# INFRARED SPECTROSCOPY AS ANALYSING TOOL FOR MATERIALS USED IN MICROELECTRONICS 1. Semiconductor substrates

Marta Klanjšek Gunde
National Institute of Chemistry, Ljubljana, Slovenia

**Keywords:** materials in microelectronics, infrared spectroscopy, semiconductor silicon, Ga-As, gallium arsenide, oxygen, carbon, hydrogen, shallow-level impurities, free carriers, surface analysis.

**Abstract:** The application of infrared spectroscopy to analyse the semiconductor substrates used for microelectronic devices has been reviewed. For the quantitative determination of various impurities involved in the bulk materials, absorption spectroscopy is used. Infrared absorption in monocrystal silicon due to oxygen, carbon, hydrogen and shallow-level impurities is examined extensively. The informations about free carriers in doped semiconductors could be obtained from bulk reflectance spectra. Some methods for characterising the semiconductor surfaces are described also. The recently published literature on this field is reviewed.

# Uporaba infrardeče spektroskopije pri analizi materialov za mikroelektronsko industrijo 1. Polprevodniški substrati

**Kjučne besede:** materiali v mikroelektroniki, spektroskopija infrardeča, silicij polprevodniški, Ga-As galijev arzenid, kisik, ogljik, vodik, primesi donorske in akceptorske, nosilci naboja prosti, analiza površinska.

**Povzetek:** Članek predstavlja pregled metod infrardeče spektroskopije, ki se najpogosteje uporabljajo za analizo polprevodniških substratov v mikroelektronski industriji. Infrardeča absorpcijska spektroskopija omogoča analizo vsebnosti nečistoč. Podrobneje je opisana infrardeča absorpcija zaradi nečistoč v monokristalnem siliciju, kot so kisik, ogljik, vodik, ter donorske in akceptorske primesi. Spekter odbojnosti dopiranega polprevodnika vsebuje podatke o prostih nosilcih naboja. Opisane so tudi nekatere metode za analizo površin polprevodniških substratov. Tematika je predstavljena v luči novejših publikacij.

## I. INTRODUCTION

Continuos improvements in technology of making microelectronic devices on the surface of a semiconductor requires special and controllable properties of all applied materials on each stage of the production /1/. Infrared (IR) spectroscopy is a powerful tool for the characterisation of these materials. Interaction of IR radiation with matter as a function of frequency provides a relatively direct probe of molecular structure via the excitation of vibrational states in molecules. This is one of the fundamental analytical techniques for obtaining qualitative and quantitative information about a substance. The advantages of Fourier-Transform IR spectroscopy together with the development of highly sensitive, rapid-response and low-noise detectors create a probe that is rapid, noncontact, nondestructive, and highly precise /2,3,4/.

This paper will consider the most frequently used applications of IR spectroscopy to analyse the fundamental microelectronic materials with special attention to the recent literature. In the first part, the characterisation of bulk materials is discussed. Mostly monocrystal silicon is considered whereas other compounds (e.g. Group III-V) are mentioned only briefly.

## II. ABSORPTION SPECTROSCOPY

The most usual way to obtain the absorption spectrum of a sample is to use the logarithm of measured normal incidence transmittance (Figure 1).

For IR radiation with energies bellow the band gap semiconductors become transparent. In this region the

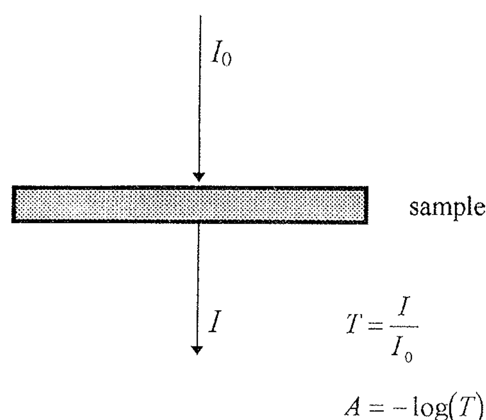


*Figure 1. Normal incidence transmittance (T) and absorbance (A) measurement.*

absorption spectroscopy play an important role. It enables to detect even low impurity concentrations in the host semiconductor material, if vibrations due to these impurities are IR active. There are two different mechanisms governing absorption of IR radiation due to impurities involved in bulk semiconductor material:

(a) *the local vibrational modes* caused by the distortion of the semiconductor crystal lattice due to electrically active or inactive impurities. The impurity species may be located either on lattice or on interstitial sites, bounded to the neighbouring host lattice atoms, and exhibiting a dipole moment.

(b) *the electronic bands* caused by the excitation of excited states of electrically active impurities exhibiting mostly shallow levels in the forbidden band-gap of the respective semiconductor.

The absorption peaks caused by vibration of impurities are not the only feature of the IR spectrum of a real semiconductor sample. The superposition of various kinds of absorptions may more or less seriously complicate detection of impurity vibrations.

a) *lattice vibration of the host semiconductor* is the main additional spectral feature. In homopolar crystals (silicon, germanium) it appears due to nonvanishing second order electric dipole moment that causes a multiphonon IR spectrum. Corresponding absorptions are the same order of magnitude as the local vibrational modes due to impurities. The vibration of polar crystal lattice (e.g. in GaAs) leads to reststrahlen bands in the far IR spectral region, representing the low-frequency boundary of the transparency region in polar semiconductors.

b) *high charge carrier concentrations*. Free carriers absorption increases continuously with increasing wavelength. The high-resistivity wafers (above 2 Ωcm) are transparent up to the far-IR spectral region whereas low-resistivity wafers (0.02-0.05 Ωcm) reflect almost all radiation in the whole IR spectral region.

c) *additional absorptions* due to surface layers such as oxides, nitrides, unintentional contamination or even fingerprint.

d) *highly scattering rough surfaces* cause a loss in transmittance. The radiation scattered by surface irregularities cannot reach the IR detector. Radiation scattering can be hardly distinguished from real absorption in a spectrum.

e) *high reflectivity of semiconductor surface* reduces the transmittance. This reduction is due to refractive index of applied semiconductor material. In silicon, it is about 50% and is almost independent on the wavelength of the impinging radiation.

These effects are shown in Figure 2, where normal incidence transmittance spectra of three silicon wafers are shown.

Spectral features of high-resistivity, high purity (float zone, FZ), double-side polished sample (Figure 2, curve a) are caused by lattice vibration of the silicon crystal lattice. The wavelength-almost-independent reduction of transmittance is caused by high reflectivity of silicon. The origin of this effect is the high value of refractive index of silicon (n=3.42). Throughout the mid IR region of high resistivity silicon, this value varies only on the fourth decimal place, practically only at frequencies of lattice vibrations /5/.

The commercial wafers for microelectronic devices are cut from Czochralski (CZ) grown ingots and polished only on one side. Typical distribution of surface irregularities of the rough rear surface causes spectral dependent loss of intensity in the measured direction for the wavelengths in the mid IR spectral region. This additional spectral feature changes the baseline of transmittance (Figure 2, curve b).

When the concentration of free carriers increases, the absorption edge due to free carrier or plasma absorption moves to shorter wavelengths. In low-resistivity silicon wafers, the free-carrier absorption dominates thus making detection of absorption due to impurity vibrations hardly or even non possible. At sufficiently high carrier concentration, the wafer is almost opaque throughout all mid IR spectral region (Figure 2, curve c).

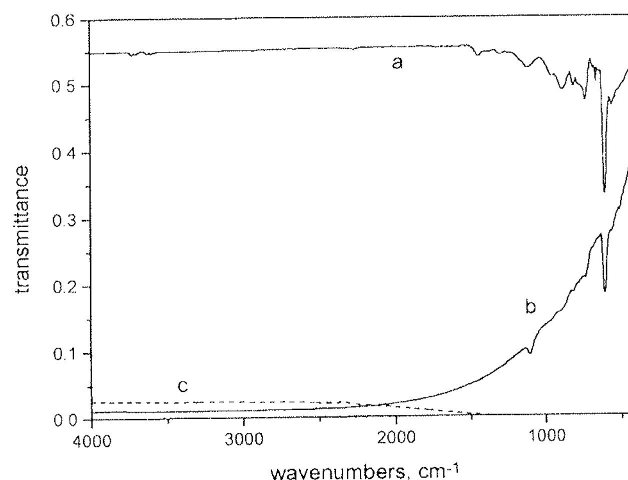


*Fig. 2. Absolute (air reference) transmittance spectra of silicon samples (room temperature measurements):*
*(a) high resistivity (~16 Ωcm), high purity (float-zone, <2x10$^{16}$ oxygen atoms/cm$^3$), both side polished wafer, thickness 502 μm,*
*(b) high resistivity (~10 Ωcm), low purity (Czochralski, 7.4x10$^{16}$ oxygen atoms/cm$^3$), one side polished wafer, thickness 480 μm,*
*(c) low resistivity (0.01-0.02 Ωcm), low purity (antimony doped, carrier concentration ~2x10$^{16}$ /cm$^3$), both side polished wafer, thickness 420 μm.*

There are some ways to avoid superposition of the above mentioned unwanted absorptions. Most simple and widely used are selection and preparation of suitable sample as well as application of known reference specimen to detect only the differences between the investigated sample and the reference.

To obtain information about the inherent impurity in a sample, the respective absorption bands have to be known. If quantitative results are wanted, the calibration factor of this absorption is necessary. Another possibility is to measure corresponding quantity of same semiconductor samples with known concentration of the same type of impurity species (calibration samples). To determine the calibration factor, detailed investigations have been performed on the commercially important semiconductor silicon, GaAs and GaP.

One sort of impurity species has various possible modes of vibration, what gives rise to various local mode absorption bands. The spectral positions of these bands shift with the sample temperature, with the respective isotopes involved, possibly even due to some entirely optical effect. Getting the most of these multitude of data offers the possibility to detect also some details about impurity species considered.

The electronic absorptions also exhibit a variety of bands due to the transitions to various excited states. The corresponding absorption coefficient and the respective full-width at half-maximum depend on the sample temperature. Detection of electronic bands requires cryogenic sample temperatures.

**The main application** of IR absorption spectroscopy in the semiconductor industry is the quantitative determination of the impurity concentrations in single crystal semiconductor material. For such analysis, the intensity of the IR absorption bands produced by the selected impurity is used as a measure of its concentration. In contrast to much more expensive techniques such as charged particle activation analysis, SIMS or the vacuum fusion method, IR spectroscopy is quite simple and fast to apply for this purpose. The former techniques were used only to calibrate the IR absorption for quantitative analysis.

The net concentration of dopants can be determined from the electrical resistivity measured at room temperature, whereas the chemical nature of impurities can be analysed by IR absorption spectroscopy. They may be classified as element impurities, pairs, complexes, and precipitates. Some of them are electrically neutral, the other are electrically active. For detection of electrically neutral impurity species, IR spectroscopy is one of the few techniques available. The presence of electrically active impurities can be detected also by means other than IR spectroscopy. These impurities generally determine the free carrier concentration and thus can be detected by electrical measurements. This technique is not very species selective, however. Different impurities give very similar results in the electrical properties, particularly in the Group III-V compounds. By IR absorption spectroscopy, on the other hand, the specific species of impurity present in the semiconductor can be identified.

## II.1. IR absorption in silicon

The Czochralski grown silicon is the most widely used semiconductor grade material for production of microelectronic devices. The major impurities present in it are **oxygen** and **carbon**. They are introduced during the growth process with maximum solubility at melting point $2x10^{18}$ atoms/$cm^3$ and $5x10^{17}$ atoms/$cm^3$, respectively. Both impurities are electrically inactive, but can seriously affect the carrier recombination process. The **oxygen** atoms occupy interstitial sites in the lattice and give rise to Si-O-Si bonds. Other oxygen species such as complexes and precipitates ($SiO_x$, $0<x\leq2$) can also exist in the silicon crystal and are detectable in the IR absorption spectrum. The **carbon** occupy substitutional sites in the silicon lattice leading to Si-C type of bonds. The absorption bands due to local vibrations of oxygen and carbon impurities are usually measured at room temperature. Lower temperatures are required only to improve delectability of very low concentrations.

**Atomic hydrogen** could be introduced into silicon due to exposure to hydrogen-containing plasma. In monocrystal silicon it can exists in various forms, that can be analysed by IR absorption spectroscopy /3/.

Dopants of the Group III-V elements are added to the silicon for manufacturing electrical devices. Commonly used are **phosphorous, boron, antimony, arsenic, nitrogen** etc. Measurement of IR absorptions due to these dopants requires cryogenic temperatures.

Only a limited number of reliable absorption bands, however, can be correlated to lattice defects /2/.

### II.1.a. Oxygen in silicon

Oxygen has been the most extensively studied impurity in monocrystal silicon and is also one of the main applications of IR spectroscopy in the semiconductor material characterisation. During the device manufacturing process, the silicon wafer is subjected to several heating cycles. During heat treatment, excess of the interstitial oxygen can precipitate to other forms. Accurate knowledge of the amount of oxygen in all forms present in silicon has become very important with respect to the development of the internal gettering technique. By this technique, it is possible to enhance the performance of devices. The result of the process depends strongly on content of oxygen involved in the crystal.

**Interstitial oxygen.** Measurement of interstitial oxygen content in silicon by IR absorption spectroscopy was developed after Kaiser et al. described the motion of a triatomic Si-O-Si "defect molecule" with the strongest IR band located at ~1107 $cm^{-1}$ /6/ (Figure 3). This band has been used for many years for the precise quantitative measurement of interstitial oxygen concentration in silicon. The method is based on the linear relationship between the oxygen content and the IR absorption due to the localised vibration of interstitial oxygen:

$$O_i = \gamma_{ox}\, \alpha_{ox}$$

where $\alpha_{ox}$ is the absorption coefficient of the interstitial oxygen vibration, and $\gamma_{ox}$ is the calibration factor. Up to now, three international interlaboratory experiments have been performed, where the precise value of $\gamma_{ox}$ for room-temperature measurements has been defined /7-9/. Some sets of certified reference materials have also been produced /9/. Determination accuracy of the ab-

sorption coefficient, $\alpha_{ox}$, depends on the particular sample. Many sources of measurement errors have been observed, beginning with multiple reflections, followed by residual oxygen content, thickness deviation between sample and reference, deviation in free carrier absorption, deviation in sample temperature, reflectivity of silicon, radiation scattering due to unpolished surface, and error due to emissivity of the samples. Most serious errors appears due to multiple reflections and due to rough surface of the wafer /10,11/.

In the standard measurement procedure, the both-side polished wafers are measured. Multiple reflections are taken into account by suitable modification of the transmission formula /7-11/.

In single-side polished wafers, the scattering of radiation from the rough side of the wafer causes intensity loss for measured spectra. In the literature, this effect is dealt with differently. One possibility is to treat it as an additional absorption process in the volume of the sample: a new term is added to the absorption coefficient $\alpha$, then the formula for both-side polished wafer is applied /11/. Another possibility is based on complete neglect of multiple reflections /10/. Instead of corrections to standard procedure, two another possibilities were proposed recently. One is to apply different experimental set-up /12-14/ and the other to use the same experiment, but different calculation /15/. Both possibilities are reported to be successful. They enable to approach the lower detection limit of the interstitial oxygen ($10^{16}$ atoms/cm$^3$ or 0.2 ppma) by IR absorption spectroscopy also for the problematical high-resistivity samples. This detection limit represents the purity level of the FZ silicon, that is required to account for vibrations of crystal lattice. When the free carrier concentration increases (i.e. the resistivity diminish), the detection limit is larger.

Applying microscopic FTIR measurement taken in a direction transversal to wafer cross section, the oxygen solid-state outdiffusion from the substrate to the epitaxial layer was investigated /16,17/. The applied direction of IR beam enables to resolve the mixing of the optical response of the epilayer and substrate. Due to use of FTIR microscope, the authors were able to map the thickness-profile of interstitial oxygen outdiffusion. The step of applied mapping was ~25 μm.

Measuring absorption of interstitial oxygen at cryogenic temperature, one can see numerous fine structure bands due to isotopic effects and due to oxygen occupying different sites in the crystal lattice /18/.

**Precipitates of oxygen.** At the relatively low temperatures used during the device manufacturing process, the oxygen-reach wafers are highly supersaturated. When such silicon wafer is exposed to sufficiently long thermal heating, oxygen concentration tends to its thermodynamical equilibrium. At temperatures above 250°C the oxygen atoms are mobile and reduce the supersaturation through the outdiffusion or the formation of oxygen precipitates. Part of this process can be followed by detecting the variation of the interstitial oxygen content /19/. In addition, IR absorption spectroscopy offers also the possibility to follow the precipitation process. This is illustrated in Figure 3. Single side polished Czochralski grown silicon wafer (initial concentration of oxygen $7.49 \times 10^{17}$ atoms/cm$^3$) was heated at 750°C in nitrogen atmosphere for 32h. The IR absorbance spectrum shows only the change in the interstitial oxygen content ($6.68 \times 10^{17}$ atoms/cm$^3$, Fig.3, curve b). Then, the sample was heated at 1000°C in nitrogen atmosphere for 16h. After that, the interstitial oxygen content diminish considerably ($3.99 \times 10^{17}$ atoms/cm$^3$) and 1229 cm$^{-1}$ band due to oxygen precipitates appears (Fig. 3, curve c) /19/.

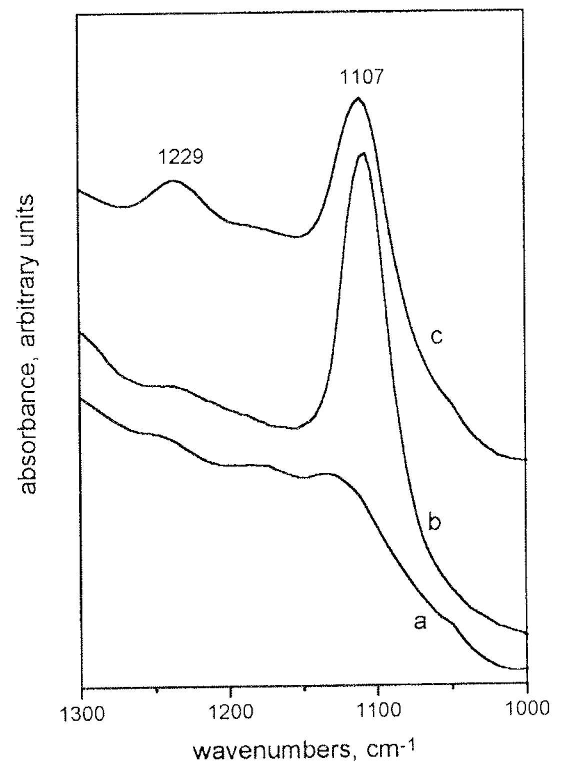


*Figure 3. Absorbance spectra of three high resistivity, one side polished silicon wafers in the oxygen stretching spectral region (room temperature measurements) /15, 19/:*
*(a) reference sample, high purity (float-zone, $<2 \times 10^{16}$ oxygen atoms/cm$^3$),*
*(b) low purity, $6.68 \times 10^{17}$ interstitial oxygen atoms/cm$^3$*
*(c) low purity, $3.99 \times 10^{17}$ interstitial oxygen atoms/cm$^3$*

The strongest IR absorption bands due to oxygen precipitates are located near 1100 cm$^{-1}$ and 1230 cm$^{-1}$. For quantitative estimates of the precipitate concentration, the 1250 cm$^{-1}$ band can be used /3/. It is possible to detect the amorphous structure of precipitates, being either in $SiO_x$ ($0<x<2$) or in $SiO_2$ form. In addition, the crystobalite crystalline type was detected as well as the conversion of one form into another with simultaneous initiation of crystal defects /20/. Applying the theory of average dielectric function of a composite medium and optical constants of silicon and of appropriate silicon oxide form (amorphous, crystalline), the connection between the measured absorption band due to oxygen

precipitates and their shape (needle, oblate, sphere, disc) was established /21/.

In more recent years, the research is even more complex, taking the full advantage of better measurement equipment. It is possible to study the hydrogen - enhanced oxygen diffusion as well as formation of thermal donors which are thought to be small aggregates of oxygen atoms /22/.

The absorption bands related to aggregates of $SiO_2$ disk-shaped precipitates were analysed in polarised IR beam. The intensity of this band depends strongly on light polarisation, what leads to conclusion that the disk-shaped precipitates lie parallel to the wafer surface /23/.

Oxygen microprecipitation was followed by micro-FT-IR mapping system /24/. It was shown, that the process depend upon initial micro-distribution profiles of interstitial oxygen.

### II.1.b. Carbon in silicon

Electrically neutral **substitutional carbon** can be detected by measuring the local mode absorption band due to stretching of C-Si bonds which appears at 607 $cm^{-1}$. The determination procedure is similar to that of interstitial oxygen. But it requires some more attention. The carbon absorption band is overlapped by the main two-phonon band of the silicon crystal lattice vibration. This absorption has to be considered more exactly in order to avoid increased experimental error. In addition, the carbon band is considerably narrower (full-width at half-maximum ~ 6 $cm^{-1}$) compared to the band due to interstitial oxygen (~ 31 $cm^{-1}$). Therefore, higher resolution has to be applied /2,3,10/.

In silicon sample, that contains oxygen and relatively large amounts of carbon, these unintentional impurities influence one another. The carbon enhances both oxygen precipitation and nucleation. the process can be followed measuring the contents of oxygen and carbon. Another possibility is to study the **carbon-oxygen complexes**. In the IR absorption spectrum, some localised vibrational modes in the spectral range of 1000-1120 $cm^{-1}$ are possible to obtain even at room temperature. These bands are typically one order of magnitude smaller than that of carbon. It was shown recently, that the study of the nucleation kinetics together with IR absorption measurements provides the model of nucleation reaction of carbon-oxygen complexes /25/.

### II.1.c. Hydrogen in silicon

The action of hydrogen in silicon is very complicated. It can binds defects and/or other impurity atoms to form many kinds of hydrogen-related defect-impurity complexes /26/. These complexes can give rise to many IR absorption bands in the spectral range between 1800 $cm^{-1}$ and 2300 $cm^{-1}$. IR data due to hydrogen in silicon are complex and not yet solved satisfactorily. The stronger absorptions are usually recorded at 2210 and 1946 $cm^{-1}$ /27/. According to the literature data, the band at 2210 $cm^{-1}$ could be assigned to silane molecule ($SiH_4$) sitting in a tetrahedral interstitial site or to four hydrogen atoms at a vacancy /3/. The 1946 $cm^{-1}$ absorption band is usually assigned to defects containing only the Si-H groups /3/. In FZ silicon that was grown in hydrogen atmosphere, the hydrogen-related vacancy-oxygen complexes were obtained at 1954 $cm^{-1}$ and 2066 $cm^{-1}$ /28,29/.

### II.1.d. Electronic bands of shallow-level impurities

The purest semiconductor-grade silicon samples contain impurities in the $10^9$-$10^{14}$ atoms/$cm^3$ concentration range. These are substitutional impurities that give rise to shallow acceptor (B, Al, Ga, In) and shallow donors (P, As, Sb, thermal donors). The dopants introduce free carriers that have high mobility at room temperatures. When the sample is cooled down to 20K or less, the electrons and holes become loosely bond to the defect centres. Their transitions give rise to characteristic absorptions in the mid- to the far-IR. For samples with thickness 2-10 mm, these absorptions can be seen in IR absorption spectrum in the region 300-550 $cm^{-1}$. Most of them are due to transitions of the electron or hole to the ground state of the neutral impurities to the pseudo-hydrogen levels below their respective and edges. Ionised centres and compensated impurities will not be detected by this method. If the sample is illuminated with photons having energy higher than the band gap of silicon, excess electron-hole pairs can be generated. These excess carriers neutralise the ionised centres and the spectrum will show absorption bands corresponding to the total impurity of the same chemical nature present in the sample. By this technique the bands that are about a factor of $10^4$ less than that of the local mode oxygen band can be detected /2,3/.

## II.2. IR absorption in III-V compound semiconductors

IR absorption in the group III-V compound semiconductors is possible in the transparent spectral region below and within the fundamental bands of the polar crystal lattice. The basic mechanism of absorption of IR radiation are the local vibrational modes. If these modes lie in the low-frequency region, they may fall in the continuum formed by the host lattice modes. Such modes are impossible to resolve.

Detection of impurities in GaAs or GaP is more complicated than the analogous analysis in silicon. The absorption bands due to most impurities are usually too weak to be detected in commercially thick wafers. Due to small full-widths at half-maximum of absorption bands (typically less than 2 $cm^{-1}$), high spectral resolution is required. With such measurement conditions, interference fringes from multiple reflections of the IR beam within the thin sample (1 mm or less) may be dominated and may cause the local mode absorption impossible to identify. For these reasons, routine control of commercially wafers is very difficult or even impossible. The problem can be solved by thicker slices. To sharpen the peaks and to increase their intensities, the samples are cooled to liquid nitrogen temperatures /2/.

The interpretation of results is more complicated as it is for silicon. There are two possible substitutional sites in GaAs: the gallium and the arsenic site. If different iso-

topes are substituted into the crystal, a pronounced frequency shift of localised vibrational modes can be observed /2/. This effect was applied to study some details of the bonding sites and of the bonding mechanism for hydrogen impurity in the GaAs single-crystal semiconductor. For this purpose, the frequencies of hydrogen-tin and deuterium-tin pairs were compared with analogous frequencies of hydrogen-silicon and deuterium-silicon pairs /30/.

## III. EXTERNAL REFLECTION SPECTROSCOPY

On the edges of the transparent spectral region of a semiconductor, the reflectance is recorded instead of zero-approaching transmittance. If the incident and the reflected light beams are outside the sample, the term external reflection spectroscopy is used for such experiment. There are many possibilities to measure the external reflectance of a sample. For analysis of homogeneous materials, the **specular reflection** (obeying reflection law) is used.

In the most simple experiment, the unpolarized light that reflects from the sample surface at **near normal incidence angle** (<8°) is measured (Figure 4). It is assumed, that all reflected light originates from reflection on the front surface of the sample only. Such reflection is called **bulk specular reflection**. These spectra are applied to determine the properties of free carriers in doped semiconductors /2/.

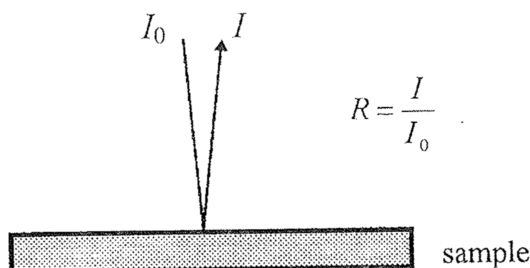


*Figure 4. Diagram illustrating near normal external reflectance measurement.*

The intensity of the reflected light changes significantly depending upon the collection (or observation) angle and upon the polarisation. This result of reflection at the surface can be predicted by laws of classical electromagnetic theory. On metal surfaces, the intensity of the reflected light reaches maximum at very large (grazing) angles whereas for other materials (e.g. Si, glassy carbon etc.) this angle is somewhat smaller /31, 32/. Combining this optimised collection angle together with polarised IR light, the information about chemical species present on the surface and their orientation can be obtained. For this purpose, the appropriate reference sample have to be measured to get the corresponding change in normalised reflectance. This **oblique incidence external reflection spectroscopy** has been referred in the literature as **IR reflection-absorption spectroscopy**. When metal substrates are used, the optimised angle is very large and therefore the name **grazing incidence reflection** is used. To enhance the sensitivity of oblique incidence reflection spectroscopy, the number of reflections could be increased /31/. Various attachments for this purpose are presented in Figure 5. The oblique incidence external reflection spectroscopy is used for analysing very thin films and surface species on samples that have considerable bulk specular reflection.

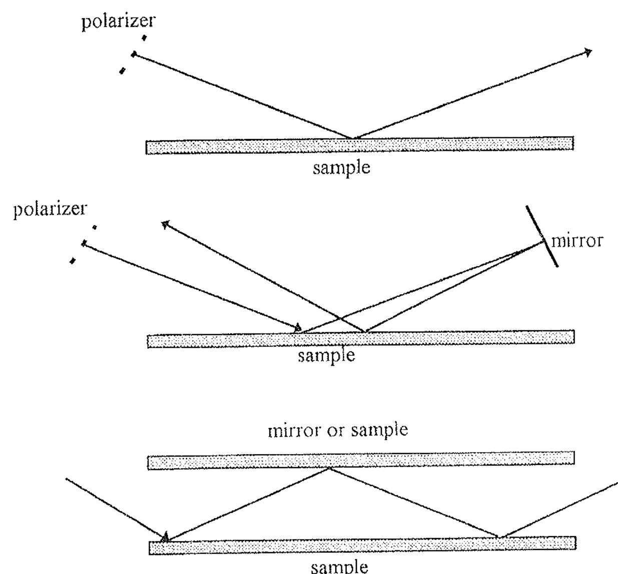


*Figure 5. Diagram illustrating oblique incidence external reflection measurement.*

### III.1. Free carriers in doped semiconductors

Electromagnetic radiation with sufficiently large wavelengths interacts with the free carriers in doped semiconductor and undergoes dispersion. In such circumstances, the light can not penetrate into the sample and therefore reflects from it. This is the basic mechanism that terminates more or less transparent spectral region of the semiconductor at large wavelengths. The bulk specular reflectance is measured usually (Fig. 4). The obtained so-called plasma reflectivity spectra contain informations about free carriers: their concentration, mobility and effective mass. The determination method has all benefits of optical spectroscopy: it is non-destructive, fast and easily performed.

Some more complicated situation arises where the interaction of free carrier plasma and phonon lattice modes have to be taken into account. In homopolar semiconductor crystals (e.g. Si and Ge) this effect is practically negligible. Coupled plasmon-phonon frequencies were observed for GaAs, GaP, CdTe, PbTe, etc. Analysing plasma reflectance of such samples, phonon contribution has to be taken into account /33/.

### III.2. Surface characterisation

The observation of vibrational spectra of species directly bound to the substrate surface is crucial to understanding the mechanism of growing good-quality thin

films on atomically flat surfaces (e.g. on Si wafers). IR external reflection spectroscopy at oblique incidence angle is one of the techniques available for this purpose. It is completely non-destructive: the commercial wafer can be measured at low vacuum or in desired atmosphere.

This technique was used recently to study the oxidation and fluorination of the Si(111) surface /34/. Reflectance of p-polarised light was related to absorptions arising from Si-H, Si-O, and Si-F bonds on atomically flat Si wafer surface.

## IV. INTERNAL REFLECTION SPECTROSCOPY

When the IR beam from optically denser medium impinges onto the optically rare medium, its reflection is called **internal reflection.** Beyond the critical angle, the incident light is totally reflected. If the rarer medium is an IR absorptive material (or if IR vibrations are located on the interface), the reflected light bears information about the absorption spectrum in the rare medium. The optically dense transparent material forms so-called **internal reflection element** (IRE). Typical shapes of IRE are shown in Figure 6. By specifical design, one internal reflection (Fig. 6 a) or multiple internal reflection (Fig. 6 b and c) can be achieved.

The decrease in total internal reflection that is observed when an absorbing material is in contact with IRE is called **attenuated total reflection (ATR)**. The big advantage of IR-ATR spectroscopy is in the investigation

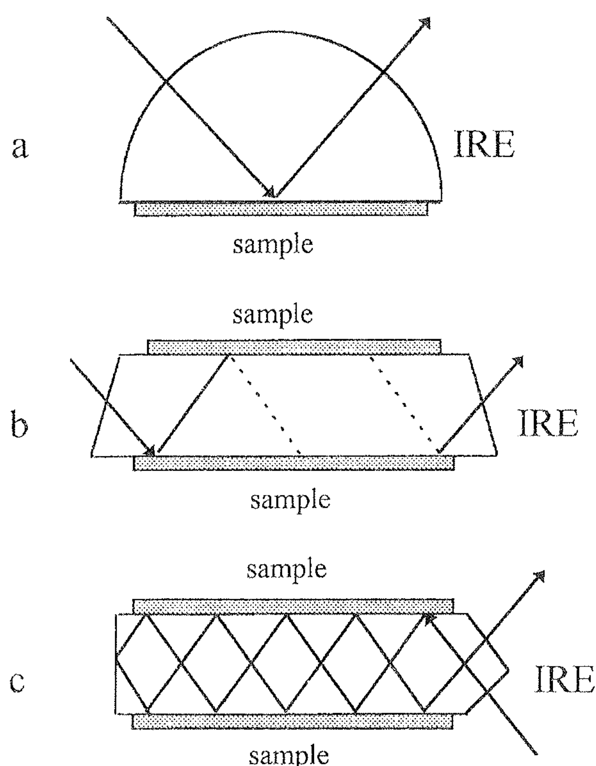


*Figure 6. Typical internal reflection elements (IRE) for one internal reflection (a), and for multiple internal reflections (b and c).*

of molecular orientation. For this purpose, linearly polarised light is applied.

### IV.1. Surface and interface morphology

In the majority of semiconductor surface analysis the semiconductor itself is used as an IRE. The wafers are bevelled at opposite ends to couple the IR beam in and out (see Figure 6 b and c) and to apply the multiple internal reflection technique. Such measurements are used to analyse the physical and chemical state of the surface. Mostly the adsorption of hydrogen due to the chemical removal of the surface oxide by hydrofluoric acid (HF) solution is studied. Such removal of oxide from silicon wafer surface produces very inert hydrogen-covered surfaces that are contaminant-free and stable at room temperature.

Recently, a series of multiple internal reflection measurements were reported to study the surface cleaning of Si wafers on a molecular level. Si-H stretching vibrations were analysed in terms of monohydrides, dihydrides, and trihydrides /35, 36, 37/.

Applying the same technique, the microscopic removal mechanism during the chemo-mechanical polishing of silicon was analysed /38/. It was shown that after this surface shaping process a surface termination by hydrogen predominates on a defect-free, atomically flat (111) and (100) Si surfaces. This H-termination is responsible for the strong hydrophobicity of the surface and its chemical stability in air.

By multiple internal reflection spectroscopy, the interface of bonded hydrophylic and hydrophobic wafer pairs were studied /39/. Analysing Si-$H_x$ (x=1, 2, 3) and SiO-H stretching modes, it was obtained that Si-H bonds might be involved in the bonding of both wafers.

## V. CONCLUSIONS

IR spectroscopy is a powerful technique for characterising bulk materials used for microelectronic devices. It is one of very few techniques available for efficient non-destructive analysis of chemical nature of the sample. A large variety of techniques are now being used to observe the spectra for many configurations of the sample. Some of this techniques are relatively simple in concept, the other are more sophisticated. The obtained results may help to understand and to control the chemical and physical processes inside the material as well as on its surfaces.

## VI. REFERENCES

/1/ M. T. Bohr, Appl. Surf. Sci. 100/101 (1996), 534-540

/2/ K. Graff, in Analysis of Microelectronic Materials and Devices, Ed. by M. Grassebauer and H. W. Werner, John Wiley and Sons Ltd. 1991, p.77-96

/3/ K. Krishnan, P. J. Stout, M. Watanabe, in Practical Fourier Transform Spectroscopy, Academic Press, Inc., 1990, p. 285-349

/4/ J. E. Franke, T. M. Niemczyk, D. M. Haaland, Spectrochim. Acta 50A, (1994), 1687-1723

/5/ M. Klanjšek Gunde and B. Aleksandrov, Appl. Optics 30 (1991), 3186-3196

/6/ W. Kaiser, P. H. Keck, and C. F. Lange, Phys. Rew. 101 (1956), 1264-1268

/7/ T. Iizuka, S. Takashu, M. Tajima, T. Arai, T. Nozaki, N. Inoue, and M. Watanabe, J. Electrochem. Soc. 132 (1985), 1707-1713

/8/ A. Baghdadi, W. M. Bullis, M. C. Croarkin, Yue-zsen Li, R. I. Scace, R. W. Series, P. Stallhofer, M. Watanabe, J. Electrochem. Soc. 136 (1989), 2015-2024

/9/ R. Murray, K. Graff, B. Pajot, K. Strijckmans, S. Vandendriessche, B. Griepink, and H. Marchandise, J. Electrochem. Soc. 139 (1992), 3582-3587

/10/ P. Stallhofer, D. Huber, Solid Stated Technol. 26 (1983), 233-237

/11/ F. Schomann and K. Graff, J. Electrochem. Soc. 136 (1989), 2025-2031

/12/ H. Shirai, J. Electrochem. Soc. 138 (1991), 1784-1787

/13/ H. Shirai, J. Electrochem. Soc. 139 (1992), 3272-3275

/14/ Y. Kitagawara, M. Tamatsuka, and T. Takenaka, J. Electrochem. Soc. 141 (1994), 1362-1364

/15/ M. Klanjšek Gunde, Appl. Spectrosc. 50 (1996), 1156-1160

/16/ M. Geddo, B. Pivac, A. Borghesi, and A. Stella, M. Pedrotti, Appl. Phys. Lett. 57 (1990), 1511-1513

/17/ M. Geddo, B. Pivac, A. Borghesi, and A. Stella, M. Pedrotti, Appl. Phys. Lett. 58 (1991), 370-372

/18/ H. Saito and H. Shirai, Jpn. J. Appl. Phys. 34 (1995), L1097-L1099

/19/ Marijan Maček, Disertacija, Univerza v Ljubljani, Fakulteta za elektrotehniko in računalništvo (oktober 1991)

/20/ K. Tempelhoff, F. Spiegelberg, R. Gleichmann, and D. Wruck, Phys. Stat. Sol. (a) 56 (1979), 213-223

/21/ S. M. Hu, J. Appl. Phys. 51 (1982), 5945-5948

/22/ R. Murray, Physica B 170 (1991) 115-123

/23/ A. Borghesi, B. Pivac, and A. Sassella, Appl. Phys. Lett. 60 (1992), 871-873

/24/ E. Iino, I. Fusegawa, and H. Yamagishi, Appl. Spectrosc. 47 (1993), 1488-1491

/25/ H. Yamanaka, Jpn. J. Appl. Phys. 33 (1994), 3319-3329

/26/ E. E. Haller, Semicond. Sci. Technol. 6 (1991), 73-84

/27/ P. Déak, L. C. Snyder, M. Heinrich, C. R. Ortiz, and J. W. Corbett, Physica B 170 (1991) 253-258

/28/ Meng Xiang-Ti, Semicond. Sci. Technol. 4 (1989), 892-894

/29/ X. T. Meng, Physica B 170 (1991) 249-252

/30/ R. C. Newman, Semicond. Sci. Technol. 5 (1990), 911-913

/31/ W. Suëtaka, in Methods of Surface Characterization, Volume 3, Plenum Press, New York and London (1995)

/32/ M. C. Porter, Anal. Chem. 60 (1988), 1143A-1155A

/33/ A. A. Kukharskii, 13 (1973) 1761-1765

/34/ M. Okuyama, M. Nishida and Y. Hamakawa, Jpn. J. Appl. Phys. 34 (1995), 737-740

/35/ L. Li, H. Bender, G. Zou, P. W. Mertens, M. A. Meuris, and M. M. Heyns, J. Electrochem. Soc. 143 (1996), 233-237

/36/ H. Ogawa, K. Ishikawa, M. T. Suzuku, Y. Hayami, and S. Fujimura, Jpn, J. Appl. Phys. 34 (1995), 732-736

/37/ C. H. Bjorkman, M. Fukuda, T. Yamazaki, Jpn. J. Appl. Phys. 34 (1995), 722-726

/38/ G. J. Pietsch, Y. J. Chabal, G. S. Higashi, Surface Sci. 331-333 (1995), 395-401

/39/ M. Reiche, S. Hopfe, U. Gösele, Q. Y. Tong, Appl. Phys. A 61 (1995) 101-105

*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*

*Prispelo (Arrived): 29.01.1997* *Sprejeto (Accepted): 25.02.1997*