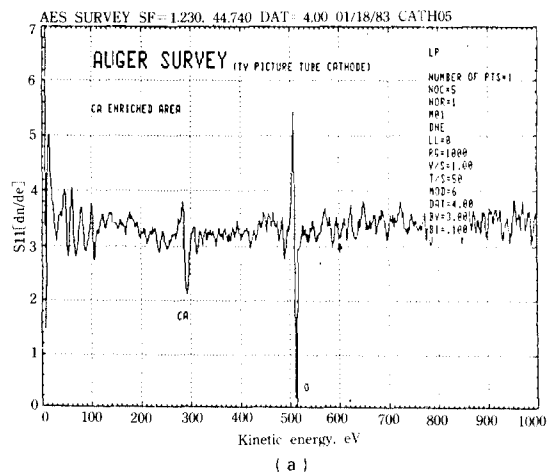
3. Electron Energy Loss Spectroscopy

Electron Energy Loss Spectroscopy (EELS) or Ionization Loss Spectroscopy (ILS) is based on the energy loss in order to produce core level ionization and gives information about empty states. The incident electron with energy E_b may be captured by a level E in unoccupied band above the Fermi level of the surface atom, and the core-level electron can be excited and directly ejected to vacuum with a maximum kinetic energy at $E = 0$ which is defined as an *edge* and can be used for elemental identification. In a simple one-electron picture, assuming constant oscillator strengths, the shape of the edge will correspond to the density of empty states near
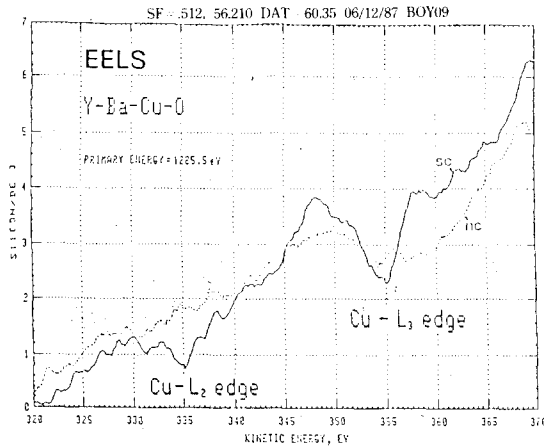
Fig. 2. EELS of two different Y-Ba-Cu-O samples.
sc: superconductive, *nc*: nonconductive.

the Fermi energy broadened by the lifetime of the core hole[1], and therefore gives information about empty states. EELS can be acquisited on an AES machine with some slight modifications. Therefore in a single equipment with a combination of AES and EELS a complimentary knowledge of DOS can be obtained.

For an illustration, EELS has been used for studying Y-Ba-Cu-O superconductive films[3]. Fig. 2 presents a comparison between two samples: *sc* is superconductive with $T_c > 90$ K while *nc* is a nonconductive bulk with the same composition but from different sintering processes. Evidently they are quite different. Compared with Cu spectra before and after oxidation (Fig. 2), *sc* is similar to the oxidized Cu and *nc* the non-oxidized Cu. This indicates that in a Y-Ba-Cu-O system the coordination between Cu and O plays an important role in superconductivity.

4. Total Current Spectroscopy

Total Current Spectroscopy (TCS) differs from AES by using primary electrons with low, scanning energy $(E_p = 0 \sim 30$ eV) and measuring the total secondary electron current which will vary rapidly at some proper E_p values. TCS of the above-mentioned *sc* and *nc* samples[4] are shown in Fig. 3, with a measured value of work function 5.3 eV. The peak positions can be explained to the interband
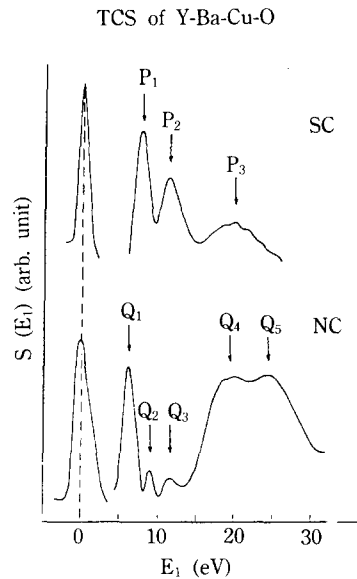
TCS of Y-Ba-Cu-O

Fig. 3. TCS of two different Y-Ba-Cu-O samples.
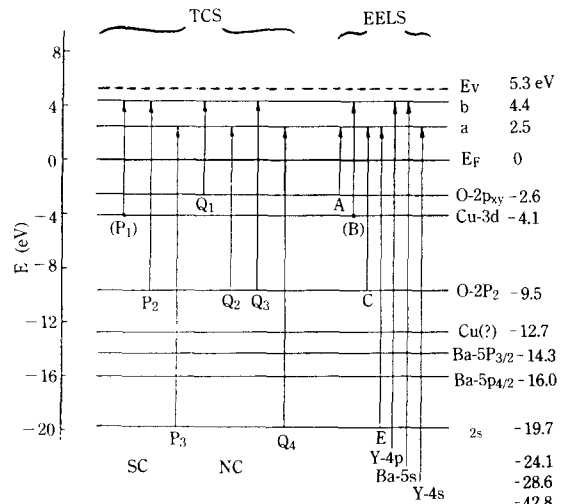*sc*: superconductive, *nc*: nonconductive.

Fig. 4. Explanation of interband transition for TCS as compared with EELS results.

transition and plasmon excitation by comparing with known results obtained from EELS[5]. As shown in Fig. 4, both *sc* and *nc* samples have many peaks with identical positions which will not attract our attention, but obviously peak P1 is different. This peak, existing only at *sc* but not *nc*, is corresponding to the transition from Cu-3d to b. It leads to the conclusion that in a high-T_c Y-Ba-Cu-O the

3d-electrons in Cu play the most important role in superconductive phase.

5. Surface Extended Energy Loss Fine Structure

EELS is not only used for DOS study. Even more important, the spectra recorded above the edge of an element with modulation in the differential inelastic electron scattering cross-section can give reliable surface structural information. This method is an analogy to the principle of Extended X-ray Absorption Fine Structure (EXAFS)[6] and thus is termed as the Surface Extended Energy Loss Fine Structure (SEELFS)[7]. SEELFS is the only method which can be used for highly disordered systems such as amorphous film surfaces.

Fe80-B20 is a conventionally used boron-contained metallic glass[8]. A factory has made a proposal to add some Si for improving the ductility of the material but the same physical properties are expected. They don't know whether, at least in principle, the properties will be changed or not. Therefore a new metallic glass, Fe78.5-Si5-B16.5 was studied in our lab[9]. The samples are very thin strips. SEELFS procedure was operated with a primary electron beam of 2.3 KeV, 1 μA. K-shell absorption spectra are most preferable because of the uniqueness of the starting electron state, the absorption coefficient of which can be described by a simple formalism. The extended portion above the B-K edge (188 eV[10]) is roughly 300 eV. The SEELFS spectra have been processed by some special procedure[7] to obtain the radial distribution function (RDF). Results are shown in Fig. 5. The distances of the nearest neighbor peaks (R1) of boron atoms in these samples were 19.4 nm and 19.2 nm, respectively. After phase-shift correction, the nearest neighbor distances are 21.4 nm and 21.2 nm respectively. This implies that an additive of Si with 5% concentration gives almost no effect on the alloy structure. This is important for practical consideration. Afterwards a report[11] said that Si is added up to 9% an amorphous Fe-Si-B alloy used for making power transformer cores in Japan.
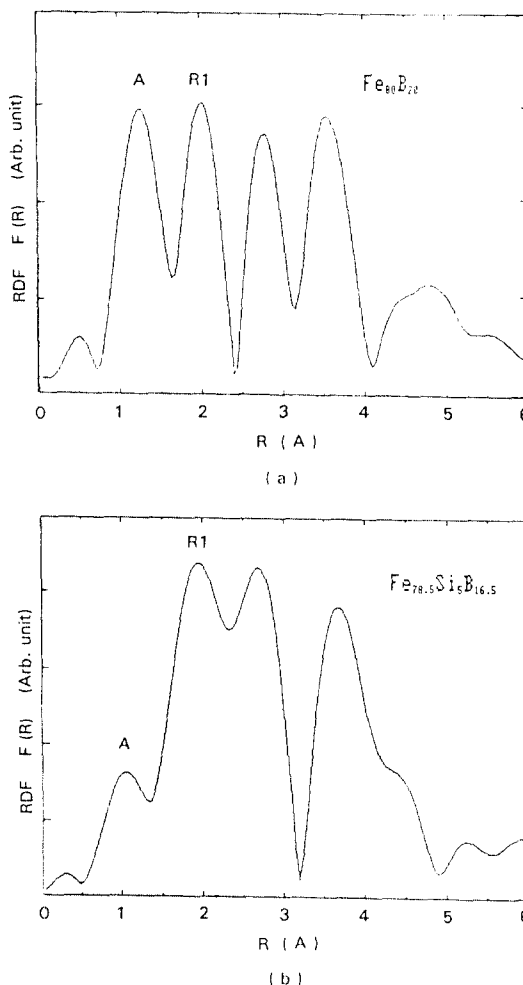
6. Appearance Potential Spectroscopy

Fig. 5. Radial distribution function (RDF) vs. distance curve calculated from SEELFS. (a) Fe80-B20, (b) Fe78.5-Si5-B16.5, R1: the first RDF peak, A: a "false" peak caused by the incomplete background substraction and/or truncate errors.

Appearance Potential Spectroscopy (APS) is the only surface spectroscopy to be obtained without an electron energy analyzer, thus dramatically simplifying the equipment. Similar to TCS, APS also uses primary electrons with scanning energy but much higher ($E_p = 100 \sim 1000$ eV). When E_p is equal to the binding energy of a core electron of the surface atom, the core electron will be excited to a level above the Fermi energy. The excitation probability above the threshold should vary as the self-

convolution of the unfilled (conduction band) DOS broadened by the lifetime of the core hole. Core electron excitations are signaled in soft x-ray appearance potential spectroscopy (SXAPS) by an increased emission of x-rays, in Auger electron appearance potential spectroscopy (AEAPS) by an increase in secondary emission, and in disappearance potential spectroscopy (DAPS) by a decrease in the elastic scattering coefficient[12]. APS has the highest resolution of any core-level electron spectrometer, since the resolution is limited only by the energy spread of the incident electrons (usually <0.25 eV). Moreover, APS has experimentally proved to be, even not clear enough, much more sensitive than AES or XPS for rare earths[13].

A very interesting fact is as follows. In China, to manufacture the rim of a train wheel, the hot steel rim was usually quenched in a cold liquid containing mixed rare earths for surface hardening. This technology has been in use for about one century. Everybody believes that on the rim there should be a thin film (or layer) containing rare earths which improves the hardness of the rim surface. But it is very difficult to find out the confused results through spectra from AES or XPS. Fig. 6(a) is one of the Auger spectra made by an AES/SAM machine. From this figure nothing can be said about the quenching process related to the effect of rare earths. But AEAPS gives all impotant members in the rare earth family, i.e. La, Ce, Pr and Nd, as shown in Fig. 6(b), which is very clear because APS contains no interband transition. The effect of this quenching technology therefore is crucial.

Very recently a preliminary experiment has shown that APS can also be used as a scanning probe to obtain an *elemental map* similar to an Auger map with same spatial resolution but no electron energy analyzer is needed[14]. Hence the vacuum chamber is much smaller and less expensive as compared with a SAM.

It is well known that a scanning electron microscope (SEM) is very useful for thin film analysis. Yet SEM can only give topographical micrographs. Some of the SEM have optionally equipped with an electron probe microanalyzer (EPAM) to deter-
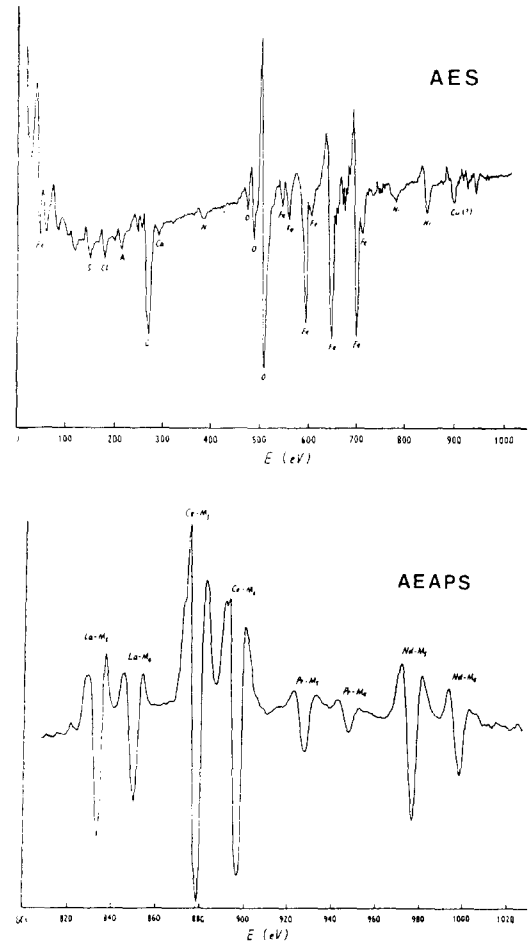

Fig. 6. Elemental analysis of quenched rim surface of a steel train wheel. (a) by AES, (b) by AEAPS.

mine the chemical composition, but the given information is only from the bulk but not from the surface, from point by point but not two-dimensional. Moreover, EPMA needs a surface-brrier detector operated at liquid nitrogen temperature for wavelength dispersive x-ray analysis, thus increasing its volume and price. Now we try to plant an APS device into SEM[15]. Only after a simple addition (*without* any energy analyzer), can a common SEM be upgraded to obtain not only topographical but also elemental micrographs (Auger maps). The only disadvantage is that the working chamber should be evacuated to ultrahigh vacuum (UHV) because of the requirement for a surface spectrometer. By the way, now there are many high-resolution SEM

already equipped with UHV systems.

7. Existing Problems for Thin Film Analysis

Problems raised for thin-film analysis with surface spectroscopy are mainly the reliability of quantitative analysis and the reliability of depth profiling. The former suffers from the matrix effects. For instance, quantitative Auger analysis requires the calculation of the percentage atomic concentration from the experimental Auger spectra, but the "relative elemental sensitivity factor (RESF)" method, which is recommended by any Auger Handbook, is only semi-quantitative since the matrix effects have not been considered. Among various matrix effects, the backscattering of primary electrons is most significant because it enhances the Auger yield. A method was described for determining the backscattering factor during AES analysis where the conventionally ignored information provided by the background was used for this purpose[16]. Complicated calculations such as the Monte Carlo method were avoided and, since both the intensity of Auger electrons and the energy distribution of backscattered electrons were obtained under the same experimental conditions, the accuracy of quantitative analysis might be further improved. For the depth profiling, the altered layer induced by intense ion bombardment during profiling (sputtering) cannot be neglected. The phenomena of ion-mixing and pile-up could play an important role and may cause some significant errors. Experimental results of the depth profiling of Ta_2O_5-Ta[17] which is conventionally used as a standard material for interface profiling showed that (1) the depth profile curve does not follow the form of an error function; (2) the dominant factor for Auger signal during the interface analysis is the altered layer with a thickness of $300 \sim 500$ nm, rather than the electron mean free path; and (3) the depth profiling resolution of interface analysis is determined by a compromise between the ion-mixing and pile-up effects. Therefore it should be very careful if high accuracy is needed for the analysis of a thin film with abruptly varied composition in the lateral dire-

ction (perpendicular to the surface). Very recently "factor analysis" method is used for Auger depth profiling[18, 19].

Multi-method synergism seems important especially for the characterization of some important analytical works. For instance, Rutherford Backscattering (RBS) is a good non-destructive technique for the reference of depth profiling. High-energy $(1 \sim 5$ MeV), low Z primary ions (mainly He^+) are used for RBS since at these energies the nuclear stopping power is negligible compared with the electronic stopping power and sputtering does not occur. Quantitative determination of the concentration is obtained with a high accuracy using databank of RBS cross-section or by empirical calibration and interpolation for different elements. The number of particles backscattered with a certain particle energy is proportional to the number of scattering centers of the corresponding mass number in a depth layer dz at the corresponding depth z. An example is shown as follows.

Recently a new category of organometallic complex used for erasable optical and/or electrical high density storage media was found. The complex can be symbolized as $M_{1-\beta}$(TCNQ)[20], where M is metal (Cu or Ag), TCNQ is an organic compound $(C_{12}H_4N_4)$, and $\beta = 0.2 \sim 0.5$. Experimental results showed that the physical properties of $M_{1-\beta}$(TCNQ) differ from that of M(TCNQ) with the exact stoichiometric ratio (1 : 1 mole), i.e. β is an important parameter for this material. The film is prepared by vacuum evaporation, M by electron bombardment and TCNQ by resistance heating. In principle the value of β can be calculated by the evaporation rate of metal and TCNQ respectively, however, for a multisource-evaporated film, the experimental determination of the final film composition seems more preferable. AES and XPS cannot do it. Dynamic SIMS is destructive. Therefore backscattering method using high-energy particles was chosen. The element for expression TCNQ was carbon. The particles used were 4.550 MeV He^+ with a scattering angle 170.5°. Under this particle energy, the scattering cross-section of metal (Ag or Cu) still obeys the RBS formula, yet for C it becomes non-Rutherford and the elastic scattering cross-section
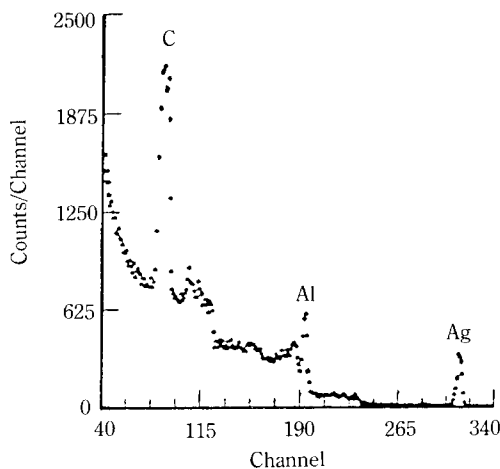
Fig. 7. Backscattering spectrum of an $Ag_{1-\beta}$(TCNQ) film. C represents TCNQ, Al comes from the covered layer (for reflection when used as a laser disc).

of C is 21.1~21.5 times larger than that in the RBS case for He^+ at 4.524~4.575 MeV[21]. The backscattering spectrum of an $Ag_{1-\beta}$(TCNQ) film, for example, is shown in Fig. 7. In this case, $\beta=0.4$. Obviously it is a good complementary mean for thin film analysis other than conventionally used electron spectrometers.

8. Conclusion

Some methods of thin film analysis based on surface electron spectroscopy have been briefly reviewed. Thin films of various kinds and purposes have been increased dramatically in recent years and the industrial development will demand more and more reliable analytical results for thin film characterization. Therefore it is a big task for vacuum scientists and engineers working in this field to meet the new requirments.

Last but not least, we should also pay more attention to laser-operated, ion-operated and ultrasound-operated analytical instruments. Since thin films with nano-structure will play an important role in the near future, scanning tunneling microscope (STM), atomic force microscope (AFM) and photon-assisted STM (PSTM) should be of top im-

portance if some of their difficulties are overcome.

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