Electron Inelastic Mean Free Path Correction for Quantitative Auger and X-ray Photoelectron Analysis of Au-Cu Alloys

S. Tanuma

Japan Energy ARC Co. Ltd., Niizo-Minami, Toda, Saitama 335, Japan
(Received 4 February 1995)

This paper describes an investigation of the inelastic mean free path (IMFP) correction for the quantitative Auger and X-ray photoelectron analysis of the three kinds of Au-Cu alloys. The author have compared two sets of the ratios of IMFPs; $(\lambda/\lambda_{std})_{obs}$ obtained from the measured intensity ratios K and $(\lambda/\lambda_{std})_{cal}$ calculated from the TPP-2 equation. The IMFP ratios of $(\lambda/\lambda std)_{obs}$ for Au coincide well with those of $(\lambda/\lambda_{std})_{cal}$. However, the curve of the ratios of $(\lambda/\lambda_{std})_{obs}$ for copper does not show the same tendency of that obtained with TPP-2. This results might suggest the existence of the ion-induced surface segregation of Au-Cu alloys. The author also have calculated absolute surface Au and Cu concentration applying density correction, backscattering correction, and IMFP correction to the measured intensity ratios. The plots of obtained surface concentration of Au versus IMFP does not show a straight line. This results also suggests the existence of the ion-radiation-induced surface segregation of the samples.

Introduction

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are widely used for surface analysis or in-depth analysis of various materials, such as those used in electronics applications, metals, etc. As for the quantitative analysis of surface composition of solids by AES and XPS, there are still problems to be solved. One of the main factors which have to be investigated for accurate quantitative analysis is the matrix effect, i.e. the non-linear dependence of the intensity of an element's AES or XPS signal on its concentration in the matrix. The matrix correction includes terms for the atomic density (n), electron escape depth (λ), and electron backscattering (R).

Quantitative AES and XPS require the knowledge of the AL (attenuation length) dependence on material at given energy. Unfortunately , the AL data now available are not sufficient for quantitative analysis and, more importantly, the available data are either of uncertain or inadequate accuracy. In the actual quantitative correction, therefore, the electron inelastic mean free path (IMFP) is usually taken into account with λ term. In this case, the elastic scattering effect should be applied to it.

The electron escape depth correction including the elastic scattering effect can be described as [1]

$$\lambda = \gamma \, \lambda_{in} \, \cos \theta = AL \cos \theta \qquad (1)$$

where γ is the elastic scattering factor, λ_{in} the electron inelastic mean free path and θ the detection angle. On Au-Cu alloys, Shimizu et al. found γ equals 5 / 6 for all alloys investigated , and pure gold and copper[1]. Then, in the actual quantitative calculation ,we could eliminate the γ factor in the quantitative AES and XPS calculations. In this report, therefore, the IMFP correction for AES and XPS were investigated using three kinds of Au-Cu alloys.

Experimental

Three kinds of alloys (Au 73.2 at.%-Cu 26.8 at%, Au 50.2 at.%-Cu 49.8at%,Au 24.7 at.%-Cu 75.3at%) were prepared as the sample to be analyzed. Pure gold and pure copper were also prepared as standards.

The AES and XPS measurements were made on 18 institutes belonging to the Japanese VAMAS-SCA working group. The measurement conditions were as follows ; for AES, primary beam energy was 5 keV, beam current about 1μA, spectrum mode dN/dE, measurement Auger lines of Au 239 eV, Au 2024 eV, Cu 920 eV. The other details were reported elsewhere[2]. For XPS, X-ray source was Al Kα , analyzer resolution ΔE = 0.5 eV, and the used peak was Au 4f (KE : 1400 eV) for gold and Cu 2p3/2 (KE : 553 eV) for copper. The details were already reported [3].

Before measurements, the surface was cleaned with Ar ions, the energy of which was 1keV for AES and 2keV for XPS.

Calculation method of intensity ratio

Assuming a homogeneous alloys constituting of N elements. The Auger peak intensity of the element i in the alloy specimen of unknown composition can be expressed as

$$I_i^{unk} = C_i^{unk} \, n^{unk} \, R_i^{unk} \, \lambda_i^{unk} k_a I_a \qquad (2)$$

where k_a is an analyzing constant assumed to be independent of composition but specific to one particular transition and instrument ,C the surface concentration, I the measured intensity and I_a is the probe current. Similarly, the Auger peak intensity of the standard specimen of pure element i can be expressed as

$$I_i^{std} = C_i^{std} \, n_i^{std} \, R_i^{std} \, \lambda_i^{std} k_a I_a \qquad (3)$$

Let the intensity ration of unknown to standard be K_i' for the element i

$$K_i' = \frac{I_i^{unk}}{I_i^{std}} \qquad (4)$$

Then, from Equations (2) and (3), an intensity ratio will be given in terms of concentration, atomic density, electron backscattering factor and IMFP as

$$K_i' = C_i^{unk} \frac{n^{unk} \, R_i^{unk} \, \lambda_i^{unk}}{n_i^{std} \, R_i^{std} \, \lambda_i^{std}} \qquad (5)$$

By analogy with Eq.(4), we define K_i in terms of corresponding observed intensity ratio for the unknown and standard.

$$K_i = \frac{I_{i,\,obs}^{unk}}{I_{i,\,obs}^{std}} \qquad (6)$$

For XPS , the K' value could be obtained by neglecting R-factor form above equations.

Results and Discussion

The measured intensity ratios K (= I_{unk}/I_{std}) for Au-Cu alloys are shown in Table 1(AES) and 2 (XPS). The measured data also have been plotted in Fig.1 as C/K vs bulk concentration of Au; C is the bulk concentration and K the measured intensity

ratio.

Table 1. Averaged K values for Au-Cu alloys measured by 18 institute with AES.

peak	Specimen	K-value	standard dev.
Au-239eV	Au75-Cu25	0.774	0.061
	Au50-Cu50	0.591	0.053
	Au25-Cu75	0.344	0.044
Au-2024eV	Au75-Cu25	0.801	0.084
	Au50-Cu50	0.619	0.070
	Au25-Cu75	0.362	0.067
Cu-920eV	Au75-Cu25	0.229	0.029
	Au50-Cu50	0.440	0.062
	Au25-Cu75	0.675	0.086

Table 2. Averaged K values for Au-Cu alloys measured by 18 institute with XPS.

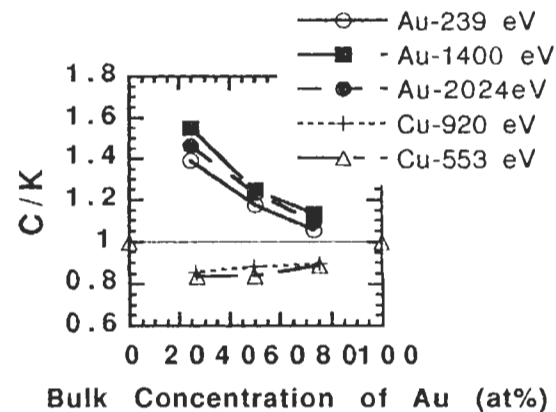| peak	Specimen	K-value	standard dev.
Au 4f	Au75-Cu25	0.830	0.048
	Au50-Cu50	0.627	0.041
	Au25-Cu75	0.383	0.028
Cu 2P3/2	Au75-Cu25	0.224	0.020
	Au50-Cu50	0.418	0.036
	Au25-Cu75	0.668	0.054

Fig.1. Plots of K/C versus bulk concentration.
K : observed intensity ratio(=I^{unk}/I^{std})
C : bulk concentration

In this figure we could find the magnitudes of the correction factors needed for quantitative AES and XPS analyses in Au-Cu alloy systems. The correction factors for Au are larger than those for Cu. Then, if the

quantitative analysis is carried out in order to obtain the normalized concentration, which are commonly used , the correction factor for Au determine the validity of IMFP correction for the quantitative analysis of Au-Cu alloy system. Then it is very important to determine absolute surface concentration of Au and Cu separately without normalizing their concentrations.

IMFP ratios

The IMFP ratio $\lambda_{unk}/\lambda_{std}$ for AES can be obtained by the following equations derived from Eqs.(5) and (6).

$$\frac{\lambda_i^{unk}}{\lambda_i^{std}} = \frac{K_i}{C_i^{unk}} \frac{n^{std} R_i^{std}}{n_i^{unk} R_i^{unk}} \qquad (7)$$

For XPS,

$$\frac{\lambda_i^{unk}}{\lambda_i^{std}} = \frac{K_i}{C_i^{unk}} \frac{n^{std}}{n_i^{unk}} \qquad (8)$$

To calculate IMFP ratio from the observed intensity ratio K with Eq.(7) or (8) , the values of n and R for AES or n for XPS must be given. For n, we have assumed that it is given by a summation of the products of atomic concentration and atomic density in the pure state for each elements as

$$n^{unk} = \sum_{i=1}^{N} C_i n_i^{std} \qquad (9)$$

For R, Ichimura-Shimizu-Langeron (ISL) equation [4] was used , and we define the mean atomic number of the alloy as

$$Z_m = \sum_{i=1}^{N} C_i Z_i \qquad (10)$$

The obtained IMFP ratios λ/λ_{std} from the observed intensity ratios with Eqs. (7) and (8) were shown in Fig. 2. The calculated results with TPP-2 equation [5] were also shown in Fig. 3. Figure 3 showed that all calculated IMFP ratios decreased according to increasing the bulk Au concentration. In Fig. 2, the ratio of $\lambda/\lambda_{Au\text{-}std}$ showed the similar tendency to that of Fig. 3. However, the IMFP ratio of $\lambda/\lambda_{Cu\text{-}std}$ showed the opposite tendency compared to the calculated results of TTP-2 as shown in Fig. 3. Figure 2 shows that the IMFP value of alloys are $\lambda_{Au25\%} > \lambda_{Au50\%} > \lambda_{Au75\%}$ at energies 239, 1400 and 2024 eV, and $\lambda_{Au25\%} < \lambda_{Au50\%} < \lambda_{Au75\%}$ at 553 and

920 eV. This results may suggest $\lambda_{Au} < \lambda_{Cu}$ at 239, 1400, and 2024 eV and $\lambda_{Au} > \lambda_{Cu}$ at 553 and 920 eV. If this is true, the $\lambda/\lambda_{Cu\text{-}std}$ ratios are larger than 1.0 at 553 and 920 eV. However, the ratios of $\lambda/\lambda_{Cu\text{-}std}$ except Au75% at 553 eV is smaller than 1.0.

The observed Auger and photoelectron peaks have the different analyzing depth. Therefore, if the concentration of Au along depth is not constant, we could understand the difference between Fig.2 and 3.

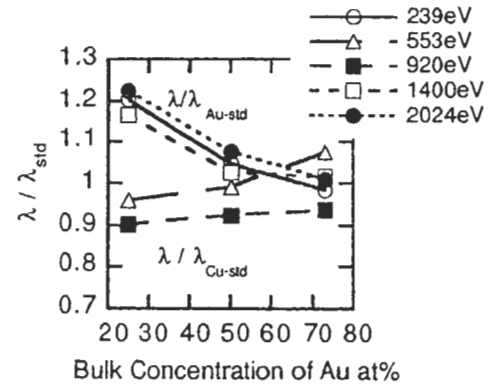Then, Fig.2 might suggest the existence of the ion-induced surface segregation of Au-Cu alloy [6,7].

Fig.2 The IMFP ratios $\left(\lambda_{Au}^{alloy}/\lambda_{Au}^{std}\right)_{obs}$ and $\left(\lambda_{Cu}^{alloy}/\lambda_{Cu}^{std}\right)_{obs}$ versus bulk concentration of Au and Cu.
The IMFP ratios were obtained the following equation and observed intensity ratios.

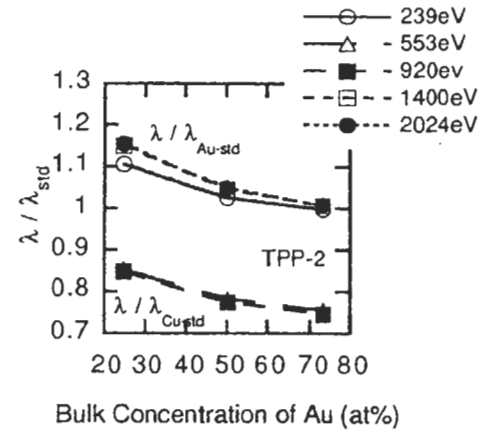$$\frac{\lambda_i^{unk}}{\lambda_i^{std}} = \frac{K_i}{C_i} \frac{n_i^{std} R_i^{std}}{n^{unk} R_i^{unk}}$$

Fig.3 The IMFP ratios $\left(\lambda_{Au}^{alloy}/\lambda_{Au}^{std}\right)_{cal}$ and $\left(\lambda_{Cu}^{alloy}/\lambda_{Cu}^{std}\right)_{cal}$ versus bulk concentration of Au and Cu.
The IMFP rations were obtained with TPP-2 equation.

Quantitative Results

The surface concentrations of Au and Cu in

Au-Cu alloys were calculated using the following equations obtained from the equations of (5) and (6).
For AES

$$C_i^{unk} = K_i \frac{n_i^{std} \, R_i^{std} \, \lambda_i^{std}}{n^{unk} \, R_i^{unk} \, \lambda_i^{unk}} \quad\quad (10)$$

For XPS

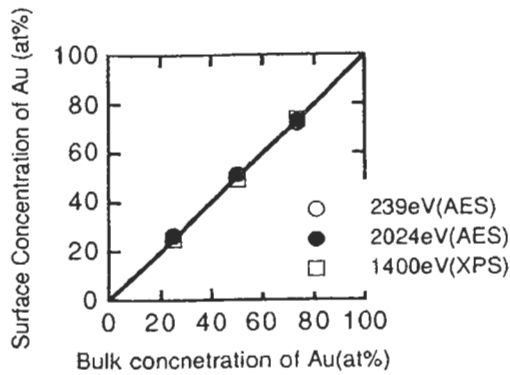$$C_i^{unk} = K_i \frac{n_i^{std} \, \lambda_i^{std}}{n^{unk} \, \lambda_i^{unk}} \quad\quad (11)$$

Fig.4 The obtained surface concentration of Au versus bulk concentration of Au.
R : Ichimura-Shimizu-Langeron equation for AES
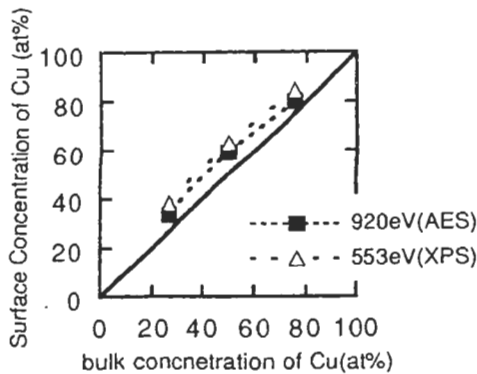λ : TPP-2 for AES and XPS

Fig.5 The obtained surface Cu concentration versus bulk concentration of Cu.
R : Ichimura-Shimizu-Langeron equation for AES
λ : TPP-2 for AES and XPS

The resulting surface concentrations of Au and Cu were shown in Fig.4 and 5, respectively. In Fig. 4, the obtained surface concentration of Au are in good agreement with the bulk concentration of Au. However,

Fig. 5 shows the surface concentration of Cu are larger than the bulk concentration clearly. In order to clarify the meanings of these figures, we have plotted the obtained concentrations of Au and Cu versus inelastic mean free path corresponding to the energy for the used peaks on three kinds of Au-Cu alloys separately. The results are shown in Figs. 6,7, and 8.

In these figures, the open marks were the rest of another element concentration, which were calculated from $C_{Au} = 1.0 - C_{Cu}$ or $C_{Cu} = 1.0 - C_{Au}$. The dashed lines indicate the bulk concentration of Au or Cu. Since the horizontal line is expressed by the inelastic mean free path in these figures, we should note the resulting concentration does not show the depth concentration profile.
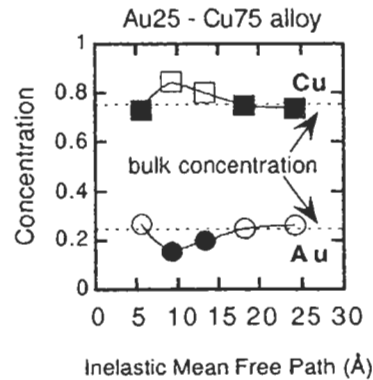

Fig.6 Plots of calculated surface concentration of Au and Cu in Au25-Cu75 alloy versus inelastic mean free path. The open circles in the figure were calculated from $C_{Au} = 1-C_{Cu}$ or $C_{Cu} = 1- C_{Au}$.
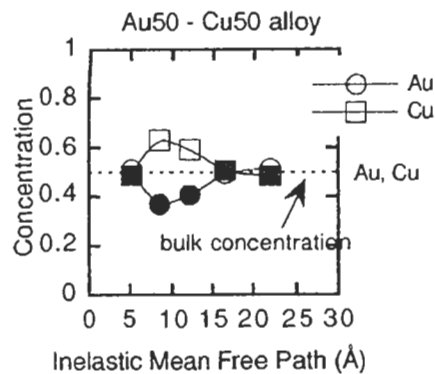

Fig.7 Plots of calculated surface concentration of Au and Cu in Au50-Cu50 alloy versus inelastic mean free path; see caption to Fig.6.
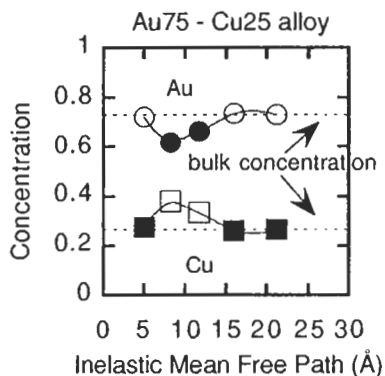
Fig.8 Plots of calculated surface concentration of Au and Cu in Au75-Cu25 alloy versus inelastic mean free path ; see caption to Fig.6.

The plots of obtained Au and Cu concentrations does not show the straight line; every line for Au have a dip. Therefore, the Au concentration profiles versus depth does not the constant, and we could conclude the Au concentration at the surface is larger than that of bulk concentration and its concentration at 2nd or more deep layers are smaller than that of bulk concentraion form above figures. Then, we conclude that the dip for observed concentration versus inelastic mean free path is a evidence of the ion-induce surface segregation. The ion-induced surface segregation for Au-Cu alloys have not been found with XPS and AES[8] although Shimizu et al.[7] and Li et al.[6] found it by ISS analysis and Auger analyses of Au-Cu thin films at the low temperature, respectively. Now, we can observe this phenomena directly with XPS and AES analysis by means of determining the surface concentration of Au and Cu separately because each observed peak has the different information depth on the alloy.

References

1) Ding Ze-jun, A. Kurokawa, R. Shimizu, The Journal of the Vaccum Soc.in Jpn., **33**,790(1990) .
2) S. Tanuma, T. Sekine, Y. Yoshihara and Members of Japanese VAMAS-SCA working group, Surf. Interface Anal. **15**, 466 (1990).
3) M. Yoshitake, K. Yoshihara and other members of the VAMAS-SCA working group in Japan, Surf. Interface Anal. **17**, 711 (1991).
4) S. Ichimura, R. Shimizu and J. P. Langeron, Surf. Sci. **124**, L49 (1983).
5) S. Tanuma, C. J. Powell and D. R. Penn, J. Vac. Technol., **A8**, 2213 (1990); Sur. Interface Anal. **17**, 911 (1991)
6) R. -S. Li, Koshikawa, K. Goto, Surf. Sci., **121**, 1561 (1982).
7) R. Shimizu, Nucl. Instr. Meth., **B18**, 486 (1987).
8) G. Betz, Surf. Sci. **92**, 283 (1980); S. Ichimura in " Technical Report on Surface Composition Analysis by Auger Electron Spectroscopy" (VAMAS-SCA Tecnnical Working Party in Japan, 1989).

査読者との質疑応答

関根：Au4f（KE: 1400 eV）のXPSピークとAu 2024 eVのオージェピークを低角度（Cu 2p 3/2 KE: 553 eV, Cu 920 eVに相当する脱出深さ）で測定したら，この結論を再確認できるのではないでしょうか.

著者：ご指摘の通り，可能であると考えます. AuのIMFPは1400 eV, 2024 eVではそれぞれおよそ1.58，2.09nmであり，一方Cuの553, 920 eVでは 1.01，1.45nmです. これらはTPP-2M式により推定しました. ここで，指摘された中からAu 1400 eV →Cu553eV相当について考えれば，IMFPの比は0.639であるからAu4fピークをXPSで法線から25度で測ったとすれば，試料を傾け54.6度で測定すればよいこになり，十分に可能です. ぜひ，試してみたいと思います.

関根：Fig. 6 - 8の横軸が"濃度vs.深さ"に展開できるとおもしろと考えます

著者：Fig. 6 - 8は当初はescape depthで目盛っていましたが，（査読意見もあり）本原稿のようにIMFP表示としました. したがって，この横軸は検出角度を考慮すればescape depthになります. この場合は，DDFがexponential decayである場合に限られますが.

原理的には，横軸を深さに換算するには逆ラプラス変換すればよいのですが，厳密には行っていません. 試みに計算した結果では最表面はAu濃度が高く，その下はCu濃度が高くなりそうです.（そのもっと深いところではAu濃度が振動しそうです）しかし，これは予備的な検討なのではっきりとは断言できません.

一村：この論文ではIMFPの計算値が正しいとして，図2と図3の違いは，Au-Cu合金でイオン誘起表面偏析が起こったためと結論ずけています. ここで偏析する元素は，Au-Cu合金でAu量が多いほうがCuに対するIMFPが大きくなる実験結果であることから考えると，Cuであるはずです.

そうすると，各計算値（n, R, λ）が正しいとして求めた表面濃度においては；特に低運動エネルギーのピークを用いた場合，Cuの濃度がバルク値よりも大きくなければならないと考えられます. しかし，図6-8を見る限り，最表面層へのCu偏析は認められません. この不一致について，考えている

表面偏析のイメージと合わせた説明が必要と考えられます.

ちなみに，ISSでAu-Cu合金の表面偏析を調べた結果では，Auが表面偏析しています.（たとえば，A. Kurokawa and R. Shimizu, Microbeam Analysis (1986) 113）.

著者：（図2，3に関しましては当初は指摘のように表現していました. ご指摘意見をいれまして，本文ではいくつかの点を変更しました. これをご承知おきください）図2，3からはご指摘の通り金の表面偏析を直接結論づけることは難しいと考えます. しかし，合金の組成が表面から内部まで一定であればIMFPの比は図3のようになるべきであり，図2にはならないと言うのが著者の考えです. すなわち，AuとCuのIMFPのそれぞれの標準試料に対する比は同じ変化をするはずだということです.

したがって，実験結果である図2を説明するには，この合金の組成は表面から内部にかけては一定ではないと考えるほかありません. また，この合金じたいは一定組成をもっているわけですから，表面クリーニングに用いたイオンスパッタリングにより偏析が生じたと結論しました.

関根：λ/λstdの挙動の精密な解析結果から見いだされたCuのIMFP比の組成依存性異常，K-value法によるCu定量値のオーバーコレクションが，イオン誘起偏析によるものと結論されたが，解析の精度を上げると見えないものが見えてくる良い例で，大変興味深い.

著者：K-value法はあまり用いられる方法ではないが，データを蓄積するには良い方法であると考えています. イオン誘起偏析が起こっていれば（実際にISS等では観測されているので）必ず通常のXPSやAESの定量分析で差がでると考えています. その差が検出されないのは，測定のの精度もありますが，定量に必要な種々のパラメータの精度の低さにも大きな責任はあると思っています.