Pure & Appl. Chem., Vol. 64, No. 5, pp. 615–622, 1992.
Printed in Great Britain.
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Electron and mass spectrometric analysis of plasma controlled surfaces and thin films

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Abstract – The application of physical methods for chemical surface and depth profile analysis to plasma controlled surface and thin film processes is elucidated by recent examples. Besides several aspects of already routinely used electron spectroscopic techniques the potentialities of Scanning Work Function Spectroscopy and Secondary Neutral Mass Spectrometry as more recent analytical methods are discussed.

INTRODUCTION

Within the last few decades a number of physical methods for the investigation of solid surfaces have evolved from surface physics and become almost routine techniques for quantitative chemical analysis of surfaces and thin films (see e.g. refs. 1 and 2). Such methods are essentially based on energy spectroscopy of Auger or photoelectrons emitted from the outermost atomic layers or on mass spectrometric identification of atoms and molecules removed from the sample surface by appropriate desorption techniques. While mass spectrometric studies aim mostly for a compositional characterization, photoelectron spectroscopy, in particular, can deliver detailed information about the chemical binding conditions at the sample surface. Depth dependent information which is most important for the analysis of thin film structures is obtained either by appropriate bevelling techniques or by employing controlled sputter removal by ion bombardment as the most sensitive microsectioning technique. Depth resolution in sputter profiling can be expanded down to a physical limit in the order of only a few atomic distances by appropriate experimental measures (ref. 3). The lateral resolution is mainly determined by the diameter of the primary beam exciting the analytical signals. While in state–of–the–art ion microprobes which often employ liquid metal ion sources beam diameters down to a few tenths of a micrometer are available, recent auger microprobes using field emission sources provide electron beams with a spot size down to the 10 nanometer range at a beam current of 1 nA. As an example, elemental mapping across an area of 1 μm x 1 μm with a lateral resolution of 50 nm is enabled with up–to–date Scanning Auger Microprobes within a few minutes (ref. 4). While the detection sensitivity in Auger and Photoelectron Spectroscopy is in principle limited by the moderate excitation cross sections to some 10^{-3}, much higher detection sensitivities down to ppb–range are achieved when the secondary ions or – postionized – sputter ejected neutral particles are used for the analytical information.

Besides Auger and Photoelectron Spectroscopy AES and XPS (resp. UPS) or Secondary Ion Mass Spectrometry SIMS, more recent techniques as Secondary Neutral Mass Spectrometry SNMS (ref. 3) or Work Function Microscopy (ref. 5) have been already established or are just being introduced in surface and thin film analysis. After some examples for recent applications of XPS and AES, Work Function Scanning Microscopy as a novel analytical method using electron spectroscopy will be discussed in some detail. Subsequently, Secondary Neutral Mass Spectrometry SNMS, in particular electron–gas SNMS as a plasma based technique, and its prospectives will be addressed. In all cases, the application of such techniques to the characterization of surfaces and thin film structures which have been treated or deposited by plasma processes will be emphasized. An important aspect is always the correlation of the sample properties with the parameters during plasma treatment of surfaces and plasma based thin film formation.

XPS AND AES STUDIES OF PLASMA CONTROLLED SURFACES AND THIN FILMS

The direct interaction of reactive and inert plasma species with surfaces is nowadays largely employed on a technical scale. Examples are the manifold applications for surface structuring by reactive or inert ion etching which makes use of the high selectivity of the chemical etch attack or the large differences between low energy sputtering yields. Another area where surface modification

by plasma treatment became an important technological process is the conditioning of polymer surfaces, for instances to improve the wetting or sealing properties. In this context, Photoelectron Spectroscopy has provided a detailed answer on the surface modification which are inferred when the surface of a polymer as polyethyleneterephtalate PET is exposed to a corona discharge in air.

Effective heat sealing of PET foils was found to be only possible after a such a treatment. Comparative XPS studies of PET surfaces have revealed that initially not present phenolic C–OH–groups are generated which are assumed to be responsible for the excellent sealing properties after the corona treatment (ref. 6).

Chemical modification of metal surfaces by reactive plasmas has been investigated to a much lesser extent although exposure to oxygen or fluorine occurs during reactive etching in microelectronic fabrication steps. This may cause potential problems as contact resistance or electrocorrosion, thus limiting the lifetime of the respective devices. In a recent study the interaction between a low pressure plasma maintained in O_2/CF_4 mixtures with copper films has been investigated by XPS and AES (ref. 7). A careful analysis of the photoelectron spectra in the region of the Cu(2p) peaks shows that a surface layer is formed which consists of a mixture of Cu_2O and CuF_2, rather than a homogeneous compound layer of $Cu_xO_yF_z$. In addition, AES sputter depth profiles of Cu films reacting with plasmas of different O_2/CF_4 ratios reveal that the oxide extends always through greater depths than the fluoride, and that consequently the treatment in CF_4 rich discharges results in thinner modified surface layers.
The production of thin films or multilayer structures with well defined properties by plasma processes has also become an important field with a strong link to widespread technological applications (see, e.g. ref. 8). As an example, amorphous hydrogenated carbon layers (a–C:H) have recently attracted much interest since their optical, electrical and mechanical properties can be adjusted in a definite manner when the deposition parameters are carefully controlled. In this context, the application of a novel plasma beam source by which the composition and the energy of the film forming plasma species can be varied in a precisely controllable manner is of particular advantage (ref. 9). This plasma beam consists of a monoenergetic ion component of variable energy and a co–travelling electron component of equal flux densities, and thus transports no net electrical current. Hence, surface or thin film processes become completely independent of the actual substrate conductivity or its changes during the process.

The properties of a–C:H films depend largely on the ratio of the sp^3– and sp^2– carbon bondings, where the π electrons connected with sp^2 refer to the graphitic fraction in such films. The films become diamond like the more the sp^3–bonds are dominating. Respective information can be achieved by photoelectron loss spectroscopy, utilizing the C(1s) photoelectrons as an internal monoenergetic electron source in the films. Corresponding loss structures are shown in fig. 1 where they appear at higher binding energies corresponding to smaller kinetic energies. These structures arise from plasmon excitations of the π and the σ valence electrons in the a–C:H films. Diamond–like conditions are approached when the structure with an energy loss of 6.5 eV being visible at the slope of the C(1s) peak and referring to the π electrons disappears, and only the plasmon losses

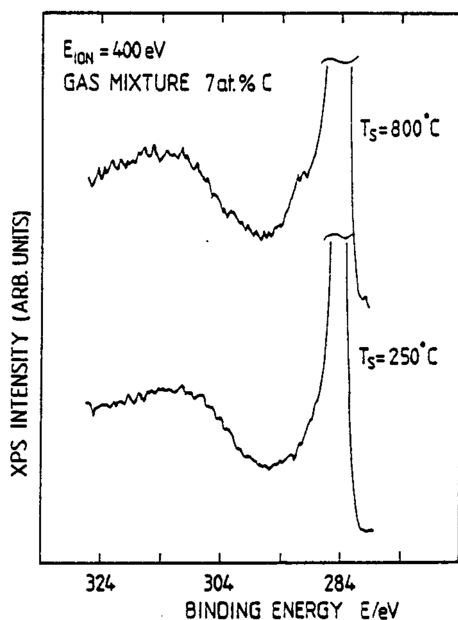

Fig. 1 Electron loss structures due to plasmon excitations in the vicinity of the C(1s) photoelectron peak. Taken from an XPS analysis of a–C:H films deposited by a plasma beam from a CH_4/H_2 plasma at an ion energy of 400 eV and for different temperatures of the (100) Si substrate. From ref. 9.

around 27 eV are left. While fig. 1 displays the transition to diamond–like films for a reduced substrate temperature T_S, fig. 2 refers to the shift of the position of the high energy plasmon losses as a function of the kinetic energy of the film forming ions. Quite obviously, loss energies around 30 eV which correspond to diamond are approached when the ion energy in the plasma beam arriving at the substrate is reduced to energies below 100 eV.

Another useful application of XPS loss spectroscopy is shown in fig. 3 which refers to the variations of plasma deposited diamond films under the etch attack of an Ar or a CF_4 RF plasma (ref. 10). Quite obviously, inert sputter etching by Ar^+ disturbs diamond like sp^3 bondings on expense of the amorphous or graphitic fraction of the film. On the other hand, when the surface of the films is etched by the CF_4–discharge, the graphitic and the amorphous component are preferentially etch removed and the typical high energy loss structure of diamond develops.

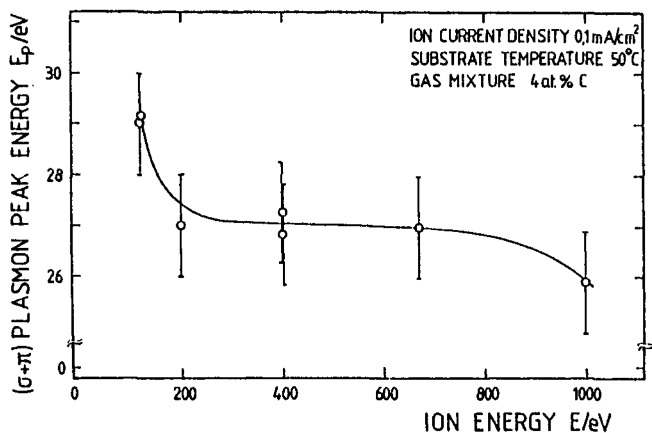

Fig. 2 Dependence of the plasmon energy E_p referring to diamond–like properties of plasma beam deposited a–C:H films on the energy E of the arriving beam ions. From ref. 9.

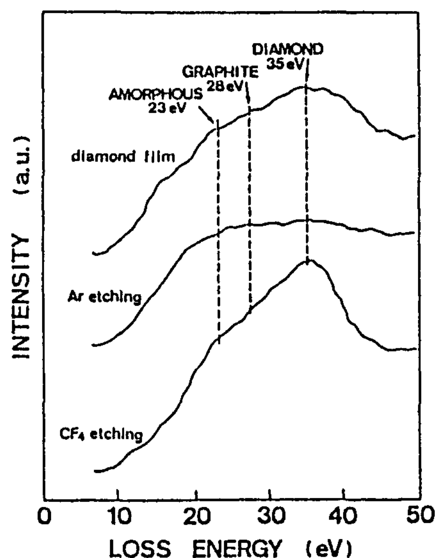

Fig. 3 XPS loss spectra of diamond films before and after Ar and CF_4 plasma etching (etch time 10 min). From ref. 10.

APPLICATION OF WORK FUNCTION SCANNING SPECTROSCOPY TO PLASMA DEPOSITED THIN FILM STRUCTURES

The monoenergetic electron signals both of Auger or photoelectrons are always superimposed on random electron energy distributions which are in XPS or AES removed as an interfering background. Such distributions originate from mostly isotropic distributions of inelastically scattered electrons or from excited conduction band electrons. When such electrons pass through the solid surface to form the well–known continuous energy distribution of "true" secondary electrons, they have to overcome a potential barrier given by the electronic work function ϕ at the actual surface. Hence, the onset energy of the secondary electron energy distributions along an arbitrary, but fixed energy scale will be determined by the ϕ–value of that surface area from which the electrons are escaping (ref. 11). Lateral work function changes across the sample surface can thus be detected from the shift of the energetic position of the onset point, when secondary electron emission is locally excited by a focused primary electron beam. Accordingly, depth dependent variations of ϕ in thin film structures are obtained when the onset technique is applied in conjunction with a controlled sputter removal. As the electronic work function varies with the experimental composition and the chemical binding conditions, spatially resolved Work Function Spectroscopy, which can readily incorporated in existing Scanning Auger Microprobes (ref. 12) can provide useful compositional and structural information. Since, in principle, all secondary electrons are utilized and not only the small amount of Auger electrons, much higher detection sensitivity should be achieved in combination with an extremely high surface sensitivity, as ϕ is almost exclusively determined by the electron density distribution at the solid–vacuum interface.

An energy diagramme for elucidating the onset method for Work Function Microscopy is shown in fig. 4 (ref. 12). An electron with the kinetic energy E_{kin} which leaves the sample at a spot with the local work function ϕ_c is measured in an electrostatic energy analyzer with an energy $E'_{kin} = E_{kin} + \phi_c - \phi_A$. The "Analyzer Work Function" ϕ_A which is an apparatus constant may serve as a constant reference point along the energy scale where the different onset points referring to $E_{kin} = 0$ and hence to the work function differences ϕ_c–ϕ_A are appearing during the analysis. For the practical performance of Work Function Microscopy the different onset points are moved back to one identical reference point by applying a variable external bias voltage U_g between the sample and the

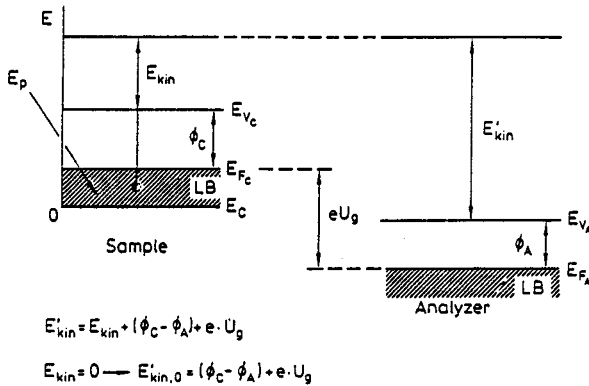

Fig. 4 Energy diagram for Work function Microscopy by the onset method. (E'_{kin} measured kinetic energy of secondary electrons from the conduction band L.B. of the sample. ϕ_c, ϕ_A sample and analyzer work functions; E_V and E_F vacuum and Fermi levels, U_g external bias voltage).

analyzer. The individual U_g–values are a direct measure for the local work functions. When they are correlated with the actual positions of the primary electron beam being scanned across the surface, work function images can be generated at a TV screen. As an example, fig. 5 displays the work function image of a small Ni particle in a Cr sublayer of a sputter deposited Ni–Cr multilayer structure with a thickness of only 50 nm of the individual sublayers. In this case, Work Function Spectroscopy in the onset mode is applied to a bevelled section through this multilayer system with an bevelling angle in the order of 10^{-5} degrees (ref. 13).

The extreme surface sensitivity of work function analysis is demonstrated in fig. 6 referring to simultaneous Auger and work function sputter depth profiling through a Ta–Si multilayer system with a double layer thickness of only 20 nm. The depth dependent work function varies by 0.4 eV between the Ta and the Si rich depth intervals. Quite obviously, distinct silicide phases with a thickness of only a few Å are identified by steps in the ϕ–profile in the very narrow interfaces between the individual sublayers (ref. 14). This is a consequence of the extremely high surface sensitivity of the work function method compared to the depth information from the AES signals which is determined by a convolution of the true concentration profile and the escape function of the electrons with mean escape depth in the order of 10 Å.

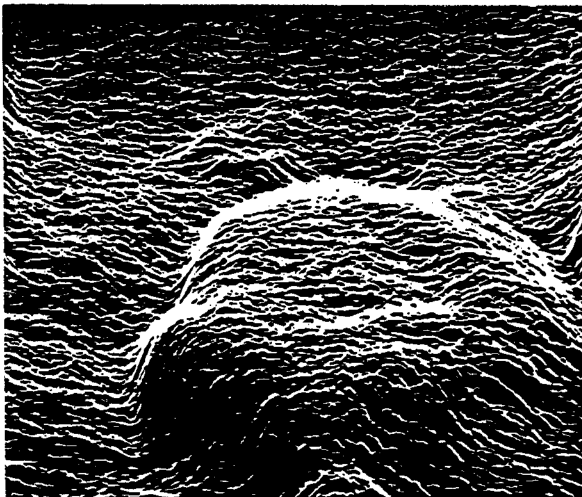

Fig. 5 Work function image of a small Ni particle in a sublayer of a sputter deposited Ni–Cr multilayer structure with an individual single layer thickness of 500 Å. From ref. 13.

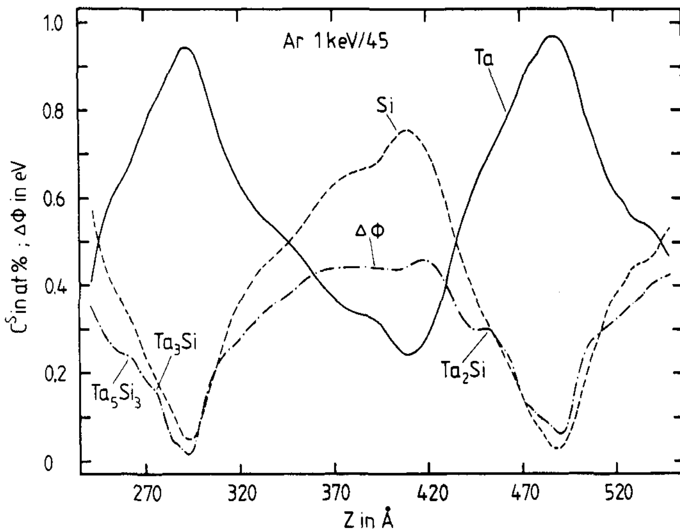

Fig. 6 Section of a combined work function sputter depth profile of a sputter deposited Ta–Si system consisting of 70 Å Ta– and 140 Å Si–sublayers. Sputter profiling by 1 keV Ar^+ ions at 45^0. (According to G. Bachmann, ref. 14).

QUANTITATIVE ANALYSIS OF THIN FILMS BY SECONDARY NEUTRAL MASS SPECTROMETRY

Secondary Neutral Mass Spectrometry SNMS, i.e. surface and depth profile analysis utilizing neutral atoms and molecules removed from the sample surface by "atomic spoons" in the form of primary bombarding ions, has developed to a strong competitor of Secondary Ion Mass Spectrometry SIMS within the last few years. The additional experimental means which have to be included for the necessary postionization of the ejected neutrals are by far compensated by the high quantifiability of SNMS (refs. 3 and 15). As contrary to SIMS the emission and the ionization process of the analyzed particles are strictly separated, the SNMS signals are directly correlated with the actual concentrations in the sample via a particle specific but constant detection factor. Hence, the well–known strong "matrix effects" which prevent the quantification of SIMS in many cases do not appear in SNMS. Small residual influences of the target composition reflect only possible differences in the energy and the angular distribution of the ejected particles (ref. 16). Those influences, however, are by orders of magnitude lower than the matrix dependence of secondary ion formation. As another advantage, SNMS can readily be applied also to the analysis of dielectric samples (ref. 17).

Besides postionization by electron impact, laser postionization by resonant or nonresonant multiphoton processes have become a major object in developing SNMS techniques. Nevertheless, postionization by a hot Maxwellian electron gas being established by the electron component of a low pressure noble gas plasma excited by an electrodynamic resonance effect is at present the most elaborated analytical method for Secondary Neutral Mass Spectrometry. There are already numerous examples for the analytical application of this technique for which the acronym SNMS has been introduced at first. We will here concentrate on a particular aspect, namely the quantitative determination of the depth dependent hydrogen content in amorphous hydrogenated carbon and silicon layers which are deposited either by the already mentioned plasma beam source (ref. 9) or by magnetron sputter deposition. It is well–known that the hydrogen content determines largely the film properties. In particular, the electronic properties of hydrogenated amorphous semiconductor films as a–Si:H which are designed for photovoltaic applications depend strongly on the saturation of dangling bonds by incorporated H (ref. 18).

An example for SNMS depth profile analysis of plasma deposited thin a–C:H–layers is presented in fig. 7 (ref. 19). The interface width between the film and the (100) Si substrate is detected to be only in the order of 100 Å. A detailed discussion of the different influences which contribute to this very small interface width reveal that about 70 Å refer to interface broadening by collisional mixing, and 15 to 25 Å to low energy ion implantation of the plasma beam ions with an energy of 220 eV during the initial stage of film growth. The remaining 15 Å have to be attributed to sputter induced microroughness which forms the physical limitation of any depth profiling employing ion sputter removal (ref. 20). The example in fig. 7 demonstrates the high depth resolution obtained by SNMS which has been shown to approach the limiting value around 15 Å, or for 4 to 5 atomic layers, when the ion bombarding energy is reduced to values around 100 eV (ref. 15).

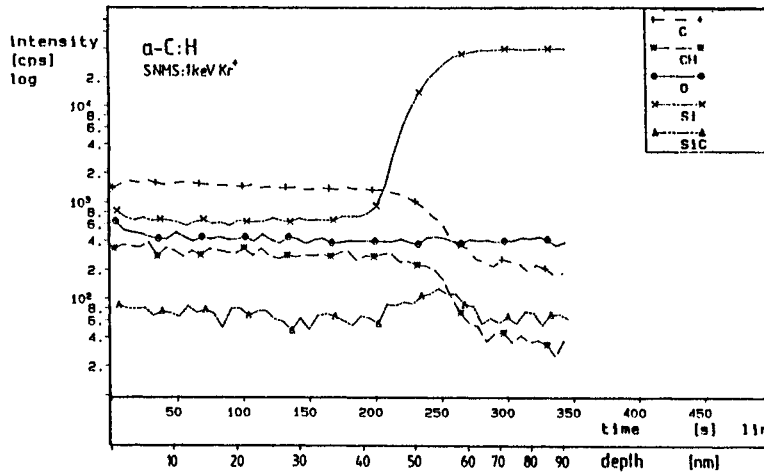

Fig. 7 SNMS depth profile analysis of an a–C:H film deposited on (100)Si with plasma beam extracted from a CH_4 plasma at an ion energy of 220 eV. Analysis under perpendicular bombardment with 1 keV Kr^+–ions. From ref. 19.

Besides C neutral CH molecules constitute another layer specific species in the SNMS analysis shown in fig. 7. According to the quantitative character of SNMS the CH or other monohydride signals should be correlated with the hydrogen concentration c_H in the sample. The corresponding evaluation makes use of the so–called direct emission model DEM which applies to the formation of sputtered molecules for strong, mainly ionic bonds and large mass differences between the atomic constituents (ref. 21). The DEM yields explicitly a monotonous relation between c_H and the ratio of the SNMS signals for the molecule and the heavier constituents, i.e. of the CH and the C signals in the present case. The results of corresponding evaluations for a number of a–C:H layers deposited for different parameters of the employed hydrocarbon plasma beam are shown in fig. 8. Since c_H determines vice versa the electrical, optical and mechanical properties of the investigated a–C:H films such numbers can now also be directly correlated with the relevant parameters for film formation.

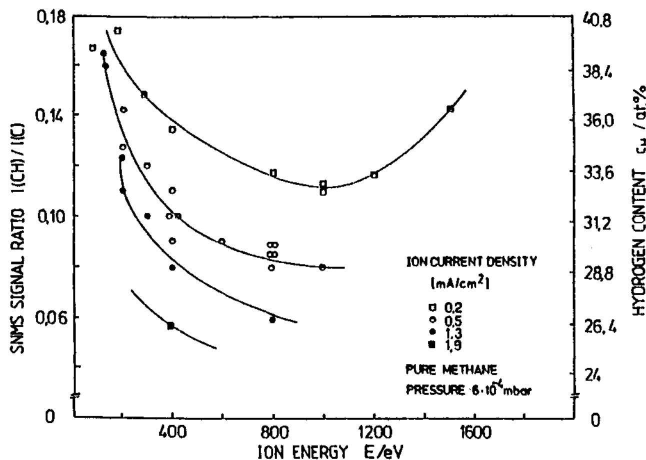

Fig. 8 Dependence of the hydrogen concentration determined by SNMS in plasma beam deposited a–C:H films on the ion energy and the current density of the beam. From ref. 9.

Another very instructive example for the hydrogen analysis with SNMS is presented in fig. 9. In the respective investigations the DEM method for the determination of c_H from the SNMS signals has been applied to hydrogenated amorphous silicon films which have been deposited by magnetron sputtering (ref. 22). For a controlled variation of c_H the hydrogen partial pressure p_H in the sputtering chamber has been varied during the deposition. The hydrogen depth profile in fig. 9 is compared with a "theoretical" profile as being expected from the variation of p_H during layer formation. In addition, the phosphorus concentration in an n–doped surface layer has been also determined quantitatively from the SNMS signals. In both examples shown here the electron gas SNMS apparatus (INA 3 delivered from SPECS GmbH) was operated in the so–called direct bombardment mode (ref. 3).

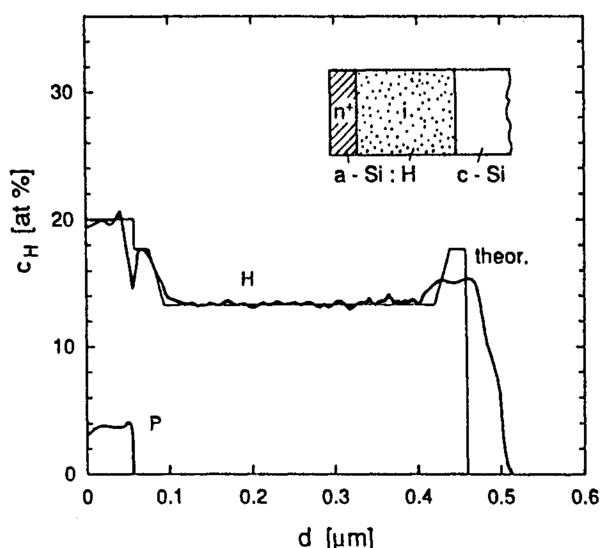

Fig. 9 Hydrogen depth profile measured by SNMS for a sputter deposited a–Si:H film, with a P–doped n–layer on top. The "theor." profile refers to the H–distribution expected from the variations of the hydrogen particle pressure during the deposition process. From ref. 22.

CONCLUDING REMARKS

The presently available physical methods for chemical surface and depth profile analysis are well suitable for detailed studies of surface modifications due to the interaction with plasma borne particles, or the precise characterization of thin film structures which in modern thin film technology are to a large extent generated by plasma controlled or assisted processes. XPS and AES as routinely applied electron spectroscopic techniques have been much improved with respect to the evaluation procedures but also to the instrumental possibilities. For example, very useful information can be derived from AES spectra if not only the first derivitive of the signals is utilized as usual. Thus, the contribution of interatomic transitions in compound layers can be readily identified by means of the second derivitives of the corresponding Auger peaks (ref. 23). Though XPS is in general considered to be applicable to insulating samples, residual surface charging by the escaping photoelectrons can cause interfering distortions in the XPS spectra. Such influences can be quantitatively controlled by incorporating an electron optical system into the photoelectron spectrometer by which the peak shifts can be imaged in dependence of the sample area from which the photoelectrons originate (ref. 24). Besides the improvements of the already established techniques, the application of novel methods as Work Function Microscopy promise further progress.

An important point being often neglected is the complementary character of electron and mass spectrometric methods for surface analysis. While electron spectroscopy monitors what is remaining at the sample surface, e.g., after the attack of bombarding ions, the mass spectrometric methods, in particular, SNMS monitors quantitatively the particle flux from the surface. Hence, AES or XPS analyze frequently a surface composition which has been changed by preferential emission of certain species. Such changes of surface stoichiometry are mostly established after the removal of a few monolayers and compensate automatically for the different ejection probabilities by an enrichment of the less ejected components. On the other hand mass spectrometric techniques offer stoichiometric information about the sample composition as soon as stationary surface conditions, for instance at "sputter equilibrium", are achieved. It is quite evident that optimum information can be obtained when different methods being complementary in that sense are applied. In this context a combination of XPS and SNMS seems favourable because quantitative compositional information is then connected with simultaneous analysis of the binding conditions at the sample surface.

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