INFRARED SPECTROSCOPY AS ANALYSING TOOL FOR MATERIALS USED IN MICROELECTRONICS
2. Thin films

Marta Klanjšek Gunde

National Institute of Chemistry, Ljubljana, Slovenia

Abstract: The application of infrared spectroscopy to analyse thin solid films used in modern technology devices has been reviewed. A variety of problems related to chemical bonding and morphology are possible to solve for amorphous, polycrystalline, and crystalline films as well as for low-dimensional structures. Determination of the sort and amount of dopants is now routinely applied to control the technological process. Together with relevant scientific hypothesis and with others appropriate characterisation methods, infrared spectroscopy may be efficiently used in research and development in material science.

Uporaba infrardeče spektroskopije pri analizi materialov za mikroelektronsko industrijo
2. Tanke plasti

Povzetek: Članek predstavlja pregled uporabe metod infrardeče spektroskopije za analizo tankih plati, ki se uporabljajo v modernih tehnologijah. Mogoče je rešiti različne probleme, ki so povezani s kemijskimi in strukturnimi lastnostmi v amorfnih, polikristalnih in monokristalnih tankih plasteh, pa tudi v strukturah s kvantnimi dimenzijami. Določanje vrste in vsebnosti dopantov se že rutinsko uporablja za spremljanje in morebitne korekcije v tehnološkem procesu. Z ustreznimi znanstvenimi hipotezami in skupno z drugimi analiznimi metodami lahko infrardeča spektroskopija nudi odlično pomoč praktično na vseh nivojih raziskav in razvoja materialov.

I. INTRODUCTION

In this paper the application of infrared (IR) spectroscopy to analyse most frequently used microelectronic materials is considered with special attention to the recent literature. In the first part, the semiconductor substrates were discussed /1/. In the second part (present article), IR spectroscopy of thin solid films deposited or formed on such substrates is reviewed. The literature published in 1990 and later is considered mostly.

Thin films are one of the crucial components of the microelectronic and other modern technology devices. To ensure high yield of devices, the films must satisfy a large set of chemical, structural, and electrical requirements. Film composition and thickness have to be strictly controlled. Defects and imperfections present in these films are critical for small device geometries, therefore their densities have to be low. Excellent adhesion, low stress, conformable step coverage, and appropriate surface topography are demanded /2/. A large variety of films are used for this purpose. They can be metals, semiconductors, or insulators. They may be crystalline, polycrystalline, or amorphous. They may have high density or they may be porous.

The formation of such films is accomplished by a large variety of techniques that can be divided into two groups: (a) film growth by interaction of a vapour-deposited species with the substrate material; and (b) deposition of film without causing changes to the substrate. The first category includes thermal oxidation and nitridation of single crystal silicon, formation of silicides by direct reaction of a deposited metal and substrate /2/, as well as electrochemical etching that forms porous layers (e.g. porous silicon, /3/). The second group includes three subclasses: chemical vapour deposition (CVD), physical vapour deposition (PVD) and coating of the substrate with liquid, which is then dried to form the solid thin film. By the CVD process single crystal thin films (epitaxy), amorphous, or polycrystalline films may be formed. The PVD includes sputtering, evaporation, and molecular beam epitaxy (MBE). For the coating of substrate with liquid, most common the spin-coating technique is applied /2/.

The crystallographic structure of prepared thin films can vary from a highly disordered (amorphous) state to a well-ordered (e.g. epitaxial growth on a single crystal substrate). Dielectrics are frequently observed in amorphous state, while most metals result in polycrystalline structure. Silicon films can be amorphous, polycrystalline, or single crystal, depending on the deposition temperature and on the substrate material /2/.

The properties of thin films are closely related to their chemical composition, material structure, order, and method of preparation and may be substantially different from those of the corresponding material in bulk. For extensive characterisation of films, a non-destructive method is desired to apply. Such demands are fulfilled by optical techniques. Among them, IR spectroscopy is potentially the ideal one for characterising thin films. It is especially essential if the nature of chemical bonds at the surface or at some interface have to be understood, where any sample preparation may induce serious artificial effects.

IR spectroscopy has been used to solve a variety of structural problems for amorphous, polycrystalline, and crystalline films and to investigate the dependence of the film structure upon the deposition parameters. The greatest volume of work was performed for silicon and silicon-containing films /4-7/.

II. THEORETICAL BACKGROUND

The spectroscopic characterisation of thin solid films and surfaces includes analysis of their chemical composition, concentration of impurities, film thickness, or/and concentration profiles. For conducting layers the properties of free electrons or holes in some cases can be determined also. The analyses are based on spectroscopic measurements of the contribution of vibronic excitations and of free carriers to the dielectric properties of the sample: the frequency dependent dielectric function includes informations about molecular vibrations and about conduction electrons. IR spectroscopy is used mainly for films that contain metal-hydrogen or metal-oxygen bonds that absorb in the mid IR spectral region. Structures of films with metal-hydrogen or metal-metal bonds or heavier oxides have IR absorptions that fall in the far-IR and can be studied by far-IR spectroscopy and Raman spectroscopy.

The goal of the successful spectroscopic analysis is to apply the optimised optical conditions of the sampling technique to obtain unambiguous data also on very thin films or on multilayered structures. Therefore, many diversified techniques to observe spectra for many configurations of the sample have been developed. Polarised and unpolarised beams may be applied with optionally chosen incidence angle. The interpretation of obtained spectra has become more and more complex especially if extracted data are expected to be very precise and as complete as possible. Samples required in modern technology applications usually include silicon in monocrystalline, polycrystalline, or amorphous forms. Their high refractive indices cause a considerable reflection of the IR beam on each surface boundary. In thin films ($d \approx \lambda$) the observed spectral features are not only due to the nature of the dielectric function, but

interferences of the partial waves reflected at the surface and/or interfaces of the layers also occur. The so-called Fabry-Perot fringes carry informations about optical constants and thickness of the layer. The interference fringe patterns obscure the baseline, impede detection of weak peaks, and alter the intensity. The broad region where anomalous dispersion in refractive index of dielectric materials takes place, shifts the position of IR absorption bands and additionally changes their shapes and intensities. All effects act simultaneously and cause strongly pronounced optical effects in IR spectra of such samples. It is well known that optical theory can predict or eliminate these effects from certain spectra /8-11/.

III. SAMPLING TECHNIQUES

A variety of techniques are available for obtaining IR spectra of different thin solid supported films. The choice of sampling technique depends on the type of the sample and on the information desired from the analysis. In the following, some more pertinent techniques for thin film analysis are described briefly. Essentially the same techniques are used as described in the previous paper /1/. To apply them on thin films and multilayers, some modifications have to be done.

III.1. Transmission

The transmission experiment is the most familiar to anyone who uses IR spectroscopy on a routine basis. During measurements, the light passes through the sample, and its absorption from the entire thickness of the film (multilayer, superlattice) and of the substrate is measured.

The substrate must be transparent or low-absorbing so that a portion of light lost due to absorption and/or scattering on them is small. Typical substrates for transmission work in the mid IR spectral region are polished crystal discs made of alkali halides (e.g. KBr, NaCl, KCl). For the modern technology applications it is of much importance, that low-level doped silicon and GaAs slices are also suitable for this purpose.

Transmission studies are used for dielectric films with thickness on the order of μm that have been deposited on transparent or semitransparent substrates. The thickness restriction is due to overdamping of intense absorption lines.

Routine quantitative analysis of transmittance spectra of thin supported films are made from their negative logarithm (i.e. absorbance spectra). The intensity diminish due to absorption in the substrate is account for by subtraction of the corresponding absorbance spectrum (Figure 1). It is assumed that the absorption bands in the so obtained spectrum are proportional to the absorption coefficient of respective vibration, concentration of the corresponding species, and optical path length (Beer-Lambert law). The approxima-tion neglects the effects of refractive index as well as all optical effects. It is routinely used for organic materials where absorptions are small, although some errors are still introduced. In precise work especially with inorganic

materials, the more complex analytical methods of chemometrics have to be applied /6/. Another possibility is to apply optical theories to account for optical effects that are strongly pronounced in spectra of these samples /8,9,11,12/. In some situations this is the only way to minimise the error of quantitative analysis.

$$T_s = \frac{I_s}{I_o} \qquad A_s = -\log(T_s)$$

$$T_{sl} = \frac{I_{sl}}{I_o} \qquad A_{sl} = -\log(T_{ls})$$
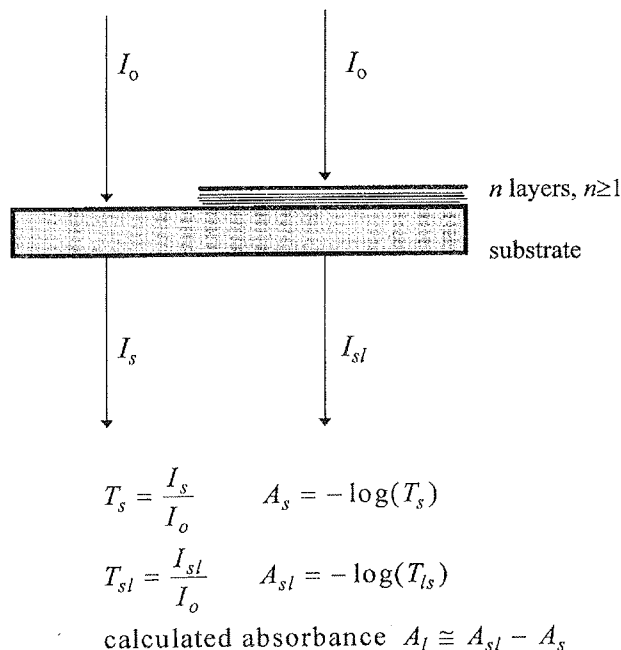
calculated absorbance $A_l \cong A_{sl} - A_s$

Figure 1. Normal incidence transmittance (T) measurement of the substrate (index s) and of n layers deposited on them. Absorbance (A) of the unknown layer (index l) is obtained by subtraction of the corresponding data for the known composition. Example for one layer (n=1).

In spite of all sorts of problems, the most simple transmission technique is very important. Before the extensive use of computers, the studies reported in the literature were done more or less only by the simple transmission measurement and even today studies using this approximate method are often reported. It is used especially to identify the basic chemical composition of the film. Many times it is the most convenient method to follow the changes in sample materials after some process (e.g. thermal annealing) qualitatively. By this procedure, very recently some small changes in spectra of superlattices were measured /13, 14/.

III.2. External reflection

When a one- or multilayered structure is deposited on a reflective substrate, the reflection of the IR beam from the sample may bear worthy information about its optical properties. If the incident and reflected beams lie outside the sample, the method is called the external reflection. Due to high refractive indices, silicon as well as III-V compound materials have considerable reflectance even in low-level doped form. Increasing doping, the reflectance of slices is increased further. Therefore,

the semiconductor substrates are appropriate reflective substrates for external reflection spectroscopy to be performed. Additional possibility to apply external reflection for thin films analysis are the metal layers used in various types of MOS devices. For the impinging light, these layers act as reflecting mirrors. For that reasons, the external reflection is relevant analysing method for most films used in microelectronic industry.

There are many ways to measure the external reflection of thin solid supported films. All of them measure the specular reflectance obeying Snell's laws. Optionally polarised beam impinges on the sample at a certain angle. The radiation passes trough the sample until it reflects on the reflective surface somewhere inside the sample. Then, the beam returns trough the sample towards the detector (Figure 2.). By increasing number of reflections on the upper surface of the sample, the sensitivity of measurement can be further increased (see /1/, Fig. 5.).

For films thicker than the wavelength (2.5 - 25 μm for the whole mid IR), the intensity of the reflected light is similar to that of the transmitted light trough the sample with an twofold effective pathlength. In such cases the term reflection-absorption spectroscopy (RAS) is usually used to describe the experiment.

For thinner films, the absorption of the radiation inside the sample will be strongly influenced by the reflecting surface, by the polarisation of the incoming radiation, by the incident angle, and by the orientation of dynamic dipoles inside investigated material with respect to the reflective surface. The polarisation of the incoming radiation influences the intensity of absorption. Most intensity is collected in the component that is polarised parallel to the plane of incidence, whereas the contribution of the perpendicular component is very small. The absorption of light inside thin film reaches its maximum when the incident angle is about equal to the Brewster's

$$R_o = \frac{I_s}{I_o} \qquad R = \frac{I_l}{I_o}$$

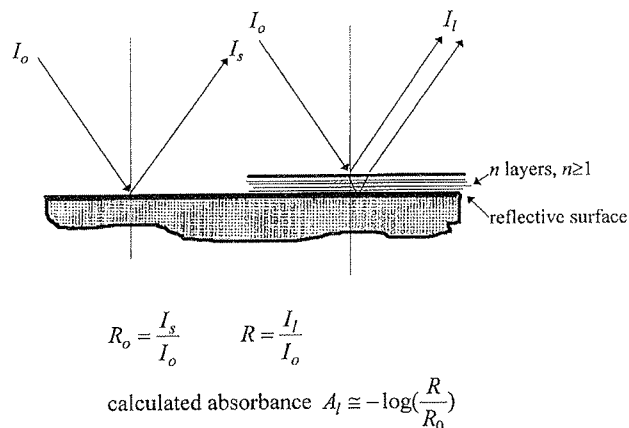calculated absorbance $A_l \cong -\log(\frac{R}{R_0})$

Figure 2. External reflection measurement of substrate (index s) and layers deposited on them (index l). Any incident angle and polarisation of the incident beam may be applied. Absorbance of the unknown layer is obtained as negative logarithm of layer reflectance that was normalised by the reference reflectance.

angle for the reflective material. For metals, this angle is very large (~90°), whereas for silicon smaller incidence angle is preferable (~60°). The largest angle that can be obtained experimentally, is about 85°. When the experiment is performed at this largest angle, the term near grazing incidence angle reflection spectroscopy (NGIA) is used.

External reflection spectroscopy of molecules that were adsorbed on metal surface was formulated 30 years ago /15/. It gained full advantage of increasing sensitivity by parallel polarisation and near grazing incidence angle. The experimental conditions together with the optical consideration of the three-phase system leads to the so-called metal surface selection rules that can be used to determine the orientation and molecular ordering at the surface /16/. A small blue shift of the adsorbate band maxima respect to the corresponding bands in transmission was thought to be due to optical effects inherent in the experiment.

For inorganic thin films, that are extensively used in modern technologies, the most important is the so-called "Berreman effect" /17/. He made an experiment with very thin (<2 μm) crystal films, deposited on metallic substrates. The component of the beam polarised normal the film (parallel to the plane of incidence), causes absorption bands at frequencies of the zeros of film dielectric function. These are the frequencies of the longitudinal optical (LO) polar modes. They depend strongly also upon intrinsic material properties, e.g. the effective charge and mass of all species participating the corresponding mode, dielectric properties of the surroundings etc. /18/. The Berreman effect is an macroscopic phenomenon of electrodynamics and offers the possibility of an precise analysing tool for very thin dielectric layers. However, the interpretation of the results is substantially different from measurement in transmission. In polar materials the band frequencies appearing in both experimental configurations are much apart so that the difference can not be described as a "small blue shift" as it is relevant for organic adsorbates. Furthermore, only some factors affecting absorption frequencies obtained in transmittance and in external reflection of parallel polarised light are the same. For all these reasons, the full understanding and interpretation of measured spectra also for thicker layers, other polarisation, incidence angles and substrates was not performed until recently when various spectral simulations with extensive computer support were accomplished /19-21/.

III.3. Internal reflection

In internal reflection spectroscopy, the incident radiation is reflected from the interface between a material with higher refractive index and a material with lower refractive index as shown in Figure 3. The higher refractive index material is called internal reflection element (IRE) and is cut to a specific geometry. In microelectronic applications, the semiconductor sub-strate (low-level doped silicon or III-V compound materials) usually represent an IRE. The material to be sampled (single layer or layered structure) is coated directly on IRE.

For total internal reflection, the incidence angle must exceed the critical angle. In this circumstances, the lower refractive index material is probed by that portion of radiation (called the evanescent wave) that passes trough the boundary of the IRE crystal surface. The evanescent field is characterised by refractive indices of the two materials, incident angle, state of polarisation, and upon the wavelength of the beam in the IRE crystal. However, the decay of this field inside the optically rarer medium (its penetration depth) is independent upon the polarisation. The obtained spectrum is similar to a transmission spectrum. The method is often called attenuated total reflection (ATR).
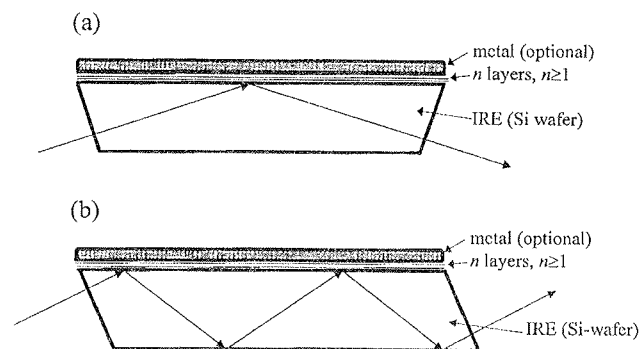

Figure 3. Internal reflection experiments with one reflection (a) and two reflections (b). For more experimental configurations, see /1/, Fig. 6.

Internal reflection spectroscopy is especially useful for films that are too thin for the spectrum to be measured in transmission. In microelectronic and photovoltaic systems as metal/oxide/semiconductor (MOS), metal/Si-nitride/oxide/semiconductor (MNOS), and metal/insulator/semiconductor (MIS) are of interest. In those systems a very thin oxide interlayer between M and S has to be characterised. In an IR experiment, the interlayer is illuminated via polished areas of the border of the Si-wafer that acts as an IRE (Fig. 3). In the oxide film, absorption of the IR light due to vibronic resonances is only possible for p-polarisation (parallel polarisation) where it is still amplified by the metal film (M). By this configuration, the 1.3 nm thick oxide on silicon within a MIS structure was measured /22/ (see also Fig. 3).

Various experimental configurations of internal reflection spectroscopy appearing in the recent literature /23-25/ are essentially ATR experiments. Among them, there is also excitation of surface polaritons, called also surface electromagnetic waves (SEW). The echo from the back of the thin layer can be avoided by residual vacuum gap of nm range between a sample and IRE (Otto geometry). The later method is not always possible to perform.

By the ATR measurements, the optical depth of the material may be profiled. The method makes use of angle-dependent penetration depth of evanescent wave /26/. The procedure represents one possibility to detect and analyse the depth-dependent composition of films.

IV. EXAMPLES

A large variety of films used in modern technologies represent relevant measurable samples for IR spectroscopy. Metal layers can not be analysed but they may play an important role in using some of the reflection techniques. All other type of films can in principle be analysed in terms of their intrinsic properties such as chemical composition, structure, order, free charge carriers, thickness, etc.

The examples of IR spectroscopy application for thin films are divided in representative groups as epitaxial layers, silicon oxide films, silicon nitride films, amorphous silicon, various glass-type films, other films, multilayers, heterostructures, and superlattices.

IV.1. Epitaxial layers

Epitaxial layers are grown on a surface of a single crystal substrate whereas its crystallographic orientation is retained. Therefore, epitaxial layer is an extension of a substrate. In homoepitaxial layers, the layer and the substrate are the same material such as silicon on silicon. Heteroepitaxial layers are made from different materials, such as silicon on sapphire or mercury-cadmium-telluride on cadmium telluride /27/. The most interesting property of epi-layers is that they can be doped to a different extent than the substrate.

Most epi-layers used in production environment are produced by CVD process involving silane halides, whereas MBE growth technique is used mostly for the research and development. Many factors of a finished devices depend upon the exact thickness of the epi-layer involved. The measurement of epi-layer thickness by the IR interference method is known from 1961 by Spitzer and Tanenbaum /28/ where the basic requirements for the interference fringes to be seen in the external reflection spectrum are defined. There has to be a suitable spectral range in which the epi-layer is transparent. Provided that on the interface between the epi-layer and the substrate the impurity concentration suddenly changes, the incident radiation will be reflected both at the surface of the epi-layer and at the interface. Since the waves transverse the layer, these so-called Fabry-Perot fringes carry information about layer thickness as well as about its optical constants. The onset of the fringes will occur at a wavelength governed by the carrier concentration of the heavily doped substrate. The spectra are measured by external reflection technique using unpolarised IR beam at normal incidence /27, 28/. To increase the sensitivity of the method, oblique incidence of polarised beam may be applied /5/.

For the method to be applied for homoepitaxial Si layers, the substrate resistivity has to be less than 0.02 Ωcm (at 23°C) and the resistivity of the epi-layer more than 0.2 Ωcm (at 23°C). In these circumstances, the technique is capable of measuring the thicknesses of both n- and p-type layers greater than 2 μm thick. With reduced precision the technique may also be applied to both n- and p-type layers from 0.5 to 2 μm thick. The external reflection spectra of some homoepitaxial Si layers are shown in Figure 4.

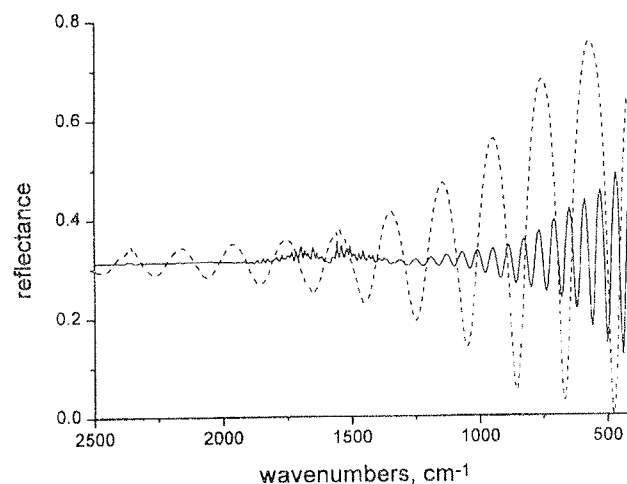Figure 4. External reflection spectra of two silicon homoepitaxial layers.

full line: substrate: 0.015 Ωcm, Sb-doped, n-type,
epi-layer: P-doped, n-type, 1-6 Ωcm, measured thickness 23.4 μm

dashed: substrate: 0.002-0.004 Ωcm, As-doped, n-type,
epi-layer: P-doped, n-type, 2.0-2.4 Ωcm, measured thickness 7.2 μm

By the same technique, the thickness of the heterostructures of III-V semiconductors epitaxially grown on GaAs substrate were measured. Simultaneously, the diffusion profile in epitaxial Si-layers were studied /5/.

IV.2. Silicon oxide films

Silicon oxide films are one of the most crucial films for the microelectronic industry. Their ability to form highly passivating, stable, and insulating films represents the basis for planar processing of silicon integrated circuits.

Silicon oxide is the simplest form of glass and appears also in most mixed glasses. Therefore, the study of its properties may help in understanding the whole group of materials. Silicon oxides fabricated in the laboratory condense into amorphous solids noted by SiO_x. If $x=0$ we have amorphous silicon and if $x=2$ the silicon dioxide was formed. The structure of amorphous layers compose of statistical mixture of $Si-(Si_yO_{4-y})$, $y=0,1,2,3,4$ tetrahedra. The final structure represents a three-dimensional random network where some of the tetrahedra joins to each other by an oxygen ion. This ion is called bridging oxygen and is shared between two touching polyhedra. In the crystalline SiO_2, all oxygens are bridging oxygens. The greatest the ratio of bridging to non-bridging oxygens in amorphous form, the better the cohesiveness of the glass /2,29/.

IR spectra of silicon oxide films can be obtained as absorbance spectra recorded in normal incidence transmission (see Figure 1). As deposited silicon oxide films are different by the stoichiometry, as well as by the porosity and bonded impurities. In Figure 5, absorbance spectra of thermal oxide and of two differently

formed CVD silicon oxide layers are shown /30/. Beside strongly pronounced vibration of bridging oxygen in SiO_4^- random network tetrahedra, also vibrations due to other species in films (e.g. SiOH, Si_2O_3, H_2O) are obtained. By thermal annealing at temperatures above 800°C for 10-15 min, densification of layers is complete and absorbance spectra of all silicon oxide films are indistinguishable from each other and from the thermal oxide which is SiO_2 /30/.

This simple form of IR analysis was frequently used to study the properties of various silicon oxide films /31,32/ also if they were very thin /33,34/. For precise analysis and to extract more data from measured spectra, optical effects have to be taken into account /35,36/. Applying optical analysis it was shown that the position of absorption peak due to asymmetrical stretching vibration of Si-O-Si bond may acts as an detector of differences among films: increasing the annealing temperature yields to stronger bonds in the oxide structure /37,38/.

To increase the sensitivity for very thin films (d<100nm), oblique incidence angles or some of the reflection techniques using polarised IR beam may be applied. This way the structural nature of the Si/SiO_2 interface was studied /39-43/. These analyses are important to understand the properties of the so-called conduction channel formed at this interface.

IV. 3. Silicon nitride films

In recent years, special attention has been devoted to the use of silicon nitride in semiconductor device technology, since it can be used safely for interlayer isolation, device passivation, and mechanical protection /44/.

The most important method to produce silicon nitride thin films is plasma-enhanced CVD (PECVD) that enables the formation of thin film dielectrics at low temperatures (200-500°C). PECVD silicon nitride films tend to be nonstoichiometric what is chemically represented as $Si_xN_yH_aO_b$ with a and b being much less than x and y. The IR absorbance spectrum of such film obtained by transmission measurement (see Fig. 1) is represented in Figure 6. The main absorption region (750-950 cm^{-1}) is dominated by the antisymmetrical stretching mode of the Si-N-Si molecular group. The symmetrical stretching of the same molecular group leads to the much smaller band at 490 cm^{-1}. An appreciable amount of hydrogen in the form of Si-H and N-H bonds is recorded at 2170 and 3340 cm^{-1}, respectively. A small band due to Si-O vibration is found at 1160 cm^{-1}.

The changes in position, shape, and intensities of absorption bands were observed at various preparation ways as well as after heat treatments. These changes are possible to relate to the properties of local environment of the constituent atoms and hence to the molecular structure of the layer. Such data may lead to conclusions about important intrinsic properties as follows: stoichiometry, identification of densification or structural loosening of the film, passivating the dangling bonds of silicon and nitrogen (these are the principal source for the localised gap states), reduction of mechanical strain within the network etc. /44/. The studies may be performed applying the normal incidence transmission /45/ or some of reflection techniques /46, 47/.

The ultrathin silicon nitride film (0.4<d<4 nm) deposited on a top of 1.3 nm thick silicon oxide film thermally grown on crystalline silicon was analysed. For this purpose, the internal reflection at grazing incidence (due
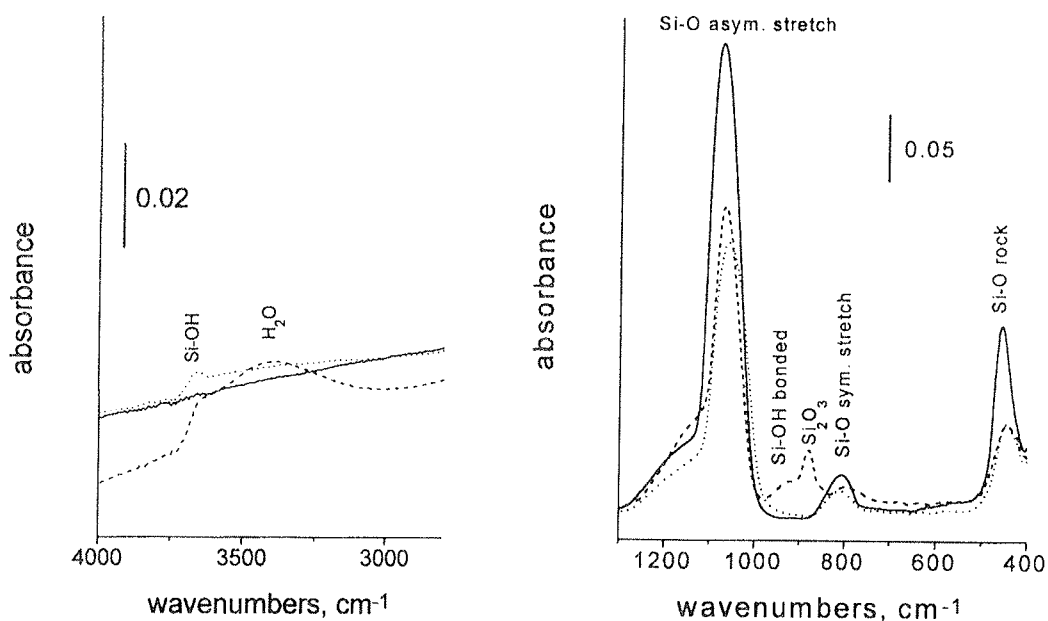

Figure 5. Absorbance spectra of as-deposited silicon oxide films formed by thermal oxidation (full line) and by CVD process (broken line, points). Thermal oxidation was performed in the diffusion owen at 750°C, the deposition rate was 0.19 nm/min and the layer thickness obtained is 114.4 nm. Data for CVD oxides: broken line: $O_2:SiH_4=1.5$, deposition at 160°C, 3.5 nm/min, final thickness 221.2 nm; points:$O_2:SiH_4=3$, deposition at 355°C, 20.1 nm/min, final thickness 168.1 nm

to metallized rear side) was applied to analyse the vibrational properties of the sample. During the direct-plasma-enhanced CVD of nitride film, the ultrathin silicon oxide layer changes due to ion bombardment. Applying the remote-plasma-enhanced CVD, this damage process did not occurre /46/.
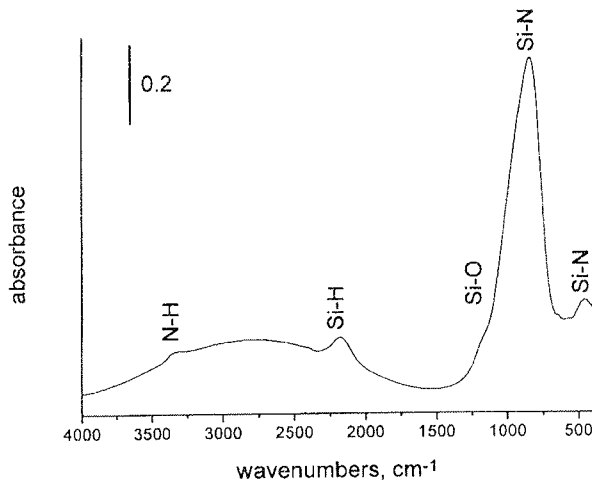

Figure 6.   Absorbance spectrum of PECVD silicon nitride film. A radial flow reactor operating at 300°C was used. Reactant gasses were N_2, NH_3, and SiH_4 at gass flow rates of 735, 405, and 173 cm^3/min, respectively. The film thickness is 0.945 µm. The spectrum was obtained by the normal-incidence transmis-sion method. The origin of absorption lines is noted in the figure. The broad absorption is due to interference in the film.

The resist pattern deformation in chemical amplification resists on SiNx layers were observed. Applying the ATR technique, the Si-OH surface groups were found to cause the pattern deformation /47/.

One of the most interesting publication is the analysis of silicon nitride which forms occasionally and can not be etched in concentrated HF. The authors analysed the 10 µm diameter nitride spot. By the help of IR spectroscopy, they were able to conclude, that this unintentionally formed etch-resistant silicon nitride has the crystalline structure /48/.

The results obtained from IR spectra may be defined precisely if optical effects were taken into account. It is well known that these effects may change the position, intensity, and shape of absorbance lines in spectra of thin films. The most prominent are changes due to film thickness /9/. Optical analysis of silicon nitride /49/ and silicon oxynitride /50/ films can be found in the recent literature.

IV.4. Amorphous silicon films

IR spectroscopy can be used to study a variety of problems related to chemical bonding and morphology in amorphous silicon films. In crystalline films, absorption bands are sharper and more resolved. Some of them may split due to crystalline phase. In most work,

the main region of interest is incorporation of hydrogen. There are several IR absorptions caused by hydrogen in amorphous silicon. An example is shown in Figure 7. These bands enables an insight into homogeneity, morphology, long-term stability, structural defects etc. Among all absorptions appearing in the absorbance spectrum of hydrogenated amorphous silicon, the most frequently studied spectral region is 2200-1800 cm^{-1} where the silicon-hydrogen stretching vibrations occur. This way the source of light-induced changes in the optical properties of hydrogenated amorphous silicon were measured. These changes are one of the key properties that determines the durability of solar cells made of amorphous silicon. On the basis of the silicon-hydrogen stretching vibrations measured by ATR method, a reversible shift in the Fermi level after light illumination for 38 hours was observed /51/.
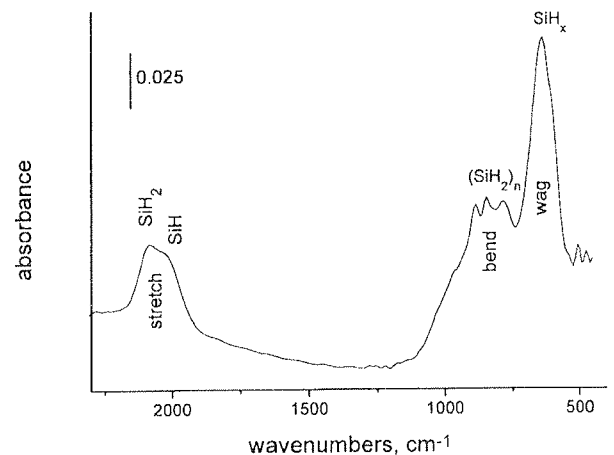

Figure 7.   Absorbance spectrum of amorphous hydrogenated silicon film. ~300 nm thick film was prepared by magnetron sputtering.

Very recently, nucleation of amorphous hydrogenated silicon on the H-terminated surface of crystalline silicon was monitored by in situ near normal transmission spectra (11° incidence angle) /52/. The film thickness was measured simultaneously by the quartz crystal microbalance. For layer thickness from 4 Å up to 150 Å, the evolution of the bonding configuration in the SiH stretching mode region was followed. The absorption bands due to stretching modes of SiH, SiH$_2$, and SiH$_3$ bonds in each spectrum were deconvoluted. From obtained results the authors were able to conclude that the coalescence point of monohydride SiH bond clusters occurs at about 20 Å layer thickness.

IV.5. Doped silicon oxide films

Dielectric thin films of doped silicon oxide glasses have some important advantages over undoped glasses as in preventing diffusion of dopants into underlying layers, passivating device junctions, reducing film stress relative to pure SiO$_2$ etc. The films used for such purpose range in thickness from 0.5 and 1.0 µm. Another use of these films is to taper and planarise irregular device topographies.

Two most important doped silica glasses are **phospho-silicate-glass (PSG)** and **boro-phospho-silicate-glass (BPSG)**. In these films, phosphorus and/or boron oxides have been added into a silicon matrix in order to achieve desired film properties. The chemical, physical and electrical properties of PSG and BPSG films are determined by the dopant levels and film thickness.

PSG consists of two compounds, P_2O_5 and SiO_2 - therefore it is a binary glass (or binary silicate). Phosphorus acts to provide trapping sites for alkali ions and thus minimises impurity penetration. PSG can be flowed at high temperatures (1000-1100°C) to create a smoother surface topography /2/.

BPSG is a ternary oxide system (three component): B_2O_3-P_2O_5-SiO_2. In such films, boron plays an important role in lowering glass viscosity: by adding boron dopant into PSG glass, flow temperatures as low as 700°C can be obtained. Increase in boron concentration of 1 wt. % decreases flow temperature by 40°C, whereas an upper limit of boron concentration is deter-mined by stability: BPSG films containing over 5 wt. % boron tends to be very hygroscopic and unstable /2/.

Flow and reflow temperatures are critical for minimising vertical and lateral diffusion of dopants. For adequate maintenance of films, the (B,P) dopant contents and other critical parameters must be precisely controlled. Small changes in film composition and thickness may lead to significant changes in the thin film properties, especially film reflow temperature.

IR spectroscopy is the most common method to measure PSG and BPSG composition. Doped silicon oxide glasses are multicomponent oxide solids where the band absorptions may be overlapped by a considerable extent. Optical effects due to reflections on the reflective silicon wafer and due to inteferences within thin film are also present. All these complexities together complicate the quantitative analysis of spectra. For this purpose, univariate as well as multivariate calibration techniques for normal incidence transmission /6,53/ or external reflection /54,55/ measurements were developed. It was found, that in chemo-mechanical polishing, boron is more effective than phosphorus /56/. A simple method for quantitative and simultaneous determination of composition and thickness of BPSG films based on IR ellipsometry was described with precision of the order of 0.1 wt. % on thė boron and phosphorus /57/. All of these IR methods are based on measuring heights and/or areas of two absorption peaks for each component determination: net B-O (at ~1370 cm-1) to total Si-O (at ~1090 cm-1) for boron content, and net P=O (at ~1316 cm-1) to total Si-O (at ~1090 cm-1) for phosphorus content. Absorption bands due to B-O and P=O in BPSG films are highly overlapped and the various determination methods used throughout the literature differ to each other in a way how they account for this fact.

Another form of doped silica glasses used in microelectronic industry is **fluorinated-silica-glass (FSG)**. These films show the ability to reduce the dielectric constant while providing enhanced gap fill over undoped oxide films. All these properties are in close relation to the dopant concentration within the film: increasing fluorine content, the dielectric constant decreases and the gap fill improves. Fluorine dopant levels in FSG films is commonly determined by IR spectroscopy: the ratio of the Si-F peak (at ~937 cm-1) area to the Si-O bond stretch peak (at ~1090 cm-1) area is used to quantify the fluorine doping levels /58/.

IV.6. Other films

Several solid inorganic films are used in modern technologies. The most basic are made of silicon and silicon containing materials mentioned in previous chapters. In this chapter, the application of IR spectroscopy for some of the other materials having interesting properties for many potential applications is examined. In most cases, their investigation is still in progress.

Semi-insulating polycrystalline silicon (SIPOS) has many potential applications, e.g. as a resistive plate, as an active passivating layer, for SIPOS/Si heterojunctions, etc. Understanding the phenomena that determines SIPOS characteristics and how to design their material properties is still in progress.

SIPOS is a mixture of silicon and silicon oxide phases. The Si-phase can be amorphous or microcrystalline, depending on the oxygen content, anneal, and deposition temperature. The evolution of the micro-structure is strongly related to chemical composition.

Recently, the strong relationship between microstructure and electrical conduction mechanisms in SIPOS was studied /59/. Several techniques were used for this purpose as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), IR spectroscopy, Raman spectroscopy, photoluminiscence, and electroluminiscence. By IR transmission at normal incidence, the presence of SiO_2 phase was followed. Thin SIPOS films were deposited by low-pressure CVD of SiH_4 and N_2O or SiH_4 and CO_2. As deposited materials were amorphous and may contain all five possible tetrahedra, from $Si-Si_4$ to $Si-O_4$, corresponding to the five possible oxidation states of Si. In low temperature annealed films (700-800°C), only tetrahedra of the extremes, i.e. $Si-Si_4$ and $Si-O_4$ were formed. At higher temperatures (790-1000°C) Si-nanoclusters and SiO_2 phase were formed /59/.

Aluminium oxide is an attractive material for microelectronics as well as for other applications. It has high chemical stability, high radiation resistance, high thermal conductivity, and very low permeability of alkali ions and other impurities. These properties depend upon deposition temperature and upon post-deposition heat treatment as it was reported for PECVD aluminium oxide films /60/. In this investigation, IR spectroscopy plays an important role: the chemical composition was possible to follow via functional groups such as Al-CH_3, Al-O, and O-H /51/. The most important is the possibility to detect the hydrogen bonds which are not detectable by Auger electron spectroscopy (AES) or by XPS. The concentration of hydrogen was followed by the area of O-H stretching mode in absorbance spectrum of corresponding sample /60/.

Aluminium nitride in a wurtzite crystal structure is a wide energy band gap semiconductor (6.2 eV) and has many valuable properties as high thermal conductivity, high electrical resistivity, high ultrasonic velocity etc.

There are many troubles in producing large areas of high quality AlN thin films. Dependence of material properties upon the deposition conditions were reported for ion-beam assisted deposition /61/. The most important factor that impacts the crystal quality is the stress in the film. A process-induced biaxial compressive stress in the plane of film as well as stress produced by differences in the thermal expansion coefficient among the substrate (Si(111)) and the film was examined. In IR absorbance spectra, only one peak was detected. As the ion-beam voltage employed during deposition was reduced from 200 V to 50 V, the spectral position of this transverse optical (TO) mode was shifted monotonically towards lower wavenumbers (higher wavelengths), approaching the TO mode value for bulk crystalline material. Simultaneously, the width of the peak was decreased and its intensity increased. All these results shows that decreasing the ion-beam voltage, the structural disorder decreases. Therefore, the authors concluded: to produce films approaching single crystal quality, the ion-beam voltages have to be the lowest possible.

Strontium titanate, $SrTiO_3$, is a very promising ferroelectric material for use in e.g. micro-size thin film capacitors, as a gate insulator for MIS field-effect transistors with extremely high carrier concentrations. For these applications, films with good crystallinity and high dielectricity have to be ensured. For these reasons, the correlation between IR spectra and temperature coefficient of the dielectric constant of $SrTiO_3$ thin films was studied /62/. 130-230 nm thick films were deposited on the Pt/MgO substrate by the rf-magnetron sputtering at various deposition temperatures (T_D) ranging from 350 to 710°C. IR absorption spectra were measured in external reflection mode. In obtained spectra, LO phonon modes associated with crystallinity of films were followed against T_D. A close correlation was found between dependence of the LO phonon modes upon T_D and the temperature coefficient of the dielectric constant. This is a well known phenomenon: the frequencies of the LO modes depend strongly upon dielectric properties of the medium /18/ (see also chapter III.2.).

Gallium nitride is one of the III-V compound materials with very interesting properties. As grown GaN is semi-insulating when grown in a hydrogen-rich ambient whereas in absence of hydrogen, it is a p-type conductor. The final properties of the layer are defined by the post-growth treatments whereas hydrogen play an important role.

Measuring normal incidence transmittance at cryogenic temperature, very recently the direct spectroscopic evidence of local vibrational modes of hydrogen with the shallow acceptors in Mg-doped GaN thin film (4 μm thick films, CVD deposited on double side polished sapphire substrate) was reported /63/. In spectra of undoped and Si-doped GaN, these local vibrational

modes were absent. The authors concluded, that hydrogen is able to passivate Mg acceptors in these type films. This way they were able to answer the question as to whether the high resistivity of as-grown GaN:Mg arises from compensation of hydrogen passivation.

IV.7. Multilayers, heterostructures, and superlattices

The parallel-faced piles of layers used in modern technologies are named as multilayers, heterostruc-tures, or superlattices. Heterostructure consists of different materials (e.g. Ge and Si) whereas in multilayer the same material having different properties (e.g. different doping, different porosity etc.) may appear (homolayers). The name superlattice is used to point out the quantum-sized dimensions. For an electron, such layers form quantum wells and barriers between them. Due to tunnelling, minibands of allowed energies are formed in the superlattice. Such samples may be formed by carefully controlled deposition of atomic layers onto a crystal (MBE). Applying this procedure, quantum wells, quantum wires, or quantum dots may be formed, offering admirable possibility to tune the properties of the final material. The superlattice may have properties quite different from those of any naturally occurring materials. Throughout the literature, multilayer and heterostructure are used also for samples with low-dimensional (quantum) structures /22,64,65/.

In principle, an n-layers pile may be measured by each of three basic IR sampling techniques (see Figs. 1-3). In these experiments, many complications may appear. The coherent reflections and transmissions of the IR beam trough the multilayered stack may produce all sorts of optical effects. By suitable calculation procedure (matrix formalism), they may be taken into account /66,67/. When some of the layers are thick enough to support evanescent waves, it leads to the numerical instability. The solution of this problem was proposed /68/. Such calculations were applied in problems of optical gratings and the graded-index problem, but rarely in the field of IR spectroscopy. The reason for this may be the complexity of the problem.

If IR measurements are performed enough skilful, the interpretation of measured spectra will not be too complicated. The changes in selected part of the sample may be observed only, whereas the remainder may be taken as an reference. Some experimental techniques enable to select the vibrational modes that is to be monitored. Nevertheless, the interpretation of IR spectra of these complicated structures requires much more knowledge both from the field of optics and solid state theory. For more simple samples, such knowledge is not obviously required.

In MNOS structure, the concentration of hydrogen bonds in 12 nm thick silicon nitride layer was determined. For this purpose, the internal reflection spectroscopy at grazing incidence was applied. Despite of an ohmic Al contact, silicon wafer was used as an IRE /22/.

Conducting GaAs multilayers were analysed by external reflection spectroscopy at oblique and at normal

incidence angles. From spectral position of Fabry-Perot and Berreman structures, layer thickness and free carrier concentrations in them were obtained. In the procedure, the coupled LO phonon plasmon polaritons appearing in polar semiconductors were taken into account /65/.

A GaAs superlattice incorporating 50 carbon δ-doped layers (1 nm thick) with 50 nm superlattice periode was analysed by IR spectroscopy. High resolution (0.1-0.5 cm^{-1}) spectra were measured at ~10K in normal transmission mode. By IR localised vibrational modes due to hydrogen and carbon, the sites of the superlattice occupied by the carbon atoms were detected and their bonding properties were studied /13/.

The temperature and electric field dependence of the interminiband absorption in a doped GaAs/AlGaAs superlattice was monitored /14/. To measure IR trans-mittance of the superlattice during electric field pulses used to heat the electron system, a step-scan/time-resolved extension for spectrometer was applied.

IR ATR spectroscopy in the long-wavelenght region (far IR) was used to study the phonon parameters of a short period GaAs/AlAs superlattice /69/. By ATR spectroscopy in Otto configuration (sample is separated from IRE by a small gap), it is possible to excite the modes localised at a surface of superlattice (localised surface polaritons). In special cases, ATR can excite also surface modes on the superlattice-substrate interface. This can occur only just above LO frequencies of the superlattice or of the substrate. Guided wave polaritons are confined within the superlattice and may be excited in both polarisations. These modes together with polariton dispersion curves near the centre of first Brillouin zone helped the authors to analyse the parameters of the superlattice. IR measurements were performed at 77K with a resolution of 0.5 cm^{-1} /69/.

V. CONCLUSIONS

IR spectroscopy is an efficient non-destructive analysing tool for materials used in modern technologies.

It may be applied to determine the sort and amount of dopants in the investigated materials. Some of these analysis are used routinely in the technological process. These are determination of dopants in silicon wafers (interstitial oxygen, substitutional carbon, /1/) and dopants in doped silica glasses (P in PSG and P,B in BPSG). Amount of these dopants are crucial parameters for efficient fabrication of well-operated devices.

Other applications of IR spectroscopy are strongly connected with research and development. Here, IR spectroscopy may be used as purely analytical technique, offering an insight into the chemical properties of the sample. Connected to scientific hypothesis, and accompanied by other characterisation methods, the obtained data may be of great importance to the material scientists who are able to master the fabrication techniques to high sophisticated levels.

In the preparing the future of microelectronics and all other up-to date technologies, IR spectroscopy may play a considerable role. Provided that more and more knowledge about surface chemistry and chemistry of local environments, about optics, electromagnetics, and solid state theory will be incorporated, the role of IR spectroscopy may be more and more prominent. For the researchers, it is important due to all advantages of IR spectroscopy. Simultaneously, the important parts of Fourier-transform spectrometers (the source and detecting systems, interferometer, scanning mecha-nism, computing power, beamsplitters, polarisers etc.) are improving to so high level that they may fully support high demands of specialists applications.

VI. REFERENCES

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dr Marta Klanjšek Gunde, dipl. ing.
Kemijski Inštitut,
Hajdrihova 19
1115 Ljubljana, Slovenija
tel. +386 61 1760 291
fax: +386 61 1259 244
e-mail: marta.k.gunde@ki.si