Auger electron spectroscopy sputter depth profiling technique for binary solids

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Abstract

In this work the Auger electron spectroscopy (AES) sputter depth profiling technique for binary solids has been discussed and exemplified by its application to reveal composition profiles generated in Ni_{0.7}Mo_{0.3} by pre-bombardment with Ar^{+} ions of 1 through 5 keV. Two element-specific, surface-sensitive Auger transitions are employed to monitor the surface composition. The linear correlation between the Auger intensities provides the relative sensitivity factor for the quantification of AES data. A model proposed by Ho and co-workers is reformulated for the conversion of the measured temporal variation of surface concentration C_s(t) into the original composition profile C(x). Radiation-enhanced diffusion caused by high-energy ion bombardment turns sputter depth profiling into an underdetermined inverse problem. On the other hand, experiments show that the strong preferential sputtering effect accompanying low-energy sputter may veil the detail of the composition profiles. An intermediate energy between about 100 and 300 eV is found to be optimum for the purpose of sputter depth profiling.

Keywords: Alloys; Auger electron spectroscopy; Ion bombardment; Molybdenum; Nickel

1. Introduction

Auger electron spectroscopy (AES) in conjunction with ion sputtering has proven to be a widespread depth profiling tool in the past decades [1–4]. The careful control of the etching velocity by adjusting the ion energy and/or the current density enables a uniform removal of the sample. Henceforth the depth profiling can be achieved with a well-defined depth resolution. Application of plasma ion sources with a current density up to 1 mA/cm^2 allows for sputter etching with ion energy often lower than 100 eV, which essentially improves the depth resolution of the method [5]. It is noticed, however, that the AES sputter depth profiling technique has found application only to a limited range of problems because of its inherent complexity. Two detrimental factors to this technique are the quantification of the AES data and the conversion of the concentration variation C(t) measured at the receding surface into the original composition profile C(x). The latter shows strong dependence on the bombardment-induced processes involved in the alteration of composition profiles; therefore, the energy for the sputtering ions plays a critical role in determining the quality of sputter depth profiling.

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The intensity of an Auger transition from an alloy is given by
\[ I_A = \int_0^n \frac{N_A(x) \exp \left( \frac{-x}{l \cos \theta} \right)}{x} \, dx, \quad (1) \]
where \( N_A \) is the atomic density of atomic species \( A \), \( x \) is the inelastic mean free path (IMFP) of the applied Auger electrons in this sample, and \( \theta \) is the acceptance angle of the analyser. As indicated by both theory and experiments, the IMFP of electron in metals and metallic alloys displays universally a minimum at energies between 40 and 100 eV [6,7]. If fine depth resolution is to be achieved, deconvolution of the integral in Eq. (1) is thus necessary since the IMFP generally extends beyond four monolayers. However, this has been more often said than ever done, since the data of IMFP in a multicomponent solid are often unknown. In case of smaller IMFP such that Eq. (1) can be reasonably reduced to
\[ I_A = C_A, \quad (2) \]
where \( C_A = \sum N_i/S_iN_i \) is the fractional concentration, calculation of the fractional concentration from Auger intensities still require the AES data for elemental standards and a so-called matrix correction factor [8,9]. This has caused the measurement to be quite troublesome. A quantification method based only on AES data of the binary solids themselves will undoubtedly make the technique more practical. Another problem concerning sputter depth profiling arises from the bombardment-induced effects, i.e. preferential sputtering effect, collisional mixing and radiation-enhanced diffusion, which may distort the original composition profile to a certain extent. All these effects are ion energy dependent. Hence the energy for the sputtering ions should be carefully chosen in the light of the interaction in the specific ion–target system. A conversion scheme pertinent to the bombardment-induced processes is indispensable to recover the original composition profile. Hofmann made a pioneering attempt by introducing the concept of resolution function \( g(z - z') \) [10]. Unfortunately, it is not easy to find out the resolution function \( g(z - z') \). For most bombardment-induced processes, whether the distortion can be described with such a resolution function is still an open question. In a considerable number of publications, the temporal composition variation measured at the receding surface, \( C(t) \), after being properly depth-calibrated, has been simply taken as the original composition profile. In this paper the AES sputter depth profiling technique will be discussed in detail. To choose a proper energy for the sputtering ions, bombardment-induced effects will be carefully inspected. For the case of sputtering with a moderate energy (about 100 to 300 eV), the model proposed by Ho et al. [11], which describes the composition evolution at the surface due to exclusively the preferential sputtering effect, will be reformulated to convert \( C(t) \) into \( C(x) \). As an illustrative example, we applied this technique to the \( \text{Ni}_{0.7}\text{Mo}_{0.3} \) alloy, in which composition profiles had been generated by pre-bombardment with 1 through 5 keV \( \text{Ar}^+ \) ions. Throughout the text the ‘temporal variation’ is always mentioned, but in Figs. 2 and 4 the Auger intensity and surface concentration are plotted versus ion fluence following the convention in literature. By constant current density the ion fluence is proportional to the sputtering time.

2. Experimental
The sample was polycrystalline bulk \( \text{Ni}_{0.7}\text{Mo}_{0.3} \). A specular surface was established by mechanical polishing before the sample was introduced into the ultrahigh vacuum chamber. The base pressure in the chamber was \( 1 \times 10^{-9} \) mbar. During the experiment the pressure was raised to \( 2 \times 10^{-7} \) mbar when the electron–cyclotron–wave–resonance (ECWR) plasma was operated within a coaxial glass cylinder at a pressure of \( 8 \times 10^{-7} \) mbar. The working gas was high-purity argon (99.999%). To remove the contaminant C and O from the surface, the sample was sputter cleaned with a 2 keV \( \text{Ar}^+ \) ion beam from an ion gun (Leybold IQ36) repeatedly until the C (KLL) and O (KLL) Auger peaks were no longer detectable.

Prior to the sputter depth profiling, a steady-state composition profile was generated by pro-
longed bombardment using 1 through 5 keV Ar \(^+\) ions from the ion gun. By ‘steady-state’ we mean that the peak-to-peak intensities of all Auger transitions available fluctuate within 0.5\%. AES sputter depth profiling was then performed, by which the sample was sputter etched with low-energy Ar \(^+\) ions extracted from the ECWR plasma source operated at 27.12 MHz while the AES spectra were recorded with a single pass cylindrical-mirror-analysyer (CMA, PHI10-155) in E::N(E) mode. During sputter etching the ion current density was kept at 0.40 mA/cm\(^2\). The energy of the Ar \(^+\) ions extracted from the plasma could be adjusted by varying the biasing voltage at the target, and it was determined with a self-made retarding-field-analysyer. For the principle of ECWR plasma and its application as an ion source, the readers are referred to Refs. [12,13]. The sample temperature was monitored using a PT100 thermosensor buried in the sample holder. For typical sputtering conditions at an ion energy of 150 eV and an ion current of 120 \(\mu\)A for 1 h, the sample temperature increased from the room temperature to 90 °C.

3. AES sputter depth profiling technique

3.1. Sputter etching

As mentioned above, a successful sputter depth sputtering relies on the development of a conversion scheme to transform the measured \(C(t)\) function into the original composition profile \(C(x)\). This is certainly impossible for the case when the bombardment-induced processes are in principle not inversely solvable. On the other hand, since in practice all analysing tools have their own detection limits, some structures in \(C(x)\) may find no perceptible correspondences in \(C(t)\) if the bombardment-induced process has the tendency to diminish the composition variation. A conversion scheme is then incapable of restoring those structures in \(C(x)\). An ideal sputtering energy should both allow the development of a conversion scheme and retain the detailed structures in \(C(x)\).

Firstly, we find that the energy for the sputtering ions should be below a critical value so as to avoid strong cascade mixing and radiation-enhanced diffusion. In case that radiation-enhanced diffusion is the dominant factor altering the composition profile, the composition evolution in the residual solid is governed by the diffusion equation [14]

\[
\frac{\partial C(x, t)}{\partial t} = \frac{1}{D(x)} \left( \frac{\partial}{\partial x} \left( D(x) \frac{\partial C(x, t)}{\partial x} \right) + v(x) \frac{\partial C(x, t)}{\partial x} + f(x) \right)
\]

or similar ones [3,15]. In Eq (3), \(D\) is the depth-dependent diffusion coefficient, \(v(x)\) is the sputtering velocity and \(f(x)\) is a term related to the driving force responsible for segregation. In this model the isotropic part of cascade mixing is incorporated into the diffusion term. For the derivation of Eq. (3), the surface is taken fixed at \(x = 0\); consequently, the bulk of the target moves towards surface with the sputtering velocity \(v(x)\). Depth profiling is then to infer the initial condition \(C(x, t = 0)\) from the function \(C(x = 0^+, t)\) monitored during sputter depth profiling. Clearly, this is an undetermined inverse problem. In other words, sputter depth profiling is infeasible so long as the energy for sputtering ions is high enough that the radiation-enhanced diffusion is the prevailing factor responsible for the composition alteration. Therefore, a lower energy should be chosen for sputtering ions to suppress the radiation-enhanced diffusion, otherwise the raw data of \(C(t)\) could in no way be converted into the original composition profile \(C(x)\). For typical depth profiling conditions, \(10^{-17} \text{cm}^2/\text{s}\) is the critical value of \(D\) for radiation-enhanced diffusion to play a part. That is to say, the energy for sputtering ions has an upper limit below which the radiation-enhanced diffusion coefficient does not exceed \(10^{-17} \text{cm}^2/\text{s}\). This upper limit for sputtering energy certainly depends on the specific ion-target combination.

If, to the other extreme, a very low energy for sputtering ions (less than 100 eV or even down to the sputtering threshold) is applied, the consequent strong preferential sputtering effect can drastically distort the composition profile. Namely, the strong preferential sputtering would terminate the sputter depth profiling, i.e. when the variation of surface concentration is below the detection limit of the...
one can calculate the ratio $Y_{cNi}/Y_{cMo}$. It was found to descend from 9.3 at 80 eV to 3.3 at 200 eV. That is to say, the preferential sputtering effect tends to be less drastic in so far as the ion energy increases to a moderate value of 200 eV. Later we will show that with a sputtering energy of 120 eV the valley in Ni composition profiles characterising the Ni-depleted zone may be absent. Therefore, the energy for the sputtering Ar$^+$ ions should be chosen higher than 120 eV for the sputter depth profiling of Ni$_{0.7}$Mo$_{0.3}$.

3.2. Quantification of Auger data

Quantification of the AES data will be substantially simplified if surface-sensitive Auger transitions, for which the proportionality in Eq. (2) is justified, are employed. It is also recognised that, for binary solids, sputter depth profiling itself can provide the relative sensitivity factor so long as the intensities of the two Auger transitions are linearly correlated.

Starting with Eq. (2), since per definition $C_A + C_B = 1$ (6)

one obtains immediately

$$I_B + r_{AB} I_A = \text{const.}$$

where $r_{AB}$ has the meaning of relative sensitivity factor for the two Auger transitions under the specific experiment conditions. If $I_B(t)$ and $I_A(t)$ measured during sputter depth profiling is linearly correlated, $r_{AB}$ in Eq. (5) is then well defined and can be determined from the plot $I_B(t)/I_A(t)$. With given $r_{AB}$ the calculation of the surface concentration is quite straightforward:

$$C_B = \frac{I_B}{I_B + r_{AB} I_A}.$$  

The IMFPs of the 61 eV (Ni, MVV) and 185 eV (Mo, MNN) Auger electrons in Ni$_{0.7}$Mo$_{0.3}$, calculated from the semi-empirical formula given by Seals and Dench [7], are about 0.38 nm and 0.609 nm respectively. Considering that the acceptance angle of the CMA is 42°, these two Auger transitions are very surface sensitive. To make it more clear, over 80% of the intensity for the Ni

61 eV Auger peak comes from the first two atomic layers. Hence, the above quantification scheme is justified. Fig. 2 depicts the intensity variation of these two Auger transitions during sputter etching the composition profiles generated by pre-bombardment with 1 through 5 keV Ar$^+$ ions. The energy for the sputtering Ar$^+$ ions was 180 eV.

In order to demonstrate the influence of the ion energy on sputter depth profiling, the results acquired by sputtering with 120 eV Ar$^+$ ions are also shown in Fig. 4b for comparison. In contrast to those in Fig. 4a, the $C_{\text{Mo}}(t)$ curves referring to the 1 and 2 keV pre-bombardments decrease monotonically to the steady-state value. The minimum, which appears on all other curves, is absent. The loss of this remarkable feature for ion-bombardment in the linear cascade regime appears irremediable.

3.3. Conversion of $C(t)$

We are now in a position to convert the $C(t)$ function into the original composition profile $C(x)$. This is the crucial step in sputter depth profiling. Many efforts have been devoted to this topic [10], yet the status quo is quite unsatisfactory. For the present case of sputtering with low energy down...
be solved for $C(x + D_{\text{alt}})$:

$$
C_A(x + D_{\text{alt}}) = \frac{N_0 J_0 \int [D_{\text{alt}} C_sA(t)] + Y_cA C_sA(t) - Y_cB [1 - C_sA(t)]}{\gamma A C_sA(t) + Y_cB [1 - C_sA(t)]}.
$$

(10)

With known component sputtering yields, the original composition profile $C(x)$ can thus be calculated using Eq. (10), together with the relations $C_sA(t = 0) = C_A(x = 0)$. (11) and

$$
x(t) = \int_0^t \frac{v(t) \, dt}{J_0}
$$

(12)

for depth calibration.

The known component sputtering yields are essential to the application of the Ho et al. model [11]. The direct measurement of component sputtering yields at very low sputtering energies is still a technical challenge. However, one may circumvent this problem by solving Eqs. (4) and (5). The ratio of the component sputtering yields can be easily inferred from the surface concentrations at sputter equilibrium, and the total sputtering yields can be either experimentally determined or assumed with a reasonable value. Errors introduced by determining the component sputtering yields in this way influence only the depth calibration, but will not bring about any profile distortion. Based on the work of Wehner on MoNi and MoCu [16], the total sputtering yield of Ni$_{0.7}$Mo$_{0.3}$ is assumed to take the value for elemental Mo, which is, together with the sputtering yields for some other 20 elements, compiled in Ref. [17]. The values of $Y_{c\text{Ni}}$ and $Y_{c\text{Mo}}$ for Ni$_{0.7}$Mo$_{0.3}$ under 180 eV Ar$^+$ ion bombardment are found in this way to be 0.57 and 0.184 respectively. A value of three mean atomic spacings was assigned to the parameter $D_{\text{alt}}$ for the following two reasons:

1. as indicated by the 'SUSPRE' code [18] simulation, over 80% of the 180 eV Ar$^+$ ions come to rest in Ni$_{0.7}$Mo$_{0.3}$ within this range;
2. the information depth of the Auger transitions applied is also about three mean atomic spac-
ings. This sets an upper limit on the depth resolution of the method.

By applying Eqs. (10)–(12) the $C'(t)$ curves in Fig. 4a were converted into the composition profiles depicted in Fig. 6. Two remarkable features of the composition profiles in Fig. 6 strongly support the plausibility of this conversion scheme. First, all curves terminate uniquely at the bulk concentration. This is not a matter of course by applying other models. Second, all curves show a minimum. The position of the minimum Ni concentration $x_{min}$ corresponds to the position of maximum deposited energy. It is related to the energy of $\text{Ar}^+$ ions having generated the composition profiles $E_0$ through a power law $x_{min} \approx E_0^{0.41}$.

This is in good consistency with the theory in Ref. [19]. The form of the curve, that it first decreases to a minimum and then gradually rises to the bulk value, indicated that both the preferential sputtering and the radiation-enhanced diffusion and segregation play a part in the generation of the composition profiles. The detailed discussions over the mechanism of compositions profile generation by ion bombardment and the numerical simulation of the profile evolution with Eq. (3) will be published elsewhere [20].

The Ho et al. [11] model is applicable in cases when the gradient of the composition profiles is small. The error brought in by this conversion scheme may be larger for the front part of the
This procedure has also been successfully applied to the sputter depth profiling of iron silicides [14]. We recognised that only for a moderate range of ion energy is sputter depth profiling feasible. For a specific ion–target combination, the detailed ion–solid interactions should be investigated prior to the choice of the energy for sputtering ions. For sputter depth profiling of iron silicides (Fe₃Si, FeSi and FeSi₂) with Ar⁺ ions, a sputtering energy down to 120 eV was also found applicable [14], since the preferential sputtering effect in iron silicides is less pronounced than in the Ni–Mo alloy.

Fig. 6. Original composition profiles for Ni derived by converting the C(t) curves in Fig. 4a using the Ho et al. [11] model. Abscissa offset: 2 nm for every curve sequentially.

Composition profiles in Fig. 6. For a composition profile with its minimum locating rather deeper than Dₓ₀, the first a few data points can be corrected by interpolation between the first data point and the data points behind this range. By calculation using Eq. (10), different Dₓ₀ values were chosen for comparison. It was found that the influence of Dₓ₀ is not severe for Dₓ₀ = 3 or 4 mean atomic spacings. The maximum difference around the minima is less than 2%, the profile tails are almost unaffected.

4. Conclusions

In summary, the AES sputter depth profiling technique for binary solids presented above consists of three steps:
1. Choosing an appropriate energy for the sputtering ions.
2. Calculating the function C(t) from the measured intensities of two surface-sensitive Auger transitions. The linear correlation of these two sets of data provides the relative sensitivity factor.
3. Using any model that relates the temporal surface concentration with the original composition profile in a straightforward manner, e.g. the Ho et al. [11] model used in this work, to convert C(t) into C(x).

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References