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Fundamentals of Depth Profiling by Ion Sputtering

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Abstract: An outline of the fundamental principles of compositional depth profiling is given, emphasizing first the importance of optimized experimental conditions to obtain high resolution depth profiles and then the basic approach to profile evaluation and quantification. The role of the depth resolution and of the depth resolution function is elucidated and an example of experimental and theoretical determination of the latter in AES depth profiling of a GaAs/AlAs multilayer structure is presented.

1. Introduction

Many areas of advanced materials technology are based on the specific properties of thin films and interfaces. Chemical characterization of these structures requires analysis of the depth distribution of composition with high spatial resolution. To achieve this, ion sputtering in combination with a surface analytical method is most frequently applied. During the past two decades, the steady progress in our knowledge about the physical processes involved in both ion-sample interactions and quantitative surface analysis resulted in a fairly accurate understanding of the basic phenomena in sputter depth profiling, despite some still existing cases where predictions can hardly be made.

The aim of this paper is to outline the fundamental conditions for optimized high resolution depth profiling/1-4/ in view of past and more recent experimental and theoretical developments/5-21/.

2. Principles of Sputter Profiling

Depth profiling by sputtering is a destructive method. Bombardment of a solid surface with energetic particles (usually argon, oxygen or cesium ions with energies between 0.5 and 5 keV) causes damage of the surface structure and ejection of secondary particles. By continuous ion bombardment, the topmost layers are removed and layers beneath the surface are subsequently exposed as surface layers. Therefore there are two different ways to obtain the in depth distribution of composition as a function of the sputtered depth: either (a) by analysis of the sputtered material (as e.g. in SIMS and SNMS) or (b) by analysis of the remaining surface (as e.g. in AES, XPS and ISS). Both methods give the same results if all components are removed with the same sputtering yield; the results are different for preferential sputtering of one component. In this case and for homogeneous composition, methods (a) provide the bulk composition whereas methods (b) measure the composition of the altered surface layer generated by atomic mixing and preferential sputtering. In any case, the sputter erosion process itself is independent of the analysis method but it ultimately limits the accuracy by which the depth distribution of composition is obtained.

3. Optimized Profiling Conditions

The aim of any profiling experiment is to get a sputter depth profile (intensity versus sputtering time) which resembles as closely as possible the original elemental distribution with depth. While it is obvious that the instrumental setup requires correct adjustment of ion beam impact area and analysis spot as well as stable operation of the equipment with time, a number of additional conditions have to be considered in order to ensure minimum degradation of the measured profile. These conditions are compiled in Table 1.

A measure of profile broadening is the depth resolution Δz. Therefore establishing optimized profiling conditions means minimizing all the effects which tend to increase Δz. IUPAC and the ASTM E 42 committee have adopted its definition by "the depth range over which a signal increases (or decreases) by a specified amount when profiling an ideally sharp interface between two media. By convention, the depth resolution corresponds to the distance over which a 16% to 84% (or 84% to 16%) change in signal is measured"/5/.

Table 1
Guidelines for optimized sputter depth profiling conditions and methods

Sample ambient	Low residual reactive gas pressure ($< 10^{-8}$ Pa); "free" sample mount to prevent redeposition
Ion beam	Constant uniform intensity (scanning); low beam energy (≤ 1 keV); high mass ion species (or reactive species); large incidence angle for smooth sample ($> 60°$)
Analyzing conditions	Analyzed area centered in and small against sputtered area; sample rotation; minimized information depth
Sample characteristics	Smooth, polished surface; non-crystalline, no 2nd phases; oxides, semiconductors; components with similar sputtering yields; negligible diffusion and segregation and good electrical and thermal conductivities

If the shape of the interface profile can be approximated by an error function, this definition means $\Delta z = 2\sigma$ where σ is the standard deviation of the corresponding Gaussian resolution function/1-4/. Note that a Gaussian depth distribution function is most simple and is characterized by only one parameter ($\sigma = \Delta z/2$) in contrast to more complicated, asymmetric resolution functions discussed below.

The measured Δz is composed of contributions from different physical phenomena. Assuming depth resolution functions of approximately Gaussian shape and mutual independence, the main contributions add up in quadrature/6/:

$$\Delta z = \left(\Delta z_o^2 + \Delta z_s^2 + \Delta z_m^2 + \Delta z_r^2 + \Delta z_\lambda^2 + \Delta z_i^2 \right)^{1/2} \tag{1}$$

Equation (1) explicitly contains the following main contributions: lateral inhomogeneity of the depth distribution of the original sample (e.g. roughness and/or interface width of layered structures) Δz_o, surface roughening by sputtering statistics Δz_s, atomic mixing Δz_m, ion beam induced roughening Δz_r, information depth Δz_λ, and inhomogeneous ion beam intensity Δz_i. Whereas Δz_λ and, after sputtering removal of the first few nanometers, Δz_s and Δz_m are practically constant, Δz_r and Δz_i generally increase with sputtered depth. Therefore, equ.(1) can be used to extract the amount of the different contributions to the measured Δz in test structures as recently shown by Cirlin et al./7/, thus giving directions for further improvement of Δz.

Usually, a test of optimized instrumental adjustment for high resolution depth profiling is performed with a certified reference material consisting of anodic oxide layer of Ta_2O_5 on Ta of 30 nm thickness, for which $\Delta z \leq 2$ nm should be attained when sputter profiling with 1~3 keV Ar^+ ions/8/.

By using low ion beam energy (<1 keV), large incidence angle (> 70°), and minimum information depth (e.g. low kinetic energy peaks in AES and XPS), a depth resolution in the range of a few atomic monolayers can be obtained/9/. In particular for metallic materials, sample rotation during sputter profiling is extremely helpful to suppress ion beam induced roughening/10,11/.

After acquisition of the sputter depth profile, evaluation and quantification has to be done.

4. Evaluation and Quantification of Sputter Depth Profiles

The measured depth profile usually consists of an elemental signal intensity as a function of the sputtering time. To convert these raw data into the original in depth distribution of composition, e.g. by profile reconstruction or deconvolution, the following three main tasks have to be performed:

(1) Calibration of the sputtering time scale

(e.g. min.) in units of depth (e.g. nm)
(2) Calibration of the intensity scale (e.g. counts per second) in units of concentration (e.g. atom-%)
(3) Estimation of the depth resolution and/or determination of the resolution function.

Let us consider the above three tasks in some more detail:

(1) Calibration of the sputtering time (t) in terms of sputtered depth (z) requires knowledge of the instantaneous sputtering rate $\dot{z} = dz/dt$. For constant z, the sputtered depth is proportional to the sputtering time, i.e. $z(t) = \dot{z} \times t$. An estimation of $\dot{z}$ is possible by measurement of the depth of the crater generated by sputtering after a certain sputtering time. In practice, profiling of a metallic evaporation layer or an oxide layer with known thickness (such as the NPL/BCR certified tantalum pentoxide layers of 30 nm and 100 nm thickness/8/) under identical conditions yields the sputtering rate for the reference material which of course has to be corrected by multiplication with the sputtering yield ratio with the material studied.

Due to the dependence of the sputtering rate on the instantaneous surface composition, a non-linear time/depth relation may result. In this case, only in situ measurements of the receding surface can provide the correct answer, which are however complicated and generally not available. A first-order correction of the time/depth relation can be made by assumption of a linear dependence of the sputtering rate on the surface composition, as e.g. demonstrated for depth profiling results of a Ni/Cr multilayer sample with nitrogen ions/3/.

(2) Calibration of the intensity scale covers the general topic of quantitative surface analysis which is treated in special publications/1/. Important with respect to depth profiling are the effects of sputtering induced changes of surface topography and composition. In particular, the fundamental effect of atomic mixing inevitably leads to a deviation between the instantaneous surface composition and the original sample composition. In general, this deviation is modified by the concentration distribution within the mixing zone, which can be significantly influenced by preferential sputtering and/or segregation /12/. These effects can only be represented by an appropriate depth resolution function if there is a linear relationship between signal intensity I(t) and concentration X(z). Most often, the exact composition of the mixing zone can hardly be predicted and it is one of the fundamental limitations of accuracy in quantitative depth profiling/13/.

(3) Estimation of the depth resolution or - for increased accuracy - determination of the depth resolution function is, in addition to tasks (1) and (2), necessary to obtain a quantitative compositional profile.

Broadening of a profile can be mathematically described by a characteristic depth resolution function g(z-z'). If the integral over g(z-z') is normalized to unity, the measured, normalized intensity $I(z)/I_0$ is given by the convolution integral/14/

$$I(z)/I_o = \int_{-\infty}^{+\infty} X(z') \times g(z-z')\,dz' \qquad (2)$$

If the depth resolution function g(z-z') is known, the compositional depth distribution X(z) is obtained from equ. (2) by deconvolution.

The depth resolution function can be determined by profiling test structures with sharp interfaces. For bilayers, the Δz(84% ~ 16%)-value is easily measured and can be used for deconvolution of the sputter profile with a Gaussian depth resolution function with $\sigma = \Delta z/2$. This has been already successfully demonstrated in the seventies/14,15/. When Δz_r, attributed to sputtering induced roughness, is the decisive term for the measured Δz according to equ. (1), it is generally found to be larger than about 5 nm, and a Gaussian depth resolution function is fairly accurate. At more improved depth resolutions, the contributions of atomic mixing and of information depth become preponderant, both of which can be represented by exponential functions. As already shown in ref. /6/, an exponential resolution function can be approximately described by a Gaussian with $\Delta z_\lambda \approx 1.6 \cdot \lambda$ with the exponential decay length, λ. Of course, higher precision requires the exact shape of the depth resolution function to be taken into account in order to perform accurate deconvolution or profile reconstruction.

The depth resolution function g(z-z') in equ. (2) is experimentally obtained by profiling through an infinitesimal thin so-called delta-layer (in reality one monolayer). Another possibility is similar to the determination of Δz on a step function concentration distribution. However, a higher precision of the data is necessary here because for this case, according to equ. (3), g(z-z') is obtained by differentiation of I(z):

$$g(z-z') = \left| \frac{d(I(z)/I_o)}{dz} \right| \qquad (3)$$

High accuracy AES depth profiles performed at GaAs/AlAs multilayers/16,17/ have shown to be appropriate to derive the experimental resolution function after equ.(3)/13,18/. Fig. 1a gives an example for the sputter profile of the first three layers using both the high (Al2, 1396 eV) and the low (Al1, 68 eV) energy Auger peak and Fig. 1b depicts the results of a profile calculation using an appropriate resolution function/17/. Fig. 2 shows the experimental depth resolution determined from Fig. 1a with equ. (3) after calibration of the depth scale from the known layer thickness/17/. With such a (smoothed) depth resolution function, an arbitrary depth distribution of composition can be

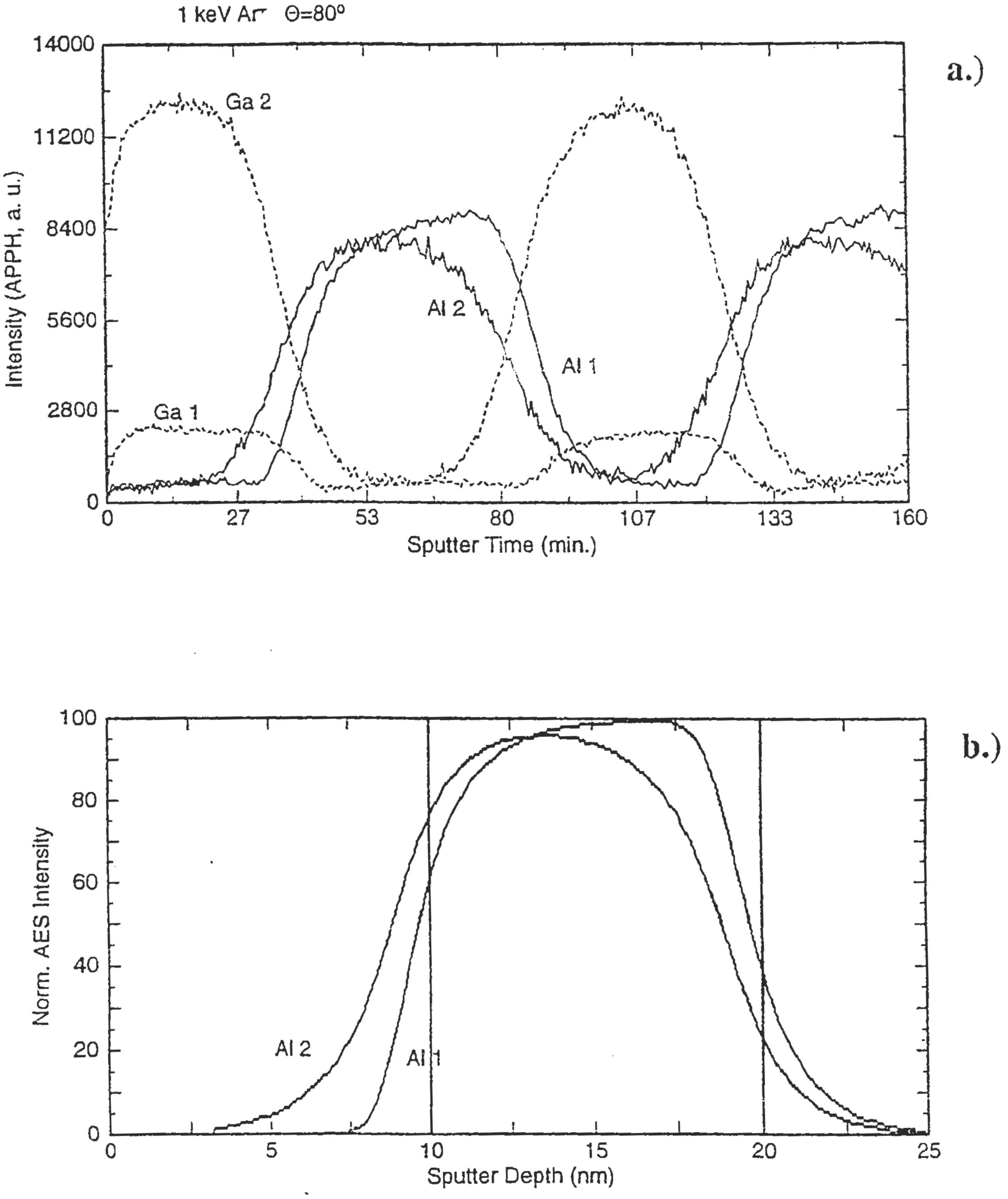

Fig. 1: a) Measured AES depth profiles (Al1: 68 eV, Al2: 1396 eV) of the first layers of a GaAs/AlAs superlattice structure with 8.8/9.9 nm layer thicknesses, respectively, using 1 keV Ar ions at 80− incidence angle

b) MRI- model calculations of the Al1, Al2 profiles with w=1.5 nm, σ=0.6 nm and λ(Al1)=0.4 nm, λ(Al2)=1.7 nm. Adapted from ref. /17/.

reconstructed/18/.

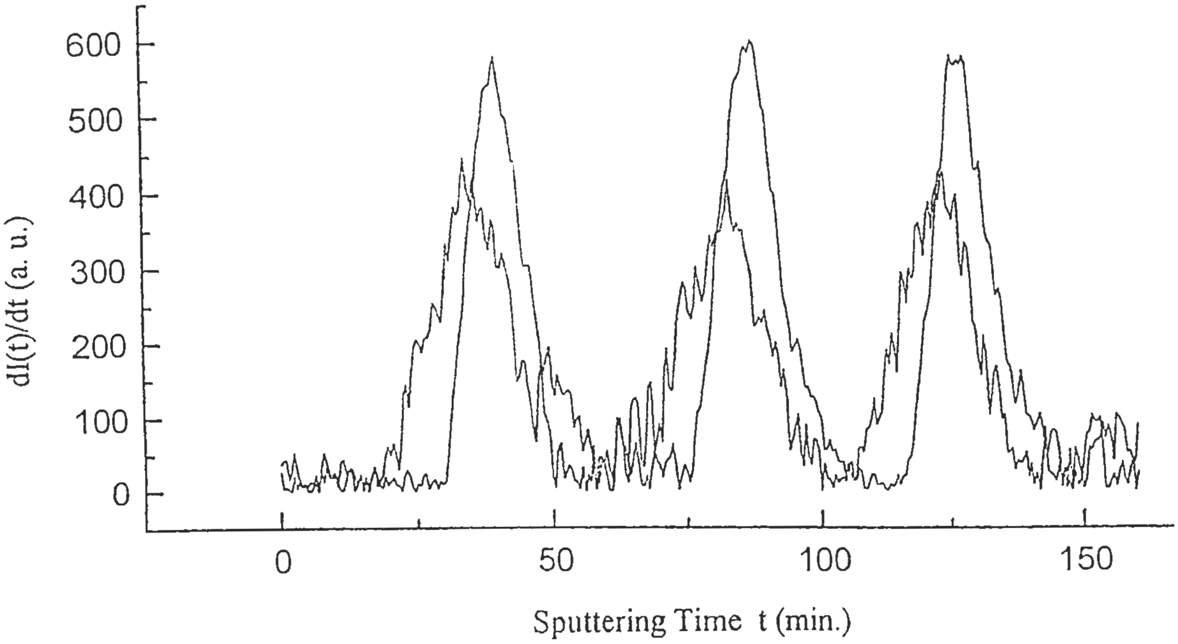

Fig. 2: Experimentally determined depth resolution functions obtained by differentiating the data in Fig. 1a) after equ.(3) showing constancy with depth.

While the depth resolution function can be fitted by any suitable analytical expression, it is useful to represent it by a set of physically meaningful parameters, as shown earlier by the so-called MRI-model/2-11,17/. This model takes into account the following three essential parameters: atomic mixing (w), surface roughness (σ) and information depth (λ). In case of Fig. 1 (1 keV Ar^+ ion sputtering) the parameters where found to be w=1.5 nm, σ = 0.6 nm, λ(Al1) = 0.4 nm and λ(Al2) = 1.7 nm. Fig. 3 shows a comparison between the experimental and theoretical depth resolution functions for the first interface. Note the good fit with a typical deviation of less than 0.3 nm, that is about one atomic monolayer.

It was shown recently that the slight discrepancy in the mutual shift of the Al1 and Al2 profiles is due to the fact that the assumption of homogeneous mixing is somewhat oversimplified because in reality probably a depletion of Al in the first surface layer occurs which is predicted by Monte Carlo calculations/13/.

Recently, similar depth resolution functions with four fitting parameters have been used for profile reconstruction of SIMS dopant profiles/19/. Because of the low concentration, nonlinear (matrix) effects

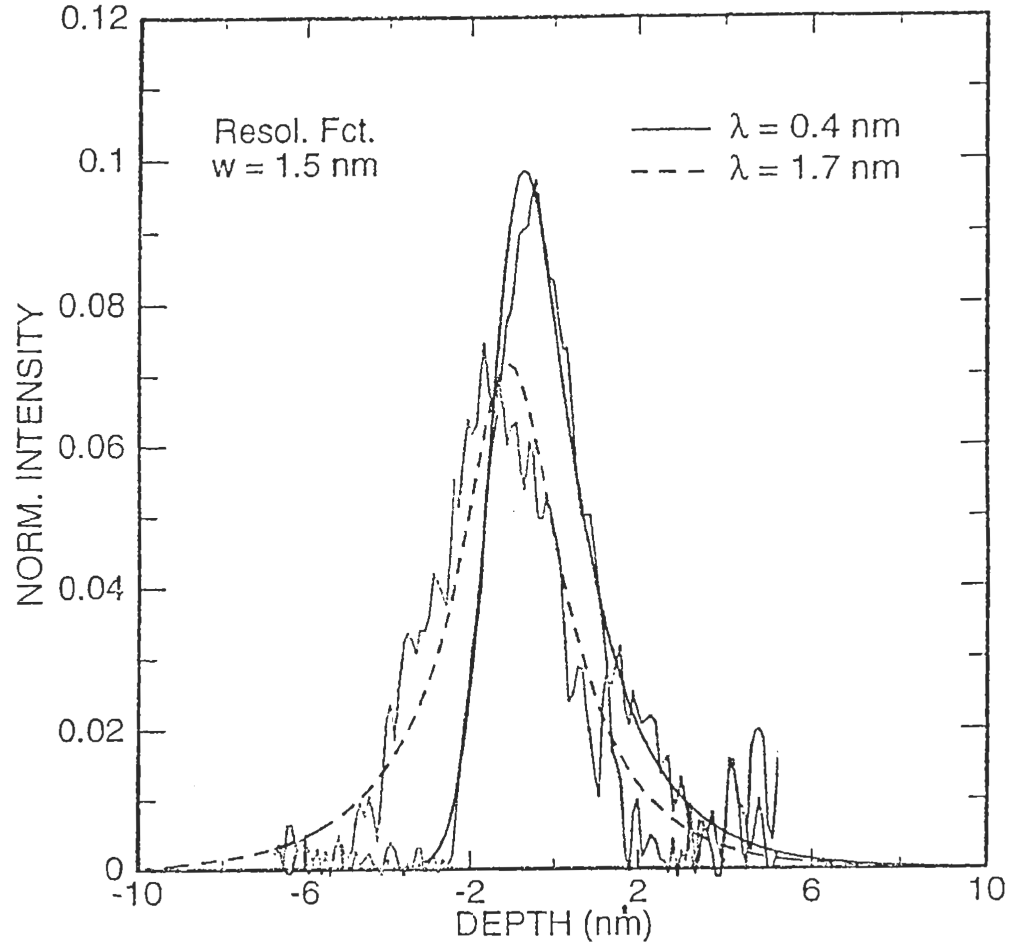

Fig. 3: Comparison of the experimental depth resolution functions from the first interface in Fig. 2 with the theoretical ones (smooth curves) calculated by MRI and the data given in the caption of Fig. 1b).

changing the shape of the resolution function with concentration are effectively diminished. However, nonlinear effects are quite common in general depth profiling, particularly at the initial stages of the sputtering process, as for thin oxide or shallow dopant layers. They can also be taken into account by appropriate model assumptions. One of the first true profile reconstructions using a resolution function which develops like a Poisson distribution with atomic layer number was shown in AES depth profiling in refs./20,21/ including also information depth and preferential sputtering effects.

5. Conclusions

High resolution depth profiling by ion sputtering requires careful optimization of the experimental profiling conditions. This procedure is based on a thorough understanding of the various detrimental effects of instrumental factors, of ion beam-sample interaction and of specific sample characteristics, a knowledge which was derived from studies with well defined reference materials. In particular, for metallic samples, sample rotation during profiling gives optimum depth resolution which is generally improved by using low energy primary ions (< 1 keV) and high incidence angle (> 70°). Quantification of the measured sputter profile in terms of original depth distribution of composition is usually performed in the three calibration steps for the sputtering time/depth relation, the intensity/concentration relation and for the profile shape. Depending on the required accuracy, the depth resolution and/or the depth resolution function can be determined with suitable reference samples and can be used to retrieve the original depth distribution by solving the convolution integral. Thus, the fundamentals of depth profiling are well established and current research focuses mainly on such topics as nonlinear matrix effects, radiation enhanced diffusion and segregation to improve our understanding and to improve the analytical capabilities of depth profiling by ion sputtering.

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