Wet chemical analysis consists of passing the film into solution and then termining the trace or major constituents by using gravimetric or volu-tric analysis. This technique has been applied, for example, to determine e boron concentration in doped polysilicon layers [3717] and the two con-tuents of Si_3N_4.

Emission and atomic absorption spectroscopy is based on the principle the optical analysis of excited vapours obtained from thin film. Emission ectroscopy relies on the identification and measurement of characteristic v and visible radiation intensity which is produced by subjecting the sample a high temperature source, such as an arc, a flame, or a spark.

Atomic absorption spectroscopy relies on the absorption measurement radiation emitted from a high-intensity light source, containing emission es of the specific element to be analysed, by means of a gas burner flame o which the sample has been injected. The latter method has been used determine the Na content in SiO_2 films [905—909] , the O content of POS films [910], and the B content in *a*-Si: B:H films.

Neutron activation analysis consists of irradiating the sample with neu-ons, which converts some impurities into radioactive species, whose activity d half-life is then measured.

Examples illustrating the application of this technique are the deter-nation of trace metallic impurities in epitaxial silicon [911], the investi-tion of Na migration in SiO_2 [919] and Si_3N_4 [912—915] films, the study the anodic oxide of GaAs [916] and the analysis of P content in PSG ns [917].

Radioactive-tracer analysis [918] uses the radiation detection of a radio-tive isotope of a particular element for tracking its movement as a function processing. This method is, therefore, useful for elucidating the mechanism various processes related to the preparation and properties of CVD films ch as Na migration in SiO_2 [919] and Si_3N_4 films [920, 4382, 4383], H incor-ration in SiO_2 films, the blocking of the p- and n-type impurity diffusion Si by Si_3N_4 layers [920], and P incorporation in epitaxial silicon [921].

3 Analysis Techniques of Thin Film Surfaces

esently in the field of electronic materials, interest has shifted from bulk surface analysis. There is a number of modern techniques which will be esented further according to the type of their primary excitation: X-rays -ray fluorescence spectrometry and X-ray photo-electron spectroscopy), ermal radiation (spark source mass spectrography), electrons (electron-probe croanalysis, Auger electron spectroscopy and scanning Auger microana-is), ions (ion-probe microanalysis, secondary ion mass spectrometry, and n scattering spectrometry), and nuclear particles (Rutherford backscatter-g spectrometry and nuclear reactions).

9.3.1 Techniques Based on X-Ray and Radiation Interaction with Matter

X-ray fluorescence spectroscopy. X-ray fluorescence occurs when an inner-shell electron is knocked out of orbit by a primary X-ray and the resulting vacancy is filled with a higher energy outer-shell electron; this electron transition leads to the emission of a secondary X-ray that is characteristic of the excited element.

In a typical XRF spectrometer (Fig. 9.1) X-rays from an X-ray tube bombard the sample and the secondary X-ray emitted are detected and analysed by means of an X-ray detector and an X-ray spectrometer, respectively.

This technique is nondestructive, quantitative, fast, fairly sensitive, and readily applied to insulators. It has a sampling depth in the micrometer range, no lateral resolution and cannot detect elements below fluorine in the periodic table.

XRF spectrometry [922] has been used to analyse the phosphorus content of reflow and passivation glasses [924], the Cu, Si, or Mg concentrations in Al films, the composition of metals (Mo, Au, Ag, Pd, Pt, Ta) or alloys on Si or SiO_2, the composition of Mo, Ta, W, and Ti silicides, the composition of HgCdTe wafers and films, and the Sb/Sn ratio in SnO_2: Sb films [925, 926].

X-ray photoelectron spectroscopy. This technique is based on the measurement of the kinetic energy of electrons, which are ejected from the sample surface by a primary beam of X-ray photons of known high enough energy, $h\nu$ [927—930] . From the measured kinetic energy E_k one can immediately derive the electron binding energy E_B (defined as the difference in energy between the vacuum level and the initial electron energy level) which is characteristic of the kind of atom present in the sample and the particular electron level involved in the transition, also giving information concerning its molecular state ($E_B = h\nu - E_k$).

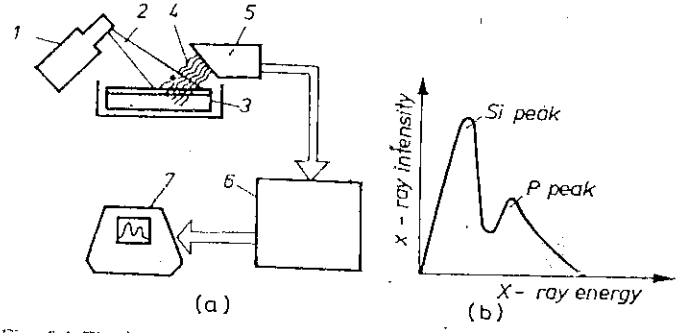

Fig. 9.1 Elemental analysis using XRF spectrometry ([923]; reproduced by permission of Kevex Corporation):
a — XRF spectrometer: *1* — X-ray tube; *2* — primary X-rays; *3* — specimen (P-doped SiO_2); *4*—characteristic secondary X-rays (P and Si X-rays from SiO_2 layers and Si X-rays from pure Si substrate); *5*—X-ray detector; *6* — X-ray spectrometer analyser; *7* — data displayer;
b — XRF spectra corresponding to a phosphorus glass layer.

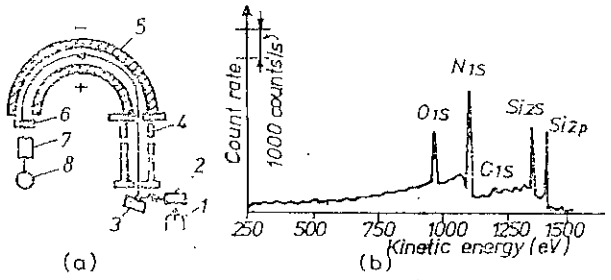

Fig. 9.2 Analysis using X-ray photoelectron spectroscopy:
a — schematic diagram of a photoelectron spectrometer (after Kelly and Tyler [931]. © 1973 Hewlett-Packard Company; reproduced with permission): *1* — X-ray source; *2* — crystal monochromator; *3* — target; *4* — retardation lens system; *5* — energy analyser; *6* — multichannel detector; *7* — multichannel analyser; *8* — output display;
b — photoelectron spectrum of a silicon nitride target. In addition to nitrogen and silicon photoelectron lines, owing to carbon and oxygen contamination, the C_{1s} sand O_{1s} lines are also observed (after Raider *et al.* [939]; reprinted by permission of the publisher, The Electrochemical Society, Inc.).

XPS, also called electron spectroscopy for chemical analysis (ESCA), equires complex instrumentation [931] consisting of an X-ray source, a rystal monochromator, a sample manipulator, a retardation electrostatic lectron lens system, an electron spectrometer, a multichannel detector and a ultichannel energy analyser system (Fig. 9.2*a*). A typical XPS spectrum Fig. 9.2*b*) shows the electron number signal intensity $N(E)$ as a function of he binding electron energy E.

XPS is the only method capable of yielding (via electronic bonding nergies) information concerning the chemical structure of atoms located within the first few layers of a solid surface. The method can readily be pplied to insulators, but has no lateral resolution, is slow, and has only limited etection sensitivity.

Some typical examples of the application of this technique in the field f CVD are the determination of the chemical composition and structure f *a*-Si: H [933, 934], *a*-SiC: H [935], silicon oxynitride or plasma deposited silicon itride [936], the observation of the thermal nitridation of SiO_2 [937], the urface oxidation of Si_3N_4 films at room temperature [939, 940], the lasma oxidation of GaAs [938], the study of the interfaces Si—SiO_2, SiO_2—Si_3N_4, and Pd—*a*-Si: H [933], the analysis of the O content and chemical tate of Si (elemental Si, Si_2O and Si_2O_3) in SIPOS layers [932], the investiation of the CVD-SiO_2—GaAs interface [941], and the depth profiling of nterfaces obtained by thermal, anodic or plasma oxidation of III—V compound semiconductors.

Spark source mass spectrometry. This method relies on the analysis of ons emitted from a sample excited by thermal radiation [942—944].

The basic components, as shown in Fig. 9.3, are a spark RF circuit for aporizing and ionizing the sample, spark source electrodes, a surface scanning

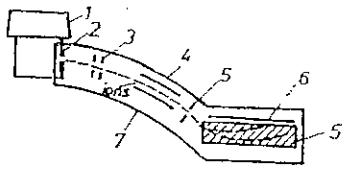

Fig. 9.3 Schematic layout of a spark source mass spectrometer (after Honig [897]; reprinted with permission from THIN SOLID FILMS. © 1976 Elsevier Sequoia S.A.):
1 — pulsed RF spark circuit; *2* — sample electrodes; *3* — accelerating electrodes; *4* — electrostatic analyser; *5* — magnetic analyser; *6* — ion-sensitive photographic plate; *7* — vacuum enclosure.

unit, the sample, accelerating electrodes, an electrostatic analyser for energy selection, a magnetic analyser for mass selection, an ion sensitive plate — or better an electrical detection system — and a vacuum enclosure.

SSMS is a relatively fast, quantitative, very sensitive, but destructive technique with a sampling depth in the micrometer range.

Examples of the use of this technique in CVD film analysis are the determination of H content in *a*-Si: H films and in plasma $Si_xN_yH_z$ films [945], trace impurities in $Si_xO_yN_z$, SnO_2: Sb and In_2O_3:Sn films, as well as background impurity (Si, etc.) concentrations in $GaAs_{1-x}P_x$ and $In_{1-x}Ga_xP$ layers.

9.3.2 Techniques Based on Electron Interaction with Matter

Electron-probe microanalysis. Electron-probe microanalysis (EPM) is based on the emission of X-rays characteristic of each element caused by the impact of a high energy beam of electrons [946—950].

A scheme of the equipment, which is often combined with SEM, is given in Fig. 9.4. It contains an electron beam source, an electrostatic or magnetic beam deflection system, a sample mount, a crystal detector combined with a pulse analyser (or a monochromator plus a conventional X-ray detector), and a display system.

This method is fast and quantitative and allows the elemental analysis of sample volumes of micrometer range dimensions to be nondestructively performed. It has an excellent lateral resolution (but is applicable only to elements with $Z \geqslant 4$), has a poor detection sensitivity, is not readily applied to insulators owing to surface charging problems, requires standards for comparison, and suffers from a negative effect due to the matrix sensitivity to impurities.

This technique is one of the most extensively used technique in the analysis of CVD film. The composition of films such as SIPOS, Si : SiO_2, Si : Si_3N_4,

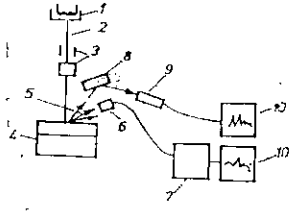

Fig. 9.4 X-ray microprobe:
1 — electron-beam source; *2* — electron beam; *3* — deflection plates; *4* — sample; *5* — X-rays; *6* — crystal detector; *7* — pulse-height analyser; *8* — crystal monochromator; *9* — X-ray detector; *10* — display (cathode-ray oscilloscope).

iO_2 [951], PSG, AsSG, Si_3N_4, AlN, Ta_2N, TaN, Al_2O_3, SnO_2 : Sb, SnO_2 : P, aAs, $Al_x Ga_{1-x}$ As, ZnSe and many others is easily determined.

Auger electron spectroscopy and scanning Auger microanalysis. Auger elec-on spectroscopy is an analytical technique used to determine the elemental mposition of the top of a surface (0—50 Å). It involves the measurement f the energy distribution of secondary electrons emanating from the sample. he secondary electrons are generated by bombarding the sample with a eam of primary electrons. Of interest in AES are only the secondary elec-ons generated in Auger transitions. The Auger electrons have specific ener-es that are characteristic of the atoms from which they originate. These ectrons produce small peaks in the secondary electron energy distribution id the measurement of the energy at which these peaks occur provides direct lentification of the type of atom producing them. Since the height of an uger electron peak is proportional to the number of atoms producing it, uantitative measurements can be made by calibrating the system [952—957].

The major components of AES equipment [Fig. 9.5*a*) include a primary ectron gun, an electrostatic cylindrical mirror system enclosed in a magnetic ield used to measure the energy distribution curve of the electrons ema-ting from the specimen surface, a carousel sample holder, a sample mani-ulator, a sputter ion gun used for depth profiling, an ultra-high vacuum

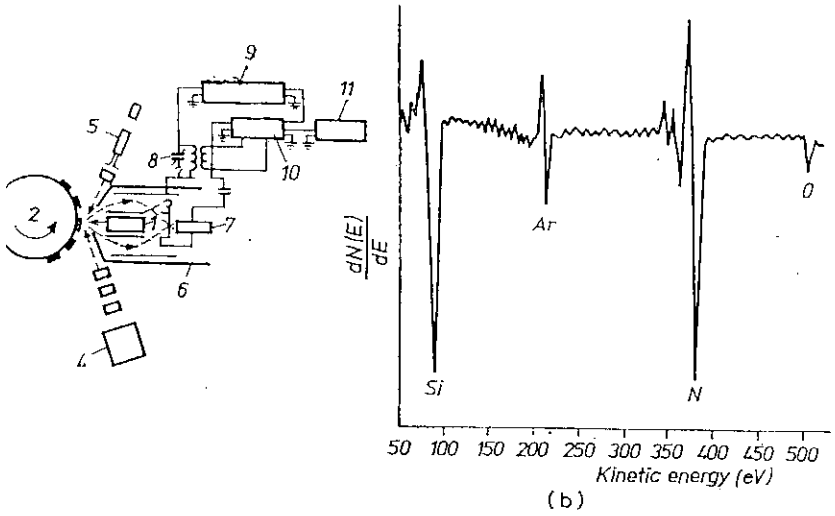

Fig. 9.5 AES analysis:

– schematic diagram of AES equipment (after Palmberg *et al.* [954]; reproduced by permission of Perkin Elmer—Physical Electronics Division):

– primary electron gun; *2* — carousel target holder; *3* — cylindrical mirror analyser; – sputter ion gun; *5* — electron gun; *6* — magnetic shield; *7* — electron multiplier; *8* — eep supply; *9* — X-Y recorder or oscilloseope; *10* — lock-in amplifier; *11* — multiplex control;

– AES spectrum of CVD silicon nitride film (after Wittberg *et al.* [936]; reproduced by permission of The American Institute of Physics).

system, and associated electronic equipment. The latter is composed of an electron multiplier, an oscilloscope, an $X-Y$ recorder, a system of standard modulation and phase sensitive detection electronics allowing electronic differentiation, as well as a multiplex control permitting in-depth profiles to be obtained for up to six different elements.

The output of the system, shown in Fig. 9.5*b*, is the energy distribution of the electrons, the curve $N(E)$. Because the Auger peaks are very small, the standard approach to data analysis is the derivative of the upper curve $\frac{dN(E)}{dE}$ obtained by electronic differentiation where the energy positions of the Auger transitions are defined as negative peaks in the spectrum.

AES is strictly a surface analysis technique because of the shallow escape depth of Auger electrons, which necessarily originate within approximately 50 Å of the surface. This technique is fast, nondestructive, free of matrix effects, capable of giving three-dimensional concentration profiles and extremely sensitive, allowing the detection of 10^{-14} g of an element, but can induce chemical changes in certain samples.

Scanning Auger microanalysis (SAM) [971] uses smaller electron-probe diameters and an electronic rastering circuit for obtaining area and line scans which provide concentration profiles within the plane of the surface for any selected element.

The method is fast, but its detection sensitivity is an order of magnitude lower than that of AES. When combined with ion sputtering, in-depth concentration profiles can be obtained.

Insulators, semiconductors, and conductors are easily analysed using Auger electron spectroscopy or scanning Auger microprobe analysis. The problems studied are the investigation of the chemical composition of the films, the width of the interface between insulator and semiconductor or metal in MIS structures as well as between two semiconductors in semiconductor heterojunctions, the distribution of dopants and impurities in insulating films, and interdiffusion between different layers. Representative examples are the determination of component ratios for *a*-Si: B, plasma Si_3N_4 [958—965], SIPOS [932], $Si_xO_yN_z$, ZnO, BN, SiO_2, ZnSe; the determination of trace contaminants, such as O in Si_3N_4 [963]:, Ga in SiO_2, $Si_xO_yN_z$, Si_3N_4, and $Al_xO_yN_z$ films [962] used as encapsulants for annealing implanted GaAs; the study of film interfaces, such as Si—SiO_2, Si_3N_4—SiO_2, Pd—*a*-Si: H [933], SiO_2—Al, Si_3N_4—Al; the study of the thermal, wet, or plasma anodization of III—V compounds (GaAs, GaP , InP, InAs, InSb, GaSb [966—968]; the study of various metal-semiconductor, metal-metal or epitaxial III—V compound interfaces [969]; and the evaluation of dopant profiles in semiconductor films, e.g. P profiles in P-doped *poly*-Si[970].

9.3.3 Techniques Based on Ion Interaction with Matter

Ion scattering spectroscopy (ISS). In this technique, the energy distribution of low energy ions scattered from the first atomic layer of the sample is measured. The mass of the scattering centre can be deduced from the energy of the scattered ion [972, 973].

An ion scattering spectrometer [974, 975] contains the following components mounted in an ultra-high vacuum system: a primary ion source, a target assembly, a charge neutralization filament, an electrostatic energy analyser and a channel electron multiplier.

The main advantages of ISS are that the composition of the outermost surface layer can be determined without resorting to sputtering (which is preferential and therefore results in the distortion of the composition of the underlying layers). It can analyse insulators without surface charging problems, yield the surface atom and impurity densities of semiconductor substrates and films, and determine the polar crystal orientation. Its main limitation is poor lateral and depth resolution. Application of ISS to the CVD field is limited to the surface analysis of silicon, the determination of polar crystal orientation (CdSe) [976], and the analysis of GaAs anodic oxide [977].

Ion-probe microanalysis (IPM). Ion-probe microanalysis is based on the sputtering process (the emission of neutral and charged particles from the surface region of a solid) by means of ion impact, which results in the production of secondary ions which are then mass analysed [978].

Ion probe microanalysers are grouped into two classes: direct imaging mass analysers [979, 980], and the scanning ion microprobes [981, 982].

The direct-imaging mass analyser commercially available from Cameca (Fig. 9.6) consists of a duoplasmatron for producing primary positive or negative ions, a system for focusing and deflecting the primary ion beam on the sample surface, the sample, an immersion lens for extracting and imaging the secondary positive and negative ions, a magnetic analyser and an electrostatic mirror for image mass analysis, a lens for image acceleration and projection, an imaging camera, an ion-to-electron converter, and a detector (fluorescent screen, ion counter or recorder).

The scanning ion microprobe available from ARL (Fig. 9.7) uses a duoplasmatron ion source, a ion mass spectrometer for mass selection, a focusing and rastering system for the primary ion beam, the sample, an optical system for extracting secondary ions, a double focusing mass spectrometer consisting of an electrostatic and a magnetic analyser, an ion detection system (ion image

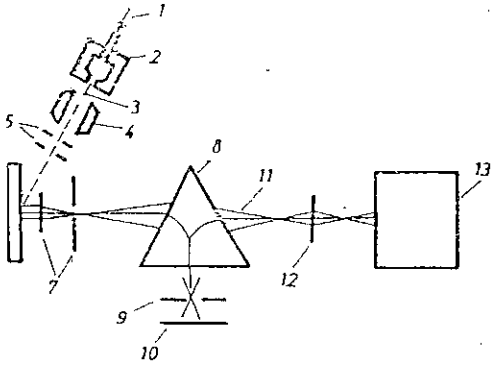

Fig. 9.6 Schematic diagram of the Cameca direct-imaging mass analyser (after Evans [978]):
1 — gas; *2* — primary ion source (duoplasmatron); *3* — primary ion beam; *4* — beam steering plates; *5* — beam focusing lenses; *6* — sample; *7* — ion lens and aperture; *8* — magnetic prism; *9* — mass resolving aperture; *10* — electrostatic mirror; *11* — secondary ions from sample; *12* — ion projection lens; *13* — ion image converter.

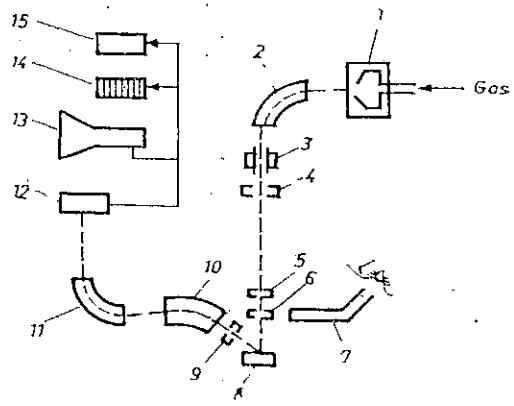

Fig. 9.7 Schematic diagram of the ARL scanning-ion microprobe (after Evans [978]):
1 — primary ion source; *2* — primary ion mass spectrometer; *3* — beam centering plates; *4* — condenser lens; *5* — deflection plates; *6* — objective lens; *7* — provision for viewing the sample; *8* — sample; *9* — secondary ion extraction optics; *10* — electrostatic analyser; *11* — magnetic analyser; *12* — ion detector; *13* — ion image; *14* — ion counter; *15* — recorder.

ger, ion counter or recorder), and provision for viewing the sample during bombardment.

Both secondary ion microanalysers have excellent lateral and in-depth resolutions, high sensitivity, high sample consumption, provide area and line scans of samples, and allow depth profiles to be obtained. However, they are destructive, very expensive, and the matrix effect is very pronounced; secondary ion yields are very different from element to element, making a quantitative evaluation of depth profiles difficult.

Ion-probe microanalysis has been applied only on a limited scale to CVD systems: the analysis of impurity distributions in homoepitaxial GaAs films, the study of the plasma oxidation of GaAs, and the study of depth profiles of B, P, and As ion concentrations implanted in silicon.

Secondary ion mass spectrometry (SIMS). This is based on the same principle (the emission of secondary ions under ion bombardment of solid surfaces) as in ion probe microanalysis, but the system is simpler and less expensive, having a poor lateral resolution, and a low sample consumption [983—987].

SIMS equipment consists of a primary ion gun, a sample manipulator, a secondary ion electrostatic analyser, and a quadrupole mass spectrometer, all mounted in an ultra-high vacuum envelope (Fig. 9.8).

The main advantages of SIMS are the following: the information depth comes from one monolayer, it can detect isotopes or compounds (by means of the molecular ions emitted), and hydrogen as well.

This method is used almost exclusively for measuring dopant and impurity distributions by sputter depth profiling in semiconductors. It has also been applied to the measurement of the transition width and the study of the distribution of contaminants in heterojunctions and superlattices. Other studies have been concerned with dopant and alkali impurities in the SiO_2/Si interface, thermal, plasma and anodic oxidation of GaAs and other III—V compounds, and metal contact films.

Typical CVD investigations include the impurity depth profiles and surface contamination of epitaxial and heteroepitaxial silicon [988], oxygen

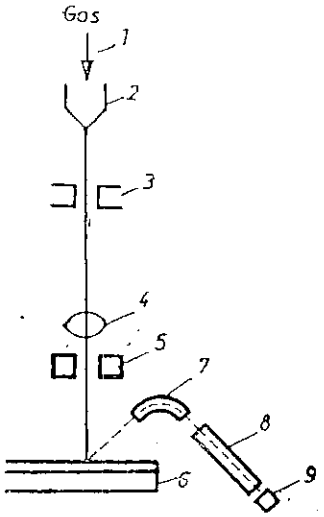

Fig. 9.8 Schematic diagram of a SIMS system (after Reuter and Baglin [986]):
1 — gas inlet; *2* — ion gun; *3* — mass analyser; *4* — Einzel lens; *5* — raster plates; *6* — sample; *7* — energy filter; *8* — mass spectrometer; *9* — secondary ion detector.

ontamination in epitaxial $Ga_{1-x}Al_xAs$ layers, the contamination of epitaxial emiconducting layers of GaAs and $ZnSiAs_2$ due to outdiffusion of Cr and a from Cr-doped semi-insulating GaAs substrates, the study of $Si_xO_yN_z$ yers on InSb substrates, the H profile in *a*-Si: H [989], BSG composion [990], the chlorine profile in silicon oxides prepared in HCl ambients 91], Si surface contamination [992, 993], and the composition of GaAs xides [994].

Glow-discharge mass spectrometry (GDMS). Recently proposed, this echnique is a combination of d.c. or RF glow discharge sputtering and mass pectrometry [995—998]. The sample to be analysed forms the cathode f the discharge, which is maintained in a rare gas such as argon and the onized sputtered atoms are monitored by means of a mass spectroeter. The instrument comprises three main parts: an ion source (a glow ischarge), an analyser (a high resolution mass spectrometer), and a detection ystem (two complementary detectors for high or low intensity signals). GDMS is a very sensitive method for determining trace elements and the omposition of thin surface layers of solids. An example is the detection of mpurity elements in GaAs epitaxial layers. Also, the stoichiometry of III—V ompound semiconductors can be determined by using this technique.

Glow-discharge optical spectroscopy (GDOS). This technique is a combiation of glow-discharge sputtering and optical spectroscopy [999—1002].

Neutral atoms ejected from the sample, which is mounted on the cathode f d.c. glow discharge, are collisionally excited and emit light of characteistic wavelengths. The intensity of an atomic emission line has been shown o be proportional to the elemental concentration in the sample. With appropriate calibration, monitoring the emission intensity as a function of time ields a profile of concentration versus depth.

The GDOS system contains a discharge chamber provided with a UV transmitting window and an impurity detection system consisting of a UV quartz lens, a double grating monochromator and a photo-multiplier tube. GDOS has been used to measure implanted and diffused impurities in silicon and to analyse various thin films.

9.3.4 Nuclear Techniques

Ion beam backscattering. Ion beam backscattering [1003—1005], also called Rutherford backscattering spectroscopy (RBS), is based on the energy loss of light ions (p, He) elastically scattered from atoms in the analysed sample. The equipment contains a particle accelerator, a magnetic analyser required to provide monoenergetic ion beams, a collimator, a target enclosed in a vacuum system, a detector (a surface barrier-type detector with an electrostatic or magnetic analyser), an amplifier and a pulse-height analyser (Fig. 9.9). The method is best suited to the nondestructive determination of the depth distribution of heavy elements in a light matrix, the accessible depth being about 1 μm. The major disadvantages of this technique are its poor sensitivity to trace amounts of light elements, its high cost, and the large space required.

Applications of this method to solid-state technology are the following: the investigation of implanted impurities and diffused dopants in substrates and films, trace impurities on surfaces, the analysis of dielectric layers such as SiO_2, Si_3N_4, Al_2O_3, Ta_2O_5, and the study of silicide formation in the metallization of silicon substrates. Typical CVD applications are the determination

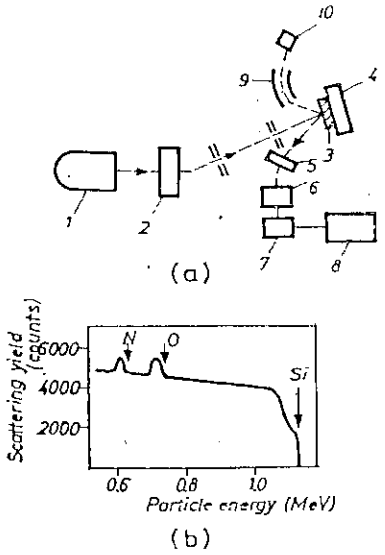

Fig. 9.9 Analysis using ion beam backscattering:
a — equipment: *1* — particle accelerator; *2* — ion beam magnetic analyser; *3* — target; *4* — current integrator; *5* — surface barrier detector; *6* — preamplifier; *7* — amplifier; *8* — pulse-height analyser; *9* — electrostatic analyser; *10* — ion detector;
b — backscattering spectra of silicon oxynitride on silicon. Inserted arrows indicate the energy of 2MeV He^+ ions backscattered from each element.

: the composition of Si_3N_4, $Si_xO_yN_z$ [1007, 1008] layers, the study of the anoization of Si_3N_4 and Al_2O_3 films on Si [1009], the investigation of the interction of Al and *poly*-Si layers [1010], the analysis of the distribution of imanted ions in SiO_2, Si_3N_4 and Al_2O_3 layers used as encapsulants for GaAs ıbstrates [1011], the depth profiling of residual chlorine in SiO_2 grown or ?posited in HCl-containing ambients [1006], and the evaluation of *a*-Si density [1012].

Nuclear reaction analysis. In nuclear reaction analysis [1013], the energy the bombarding ions (usually protons) can be varied in such a way that ıe energy required for a nuclear reaction with a sharp resonance in the oss section is reached at a given depth. The intensity of the emitted signal ısually γ-rays) is monitored as a function of the bombarding ion energy, ıus providing the concentration of the bombarded atom versus depth.

An exemple is the ^{19}F (^1H, $\alpha\gamma$) ^{16}O nuclear reaction which is used for easuring hydrogen in CVD films such as Si_3N_4 [1014, 1015]. For this reacon, ^{19}F incident on ^1H results in α-particle and X-ray emission and leaves sidual ^{16}O nuclei. By using an ^{19}F beam with energy greater than the resoance energy ($E > 6.4$ MeV) incident on the target, the ions lose energy until some depth in the solid their energy is equal to the resonance energy .4 MeV). At this energy and at the corresponding depth there is a large oss section for resonant nuclear reaction between the ^{19}F and ^1H. Measurment of the yield of the γ-rays produced versus energy therefore gives the ydrogen concentration versus depth (Fig. 9.10).

The main advantages of this method are its ability to detect low Z conminants in hosts of high Z and to distinguish isotopes, the accesible depth eing about 1—5 μm. Its limitations include generally poor depth resolution

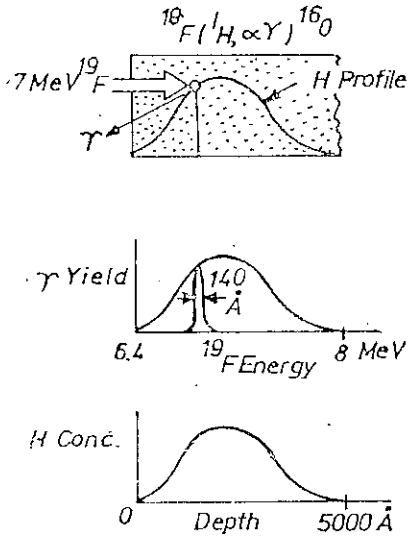

Fig. 9.10 Schematic illustration of nuclear reaction analysis of hydrogen in solids (e.g. Si_3N_4) using the ^{19}F (^1H, $\alpha\gamma$) ^{16}O resonance near 6.4 MeV (after Peercy *et al.* [1014]; reprinted with permission from JOURNAL OF ELECTRONIC MATERIALS, Vol. 8, pg. 11, 1979, a publication of The Metallurgical Society, Warrendale, Pennsylvania).

(except in cases with sharp resonances) and its application is restricted to low Z elements.

Nuclear reactions such as ^{16}O (d, p) ^{17}O and ^{14}N (d, α) ^{12}C have been used to measure the total amounts of oxygen and nitrogen in $Si_xO_yN_z$ films. Another resonant nuclear reaction (^{15}N (p, $\alpha\gamma$) ^{12}C) has been applied to the quantitative H profiling of plasma-deposited $Si_xN_yH_z$ and *a*-Si: H.

9.4 Film Composition Measurement

The importance of determining the composition of a CVD film arises from the following reasons:

(1) the properties of many nonelemental or multicomponent CVD films may depend on composition; (2) films of dissimilar composition may be deposited in different deposition system under identical deposition conditions; (3) films deposited by some CVD techniques such as PECVD are nonstoichiometric and have variable stoichiometry; (4) it is desirable to understand in detail processes involving CVD films. As already mentioned, the composition may be determined by using the methods of bulk and thin film analysis such as XRF, XPS, EPM, AES, SIMS, RBS, and the nuclear reaction technique. But, it is more convenient to ascertain the film composition by using a simple, rapid and nondestructive determination which is provided by optical methods, such as infrared absorption spectroscopy, Fourier transform infrared spectrometry, multiple internal reflection infrared absorption spectroscopy, attenuated total reflection infrared spectroscopy and UV and visible optical absorption spectroscopy. Also, the etch rates of a CVD film (especially a glass) in selective etchants have proved to be a useful means of determining film composition, all the more so as little instrumentation is required. However, this method is destructive and complicated, since the etch rate strongly depends on the specific preparation conditions. A typical example is the determination of phosphorus concentration of CVD PSG. The tedious and expensive techniques (neutron activation, electron microprobe, XRF, etc.) can be replaced by various fast and inexpensive techniques, such as the gravimetric, infrared spectrometry, etch rate variation, and diffusion techniques [917, 4138].

It has been proved that composition determinations based on IR absorption spectra are useful in the case of vapour-deposited borosilicate [1016, 1017, 4185], phosphosilicate [1018, 1019] and arsenosilicate [1020, 4191] glasses. FTIR can be used to determine the P concentration of reflow and passivation glasses [925]. Optical absorption [1021] and MIR [1022, 1023] spectroscopy enables the N—H and Si—H bonding in CVD Si_3N_4 to be measured. ATR spectra of $Si_xO_yN_z$ films deposited on Si exhibit several bands which may be related to N, O, and H in the films [1024]. The position of a defined optical absorption edge in the near UV and visible spectra can be useful for measuring the Si/N ratio as well as the thickness of glow-discharge deposited Si_3N_4.

9.5 Depth Concentration Profiling

Methods used for the measurement of elemental concentration as a function of depth (depth concentration profiling) have increased in importance for the measurement of microelectronic structures [1025—1029].

Depending on whether the removal of sample surface is required or not, depth profiling methods can be regarded as destructive or nondestructive. Destructive methods rely on the removal of the surface by using a mechanical (small-angle lapping, ball cratering), chemical (chemical dissolution, anodic sectioning), or sputter etching [1027] procedure. In all destructive methods, either the remaining sample surface (neutron activation analysis, Auger electron spectroscopy, scanning Auger microanalysis, X-ray photoelectron spectroscopy, ion scattering spectroscopy), or the removed material (secondary ion mass spectroscopy, glow-discharge optical spectroscopy, glow-discharge mass spectroscopy) is investigated. In nondestructive methods, the sample interior is probed by means of a penetrating ion or electron beam. Depth information is obtained from either the energy loss of ions (Rutherford backscattering spectroscopy — RBS, nuclear reaction analysis) or the attenuation of the electron signal by varying the take-off angle of electrons with respect to the sample surface (AES and XPS).

Sputter sectioning (i.e. sectioning caused by the emission on ion impact of neutral and charged particles from the surface region of a solid) has become the most important method of sectioning for depth profiling. Its main advantages are simplicity, speed, and the possibility of performing sectioning and analysis in the same high vacuum environment. However, there are many inherent negative factors depending on the instrumentation, the sample, the ion beam, and the method of analysis. The measurement of a sputter depth profile means recording a signal versus time which is then converted into concentration as a function of depth. Sputter depth profiling has been extensively applied to the measurement of elemental distributions in substrates, films and interfaces (such as dopants and impurities in semiconductors), the study of the insulator/semiconductor and insulator/metal interface, the measurement of metal films, and the study of the metal/semiconductor and metal/metal interface.