Section 5 : Material Analysis

Materials manufacture and characterisation are today top branches of activity inherent to the development of any new technology. The development of modern characterisation using nuclear type techniques is associated to the study and understanding of basic phenomena, often undertaken around large scale facilities. The number of applications of such know-how to material science has been continuously growing. This is particularly evident in the case of neutron scattering and synchrotron radiation applications, which have developed to the status of standard techniques, providing, among others, information on magnetism, crystallographic and molecular structures. Today, the number of subjects and user requests of beam time for material science purposes justifies alone the development of new facilities with increasing power and improved beam quality i.e., bunching, polarisation and micro beams.

On the other hand, the present needs for increased integration in electronics, photonics, nanostructured materials and micro-robotics is a fertile ground for the application and development of nuclear techniques, which provide local information, scaling from the atoms neighbourhood to micrometers. Phenomena and technologies, which are extremely dependent and relying on the submicron nature of doping, thin films, micro and nano-structures, have found in techniques like Muon Spin Resonance (μSR), ion beams microprobes and in new radioactive ion beams, the ideal source of microscopic information.

Four subsections are developed which emphasise the perspectives opened by recent technical developments, new methods and applications [1]: neutron scattering study of condensed matter; exotic beams – positron and μSR methods-; ion beam techniques; radioactive ion beams and techniques for solid state research. Among the four techniques presented in this section, the last two, which make use of ion beams, take particular benefit from the knowledge on atomic collisions and on material induced modifications that is the subject of sections 3 and 4.

5.1 Neutron scattering study of condensed matter

A very broad community of some 7000 people uses neutron scattering worldwide, 5000 in Europe, for studies ranging from mechanical engineering to life sciences. A number of unique properties of slow neutron radiation make it an indispensable tool in the study of materials. These include particularly, neutron sensitivity to light elements as H and the direct interaction with magnetic samples via its magnetic moment. In addition, due to the value of the neutron mass, the wavelength of thermal neutrons, with energy in the 5-80 meV range is comparable to the energies associated with atomic motions in condensed matter, happens to coincide with the length scale of interatomic distances (a few Å). Therefore, neutrons provide the unique capability of exploring both atomic structure and atomic motion.

Relevant examples of applications can be presented in the fast growing field of soft matter research. In these materials the macroscopic properties are strongly determined by the microscopic dynamic behaviour on the molecular level. For example in polymers the intermingled chain molecules mutually limit each other’s motional freedom, leading to the reptation process that has been the object of fundamental theoretical studies by de Gennes. Recent Neutron Spin Echo experiments have unquestionably evidenced and characterised this type of motion [2], after all other experimental attempts remained inconclusive.

Neutrons have constantly played a major role for the study of magnetism in condensed matter. In the last decade a strong activity and important findings concerned high Tc superconductors and superconductivity. In this field a recent breakthrough was the observation of vortex lattice melting in superconducting Nb [3]. In this type of superconductor, the magnetic field penetrates in channels called vortices whose core has a
normal conductance. At low temperature, the interaction between these vortices results in the formation of a periodic ordered lattice. Neutron small angle scattering diffraction studies, performed as a function of temperature, evidence supercooling and superheating effects and thus demonstrate that the vortex lattice undergoes a first order phase transition.

The sensitivity of neutrons to light elements, such O in high T\textsubscript{c} superconductors or H in biological matter, is in strong contrast to X-rays where the lattice of the heaviest elements of a compound mainly determines the diffraction pattern, and little or no information can be found on the position of the lightest elements. This confers an important complementary role to neutron diffraction, particularly useful in the study of biological samples. After the backbone of the structure formed by the heavier elements has been determined with synchrotron radiation, the position of H atoms associated, for instance, with hydration water, is elucidated by neutron scattering. This latter information is of particular importance for studying biological functions [4].

Traditionally, the preferred neutron sources used for producing beams of slow neutrons for the neutron scattering instruments are research reactors using enriched U fuel for fission. Most reactors switched, or are in the process of switching, to Low Enriched Uranium, in the spirit of the Nuclear Non-proliferation Treaty, but those with the highest neutron flux still use High Enriched Uranium. Higher density Uranium-Molybdenum fuel should be available in a decade or so, which will open up the possibility for the highest flux research reactors too to switch to Low Enriched Uranium fuel without substantial loss in their neutron flux.

The ISIS (Didcot, UK) and SNQ (Villingen, Switzerland) neutron centres use spallation for neutron production. In this more recent technique fast neutrons in the 2 – 10 MeV energy range are produced as the results of a number of secondary nuclear processes following the irradiation of a heavy metal target by protons in the 800 MeV energy range. The fast neutrons are moderated to the typically 1 meV to 500 meV energies required with very few exceptions, for the study of condensed matter by scattering experiments. Spallation offers two principal advantages over fission: the heat deposited per extractable neutron is about 30 MeV as opposed to 190 MeV, and a spallation source can easily operate in pulses, which enhances the efficiency of using the available neutrons produced in the source. The principle is illustrated in Figure 5.1.1 [5]. In time-of-flight neutron scattering spectroscopy, pulses of neutrons arrive at the sample at a frequency determined by the time needed to analyse the velocity distribution of the scattered neutrons, typically 2 – 20 ms. In order to deliver the series of pulses, illustrated in the figure, a continuous reactors source will produce neutrons all the time; most of which will be eliminated by the neutron absorbing mechanical chopper system. In contrast, on a pulsed spallation source, neutrons will emerge from the moderators only for a fraction of the total time, and neutrons emanating from the same pulse with different velocities (different slopes in the time-distance diagram in the figure) will arrive at the sample at different times, with a repetition rate as required by the

![Fig. 5.1.1: The figure represents a sequence of monochromatic pulses shaped by mechanical chopper devices (#1…#6, illustrated by horizontal lines for "closed" positions, interrupted by "open" periods). In this distance-time diagram the straight lines whose slope corresponds to the neutron velocity illustrate neutron trajectories. On a pulsed source, neutrons originating from a pulse will arrive at the sample over the whole period between pulses.](image)
spectrometer. The desirable duty factor being around 1 – 5 %, the neutron flux released by the source during the short time, can be by orders of magnitude larger than the time average flux, relevant for the average power. For example, at 5 MW proton beam power the time average cold neutron flux of coupled liquid H$_2$ moderators achieves the steady flux of the most powerful reactor in existence. Its instantaneous "peak" flux during the pulses, which matters mainly for most experiments, can achieve 30 – 60 times this time-average flux value [6]. In the next 5-10 years, different projects in Europe, USA and Japan aim to construct very powerful spallation neutron sources, with effective neutron fluxes much greater than those of the most powerful reactor.

Progress in neutron scattering experimental techniques has provided for most of the spectacular gain in performance and sensitivity in neutron scattering work over the past decades. Most recently the use of so called supermirror coatings in neutron guides is in the process of revolutionising neutron beam extraction and delivery, producing 5 – 7 fold beam intensity gains on the sample. The combined effect of improved source performance, improved neutron optical beam delivery and improved detector solid angle coverage will enhance data collection rates in the next decade by a very substantial factor, between 10 and 1000 times, in all types of neutron scattering applications. Such a tremendous gain in sensitivity and the fact that spallation sources in the range of several MW proton beam power have now become technically feasible will open up completely new fields of applications in neutron scattering research.

5.2 Exotic beams – Positron and Muon Spin Resonance Methods

Positron Spectroscopy techniques are powerful tools with a large spectrum of applications, providing microscopic information on the electronic, crystallographic and chemical properties of materials. Recently, progress has been made mainly in positron beam techniques. The availability of a MeV positron beam at the Max Planck Institute für Metallforschung (Stuttgart, Germany) allowed new experiments with the age-momentum correlation method [7,8], which correlates positron and positronium lifetime and Doppler-broadening spectroscopy. This allows in particular, the characterisation of transient processes in matter such as thermalisation, bubble formation in liquids, and slow trapping of positronium in polymers [9]. Low-energy positron beams, typically up to 30 KeV are used for studying depth profiles of positron trapping defects such as vacancies, dislocations, voids, as well as layered structures. The most recent development is the pulsed low energy positron beam which was developed at the Universität des Bundeswehr (München, Germany) and which allows depth profiling of positron lifetimes. At least 3 more pulsed low energy positron beams are under construction in Europe, i.e. at Ghent, Goteborg and Helsinki. An overall review of today’s research and development on new techniques can be found in refs [10,11].

Muons and Muonium spin resonance (µSR) methods are an outcome of particle physics, which are now well established as universally applicable microscopic magnetic probes in solid-state physics, chemistry and materials science. Nowadays, muons can be implanted at very low number and energy in any material without producing radiation damage, under a large variety of external conditions (temperature, pressure, magnetic or electrical fields, etc.). Polarised muons are an important probe of static and dynamic magnetic properties of materials. Its large magnetic moment (three times that of the proton) and mean lifetime of 2.2 microseconds make local magnetic fields and field distributions accessible in the range of µTesla to several Tesla, the time scales for dynamic properties ranging from pico- to milliseconds. As a 'light isotope' of the proton, the positive muon can form the hydrogen-like atom muonium, which may substitute for hydrogen in insulators, semiconductors and organic materials, thus providing a very sensitive spin label.
Research applications of muon-spin rotation, relaxation and resonance (μSR) include the study of magnetic, superconducting, metallic, semiconducting, ion-conducting, amorphous and molecular materials. The advent of low energy muon beams extends the applications to depth-resolved studies of magnetic properties (on a nanometer scale) of thin films, multilayers, nanometer-sized clusters, and near-surface regions.

The advantage of continuous-beam μSR is its high (sub-ns) timing resolution allowing one to study fast dynamics and high magnetic fields, whereas a pulsed beam offers the ability to determine very weak atomic magnetism and is well suited for examining materials in pulsed environments such as magnetic and electric fields, laser or radio-frequency radiation. Two worldwide unique special facilities have been developed at the continuous-beam μSR facility of the Paul Scherrer Institute (Villigen, Switzerland):

(a) A Low Energy Muon Beam (LEMB) allowing to implant muons at very small and controllable depths, a few to a few hundred nanometers below the surface of a sample. A wealth of new applications become possible by extending the studies to very thin films, multilayered structures, surface regions and by measuring material properties as a function of the implantation depth on a nanometer scale. An example of application of LEMB is shown in Figure 5.2.1 where the penetration of a magnetic field into a superconductor in the Meissner state is studied [12]. The measurements were performed on a 700 nm thick, c-axis oriented and epitaxial YBa$_2$Cu$_3$O$_7$ film. A vertical magnetic field of 10 mT was applied after cooling the sample to 20 K so that no flux lines were trapped inside and the field below the sample surface was due to the finite value of the penetration depth. The depth of the muon implantation was controlled between 20 and 150 nm by tuning the incoming muon energy from 3 keV to 30 keV. The depth dependent field profile B(z) within such a semi-infinite superconducting slab follows the well-known London exponential decay law.

(b) The extraction of one muon at a time from a continuous beam (Muons on Request) reduces background to the level of a pulsed muon source while keeping nanosecond time resolution. This provides unique sensitivity to small magnetic field differences and extends the measurable characteristic times into the milliseconds range.

Despite the increasing users demand, there is presently no dedicated facility for μSR methods alone. Production facilities optimised for μSR would provide at least one order of magnitude improvement in data collection time, flexibility in beam arrangements and availability to simultaneous users what would allow routine materials characterisation.

5.3 Ion Beam Techniques: High depth and lateral resolution for materials analysis and microfabrication

The tremendous progress in the computer, communications, imaging and micro-machining fields can largely be linked to the art of creating ever-finer structures in a variety of materials. After reaching the boundaries of photon and electron lithography, finely focused ion beams are expected to play an increasingly important role in the next generations of
integrated circuits, where geometric features in the range of 10 - 100 nm are required to satisfy the needs of gigascale integration. In mesoscopic systems, i.e., structures between the single atom with discretely spaced electronic energy levels and bulk material with a delocalised electronic energy band structure, the band gap may be tuned by the geometrical design of nanostructures, rather than by impurity doping. High depth and spatial resolution ion beam analysis (IBA) techniques are contributing to this evolution, with hundreds of IBA laboratories around the world closely involved with industrial and basic research.

Important recent developments have also been made in IBA data analysis. The development of new fitting procedures using computer techniques such as Simulated Annealing [13], Bayesian Inference with the Markov chain Monte Carlo algorithm [14] and the application of neural networks to Rutherford Backscattering Spectrometry (RBS) data [15], has drastically reduced analysis time through automation. This opens the way to implement on-line RBS data analysis, particularly relevant for industrial applications.

Very high depth resolution IBA is finding increasing use in investigations of ultra-thin films, with particular interest for thin (1 to 5 nm) dielectrics on semiconductors for MOSFET technology. Several methods are used: narrow nuclear resonance profiling, RBS with time of flight, magnetic, or electrostatic detectors to provide high energy resolution. Another method is high energy resolution elastic recoil detection, using heavy incident ions such as iodine at energies of some tens of MeV [16]. In contrast to sputter-based profiling methods such as Secondary Ion Mass Spectrometry, IBA can have nm depth resolution from the surface, without being destructive. IBA is a quantitative technique and in addition to elemental sensitivity, also offers isotopic discrimination, which is exploited in stable isotopic tracing studies. An example of such sub nm resolution near the surface is illustrated in Figure 5.3.1 where narrow nuclear resonance profiling with $^{18}$O(p, $\alpha$)$^{15}$N (full width at half-maximum ~100 eV) is used to perform isotopic exchange studies of $^{18}$O in the outer few nm of a Si$^{16}$O$_2$ film [17]. The incident beam energy is scanned around the resonance energy to obtain the excitation curve, which is an image of the $^{18}$O concentration profile, yielding information on growth mechanisms of ultra-thin SiO$_2$ MOSFET gate dielectrics. The addition of small amounts of nitrogen at the SiO$_2$/Si interface leads to substantial improved electrical properties of ultra-thin SiO$_2$ films. Such systems are also studied, with very high depth resolution, by Medium Energy Ion Scattering [18] in which ~100 keV protons are elastically scattered from the sample and their energy spectra recorded with high-energy resolution. Concentration profiling of ultra thin oxynitride films on silicon with sub nm depth resolution has also been obtained by high energy-resolution RBS and elastic recoil [19]. In fundamental condensed matter physics studies, electrostatic energy analysis of 100keV protons, in channelling-blocking geometry, has been applied to achieve sub nm resolution and to study the surface relaxation (variation of the interplanar spacing) and thermal vibrations of each of the outer few atomic layers of a copper single crystal [20]. Atomic monolayer resolution has also been demonstrated for RBS on single crystal PbTe(001) with 300 keV $^4$He incident beam and a purpose-built magnetic spectrometer [21] at a grazing exit angle of 2.6°. It is shown that the first and second Pb layers may be distinguished in this case.
The technology underlying the ability to focus MeV ion beams to spot sizes between 100 nm to 1 µm, using nuclear microprobes, has also continually evolved, opening up new applications for the characterisation of crystallographic and electronic properties of materials and increasing understanding of ion-solid interactions [22]. The nuclear microprobe operates similarly to a scanning electron microscope: a focused beam of charged particles is swept over the sample surface to produce spatially resolved images using an analytical signal produced by the particle-solid interactions. While it is relatively difficult to focus MeV ions to small spots, the beneficial side-effect is that the beam tends to stay focused through tens of microns in the sample owing to the large ion mass. Strong-focusing magnetic quadrupole lens systems can now focus MeV ions with a focal length of 10–20 cm, giving a demagnification of 10–100, and hence a small focused beam spot size. The best resolution of 100-200 nm with a small current, and 300-400 nm with higher currents for conventional IBA techniques, have been achieved by the Singapore group [23] and, recently, in Europe by the Leipzig group [24]. There are now some 50 to 60 microprobe groups in the world, of which about half are in Europe. A review of IBA microprobe applications in biomedicine, geology and archaeology, and the microprobe hardware may be found in [25,26,27,28].

The most promising recent developments are related to experiments with low current ion beams (in the ~1 fA range), in which one exploits the penetration in matter of each single ion. For material analysis, such experiments are not affected by beam-induced damage, which is sometimes the case when studying, as in conventional IBA, events with relatively low cross sections. Also, working with low currents allows one to limit the beam emittance and thus to produce parallel microbeams that can be used for the study of sample defects and crystallographic structure, using channelling. Low current nuclear microprobes are used in materials science for a wide range of applications. Many of such recent applications are reviewed in [29]. In the text below, we refer to some of the most promising.

**Applications of Ion Beam Induced Charge (IBIC) microscopy:** This has become a well-used microprobe technique in recent years because it gives a method of analysing working integrated circuits, radiation detectors, solar cells etc, through any thick surface layers. The resultant IBIC images can be interpreted to give information on the physical and electronic properties, such as layer thickness, the distribution of the underlying pn junctions, mask misalignment errors, radiation hardness and upset sensitivity. One example from ref. [30] is shown in Figure 5.3.2 where IBIC and Ion Beam Induced Luminescence (IBIL) images of polycrystalline diamond detectors are shown. These detectors, elaborated by chemical vapour deposition, are designed as alpha particle and UV sensors. They were constructed with a co-planar electrode structure, fabricated only on the growth side of the diamond film. IBIC results show the different efficiencies of individual 10 to 20 µm wide grains at facilitating charge transport at different locations away from the surface metallisation. IBIL results show that some of the large grains, which exhibit poor charge collection, give a high luminescence yield, whereas other regions exhibit both a low IBIC and IBIL signal. These results directly show that the charge collection efficiency in the inter-electrode region is limited both by the size of the diamond crystallites and by the high luminescence yield of certain grains.

**Measurement of small lattice strains using “beam rocking”:** There, measurements that use the ion channeling process in conjunction with a microprobe, have recently been developed for the analysis of small strains from micron-size areas of a crystal. A focused MeV ion beam is rocked in angle about a stationary point on the crystal surface. When the lattice strain varies along the surface, the direction associated to the best channeling effect is not the same on each surface point. The measurement of these small angular shifts permits to quantify small lattice strains across uniform composition and graded silicon-germanium layers.
Fig. 5.3.2 (a) to (c): IBIC images acquired on a polycrystalline diamond detector using 2 MeV protons over a 200 x 200 µm area as a function of the detector bias voltage from 60 V to 180 V. These images show the total number of counts measured above a threshold on the charge pulse height spectrum. Light areas correspond to a high measured number of pulses and dark areas correspond to a small number of measured pulses. Each image was collected for 5 minutes; (d) to (f) PIXE, IBIL and IBIC images from a 150 x 150 µm area of this detector. The three types of boxes on the images e-f correspond to the same area on each image and show different types of behaviour exhibited within this area [30].

-Imaging crystallographic defects using transmission channelling: Defects within the crystal lattice disrupt the regular atomic arrangement and so affect the ion channeling process. This allows the production of images of defects using a scanned, focused MeV ion beam, which is transmitted through a crystal 50 µm thick.

-Maskless patterning and fabrication of high aspect ratio features: The use of focused MeV ions using a microprobe to produce microstructures in resist materials such as polymethylmethacrylate, mica or glass, is an important step in the production of microelectromechanical components and other microstructures. MeV ions have the ability to produce features such as cogwheels, gears and turbines which are tens of microns in diameter in resist thickness up to one hundred microns, due to the high penetrating power and low lateral scattering. Curved surfaces, buried, angled features and multilevel structures can also be produced.

By the time writing this report a superconducting multipole lens has gone into operation at the Munich tandem accelerator [31], which focuses ions of 3 times larger rigidity than standard microprobes to a submicron beam spot at large beam currents (> 10 pA). A prominent improvement is gained in 3D-hydrogen microscopy utilizing proton-proton scattering of 10 - 20 MeV protons, which can now be applied to any micro-structured sample with simple preparation schemes. Ten times better position resolution and many orders of magnitude improved sensitivity is obtained compared to any other nondestructive technique for hydrogen microscopy.

5.4 Radioactive Ion Beams and Techniques for Solid State Research

Sophisticated nuclear techniques, which were developed for detecting particle radiation and to study the interaction of nuclear moments with external electromagnetic fields, were introduced in solid-state research in the late sixties. However, the limited number of adequate probe isotopes, particularly in off-line experiments has restricted their acceptance by the solid-state research community and their applications to a small number of subjects. The
on-line production of radioactive isotopes is the technical approach that best fulfils this gap. Nowadays, mainly due to the needs of nuclear physics research, several radioactive facilities have been built around the world [32] that can be used for nuclear solid-state physics research. Europe has strong traditions on the field, with daily running radioactive isotope facilities, which offer specific complementary features [33]. So far, due to the high diversity, elemental-isotopic purity and high yields of the radioactive beams the world’s best laboratory is the ISOLDE facility at CERN/Geneva [34]. Currently, a large scope of techniques and subjects are studied there that cover a vast range of subjects in metals, semiconductor, oxides with electronic correlations (superconductors, manganites...) and surfaces and interfaces.

Solid-state nuclear techniques can be ordered in three groups: a) The “Hyperfine Interaction” techniques, which rely on specific properties of excited nuclei, are extremely sensitive at the nanometer scale to the materials local fields, via their interactions with the nuclear moments [1]. Applications of Mössbauer Effect, Perturbed Angular Correlations, Nuclear Orientation and the β-Nuclear Magnetic Resonance have been the object of many proposals and publications within the last few years which are reviewed in [35]; b) The “Emission Channeling” techniques make use of the fact that charged particles (α, β+, c.e.) emitted from very low concentration of radioactive isotopes in single crystals experience channeling or blocking effects along low-index crystal directions [36]. This leads to an anisotropic particle emission yield from the crystal surface that depends in a characteristic way on the lattice sites occupied by the emitter atoms. Recently, a new 2D Si pad detector system has been developed at CERN under the scope of high-energy physics experiments [37], which has been adapted for use in electron emission channeling experiments [38]. Since then, the number of available probe nuclei has tremendously increased, being extended to all relevant element groups in the periodic table. Figure 5.4.1 shows (a - c) normalised emission yields of the integral β− intensity in the vicinity of low-index principal directions following room-temperature implantation of about $10^{12}$ cm$^{-2}$ of $^{67}$Cu into n$^+$-Si:As and post-annealing at 600°C. Figure 5.4.1 (d - f) shows best fits of simulated patterns to the experimental yields, with roughly 85% of $^{67}$Cu on ideal substitutional (S) and 15% on displaced S sites [39]; c) The so-called “tracer” techniques, where the element transmutation due to the radioactive decay changes the concentration of impurity atoms in the sample on a well-known time scale that is defined by the nuclear half-life of the used isotope. This transmutation process represents an extremely useful analytical tool for the understanding of the opto-electronic properties, particularly in semiconductors, since these properties are sensitive to the presence of small amounts of impurities. Currently, Deep Level Transient Spectroscopy [40], Hall effect [41], Capacitance-Voltage measurements [42] and Photoluminescence Spectroscopy [43] use radioactive isotopes to overcome the chemical “blindness” of the non-radioactive versions, in studies of the electrical and optical properties of impurities in elementary [44], III-V [45], and II-VI [46] compound semiconductors. Figure 5.4.2 shows (left) photoluminescence spectra of $^{111}$Ag doped GaN recorded at 4 K at different times in the time range between 1 d and 68 d after the implantation and annealing step. All spectra are normalised to the intensity of the yellow luminescence at 1.97 eV; (right) Normalised Photoluminescence intensities of the Cd band

Fig. 5.4.1: (a), (b) and (c) normalised emission yields of the integral β− intensity in the vicinity of ⟨111⟩, ⟨100⟩ and ⟨110⟩ directions of $^{67}$Cu into n$^+$-Si:As after annealing at 600°C; (d), (e) and (f) are best fits of simulated patterns to the experimental yields (see text) [39].
Fig. 5.4.2: (left) photoluminescence spectra of $^{111}$Ag doped GaN recorded at 4 K at different times as a function of luminescence wavelength or energy; (right) Normalised Photoluminescence intensities of the Cd band (circles) and the Ag band (squares) in GaN as a function of time [47].

(circles) and the Ag band (squares) in GaN as a function of time. The solid lines correspond to exponential fits to the experimental data resulting in time constants in perfect agreement with the decay constant of $^{111}$Ag. From these observations, it is clear that the photoluminescence transitions that exhibit a decreasing and increasing intensity as a function of time, have to be correlated with defect centres containing exactly one Ag or Cd atom, respectively [47].

The success of nuclear radioactive solid-state physics research depends essentially on the availability of a broad range of appropriate radioactive isotopes and on adequate sample preparation. This requires increasing the access to beam time in large-scale radioactive facilities and on a good interaction between the solid-state community and the physicists that have the expertise of the continuously developing nuclear science and nuclear experimental techniques.

References
