X-ray absorption fine structure in the study of semiconductor heterostructures and nanostructures

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**Abstract**

X-ray absorption fine structure (XAFS) is a powerful tool in the study of the local atomic environment in condensed matter. It has been often applied to the study of semiconductor heterostructures and nanostructures, significantly contributing to their characterization at the local level and to the understanding of the relation between atomic structure and physical properties.

This chapter begins with an introduction to XAFS as a tool for the determination of local structure; the physical origin of the fine structure is illustrated and the present understanding of X-ray absorption spectra in the framework of multiple scattering theory is outlined. The second section contains a description of the diverse experimental set-ups and detection schemes which can be used in the field of semiconductor science; an effort has been made to make this section both as complete and up-to-date as possible, so that it can serve as a useful reference, also outside the field of semiconductor physics. In the third section, a review of the use of XAFS to study semiconductor heterostructures and nanostructures is presented, covering bond length variations in strained heterostructures, local atomic environments in nanostructures (Ge islands, embedded nanoparticles, porous Si, and related systems), nitride heterostructures and thin films, and finally dilute alloys heterostructures, that is dilute nitrides and dilute magnetic semiconductors.
1. Introduction to X-ray absorption spectroscopy for local structural studies

In this section an introduction to X-ray absorption fine structure is reported. After a review of some basic phenomenology, the origin of the fine structure in X-ray absorption spectra is described. An outline of multiple scattering theory is presented and, in this framework, the extended and near edge regions of the X-ray absorption spectrum are discussed.

1.1 Outline and origin of the fine structure in X-ray absorption spectra

In the X-ray and vacuum ultra-violet (VUV) spectral regions, photoelectric absorption is the dominant interaction mechanism between electromagnetic radiation and matter. An X-ray absorption spectrum is a measurement of the absorption coefficient of a sample, \( \mu(h\omega) \), or of a quantity to which it is directly proportional, as a function of the energy of the impinging photons \( h\omega \). One can determine (conceptually and experimentally) the absorption coefficient by measuring the flux of monochromatic photons incident on and transmitted by a sample of thickness \( x \), \( I_0 \) and \( I_T \), respectively; these quantities are related by

\[
I_T(h\omega) = I_0(h\omega) e^{-\mu(h\omega)x}. \tag{1}
\]

The product \( \mu(h\omega)x \) (a quantity proportional to the absorbance commonly used in VUV and visible spectroscopy) can be obtained by inverting Eq. (1). The overall absorption coefficient of a sample is related to the atomic concentrations and absorption cross-sections of the constituent atoms, \( \rho_i \) and \( \sigma_i(h\omega) \), respectively, by:
\[ \mu(h\omega) = \sum_i \rho_i \sigma_i(h\omega). \] (2)

X-ray absorption spectra exhibit sharp absorption edges which occur at the energies at which excitation of particular core levels becomes energetically allowed. The energies of absorption edges are characteristic of each element; for example, excitation of electrons from 1s, 2s, 2p \( \frac{1}{2} \), and 2p \( \frac{3}{2} \) states correspond to the K, L\(_1\), L\(_{II}\) and L\(_{III}\) absorption edges, and so on, according to the established X-ray nomenclature.

The presence of fine structure in X-ray absorption spectra has been known since 1920; this fine structure shows up as a modulation of \( \mu(h\omega) \) at energies greater than the absorption edge, the relative magnitude of which can be as high as \( \sim 10\% \) and decays with increasing energy from the edge itself. Until the 1970’s the field was plagued by contradictory experimental data and uncertain physical interpretation. Two decisive factors subsequently contributed to asserting X-ray absorption fine structure (XAFS) as a valuable structural tool: the availability of brilliant and broadband synchrotron radiation sources and the development of an approximate but simple and useful point scattering theory. The “modern” era of XAFS is usually traced to the paper by Sayers et al. [1] Some historical reviews have been published recently [2,3] and the interested reader is referred to them for details on the evolution of the technique; the introductory paragraph of the paper by Filipponi [4] contains a compact historical summary.

The physical origin of XAFS in the framework of scattering theory can be understood quite easily. Consider an atom bound in a molecule or solid. In the one-electron approximation, the core level photoelectric absorption process is described in terms of the initial state consisting of the impinging photon of energy \( h\omega \) plus the electron in the core atomic orbital characterized by a wave function \( \psi_i \) with a binding energy \( E_B \) and a final state consisting of a core hole plus an excited electron characterized by a wave function \( \psi_f \) with an energy \( E_f \). Depending on the photon energy,
the electron can be excited to a discrete and bound final state or to a continuum and unbound final state. The final energy of the photoelectron is dictated by energy conservation,

\[ E_f = \hbar \omega - E_b. \]  

(3)

In the dipole approximation, the atomic absorption cross-section (just as for electronic transitions in the optical and UV region) is proportional to the square modulus of the matrix element of the position operator between the initial and final states,

\[ \sigma(\hbar \omega) \propto |\langle \psi_f | \hat{\mathbf{r}} \cdot \mathbf{e} | \psi_i \rangle|^2, \]  

(4)

where \( \hat{\mathbf{e}} \) is the unit vector defining the direction of the electric field of the exciting X-ray beam and \( \hat{\mathbf{r}} \) is the position operator. Let us consider only continuum final states. If the atom were not embedded in a matrix (e.g. a monoatomic gas) the final state wave function would be, at sufficiently high energies, that of an outgoing spherical wave and no fine structure would result. The relation between wave number \( k = \frac{2\pi}{\lambda} \), with \( \lambda \) the wavelength) and kinetic energy for such a free electron is

\[ k = \sqrt{\frac{2mE_f}{\hbar}} = \sqrt{\frac{2m(\hbar \omega - E_b)}{\hbar}}, \]  

(5)

where the second equality uses Eq. (3). If the atom is bound in a molecule or solid the photoelectron wave function will be modified by the presence of the surrounding atoms’ potential; one describes this modification as due to the scattering (one or more times) of the photoelectron by the surrounding atoms. The final state wave function is now the outgoing spherical wave plus the
scattered waves; the scattering process due to the presence of two neighbors to the excited atom is pictorially represented in Fig. 1. Depending on the photoelectron wave number and on the relative atomic arrangement, the scattering process may lead to an enhancement or a decrease of the amplitude of the final state wave function close to the core level orbital and thus to an increase or decrease of the cross-section described by Eq. (4). This is an interference effect between the outgoing and scattered wave functions; the scattered field is the electron wave function while the scattering “objects” are the neighboring atoms. As for any interference effect (e.g. in optics) the position of maxima and minima in reciprocal space depends on the wavelength of the scattered field and on the geometry of the scattering object (e.g. slits, grating or atomic lattice). In the present case, for a given atomic structure, since the wave number depends on the photon energy via Eq. (5), the cross-section varies with photon energy, exhibiting characteristic oscillations which are quasiperiodic as a function of the wave number. The structural sensitivity stems from the dependence on the relative atomic positions between absorbing (“central”) atom and scattering (neighboring) atoms. In Fig. 2 we report a typical XAFS spectrum, in this case of crystalline GaAs at the Ga edge: the presence of fine structure modulations is clearly visible.

The preceding discussion easily allows us to illustrate the common separation of an XAFS spectrum into extended and a near-edge region. If the energy of the photoelectron is high it will be only weakly affected by the neighboring atoms’ potential; usually, it will be scattered a very limited number of times by the neighboring atoms and single scattering processes will be dominant. This is the so-called Extended X-ray Absorption Fine Structure or EXAFS region. In this region one defines the EXAFS spectrum \( \chi(k) \) as

\[
\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)},
\]  

(6)
where $\mu_0(k)$ is the absorption coefficient in the absence of neighboring atoms. The EXAFS spectrum for GaAs at the Ga edge is shown in the top inset of Fig. 2.

As the photoelectron energy decreases, closer to the absorption edge, photoelectron scattering by the neighboring atoms’ potential will become increasingly important and multiple scattering (MS) processes will give a greater contribution to the fine structure. This spectral region, which extends from the edge to roughly 50 eV above it, is commonly referred to as X-ray Absorption Near Edge Structure (XANES) or Near Edge X-ray Absorption Fine Structure (NEXAFS). It must be stressed that the distinction between the two regions is largely arbitrary and that there is no difference in the basic physical mechanism which gives rise to the fine structure; however, the analysis methods for EXAFS and XANES are different and thus it is reasonable to maintain the nomenclature. In the next section the separation between the two spectral regions will be discussed in more quantitative terms in the framework of multiple scattering theory.

In the past 30 years XAFS has evolved into a reliable tool which is able to provide a quantitative measurement of the local structure in condensed matter and has been applied to fields ranging from solid state physics to cultural heritage materials. A number of review papers [5-10] and books [11,12] on XAFS have been published and the reader is referred to them for a thorough description of experimental, theoretical and data analysis aspects.

The purpose of this chapter is to report on the application of XAFS to the subject matter of the present book, semiconductor heterostructures and nanostructures. After description of theoretical and experimental aspects of XAFS a review of applications and results is reported. The use of synchrotron radiation techniques for the characterization of semiconductor heterostructures has been recently reviewed by Lamberti [13]. Fine structure is also observed in electron energy loss spectra (e.g. in the transmission electron microscope) and this is also a powerful tool in semiconductor research offering spatial resolution of the order of 1 nm (but generally a lower
signal-to-noise ratio which does not allow recording extended spectra, especially for absorption edges of high Z atoms); interested readers are referred to the review by Spence [14].

1.2 Multiple scattering theory framework and key approximations

In this section the basis of XAFS in the framework of multiple scattering theory [15-21] is briefly outlined, with the objective of providing a guide for the reader [4].

Photoelectric absorption is treated [22] in time-dependent perturbation theory to first order in the perturbation $\vec{A} \cdot \vec{p}$ (the scalar product of the vector potential of the radiation field and the electron momentum operator). Application of Fermi’s golden rule gives the transition rate between discrete initial and final many electron states, $\Psi_i$ and $\Psi_f$ respectively, as

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} \sum_j \left| \langle \psi_i | \sum_{j} \frac{e}{m} \vec{A}(\vec{r}_j) \cdot \vec{p}_{j} | \psi_f \rangle \right|^2 \delta(E_f - E_i - \hbar \omega),$$

(7)

where the index $j$ covers all the electrons in the system and the label $f$ identifies all final states compatible with the energy conservation dictated by the Dirac delta function. This intractable problem is greatly simplified in the one electron approximation, in which it is assumed that only one electron is involved in the process, the others being unaffected; many-body corrections are added a posteriori (see below). In this approximation, it is assumed that one electron makes a transition between a localized core atomic orbital (e.g. the 1$s$ orbital), described by a wave function $\psi_c$, and a final state described by a wave function $\psi_f$; in ab-initio calculations, the presence of the core hole can be taken into account in calculation of $\psi_f$. A further common simplification is the dipole approximation, which neglects the spatial variation of the vector potential across the extent
of the core level orbital. The photoelectric absorption cross-section for transitions to continuum final states can be written\textsuperscript{23} in these approximations as

\[
\sigma(h\omega) = 4\pi^2 \alpha \hbar \omega |\langle \psi_c | \vec{E} \cdot \vec{p} | \psi_f \rangle |^2 \rho(E_f),
\]

where \(\rho(E_f)\) is the density of the final states, the energy of which is given by energy conservation as \(E_f = E_c + \hbar \omega\) and (in S.I. units) \(\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \approx \frac{1}{137}\) is the fine structure constant, which is thus seen to determine the order of magnitude of the cross-section. Important consequences of the dipole approximation are the selection rules which determine, on the basis of symmetry, which final states are allowed for a given initial state; for a free atom they are

\[
\Delta l = \pm 1 \\
\Delta m_l = 0, \text{ linearly polarized radiation} \\
\quad = \pm 1, \text{ circularly polarized radiation}
\]

here \(l\) is the orbital angular momentum quantum number and \(m_l\) determines its projection on the quantization axis. Thus, for a K absorption edge, the transition will be to \(p\) states.

One must now treat the modification of the final state due to the presence of neighboring atoms, that is, to the scattering of the photoelectron by their potential. Since the principal interaction of the photoelectron is with the core level electrons of surrounding atoms, the \textit{muffin tin approximation} for the scattering potential is commonly adopted. This consists in spherically averaging the potential around each atom and adopting a constant interstitial potential in between. In this approximation, the calculation of the absorption cross-section is simplified into a multiple
scattering problem of the final state wave function by a collection of spherically symmetric
scattering centers.

Under the previously stated assumptions, it has been demonstrated [16-18] that for a randomly
oriented polycrystalline sample the polarization averaged cross-section for a transition to a final
state of angular momentum $\ell$ is

$$
\sigma(h\omega) = \frac{\sigma_0(h\omega)}{(2\ell + 1) \sin^2(\delta^0)} \text{Im} \left\{ \sum_m \left[ (I - TG)^{-1} T \right]_{L,L}^{0,0} \right\},
$$

where $\sigma_0(h\omega)$ is the atomic cross-section. Each element of the matrices which appear in Eq. (10) is
identified by four indices: $i, j$ running over the sites of the atoms surrounding the central one and $L, L'$ (where $L = \{ \ell, m_i \}$) being angular momentum indeces. $I$ is the unit matrix while $T$ and $G$ are the
atomic scattering and propagator matrices in a local basis, respectively. The $T$ matrix is diagonal in
the atomic site and angular momentum indeces, $T_{L,L}^{i,j} = \delta_{ij} \delta_{LL'} e^{i\delta_\ell} \sin \delta_\ell$ where $\delta_\ell$ is the phase shift
for the partial wave of angular momentum $\ell$ centered on the $i$-th atom. The $G$ matrix is composed
of null diagonal blocks in the site indeces $i, j$ ($G_{L,L'}^{i,j} = 0$ ) and describes the free propagation of the
electron from site $i$ to site $j$. Thus, the $T$ matrix depends on the atomic composition of the sample
while the $G$ matrix depends on the geometrical arrangement of the atoms.

At sufficiently high energies above the edge (say 50 eV) the formal matrix expansion

$$
T(I - GT)^{-1} = T(I + GT + GTGT + GTGTGT + \ldots.)
$$

1

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in Eq. (10) is convergent; this leads to the *multiple scattering series* (MS series) whereby the cross-section can be written as the sum of a limited number of terms, each relative to a particular scattering path. This is the EXAFS region in which the cross-section can be written as

\[
\sigma(h\omega) = \sigma_0(h\omega) \left(1 + \sum_{i=0}^{m} \sum_{j=0}^{n} \chi_{2}^{0,0} + \chi_{3}^{0,0} + \ldots \right)
\]

where 0 identifies the central atom, the subscripts indicate the number of scattering “legs” and the superscripts indicate the scattering path, starting and ending on the central atom via atoms \(i\) and \(j\). Scattering paths with 2 and 3 legs are pictorially represented in Fig. 3; scattering paths with 2 legs are usually termed Single Scattering (SS) paths while those with 3 or more legs are termed Multiple Scattering (MS) paths. An alternative decomposition of the cross-section in the EXAFS region into irreducible \(n\)-body signals has been used by Filipponi *et al.* [21].

The matrix expansion Eq. (11) is not convergent in the near edge, or XANES, region. Here a calculation of the spectrum implies the inversion of the matrix \((I-TG)\); this is the Full Multiple Scattering (FMS) regime because an infinite number of scattering paths contribute to the XAFS cross-section.

### 1.3 EXAFS or extended X-ray absorption fine structure

Sufficiently far from the edge, in the EXAFS region, the MS series is convergent and this leads to a compact expression for the EXAFS function, Eq. (6), which is used for quantitative structural refinement. Before proceeding, we must take into account some effects which have been neglected up to now. Despite the success of a one-electron picture, many body effects do have an appreciable influence on the fine structure and it is necessary to introduce some corrections to
improve agreement between theory and experiment, the most important of which we now briefly discuss. The first correction is due to the relaxation of the wave function of electrons not directly involved in the transition and leads to a reduction of the amplitude of $\chi(k)$ by a factor

$$S_0^2 = \left| \langle \Psi_{N-1}^f \mid \Psi_{N-1}^i \rangle \right|^2$$

(13)

where $\Psi_{N-1}^i$ and $\Psi_{N-1}^f$ are the many-body wave functions of the “passive” electrons before and after excitation of the “active” electron; the value of this amplitude reduction factor is usually between 0.7 and 0.9. The second correction is due to the limited range of the excited electron with the matrix (at most ~ 10 Å) and to the limited lifetime of the core hole (~ 1 fs); both have the effect of damping the contribution to $\chi(k)$ from distant atoms and this is, in fact, the origin of the local sensitivity of XAFS. One may model these two effects with an effective electron mean free path $\lambda(k)$, the value of which is energy dependent and ranges from a few Å’s to ~ 10 Å. In up-to-date data analysis schemes these effects are included in the effective scattering amplitude (see below).

The third correction is due to thermal motion of the atoms. The photoabsorption process occurs on the time scale of ~ $10^{15}$ s, in which the atoms may be considered as fixed in their instantaneous positions; hence, a XAFS spectrum, due to a very high number of excitation processes, probes the configurational average of the atomic position. Thermal motion gives rise to the so-called Debye Waller (DW) factor, which for a SS contribution to $\chi(k)$ involving atoms 0 and $i$ and for motion in a harmonic potential is

$$\sigma_i^2 = \langle \hat{r}_m \cdot (\hat{u}_0 - \hat{u}_i) \rangle \rangle^2,$$

(14)
where \( \langle \ldots \rangle \) denotes a configurational average, \( \hat{r}_{oi} \) is the unit vector joining atoms 0 and \( i \), and \( \vec{u}_i \) is the instantaneous deviation of the position of atom \( i \) from its average position. An important point is that the XAFS DW factor depends on the degree of correlation of the vibration of the two atoms, while the DW factor which affects the intensity of XRD peaks depends only on the mean square deviation of each atom’s position with respect to its equilibrium value, projected in the direction of the wave vector difference. The effect of moderate static structural disorder can also be taken into account by a supplementary DW factor.

With these approximations, the SS contribution the EXAFS function can be written in a compact form. With the central atom taken as reference, the neighboring atoms are grouped into coordination shells labelled by the index \( j \) and consisting of \( N_j \) identical atoms at the interatomic distance \( r_j \); in the harmonic approximation for thermal motion and for a randomly oriented crystalline powder sample we have

\[
\chi_2(k) = S_0^2 \sum_{j=\text{shells}} N_j f_j(r_j, k) \frac{1}{k^2 R_j^2} \sin [2kr_j + \varphi_j + 2\delta] e^{-2\kappa \sigma_j^2},
\]

(15)

where \( f_j(r_j, k) \) and \( \varphi_j \) are the modulus and argument of the effective scattering amplitude of atoms in shell \( j \) and \( \delta \) is the phase shift due to the central atom. The scattering amplitude depends also on the interatomic distance \( r_j \), since the curved wave nature of the photoelectron wave function is taken into account; in the \textit{plane-wave approximation}, adopted in more elementary treatments, this dependence no longer exists. If the sample is an oriented single crystal and if, as usual, a linearly polarized photon beam is used, each atomic correlation will contribute to \( \chi(k) \) with a weight \( w_{0i} \) which depends on the relative orientation of \( \hat{r}_{oi} \), the unit vector joining atoms 0 and \( i \), and the direction of polarization \( \hat{\varepsilon} \); a simple expression for this weight can be obtained in the \textit{small atom}
approximation in which the spatial extension of scattering region associated to each neighboring atom is neglected with respect to photoelectron wavelength:

\[ w_{oi} = 3 \hat{e} \cdot \hat{r}_{oi}. \]  

(16)

Despite the apparently crude approximation, this weighting factor is very useful to estimate linear dichroism effects.

Contributions to \( \chi(k) \) due to MS paths have a form similar to Eq. (15). It can be shown that the MS contribution of order \( n \) due a set of atoms the coordinates of which are identified by a path index \( \Gamma = \{ r_i \} \) and for which the total scattering path length is \( r_\Gamma \) are of the form

\[ \chi_n^\Gamma = A_n(k, \Gamma) \sin[k r_\Gamma + \phi_n(k, \Gamma) + 2\delta]. \]  

(17)

The total EXAFS function will be the sum of all the SS and MS paths, as indicated by Eq. (12). In principle, there is an infinite number of such paths, but, in practice, their number is limited by the rapid damping of the signal for long path lengths (usually paths the length of which is greater than \( \sim 10 \) Å have negligible amplitude) and the fact that the amplitude of MS signal quickly decreases with the order \( n \) (usually paths with \( n > 4 \) can be neglected). MS paths are weak in the EXAFS region but must be taken into account for an accurate structural determination; collinear paths due to three atoms in a row give rise to strong contributions to \( \chi(k) \) due to scattering paths composed of three or four legs as, for example, in the case of rocksalt structures [24]. In the diamond structure, the importance of MS paths in the EXAFS region was first pointed out by Bianconi et al. [25].

Since the EXAFS function is the sum of sine functions, the argument of which is \( kr_\Gamma \), a Fourier Transform (FT) of \( \chi(k) \) will exhibit peaks in correspondence to the path length; the FT is
usually plotted as a function of the half path length which, for SS paths, is equal to the interatomic distance. In Fig. 4 we report the magnitude of the FT of the EXAFS spectrum shown in the top inset of Fig. 2, relative to GaAs at the Ga K-edge; the main contributions to the first three peaks are due to the first, second and third coordination shell of the zincblende structure.

From the analysis of an EXAFS spectrum the following local structural parameters can be obtained: interatomic distances ($R$, typically $\pm 0.005$ Å for the first shell), identity of neighboring atoms and their coordination number ($CN$, typically $\pm 10\%$) and, provided a Gaussian model for the radial distribution function is appropriate, the DW factor ($\sigma^2$, typically $\pm 5 \times 10^{-4}$ Å$^2$).

EXAFS analysis requires an adequate starting structural model, which can be obtained from prior knowledge of the sample. An up-to-date analysis usually is based upon a simulation of the EXAFS signal and a subsequent refinement of the local structural parameters via a least squares routine. A description of data analysis methods is outside the scope of this paper; the interested reader is referred to existing literature and manuals [26].

1.4 XANES or near edge X-ray absorption fine structure

In the near-edge spectral region, the MS series Eq. (12), does not converge and thus it is not possible to express the cross-section as a sum of sine functions. A simulation of the XANES region requires inversion the matrix ($I - TG$) and it is a relatively lengthy matter in terms of computer time. The XANES lineshape is sensitive both to the details of the scattering potential (because of the low energy of the photoelectron) and to the three dimensional position of atoms contained within a radius greater than that necessary to reproduce EXAFS. As a consequence, quantitative analysis of the XANES is not generally possible at present.

An interpretation of XANES spectra in term of electronic structure is also possible. In fact, referring to Eq. (8), if one neglects the energy dependence of the matrix element in a limited range
of the near edge region, one can see that the absorption cross-section is proportional to the density of final states (in the presence of the core hole), selected in angular momentum by the rules given by Eq. (9) and projected on the absorbing atomic species. This kind of interpretation links XANES to electronic structure calculations [27,28] and is often used in the case of small molecules [29].

XANES finds widespread application in many different fields, in which it is often used with a “finger-printing” approach whereby the spectrum of a sample is compared to those of a number of reference compounds of known structure; for example, the XANES spectra of transition metal compounds exhibit clear and significant differences with oxidation state and coordination, the most extensive compilation of which has probably been performed in the field of mineralogy [30]. An analysis of the XANES spectrum provides information on the site symmetry of the absorbing atom (e.g. tetrahedral or octahedral) and on its oxidation state.

Since XANES is sensitive to the three dimensional atomic geometry (while the dominant contributions to EXAFS are of a one-dimensional character) and because XANES spectra are more easily recorded than EXAFS ones, especially for dilute elements, a quantitative interpretation of XANES would be of great interest. In the field of semiconductors, we quote the recent paper by Ciatto et al. [31], in which, by making a comparison between experimental spectra and ab-initio simulations, it was possible to determine the three dimensional structure of the nitrogen-hydrogen complex responsible for the elimination of the red-shift of the band gap in the dilute nitride alloy GaAsN. In an significant paper, Della Longa et al. [32] have described a structural fitting of XANES spectra for bio-molecules; the extension of this method to solids would be a very important step forward in the investigation of dopants and defects in semiconductors.

Let us conclude mentioning that in the important case of the L edges of transition metals, in which a $p$ electron makes a transition to a narrow $d$ band, because of the strong electron correlation effects multiplet theory is used to interpret the spectra. A useful review paper on these aspects has
been written by de Groot [33]. L-edge spectra have been used to study the local structure of Mn in dilute magnetic semiconductors, as will be described in section 3.

2. Detection schemes and experimental set-ups relevant for semiconductor research

In this chapter the main experimental set-ups which are relevant for semiconductor research are described. Of course, an essential requirement to perform an XAFS experiment is that of a brilliant synchrotron radiation source and appropriate optics, the role of which is to provide a focal spot on the sample of the required characteristics in terms of photon flux, bandpass, stability, divergence and spot size. There has been great progress in this field in the past years and a great number of papers and books have been published, some of which are reported in the references [34-39].

Here, we focus our attention on the experimental chamber itself and the appropriate detection schemes. The objective of any XAFS measurement is to record, as a function of photon energy, a quantity which is directly proportional to the cross-section of the atom of interest in the particular environment or phase which is relevant for the experiment. A number of methods have been devised and will be here described. As for Diffraction Anomalous Fine Structure (DAFS) we refer to the chapter by Proietti et al. [40].

2.1 Transmission geometry

A transmission measurement of XAFS is the most commonly used in general. It relies on the measurement of the flux of monochromatic photons incident \( I_0 \) and transmitted \( I_T \) by a sample of thickness \( x \). Inversion of Eq. (1) gives
\[
\mu(h\omega)x = \ln \left[ \frac{I_0(h\omega)}{I_T(h\omega)} \right]
\]  

(18)

where \(\mu(h\omega)\) is the absorption coefficient. The main requirement for this kind of measurement is that the discontinuity in \(\mu x\) be in the range [6] of 1-2 and that the lateral homogeneity of the sample be small enough to avoid "thickness effects" [41]. In practice, this means sample thicknesses which must be in the range 1-10 \(\mu m\) and homogeneities which must be a fraction of this; therefore, the transmission technique cannot usually be used in the soft X-ray range in which the thicknesses required would be too small to make the fabrication of a homogenous sample practical. The transmission technique can be applied when the atom of interest is not dilute or at or near the surface; its main advantage is that it generally provides data of very good signal-to-noise ratio, since it relies on the measurement of rather high photon fluxes \((10^9-10^{11} \text{ photons/sec})\). The most commonly used detector for transmission measurements are gas ionization chambers.

In the field of semiconductor heterostructures and nanostructures one is mostly interested in studying the local structure of ultra thin-films, nano-layers, or low dimensional structures on, or near, the surface. Pristine samples are thus not usually appropriate for measurements in the transmission mode, since the background due to the substrate or matrix would be too high. In a notable exception, Ridgway’s group [42] have devised specific sample preparation procedures which involve the etching of the substrate and stacking of various layers of the sample of interest in order to obtain a final equivalent thickness appropriate for transmission measurements; accompanying this with a low measurement temperature (which reduces the DW factor, Eq. (14)) data of excellent signal-to-noise ratio were obtained by these authors for a number of cases.
2.2 Decay channels: fluorescence and electron yield

Reduction of the background absorption signal originating from the matrix can be obtained by selectively recording the intensity of an atom-specific signal. For example, one can exploit the decay of photo-excited atom, which occurs with the emission of either a fluorescence photon (this is the so-called “characteristic radiation”) or of an Auger electron, both of which have energies which depend on the atomic number of the photoexcited atom.

2.2.1 Fluorescence yield detection

In the fluorescence yield (FY) detection mode [43], a photon detector is used to record the fluorescence intensity as a function of energy. In the most common experimental geometry used with horizontally polarized X-rays, the detector is placed in the horizontal plane at right angles to the incident beam to minimize the intensity of elastic scattering of the impinging X-ray beam; in this geometry, the intensity of fluorescence photons, $I_f(h\omega)$ of atom $A$ embedded in a matrix $M$ for a sample thickness $d$, can be easily shown to be [6]:

$$I_f(h\omega) = I_o(h\omega) \frac{\Omega}{4\pi} \varepsilon_f \frac{\mu_A(h\omega)}{\mu_{tot}(h\omega) + \mu_{tot}(h\omega_f)\tan \theta} \times \left[1 - \exp\left[-\left(\mu_{tot}(h\omega) + \mu_{tot}(h\omega_f)\tan \theta\right)d\right]\right]$$  \hspace{1cm} (19)

where $\varepsilon_f$ is the fluorescence yield, $\Omega$ is the solid angle subtended by the detector, $h\omega_f$ is the energy of the fluorescence photons, $\theta$ is the angle between the impinging beam and the sample surface and the total absorption coefficient (see Eq. (2)) is the sum of contributions due to atomic species $A$ and that due to the matrix $M$: $\mu_{tot} = \mu_A + \mu_M$. Since $\mu_{tot}$ depends on $\mu_A$, Eq. (19) is not in general proportional to the quantity one wants to measure, that is $\mu_A(h\omega)$. This proportionality is recovered in two limiting cases: thin samples (for which the series expansion of the exponential in Eq.(19) can
be truncated at the term linear in $d$, typically below 100 nm) and for thick samples in which atom $A$ is dilute ($\mu_{\text{tot}} \cong \mu_M$, a condition which depends on the angle $\theta$ but usually occurs below a few atomic %). If these conditions are not met, fluorescence data can be corrected for non-proportionality (also known as “self-absorption”), as has been described by various authors [44-49].

Many types of detectors for FY mode have been used, but the most common are based on solid state Si:Li or (mostly nowadays) hyper-pure Ge diodes. These detectors often are in the form of multi-element arrays [50,51] and have an energy resolution in the range of 150-200 eV at 6 keV, a reasonable trade-off between counting rate and background rejection; as an example [52], the spectrum of photons emitted from a sample consisting of $\sim 10^{16}$ Sn atoms/cm$^2$ implanted in SiO$_2$ recorded on the GILDA beamline of ESRF [53] is reported in Fig. 5: elastic scattering, inelastic (Compton) scattering and Sn fluorescence are clearly identified. Since pulse counting electronics is used, care must be taken to avoid, or correct, dead-time effects [54].

Since both the probe and the detected signals are penetrating X-rays, FY is the best choice to study dilute elements in the bulk of materials. This has lead to a wide application of XAFS to the study of dopants in semiconductors. The lowest concentration which can be measured in a FY-XAFS experiment ultimately depends on the magnitude of the inelastic scattering background in the specific experimental geometry. Takeda et al. [55] have recently studied the factors which determine the lowest concentration which can be detected; they have come to the conclusion that, for the specific case of the L$_{\text{III}}$ edge of Er in GaAs or InP, the lowest dose measurable is $1-5 \times 10^{14}$ atoms/cm$^2$. In the more general case, the lowest detectable dose or thickness depends on the absorbing atom, the matrix and the experimental geometry; XAFS spectra on thicknesses equivalent to 1-0.1 monolayers are nowadays measurable with adequate signal-to-noise ratio and even lower concentrations can be measured in specific cases [55].
2.2.2 Electron yield detection

The decay of the core hole can occur also with the emission of an Auger electron. This Auger electron creates a cascade of lower energy (“secondary”) electrons due to multiple ionization and inelastic scattering processes. Various electron yield detection methods exist, depending on which electrons are detected and the detection method. The experimentally simplest method, often used in the soft X-ray region, consists in measuring the drain current using an electrometer which connects the sample to ground; this method, termed Total Electron Yield (TEY) can be traced back to the pioneering investigation by Gudat and Kunz [56]. A variation on TEY is Partial Electron Yield (PEY) in which only electrons of a given energy range are detected, with the use of retarding grids and electron detectors. In the hard X-ray range, cross-sections are smaller than at lower energies and the most common method consists in recording the signal due to radiationless decay using a He-filled ionization chamber in which the sample acts as the anode [57-60]: He gas acts as an electron multiplier and an amplified signal is recorded from the cathode; this method is also termed Conversion Electron Yield (CEY). Finally, the conceptually simplest method consists in directly recording of the number of Auger electrons themselves [61,62] (Auger Electron Yield, AEY); this is only employed in surface XAFS experiments, since it requires an electron analyzer operating in ultra-high vacuum conditions.

The main peculiarity of all electron detection modes is the surface sensitivity, which is guaranteed by the limited electron mean free path. Hence, these modes are particularly useful for the investigation of the near surface region or of interfaces. Erbil et al. [63] have reported a detailed study of the depth sensitivity of TEY mode, concluding that it depends on the range of the original Auger electrons and that it generally is in the range of a few 100 to a few 1000 Å. Schroeder et al. [64] have compared TEY and CEY in detail, concluding that the former is more surface sensitive than the latter.
Spectra recorded using electron detection methods may suffer from “self absorption effects”, the origin of which is identical to that previously illustrated for FY; usually, the effect is less severe than in FY since the electron absorption coefficient is much higher than the photon absorption coefficient and thus it dominates the denominator in Eq. (19). Correction procedures have been described by Nakajima et al. [65] and Regan et al. [66].

2.3 Alternative detection methods

A number of “non-conventional” methods to detect XAFS have been proposed, each with its own advantages, limitations and pitfalls. We briefly review the ones which have relevance to the investigation of semiconductors, leaving a discussion of results on specific systems to section 3.

2.3.1 Optical detection

When excited by an X-ray beam, many samples emit visible or near visible radiation. The use of this X-ray excited optical luminescence (XEOL) and the measurement of the XAFS spectrum via the resulting photoluminescence yield (PLY) have attracted considerable attention, in view of the possibility of determining the local structure of only the atoms involved in the luminescence emission, thus adding site selectivity to XAFS.

XEOL was first observed by Bianconi et al. [67] in CaF$_2$; their PLY-XAFS spectrum actually exhibited an inverted jump (i.e. a decrease, rather than an increase, of the PLY at the edge). The role of the attenuation lengths for the x–ray and optical photons and the sample composition in determining this behavior was subsequently understood and discussed by Goulon et al. [68] and Emura et al. [69]
A fundamental issue is the effective site-selectivity of PLY-XAFS: it should be verified that the change of the PLY at the absorption edge of a particular atom is only due to absorbers in the optically active centers. In many cases, particularly in scintillators or ionic crystals, the optically active center may be different or distant from the selected absorbing atoms. In the case of a sample consisting of a mixture of ZnS-ZnSe powders, in which the two components emit at different wavelengths, site selectivity was clearly demonstrated by Pettifer and Bourdillon [70]. On the hand, the important role which can be played by inter-ion excitation was shown by Sonderholm et al. [71], who studied, among others, a Gd₂O₂S sample doped with 0.4% Tb; they observed a XAFS signal in the Tb luminescence yield at energies corresponding to the Gd edge. The importance of inter-atomic excitations has also been stressed by Pettifer and co-workers [72]. A thorough, but quite critical, review on PLY-XAFS has been reported Rogalev and Goulon [73]. It is clear that site-selectivity in PLY-XAFS should be checked for every sample examined.

PLY-XAFS has found an important application in the study of porous Si, which emits in the visible range, and specific results will be illustrated in section 3. Recently, PLY-XAFS has been applied in the study of ZnO nanostructured materials both at the high energy K-edge [74] and at low energy [75].

2.3.2 Electrical detection

The electrical detection of XAFS has been investigated by some groups with the objective of determining whether the local structure of only those atoms contributing to the electrical signal due to defects could be determined, leading to another attractive site-selective version of XAFS.

Photocurrent detected XAFS spectra has been reported by Boehme et al. [76] and Hu et al. [77] for an Al-GaAs diode and for bulk GaAs, respectively. Their common conclusion is that these
spectra contain, for these concentrated samples, the same structural information as the more traditional transmission mode ones, once corrections for sample thickness are taken into account.

Ishii et al. [78] have proposed a capacitance-detected version of XAFS, the specific system studied being a Se-doped AlGaAs-Al diode in which the semiconductor exhibits the so-called DX deep level electron trap. It is argued by these authors that, since changes in capacitance are due to electrons localized in the traps, it is possible to determine the local structure of only those atoms at a short distance from the trap itself. In fact, their spectra at the Ga edge recorded in the fluorescence and in the capacitance mode exhibit significant differences. Ishii has also proposed variations of the capacitance method; by varying the diode bias potential a depth selectivity is proposed [79], while use of scanning capacitance probes is proposed to provide lateral resolution on the length scale of the AFM [80, 81].

The site-selectivity of capacitance-detected XAFS has been challenged in detail by Bollmann et al. [82]. These authors have examined samples exhibiting both the DX deep level and antisite defects; spectra measured in the fluorescence and capacitance mode do not show any significant differences. Also by modeling the X-ray induced current and capacitance changes, Bollmann et al. conclude that, since the defect centers can be ionized also by electrons (directly or indirectly) generated by core ionization of atoms distant from the defect center themselves, no site-selectivity results. It is clear that in order for this detection mode to be accepted by the scientific community more work is necessary to resolve the issue of selectivity.

2.3.3 Beta environmental fine structure

We mention briefly a method which is potentially of great interest for the study of defects and dopants in semiconductors. In the context of precise measurements of the neutrino mass, it has been suggested [83] that the β decay spectrum of a nucleus belonging to an atom embedded in a crystal
or molecule could be affected by a fine structure similar to that which gives rise to XAFS. In fact, the emitted $\beta$ particle (an electron) will be scattered by neighboring atoms and the decay rate might be affected by the resulting interference, resulting in so-called beta environmental fine structure (BEFS).

BEFS was detected [84] in the decay spectrum of $^{187}$Re and since $\beta$ emitting nuclei include tritium, $^{14}$C and a number of metals it was realized that BEFS could potentially be of great interest in materials physics and chemistry [85]. The Re BEFS spectrum was later quantitatively analyzed [86], finding good agreement with the known crystal structure. An open issue, the angular momentum of the final state ($s$ or $p$) was addressed more recently [87]. BEFS is potentially very powerful, especially for the study of the local environment of hydrogen in semiconductors (for which traditional XAFS is impossible because of the low binding energy of the K edge) but has yet to prove to be a practical tool.

2.4 Specific experimental set-ups

2.4.1 Grazing incidence

The interaction between an electromagnetic wave and a sample can be described, in a macroscopic picture, by the index of refraction. The propagation of a wave traveling in the direction $\vec{x}$ is determined by the phase factor

$$\exp\left[i\left(\omega t - \vec{k} \cdot \vec{x}\right)\right]$$

(20)
where \( \omega \) is the angular frequency and \( \vec{k} \) is the wave vector, with the wave number being \( |\vec{k}| = k = \frac{2\pi}{\lambda} (\lambda \text{ is the wavelength)} \); the velocity of propagation is \( v = \frac{\omega}{k} \). In the X-ray range the index of refraction can be written as

\[
\begin{align*}
n(\hbar\omega) &= 1 - \delta(\hbar\omega) + i\beta(\hbar\omega) \tag{21}
\end{align*}
\]

where both \( \delta \) and \( \beta \) are positive and \(< 1\); \( \delta \) and \( \beta \) describe dispersion and absorption processes, respectively, and, like the real and imaginary part of the permittivity, are related by the Kramers-Krönig relations. For Si at \( \lambda \sim 1.2 \text{ Å} (\hbar\omega = 10 \text{ keV}) \) \( \delta \approx 9.8 \times 10^{-6} \) and \( \beta \approx 1.5 \times 10^{-7} \). As a consequence, an x-ray beam impinging on the flat surface of a sample may undergo total external reflection if the angle of incidence (\( \alpha \), taken to be the angle between the beam’s direction and the surface) is smaller than the critical angle,

\[
\alpha_c = \sqrt{2\delta} \tag{22}
\]

For Si at \( \lambda \sim 1.2 \text{ Å}, \alpha_c \approx 4.5 \text{ mrad}. \) For \( \alpha < \alpha_c \) the reflectivity approaches 1 and inside the sample the beam is confined to the near surface region; compact expressions for the penetration depth \( \Lambda \) in the direction normal to the surface can be derived [38] for three cases (the values listed are for Si at \( \lambda \sim 1.2 \text{ Å} \):
\[ \alpha \ll \alpha_c : \quad \Lambda = \frac{1}{2k\sqrt{2\delta}} \approx 2.2 \text{ nm} \]
\[ \alpha = \alpha_c : \quad \Lambda = \frac{1}{2k\beta} \approx 26 \text{ nm} \]
\[ \alpha = 10 \alpha_c : \quad \Lambda = \frac{\alpha}{2k\beta} \approx 29 \mu m \]

The last expression in Eq. (23) is just the usual penetration length determined by the absorption coefficient \( \mu = 2k\beta \) projected on the surface normal. Moreover, it can be shown that for \( \alpha = \alpha_c \) the beam intensity at the surface is four times the intensity of impinging beam. The reflectivity is a complicated function of \( \alpha, \delta \) and \( \beta \), which approaches 1 for \( \alpha \ll \alpha_c \) and 0 \( \alpha \gg \alpha_c \). It is clear that a strong confinement of the X-ray beam in the near surface region can be obtained by using grazing incidence.

The possibility of using grazing incidence to probe the surface region of materials was illustrated by Parratt [88]. As far as XAFS is concerned, Barchewitz et al. [89] were the first to record fine structure via the reflectivity, \( R(h\omega) \), and to suggest the relation with the absorption spectrum. Subsequently, Martens and Rabe [90] provided an in-depth discussion, opening the way to what has been called the “RefleXAFS” technique. The fine structure in \( R(h\omega) \) is related to the “usual” XAFS spectrum \( \chi(k) \). However, it is not straightforward, in the general case, to obtain \( \chi(k) \) from \( R(h\omega) \) since the latter quantity depends in a complicated way on both \( \delta(h\omega) \) and \( \beta(h\omega) \); of course, the “usual” XAFS spectrum is contained in \( \beta(h\omega) \). A simplification arises sufficiently far from the edge and for \( \alpha < 0.8 \alpha_c \), since it can be shown [91] that

\[ \mu(h\omega) = \frac{1 - R(h\omega)}{1 + R(h\omega)} \]

(24)
A number of methods have been proposed to extract an XAFS spectrum from the reflectivity, each with its advantages and limitations [90-93]. Instead of measuring the reflectivity, FY or TEY may be used, of course [94]; in the case of a dilute or thin sample, a spectrum recorded in this way is directly proportional to $\mu(\hbar\omega)$ and does not require corrections [95]. Grazing incidence XAFS is a powerful tool to study surfaces and interfaces and has been used also to study semiconductor nano and hetero-structures.

2.4.2 Surface X-ray absorption fine structure

The potential of XAFS to determine the local structure of interfaces deposited \textit{in-situ} in an ultra-high vacuum environment was realized early on [61,62]. As far as use of the EXAFS spectral region is concerned, this has lead to the acronym SEXAFS for “Surface EXAFS”. The specific advantage of surface XAFS for the study of heterostructures is the possibility of determining the atomic environment in the first few coordination shells of an excited atom in the epi-layer (with an error of the order of 0.01 Å for the interatomic distances), during the formation of the interface, without exposure to the atmosphere. This information is crucial for a correct physical modeling of interface properties and now can be usefully compared to \textit{ab-initio} structural simulations. By exploiting the dependence of the XAFS cross-section on the relative orientation of the sample and the linearly polarized synchrotron radiation beam the structure parallel and perpendicular to the growth plane can be determined [96,97]. When information on the long range order is necessary, surface XAFS can be usefully coupled to grazing incidence X-ray diffraction. Surface XAFS has been reviewed a number of times and some of these reviews are listed in the references [98-100].

Surface XAFS relies on detection schemes which are able to distinguish the signal originating in the interface from that originating from the bulk: TEY, PEY or FY, often combined with grazing incidence, all of which have been previously described. Of course, the further requirement is of an
ultra-high vacuum chamber connected to the beamline and equipped with all the instrumentation required to prepare an atomically clean and ordered surface and to deposit and characterize ultra-thin epilayers. A particularly detailed description of a well equipped surface XAFS apparatus has been reported by Oyanagi et al. [101].

2.4.3 Micro-XAFS

As brighter synchrotron sources have become available it has become possible to obtain smaller focal spot sizes and to design instruments capable of increasingly higher spatial resolution. In fact, the field of X-ray microscopy has progressed very rapidly in recent years; lateral resolutions of the order of 10 nm have been obtained with photoelectron imaging techniques, e.g. the Photo Emission Electron Microscope or PEEM [102].

There is a great interest in performing XAFS with high lateral resolution (micro-XAFS) since it allows a new level of description of heterogeneous samples, combining microscopy with the atomic-scale structural information obtainable from XAFS; with sufficiently small focal spots the local atomic environment of single nanostructures might be determined. The challenge is to record XAFS spectra free of systematic errors and with sufficiently good signal-to-noise ratio. At present, XAFS spectra can be recorded with spot sizes of the order of a few \( \mu \text{m}^2 \), for example on the ID22 beamline [103] of the ESRF or on the LUCIA beamline [104] of the SLS; micro-XAFS is often complemented with micro-fluorescence mapping. Applications of micro-XAFS to semiconductors have been relatively limited so far, but it is expected much progress will be made in this field. Micro-XAFS is particularly useful when the samples investigated exhibit lateral inhomogeneities and it is not surprising that many applications in the field of semiconductors have been on samples the growth of which has yet to be optimized, for example dilute magnetic semiconductors based on GaN, as will be discussed in section 3. In several synchrotron radiation laboratories efforts are on
the way to combine the information which can be derived from XAFS with the nm-level lateral resolution which can be obtained by using Atomic Force Microscope tips [105]. While photon-based techniques might maybe never reach the sub-Å spatial resolution obtainable in electron microscopy, the advances in recent years have been really dramatic since they involve many orders of magnitude improvement in spatial resolution. In the future, micro-XAFS will certainly become a powerful tool in materials science, complementing spatially averaged techniques which have been the key to the success and widespread use of X-rays for structural determination.

3. A review of the use of XAFS in the field of semiconductor heterostructures and nanostructures

In the field of materials science, new growth and deposition schemes are continuously devised, with the objective of obtaining samples and devices with novel physical properties. The role of highly sensitive and sophisticated methods such as XAFS is to provide a description of the local atomic environment which can form the structural basis for an understanding of the physical properties. In the past twenty years, XAFS has developed from an intriguing physical phenomenon to a tool which is used in many branches of science. In this section, an attempt is made to review the use of XAFS in the study of the local atomic environment of semiconductor heterostructures and nanostructures. This is a rather wide field and the choice of examples is partially a personal one. Not all aspects of semiconductor science are covered, for example the important application of XAFS to the study of dopants, implanted atoms and defects is not included.
3.1 Bond lengths in strained III-V heterostructures

The study of the effect of strain on the local atomic structure, especially on the bond lengths, is an area in which XAFS has provided key results, clarifying what initially seemed a rather confusing situation. The applicability of XAFS to study small bond length variations in (unstrained) semiconductor pseudo-binary alloys was demonstrated in pioneering papers in the 1980’s [106,107]. The main result of these investigations is that bond lengths exhibit a variation with relative concentration which is significantly weaker than that exhibited by the lattice parameter. In fact, the lattice parameter of a pseudobinary semiconductor alloy of composition $A_xB_{1-x}C$ and zincblende structure generally obeys Vegard’s law,

$$a(x) = xa_{AC} + (1-x)a_{BC}, \quad (25)$$

where $a_{AC}$ and $a_{BC}$ are the lattice parameter of the binary compounds, quite well. It is found experimentally that the bond lengths, $R_{AC}$ and $R_{BC}$, exhibit a much weaker dependence on $x$. This can be qualitatively understood as due to the “rigidity” of semiconductor bonds and implies the existence of local distortions, i.e. variations of the bond angles. A comprehensive theory of bond length variation in semiconductor alloys, able to reproduce existing experimental results and with predictive ability, was proposed by Cai and Thorpe [108]; a basic ingredient of their work is the assumption that there are no differences between the bond stretching and bond bending force constants in elemental tetrahedra centered on different atoms and that an average value applies in all cases. It should be noted that XAFS is the appropriate tool to study this problem because of the chemical selectivity and high resolution at the short distance scale. It is interesting to note that a pair distribution function (PDF) analysis of X-ray diffraction (XRD) patterns has also recently been shown to allow the determination of interatomic distances in bulk $\text{InGa}_{1-x}\text{As}_x$ samples [109]; also, it
has been demonstrated [110] that *ab-initio* structure determination of randomly oriented nanostructures is in principle feasible and that the PDF can be obtained for bulk ZnSe$_{1-x}$Te$_x$ from neutron diffraction data [111]. An advantage of this technique is that it combines short and medium scale sensitivity while a limitation is that the applicability to thin crystalline epilayers appears to be difficult.

The issue of bond lengths in thin strained semiconductor layers grew out naturally in the context of studies of bulk alloys. It is well known that, below a certain critical thickness, when a epilayer with a cubic lattice is deposited on a substrate with a different lattice parameter its unit cell will undergo a tetragonal distortion (this is termed pseudomorphic growth). The distortion is quantified by the perpendicular and parallel strains, $\epsilon_\perp = \frac{a_f - a_i}{a_f}$ and $\epsilon_{||} = \frac{a_f - a_i}{a_f}$, respectively, where $a_f$ is the epilayer’s free (unstrained) lattice parameter; for two-dimensional growth on a (001) oriented substrate the strains are related by

$$
\epsilon_\perp = \frac{-2C_{12}}{C_{11}} \epsilon_{||},
$$

where $C_{12}$ and $C_{11}$ are the elastic constants. The open issue at the beginning of the 1990’s was the effect of this long range strain at the local scale, i.e. on the individual bond lengths. Is there such an effect (also in consideration of the known rigidity of bonds)? If so, in the case of an alloy, is it the same for different bonds and how does it combine with bond length variations induced by alloying itself? The problem is graphically depicted in Fig. 6. XAFS is clearly the technique of choice to address the problem, also in consideration of the applicability to thin epilayers; in fact, FY was used by most groups and in some cases grazing incidence was used to enhance surface sensitivity and to reject the substrate contribution [112].
Bond length strain has been studied both for SiGe alloys deposited on Si(001) and for heterostructures based on III-V semiconductors; the clearest results have been obtained in the latter case. The issue can be tackled in two ways. For a binary epilayer or for an alloy epilayer with fixed composition, the bond lengths can be measured as a function of thickness: the effect of strain should show up since strain relaxation will occur above the critical thickness. Alternatively, for an alloy epilayer below the critical thickness, the bond lengths can be measured as a function of the composition: the strain will change since the free lattice parameter varies according to Eq. (25); in this case variations of the bond length induced by strain must be distinguished from variations due to alloying.

Initially, many authors [113-115] reported negligible variations of bond lengths in strained layers, within a quite large typical error bar of ± 0.01 or ± 0.02 Å. This confusing situation was probably due to less than optimal data acquisition and analysis and/or poor sample quality or lack of characterization. Most probably, the first clear report of a strain induced bond length variation is that by Kuwahara et al. [116], who measured the In-As bond length in InAs and InAs$_{0.6}$P$_{0.4}$ layers on InP(001) (both of which are compressively strained) as a function of thickness. Their data is reported in Fig. 7: a clear compression is measured at low thicknesses while an increase is evident in a thickness range which includes the critical thickness for strain relaxation; note the reduced error bars. Later, Woicik et al. obtained a similar result for InAs/GaAs(001) [117].

A couple of years later, experiments on strained alloy layers as a function of composition allowed to gain definitive insight on strain-induced bond length variations and to propose a simple model for the effect. Romanato et al. [118] studied tensile and compressively strained In$_x$Ga$_{1-x}$As epilayers InP(001) in the range 0.25 < x < 0.75 while Woicik et al. [119] studied a buried In$_{0.22}$Ga$_{0.78}$As layer in GaAs, finding similar results. In Fig. 8 we report the data of Romanato et al. for In$_x$Ga$_{1-x}$As epilayers on InP(001), which are lattice matched for x = 0.53; filled symbols are the results for the strained alloy layers while empty ones are for unstrained alloys, measured as a check.
Data points on unstrained layers confirm the classical results by Mikkelsen and Boyce\textsuperscript{106} (the dashed line is a fit to their data) while those for the strained layers clearly exhibit the effect of strain, which actually \textit{inverts} the slope of the bond length versus concentration plots: a remarkable effect. The continuous line is the result of a model which applies to the local scale the strain tensor: to first order the strain-induced distortion for bonds in the [111] direction is predicted to be

$$\delta r_{\parallel} = \frac{a(x)}{2\sqrt{3}} \left( 1 - \frac{C_{12}}{C_{11}} \right) \epsilon_{\parallel}. \quad (27)$$

The effects of alloying and strain are summed linearly. As can be seen, the agreement with the data is excellent. A consequence of this model is that different bonds (e.g. In-As and Ga-As) actually respond to strain in the same way, despite the fact that bond stretching force constants are significantly different; this is not surprising since the alloying-induced variations were reproduced with average values of the force constants [108]. More refined methods to calculate bond lengths in strained layers, based on a valence force field potential, have been published by Woicik [120] and d’Acapito [121], with a similar degree of good success. The issue of the effect of strain on bond lengths can be considered as solved and measurements of variations of bond lengths in strained systems can now be used to \textit{determine} strain, as will be described in the next paragraph.

\textbf{3.2 Atomic environment in nanostructures}

XAFS has been used to determine the atomic environment in many semiconductor nanostructures. The applicability of XAFS to study the changes of the local environment in nanostructures as a function of their dimensions was recognized early in the development of the technique, as shown by the studies on metallic clusters performed in the eighties [122-124]. These
studies demonstrated that nanoparticles exhibit a contraction of bond lengths, a reduced average coordination number and an enhanced structural and vibrational disorder. XAFS is the technique of choice because its local sensitivity (which derives from the limited photoelectron mean free path and core hole lifetime) makes it extremely powerful in detecting even subtle changes in the local atomic environment; moreover, the method of analysis does not change with the degree of long range order even in going from a dimer molecule to a perfect crystal, a situation which must be contrasted with the case of XRD, and there are no consequences of even great changes in the morphology of a nanoparticle on the analysis formalism. Here, the most important topics addressed using XAFS are reviewed.

3.2.1 Ge quantum dots and islands on Si surfaces and related systems

The possibility of altering the physical properties of semiconductors by exploiting quantum size effects has lead to the great recent interest in nanostructures. In this field, XAFS has provided key results, especially regarding the intermixing in Ge quantum dots and islands on Si. XAFS has the advantage of providing a local view of the atomic environment of the excited atom, thus providing quantitative information on intermixing and bond length strain in a direct fashion. The chemical sensitivity necessary to obtain information on intermixing can be obtained by XRD techniques only by exploiting anomalous dispersion. In this context, anomalous XRD at high momentum transfer has been successfully applied to determine composition and strain profiles of Ge islands on Si [125]; disentangling the contributions of strain, intermixing and morphology to the XRD pattern required a significant amount of modeling. A limitation of XAFS for the ex-situ study of uncapped dots and islands is that for thin samples the contribution from the surface oxide (or from other disordered phases) can be significant, which might complicate analysis; a solution is the
use of a capping layer or performing an in-situ experiment. In view of the advantages of XAFS in this field, a great deal of papers have been published, of which we review the most significant.

Ge islands on Si(001) are among the most studied systems. It is known that, due to the 4.2% lattice misfit, heteroepitaxial growth proceeds with the formation of a two-dimensional wetting layer, followed by the formation of dots which relieve the lattice strain (at the cost of an increase in surface energy); this is the so-called Stranski-Krastanov growth mode. XAFS experiments [126] on Ge dots formed on Si(001) and Si(111) were among the first to detect the presence of atomic intermixing by any technique, a phenomenon which had been neglected up to that time; other evidence for intermixing from XAFS was provided by Kolobov et al. [127] and Erenburg et al. [128] The experimental evidence is rather clear, as can be seen in Fig. 9 which compares the FT of Ge K-edge spectra for bulk Ge, for a Ge impurity in crystalline Si and for a representative sample of Ge dots on Si(001). The asymmetrical lineshape of the first peak, which is due to the first coordination shell, indicates the presence of a significant number of Si neighbors to the average Ge atom; this indication has been confirmed by a fitting of the spectra. It is now accepted that diffusion of Si atoms from the substrate reduces the strain energy associated with the heteroepitaxial growth and is a key feature of quantum dot growth. Hence, the appropriate growth mode for quantum dots is a modified Stranski-Krastanow one. Motta et al. [129] has also monitored the evolution of the intermixing process on the Si(111) surface, finding an enhancement of interdiffusion with increasing substrate temperature. The direct information on intermixing in quantum dots available from XAFS was also nicely illustrated by the measurements by Kovats et al. [130], who found that intermixing was inhibited by the saturation of the dangling bonds on the Si(111) surface by B atoms.

The advantages of XAFS to study the local Ge quantum dots on Si in comparison to Raman spectroscopy have been described by Kolobov et al. [131], who clearly showed that the superposition of a Raman peak of the Si substrate to that of Ge implies strong limitations of this
technique in the present case. The same group also detected considerable atomic intermixing in capped Ge dots, the degree of which depends on the growth temperature of the capping layer [132] and can be eliminated by growth on SiO$_2$ [133]; the value of the second and third shell interatomic distances was found to indicate the strained state of the dots. The measurement of second and third shell was made possible by inclusion of the significant multiple scattering paths. The use of bond lengths to determine the degree of strain of Ge dots was also recently illustrated by d’Acapito et al. [134].

Atomic intermixing is not limited to the group IV dots and islands but was found also in those based on III-V compound semiconductors. Galluppi et al. [135] were the first to detected In/Ga intermixing in nominally pure InAs dots on GaAs by In K-edge XAS; these structural measurements were correlated to photoluminescence investigation of the optical properties. d’Acapito et al. [136] confirmed this result in a grazing incidence measurements on 1.3 to 3 monolayer (ML) thick samples and discussed the values of the bond lengths, finding that, also in this case, their value could provide reliable information on the state of strain of the dots. Finally, Renevier et al. [137] contrasted the case of InAs/GaAs dots to that of InAs/InP quantum wires; in the former case the authors confirmed the previously cited results while no interdiffusion was found for the group V elements in the latter case.

### 3.2.2 Embedded semiconductor nanoparticles

Semiconductor nanoparticles embedded in a dielectric medium can exhibit unique optical properties and have been actively studied recently, also in view of potential applications. Variations of the physical properties derive from quantum size effects and from the increased surface-to-volume ratio in smaller particles. Among the fabrication methods proposed, ion implantation
followed by thermal annealing is a very flexible means to realize nanoparticles in the near-surface region of a dielectric. We will focus our attention on studies of Ge, GaN and II-VI nanoparticles embedded in a variety of mostly amorphous media.

The local structure of Ge nanocrystals in silica has been studied by Ridgway’s group, who obtained two main results. Firstly, for mean nanocrystal sizes of 14 nm, these authors confirmed the tetrahedral coordination of Ge in the nanocrystals but showed that, compared to bulk crystalline Ge, an enhancement of both Gaussian and non-Gaussian disorder is present [138]; this study highlights the extreme sensitivity of XAFS to the details of the short-range radial distribution function. Secondly, the amorphization of Ge nanocrystals in Si induced by Si ion irradiation was demonstrated to occur at a dose 100 times smaller than that required for the bulk [139]. In Fig. 10 we report Fourier transforms of Ge K-edge XAFS data for (a) polycrystalline and (b) nanocrystalline samples upon Si ion irradiation (in units of ions/cm²); note the factor of 10 difference in the doses between the two panels. The strong damping of the second and third-shell signals (peaks between 3 and 5 Å) clearly shows that preferential amorphization of the nanocrystals. The authors discussed four possible origins for this behavior: preferential amorphization at the interface, the intrinsic instability of the nanocrystals, the enhanced vacancy concentration within the nanocrystals and ion-beam mixing.

An original route for the fabrication of GaN quantum dots in crystalline (quartz and sapphire) or amorphous (silica) dielectrics by sequential ion implantation of Ga and N followed by annealing in NH₃ or NH₃/H₂ has been reported by Borsella et al. [140] Ga and N doses of the order of 10¹⁷ cm⁻² and annealing treatments at 900 °C-1200 °C for ~1 h were used. The wurtzite phase GaN dots have average dimensions of ~5 nm and their optical properties exhibit quantum confinement effects. XAFS measurements have provided important information on the local structure and its relation to the sample deposition conditions. In Fig. 11 we show the FT of Ga K-edge EXAFS spectra for bulk GaN and differently prepared samples. While an overall similarity is apparent (and
confirms that the particles locally exhibit the wurtzite structure), the smaller amplitude of the second peak with respect to the first one reflects the partial incorporation of Ga atoms in the GaN clusters and indicates that a fraction of Ga atoms is also dispersed in the matrix, possibly bonded to oxygen atoms.

Studies of CdS nanoparticles embedded in glass have been reported by Hayes’s group. These nanoparticles are obtained by doping a borosilicate glass in the melt with 0.1% weight CdS and subsequent quenching and annealing (at 625 °C-900 °C); with increasing annealing temperature and time, CdS particles grow in size until they finally dissolve. These particles have typical diameters ranging from 2 to 6 nm and clearly exhibit a blue shift of the optical absorption edge due to quantum confinement. XAFS at the Cd edge showed [141] that Cd is present both in the nanoparticles and also dispersed in the glass, and that a high degree of structural disorder is present in the nanoparticles. In Fig. 12 the Fourier Transforms of an as-received sample and of a sample annealed for 14 h at 700 °C, compared to bulk CdS and CdO; a shift to higher distances of the first peak with annealing and the absence of structure above the first peak in the as-received sample are evident. The first and second shell interatomic distances were found [142] to be within 0.2% of the bulk value, which implies a low interfacial tension, suggesting that the glass matrix is able to accommodate and relax strains, increasing the particles’ stability.

3.2.3 Metallic nanostructures embedded in silica

Metallic nanocrystals embedded in amorphous SiO₂ on Si(001) have been recently investigated in view of their non-linear optical properties, with applications ranging from optical fibres, memories and switching devices. XAFS has been employed by several groups to study the
variations of the local structure as a function of particle size and processing, and its relation to the physical properties.

Spiga et al. [143] have investigated the formation and the structural properties of Sn nanocrystals produced by ion implantation in ultra thin silica films, using grazing incidence XAFS in conjunction with Mössbauer spectroscopy and transmission electron microscopy. The analysis of this system is complicated by the multiple oxidation states of Sn. Sn ion implantation was performed at 80 keV with a fluence of $10^{16}$ cm$^{-2}$, positioning the peak of the implantation profile in the middle of the 85 nm thick thermally grown SiO$_2$ film and was followed by annealing at 800–1100 °C; particle sizes were in the range 7-17 nm. It was found that in the as-implanted state all Sn ions are oxidized, with the Sn$^{+2}$ oxidation states predominant, while annealing induces the formation of β-Sn nanoclusters. Fig. 13 reports XANES and EXAFS spectra which illustrate these changes. For particle sizes less than 10 nm, a reduced coordination number and a contraction of the interatomic distances was found. The investigated annealing treatments did not lead to a complete precipitation of Sn atoms in the metallic phase, leaving a fraction of them oxidized. This study nicely illustrates the combined use of the XANES and EXAFS region of the X-ray absorption spectra; the first provides qualitative information on the oxidation state while the second measures local structural parameters. It also shows the advantage of grazing incidence to enhance the signal originating from ultra thin films.

The local structure of Au nanocrystals fabricated by ion implantation in thin amorphous silica was investigated by Kluth et al. [144] Au ions were implanted at 4.5 MeV in 2 µm thick thermally grown SiO$_2$ at fluences in the range $10^{16}$ to $3 \times 10^{17}$ cm$^{-2}$ and were subsequently annealed in forming gas for 1h at 1100 °C. Average particle sizes ranging from 25 to 100 Å were obtained. Thanks to the high XAFS data quality, the authors clearly detected a ~ 0.02 Å bond length contraction in smaller particles (each bond length was measured with an error bar stated as ranging between ± 0.002 and ± 0.005 Å); this contraction, which is consistent with previous reports on non-
embedded clusters, implies a negligible influence of the SiO$_2$ matrix. The same authors also later studied the effect of irradiation with Sb ions (2.3 MeV, doses between $10^{14}$ and $10^{16}$ cm$^{-2}$), a method proposed to tune the nanoparticles’ properties [145]. At lower irradiation doses, significant disordering is evident, with a bond length expansion; at higher doses, a significant fraction of Au atoms dissolves in the matrix and other form very small clusters (especially dimers and trimers).

### 3.2.4 Porous Si and related systems

Obtaining visible light emission (luminescence) from Si and fabricating a Si-based optoelectronic device has been a very active area of research in recent years. Porous Si (p-Si), typically obtained by anodic etching of a Si wafer in an electrochemical cell containing HF acid and exhibiting such luminescence, has been the object of intense research. The origin of the luminescence has been often attributed to a quantum size effect but competing interpretations attribute the luminescence to oxide related structures on the surface of the Si. XAFS measurements, especially conducted in the PLY (or XEOL) detection mode, have played an important role in correlating the atomic structure to the physical properties and in elucidating the origin of the luminescence.

The first study by PLY-XAFS was reported by Sham’s group [146]. They clearly showed that XAFS spectra in the TEY and PLY modes were different and that the former were much more sensitive to the oxide component of the sample. Their PLY detected spectra were qualitatively similar to those of bulk Si, so it was concluded that the optically active component of p-Si locally exhibits the diamond structure. Pettifer at al. [147] studied oxidized p-Si by collecting PLY-XANES spectra using time-resolved detection: in this way they were able to distinguish the
different environment of Si atoms because the fast blue component is only related to the presence of SiO$_2$-rich regions.

Rather extensive investigations of p-Si using XAFS have been conducted by the Trento group. In their investigations, the samples are usually freshly prepared and soaked in HF to remove the oxide component just before the measurements. A first investigation [148] was conducted in the transmission mode and allowed recording high quality EXAFS spectra; this investigation quantitatively confirmed that the local structure of p-Si is the diamond one and detected an increase in the DW factors with porosity. Subsequently [149,150], a comparison of TEY and PLY detected spectra allowed the same group to conclude that the structures responsible for luminescence in p-Si are smaller and more disordered that the average structure of the sample. This is illustrated in Fig. 14. In the left panel, the photoluminescence spectra for two samples are reported; the higher current density sample has a higher porosity and its emission is blue shifted. In the right panel, the corresponding FT’s of the Si K-edge EXAFS spectra in the PLY mode are compared to those acquired in the TEY mode; it is clear that the TEY spectra do not change, while the PLY spectra exhibit an increasing disorder with porosity, as testified by the decreasing amplitude of the first three peaks. Finally, the same group has proposed a partial PLY detection mode [151]. According to the model in which luminescence in p-Si is due to recombination of carriers localized in quantum confined structures emission at higher energies corresponds to smaller emitting clusters. By selecting the light emission energy, Dalba et al. were able to show that the position of the X-ray absorption edge increases linearly with the emission energy. Since the X-ray absorption edge is due to a transition from a dispersion-less core state to the bottom of the conduction band, this experiment supported the stated model for the origin of luminescence in p-Si.

A field related to that of porous semiconductors is that of free-standing wires (NW’s). By a variety of methods it is possible to fabricate filamentous structures with diameters ranging from a few to a few tens of nm’s and lengths up to a few hundred microns. The wires are generally covered
by an oxide layer. XAFS has provided an atomistic description of the structure of these systems. In particular, Zhang et al. [152] have studied Si NW’s obtained by laser ablation of a mixed Si/SiO₂ target. XAFS measurements at the Si K-edge of the as-deposited samples and of samples with the oxide removed showed that the core of the NW maintains the diamond local structure, with increased disorder compared to bulk Si. The same group has also more recently studied [153] Si NW using PLY detection, identifying luminescence bands originating from the quantum confined silicon crystallites, the encapsulating silicon oxide and the silicon-oxide interface.

Finally, we mention XANES studies on silicon nanodots embedded in a SiO₂ film, performed by recording TEY and PLY spectra by the Trento group [154]. The comparison has allowed to propose and validate a model for the origin of the observed enhanced photoluminescence. Both experimental and theoretical results show that the interface between the silicon nanocrystals and the surrounding SiO₂ is not sharp: an intermediate region of amorphous nature and variable composition links the Si to amorphous stoichiometric SiO₂. This region plays an active role in the light-emission process.

### 3.3 Nitride heterostructures and thin films

GaN and related materials have been intensely studied in recent years in view of the properties which make them attractive for applications: a wide band gap (in blue-violet region), good thermal and chemical stability and physical hardness. The most common crystal structure of nitrides is the hexagonal wurtzite one but cubic forms are also possible, albeit metastable. The wurtzite structure grows in the (0001) direction and therefore has a polar character which entails strong polarization fields (both intrinsic and piezoelectric). The cubic and hexagonal polytypes of GaN are very similar when viewed along the cubic (111) and hexagonal (0001) directions and since the formation of stacking faults is energetically favourable, stabilization of the hexagonal phase is sometimes
difficult. An important problem for this class of materials is the absence of substrates with comparable lattice parameters, crystal symmetry and thermal expansion coefficients; the most commonly used substrates are Al₂O₃, SiC and Si. XAFS investigations have contributed to clarify the local atomic structure of nitride alloys, determine the local effect of strain due to heteroepitaxial growth, investigate the relation between the relative fraction of cubic and hexagonal phases of GaN films and the choice of substrate, and finally study the fine details of the local structure of GaN.

Miyano et al. [155] studied the variation of interatomic distances in wurtzite structure AlₓGa₁₋ₓN alloys deposited by metal organic chemical vapour deposition (MOCVD) on sapphire, with x in the range from 0 to 0.43. The films were about 1 µm thick, so no effect of the strain due to the growth was expected; XRD showed a linear variation of the a and c lattice parameters of the wurtzite structure as a function of x. Ga K-edge EXAFS allowed the authors to measure the interatomic distances in the first and second coordination shells around Ga, finding that the first shell Ga-N bond lengths exhibit a variation with x which is much weaker than the variation of the lattice parameters. Essentially, this study extends to the wurtzite structure the classical results [106,107] on zinc-blende III-V pseudobinary alloys. The effect of strain due to heteroepitaxial growth was probed in two studies of GaN ultra-thin films grown by molecular beam epitaxy (MBE) on SiC substrates [156] and AlN layers [157], both of which exploited the polarization dependence of the X-ray absorption cross section (see discussion in section 1.3) to decouple the local structure parallel and perpendicular to the growth plane. For the case of SiC substrates the growth was found to be always relaxed while the GaN on AlN films were found to be partially strained, due to the lower lattice mismatch; the degree of strain was found to depend on the substrate temperature and the ratio between the strain parallel and perpendicular to the interface was found to be in good agreement with estimates on the basis of the available elastic constants and macroscopic elasticity theory. These studies can be viewed as an extension to nitride epilayers of the previously described ones for III-V systems (see section 3.1); it must be mentioned that nitride epilayers are intrinsically
more defective than III-V’s, so an understanding of local distortions due to the heteroepitaxial growth is extremely valuable.

The effect of the substrate on the crystal structure of GaN thin films has been studied by Paloura’s group [158,159]. By using the polarization dependence of N K-edge XANES spectra these authors were able to illustrate how an Al$_2$O$_3$(0001) substrate yields a wurtzite GaN film, that a Si(001) substrate yields a cubic film and that a Si(111) substrate yields a mixed phase. The physical basis of this kind of study is that the atomic absorption cross-section must exhibit (at least) the symmetry of the point group of the crystal structure in which the absorbing atom is embedded [160]. For zincblende films the point group is $T_d$ and the cross-section is isotropic. For wurtzite films, instead, the point group is $C_{6v}$ and the angular dependence of the cross-section is

\[
\sigma^{tot}(\hbar\omega, \theta) = \sigma^{isotropic}(\hbar\omega) + (3\cos^2\theta - 1)\sigma^1(\hbar\omega)
\]

(28)

where $\theta$ is the angle between the polarization vector and the c axis of the wurtzite structure and the two cross-section terms on the right hand side do not depend on the angle; for $\theta = 54.7^\circ$, the so-called “magic angle”, the measured cross-section will be equal to the isotropic one. It is therefore clear that angular dependent measurements can distinguish between cubic and hexagonal symmetry. An alternative explanation of the method, based on a molecular orbital framework, is reported in the quoted papers. In Figs. 15a and 15b polarization dependent XANES spectra for GaN films deposited on Si(001) and Al$_2$O$_3$(0001) substrates, respectively, are reproduced; it is quite clear the former exhibit no polarization dependence and are thus relative to cubic films, while the latter exhibit a clear angular modulation and are thus hexagonal. These papers illustrate a general method based on XANES which can be used to determine the symmetry of the investigated crystal structure. This technique has been also extended to other nitride films [161,162].
GaN films are highly defective: along with the stacking faults which lie at the origin of the possible presence of both cubic and hexagonal phases, point defects such as N vacancies and Ga antisite defects have a relatively high concentration. This defectivity has been proposed by Katsikini et al. to cause significant structural distortions in the elementary tetrahedral building block of the material. By analysis of FY-XAFS data at both the N [163] and Ga [164] K edges these authors have detected a ~ 0.25 Å elongation of a significant fraction of the four Ga neighbors to the average N atom. This distortion has subsequently been found also in ab-initio structural simulations by Dimakis et al. [165] These studies once again highlight the unique sensitivity of XAFS to the fine details of the local structure.

3.4 Dilute alloy heterostructures

In recent years there has been considerable interest in the physical properties of dilute alloy heterostructures, obtained by adding a concentration ranging from ~ 10^{-3} to ~ 10^{-2} of a foreign atom to the epilayer. Two materials systems will be reviewed: dilute nitrides and dilute magnetic semiconductors. In these fields XAFS has played an important role, both as an atomic level characterization tool in order to provide crucial feedback to optimize the growth procedures and also for providing an understanding of the physical properties on the basis of the local atomic structure.

3.4.1 Dilute nitrides

The addition to III-V semiconductor alloys of small quantities of an isoelectronic impurity characterized by very different electronegativity and size with respect to the constituents of the host lattice causes dramatic and unexpected changes in physical properties. For example, the
incorporation of a low concentration of nitrogen (~0.1-1%) into GaAs, InGaAs, or GaP (the so-called “dilute nitrides”) leads to, among others, a giant (and counterintuitive) band gap reduction and a reduction of the lattice parameter. These effects render dilute nitrides attractive for the fabrication of light emitters in the telecommunications wavelength range and of high-efficiency solar cells. XAFS has been used to address the relative atomic ordering in quaternary dilute nitrides and the structure of the complexes formed upon irradiation with hydrogen.

In the quaternary alloy (InGa)(AsN) the relative disposition of cations and anions on their sublattices is not uniquely determined by the atomic concentration. In fact, in the zincblende structure each site of the anion (cation) sublattice can be occupied by In or Ga (As or N) without any limitation. Therefore the question of the degree of atomic ordering, i.e. the relative number of each atomic bond as a function of composition, naturally arises. Specific examples of types of atomic ordering are the random case (relative number of each type of bond equal to the concentration) or short range ordering (SRO); in the relevant case of low N concentration SRO is exhibited, in the extreme cases, by a sample having only N-In or only N-Ga bonds. For (InGa)(AsN) it has been predicted [166] that precisely this type of SRO exists, with a strong preference for In-N bonds over Ga-N ones. Moreover, SRO has been predicted to cause a significant blue shift of the band gap and hence may represent an intrinsic materials limitation, since it is the red shift which has applicative interest.

XAFS is clearly the technique of choice to address the issue of atomic ordering, due to its chemical sensistivity, and in 2003 two groups published important results in this field. Lordi et al. [167] concluded that while the as-deposited alloy has a random atomic distribution, annealing favors an increase of the relative number of In - N bonds. According to these authors annealing brings the system towards a thermodynamically more stable state, characterized by a (not quantified) degree of SRO. Similar qualitative results were published by Uno et al. [168]. However, a quantitative measurement of the degree of SRO in as-deposited and annealed samples was not
provided. A quantitative determination was instead provided by Ciatto et al. [169,170] who used combined In K-edge EXAFS and N K-edge XANES and showed that SRO does exist, but is significantly less pronounced than predicted. These authors have compared the In-N coordination number with the N concentration measured by Nuclear Reaction Analysis. As-deposited samples exhibit a random atomic arrangement, while annealed samples show a statistically significant deviation towards SRO. The degree of SRO falls short of the maximum possible on a statistical basis and also of that predicted by Kim and Zunger [166]. This study nicely illustrates the power of XAFS to obtain quantitative information on ordering by comparing coordination numbers to average concentrations, a method well known in the study of amorphous systems [171].

Another fascinating physical properties of dilute nitrides alloys is that the dramatic changes induced by nitrogen in dilute nitrides can be reversed fully by hydrogen irradiation. Infact, XRD of hydrogenated GaAsN shows a disappearance of the diffraction peaks associated with the GaAsN epilayer and a recovery of the GaAs lattice parameter. Concomitantly, H irradiation leads to a nearly full reopening of the band gap. Such effects are technologically relevant since hydrogen is present in most growth processes and mass-production steps of semiconductor devices. The nature of the hydrogen complexes responsible for these alterations of the physical properties has been addressed by a number of techniques and XAFS has played a decisive role. By combining in an original way N K-edge XANES measurements with simulations of their lineshape in the Full Multiple Scattering (FMS) framework performed on the basis of atomic coordinates obtained by ab-initio simulations of the structure of the most stable N-H complexes in hydrogenated GaAsN, Ciatto et al. [31] provided convincing evidence that dihydrogen-nitrogen complexes with $C_{2v}$ symmetry are the most abundant. This finding contradicted all previous predictions of “in-line” N-H$_2$ complexes as the predominant species. In Fig. 16a we sketch the structures of some of the hydrogen complexes and in Fig. 16b the comparison between the simulations and the experiment; the best agreement is clearly found for the complexes with $C_{2v}$ symmetry. This paper nicely illustrates the
high energy resolution in XANES measurements which can be obtained in the soft X-ray range, the three dimensional sensitivity of XANES and the power of combined experimental-simulation studies [172].

3.4.2 Dilute magnetic semiconductors

A dilute magnetic semiconductor (DMS) [173] consists of a non-magnetic semiconductor doped with a few % of a magnetic ion (a transition metal, e.g. Mn or Fe). DMS thin films are typically obtained by MBE growth on an appropriate substrate. In a DMS, the ions (which ideally occupy substitutional sites in the semiconductor lattice) retain ferromagnetic alignment in the presence of spin polarized free carriers. DMSs have been studied since the 1970’s; initially much work was on II-VI based alloys, later on III-V’s and more recently on nitrides; DMSs form the materials basis of the emerging field of spintronics. There are expectations that room temperature ferromagnetism might be obtained in DMSs. In fact, in 2000 Dietl et al. [174] predicted that room temperature ferromagnetism could be obtained by doping GaN or ZnO with a few % of Mn. Three years later, ferromagnetism at 172 K was reported for p-type delta-doped GaAs:Mn [175] and in 2005 the same group reported [176] a Curie temperature of 250 K in a specially designed heterostructure.

A great amount of work has been reported on DMSs, much of it is very recent and the panorama of results is continuously changing; sample deposition procedures are far from optimized and this inevitably entails that it is difficult to draw certain conclusions. For the nitride and oxide based systems, the reader is referred to the recent and extensive review by Chambers [177] for a materials science perspective. XAFS has played an important role in studies of DMS, both initially at the level of basic characterization and then to gain insight in the relation between local structure and physical properties. This is also due to the rich chemistry and variety of oxidation states of
transition metal ions, which can be accurately characterized by the technique. Moreover, it is important to note that ferromagnetism can also be observed if ferromagnetic precipitates are present in the material—but this does not qualify as a true DMS: hence, an atomic level probe such as XAFS is of crucial value. For reasons of space, this section is limited to Mn doped III-V semiconductors and GaN, which are probably the most intensely studied class of DMSs.

As often the case, the first studies in the field were of a preliminary character; for InAs:Mn, Krol et al. [178] reported that only a small fraction of Mn atoms were actually substitutional in the InAs lattice and most formed MnAs clusters. A few years later, using optimized sample preparation procedures and more accurate data analysis, the same group [179] clearly highlighted the role of concentration and of growth temperature: at low (~ 1%) concentration and growth temperature substitutional Mn was clearly detected while clusters with the local structure of MnAs precipitated at high concentrations or substrate temperatures. The origin of this behavior is the limited solubility of Mn in III-V semiconductors; in order to avoid the formation of MnAs inclusions, the growth temperature for Mn-doped III-V’s has to be between 200°C and 300°C, i.e. very low compared to the 500-650 °C interval used for standard GaAs-based materials.

For the prototypical GaAs:Mn system more work has been reported. In this system, there is a close interplay between the local structure of Mn and the electronic properties. In fact, by using DFT simulations, Mahadevan and Zunger [180] have predicted that the formation energy of an interstitial Mn defect decreases as the Fermi level shifts towards the valence band, as can be occur as a consequence of Be co-doping. Shioda et al. [181] initially reported complete Mn incorporation in substitutional sites, for concentrations < 7% and growth temperatures quoted as 250-300 °C; also, they measured a Mn-As bond length of 2.50 Å, which is 0.05 Å higher than the value for Ga-As and thus implies considerable local distortion. Later, Bacewicz et al. [182] studied samples grown between 220 and 250 °C with Mn concentrations below 4 %; by a combined analysis of the XANES
and EXAFS regions these authors were able to detect the presence of a significant fraction of interstitial Mn atoms; no correlation with other sample properties was reported.

More complex GaAs:Mn-based heterostructures have also been studied. Two methods have recently been proposed as alternatives to the growth of bulk GaAs:Mn alloys: the growth of digital GaAs/MnAs heterostructures, obtained by alternately depositing layers of GaAs and MnAs, and δ-doping of GaAs with Mn. The latter method consists in creating a δ-like doping profile in the growth direction by inserting in GaAs a submonolayer thick Mn layer. In both cases, the basic idea is to achieve locally higher Mn concentrations where high hole densities can be trapped. Soo et al. [183,184] have studied Mn/GaAs digital alloys. They found that in samples deposited at the low temperature of 275 °C, Mn substitutes Ga and locally forms a GaMnAs alloy; upon annealing, a dramatic decrease of the first shell coordination number was found and the authors suggested that this was due to initial stages of precipitation of a MnAs phase. Later, the same group published [185] a convincing study which combined the local structural sensitivity of Mn K-edge XAFS with an atom-specific magnetic probe such as X-ray magnetic circular dichroism (XMCD) performed at the Mn L-edge. They found a high ferromagnetic alignment of the Mn atoms and a local structure exclusively composed of substitutional Mn in the Ga sites, as in a random (GaMn)As alloy. In Fig. 17 we report Fourier transforms of Mn K-edge EXAFS data for a MnAs reference compound, a GaAs:Mn digital alloy and a (GaMn)As random alloy which clearly supports this conclusion. More recently, d’Acapito et al. [186] have studied a series of Mn δ-doped GaAs samples, deposited at growth temperatures in the range 300 °C-450 °C, with and without Be co-doping. In low temperature samples, Mn was confirmed to be substitutional to Ga. Interestingly, a direct correlation between Be co-doping (which lowers the Fermi level towards the valence band) and the presence of Mn interstitials was demonstrated; this study illustrates the ability of XAFS to detect relatively small fractions of defective site and to measure their local structure quantitatively.
XAFS has also made a significant contribution for the characterization of Mn-doped GaN films; again, it should be remarked that the nitrides are a more defective materials system than III-V’s and that a significant evolution in the near future is expected as the close interplay between growth and characterization will lead to improved materials. XAFS has provided important results on the site of Mn in GaN and its oxidation state.

Soo et al. [187] studied 150 nm thick films deposited by MBE on Al$_2$O$_3$(0001) at substrate temperatures ranging between 400 °C and 650 °C, with a maximum Mn concentration of 2 %; magnetic measurements indicated that the samples were paramagnetic. EXAFS measurements indicated that Mn occupied a substitutional Ga site with a Ga-N bond length which was found to ~ 0.07 Å greater than the Ga-N one. XANES measurements on the samples were compared to several oxide and fluoride reference compounds in which Mn has known oxidation states and it was concluded that Mn has the +2 oxidation state. While this is certainly a reasonable conclusion, it should be remarked that, ideally, such comparisons should be performed with reference compounds of known structure and composition as close as possible to the samples; it is an unfortunate situation that this is not strictly possible with Mn-doped GaN. In 2004, Thaler et al. [188] reported EXAFS data on Mn-doped GaN films grown by MBE on either Al$_2$O$_3$(0001) or MOCVD GaN substrates with and without a 2 µm thick GaN buffer layers. Samples grown at 700 °C with the GaN buffer layers exhibited strong magnetization even above room temperature (but no remanence). The EXAFS measurements indicated that Mn was always substitutional, independently of the presence of the buffer layer; this result indicated the important role of the defect density of the GaN matrix in determining the magnetic behavior.

One of the concerns in the growth of Mn-doped GaN is the presence of multiple oxidation states of Mn and their spatial distribution. In this context, micro-XAFS has provided results which nicely illustrate the potential of the technique. By using an intense spot size of the order of 1 µm$^2$, Martínez-Criado et al. [189] performed a joint micro-fluorescence mapping and micro-XAFS
experiment. Mapping of the Mn and Ga fluorescence intensity demonstrated their inhomogeneous distribution. Moreover, by performing maps of fluorescence intensity at specific excitation energies which correspond to XANES features of Mn in the Mn$^0$, Mn$^{+2}$ and Mn$^{+3}$ oxidation states (chosen using as references metallic Mn, MnO and Mn$_2$O$_3$) the authors were able to show the presence in the samples investigated of all three oxidation states, thus including metallic Mn, and their strongly inhomogeneous spatial distribution. The presence of Mn$^{3+}$ in a substitutional site in MBE grown samples on a GaN buffer layer up to a concentration of 5.7% was nicely demonstrated by Titov et al. [190] using high resolution XANES measurements and their interpretation using band structure calculations. This study illustrates the usefulness of simulations in cases in which an ideal reference compound does not exist. We close this paragraph by quoting a combined X-ray absorption and XMCD study at the Mn L-edge by Keavney et al. [191]; by comparison with first principles band structure calculations these authors propose that Mn preferentially populates Ga sites neighboring N split interstitials.

4. Summary and perspectives

XAFS has established itself as a precious tool to study the local structure in the field of materials science. The underlying theory, which has been outlined in section 1, is well understood and a number of reliable analysis programs are now available. Thanks to the many possible detection modes, most of which have described in section 2, it can be applied to a great variety of systems and sensitivity to a particular phase, environment or part of the sample can be enhanced on the basis of the experimental requirements. As a consequence, applications of XAFS to a wide variety of heterostructures and nanostructures, which have been reviewed in section 3, have been widespread and have greatly contributed to the present understanding of the relation between atomic structure and physical properties.
There is no doubt that in the future XAFS will continue to be a valuable tool in this field of research. It is possible to outline specific areas in which progress is expected. The spatial resolution of synchrotron radiation techniques has greatly improved recently [102-104], and certainly further progress will occur in the near future. Micro-XAFS is expected to be very valuable in two areas: characterization of inhomogeneous samples (with possible feedback to sample growth) and study of the local atomic environment of individual nanostructures. Concerning the last point, the challenge is to record spectra of sufficient quality and energy range to allow a quantitative interpretation; a strong effort is required in this area. If this issue is resolved, it might be possible to perform “bond length maps” of nanostructures.

Time resolved XAFS has recently emerged as a very promising field, due to the full use of the time structure of storage rings and the pump-and-probe scheme [192]. Differential XANES spectra of a metastable charge transfer state of an organometallic molecule with 100 ps x-ray pulses have been reported by Saes et al. [193]. A lot of work is currently underway in synchrotron radiation laboratories and the future challenge is to use the fs pulses of the LINAC-based sources. Present time resolutions range many orders of magnitude, from the seconds to ps [192]. In the field of semiconductor science, there have been only limited application of time resolved XAFS, for example studies of photo-excitation of GaAs [194] and of melting of Si [195]. More work in this area is expected, for example to study the kinetics of annealing-induced bonding changes, crystallization and amorphization, aggregation and growth of nanostructures in real-time.

Work is in progress and interesting developments are possible also in the quantitative interpretation of the XANES region. XANES spectra contain a wealth of information, especially in view of the three dimensional sensitivity; at present, even most of the advanced work in the solid state relies on a comparison between simulations and experiments, with semi-quantitative agreement. It would be a significant advancement to develop fitting methods, which have been devised in the field of bio-molecules [32] for the quantitative determination of the three dimensional
structure of very small nanostructures, defects and complexes in semiconductors. Finally, it must be mentioned that great progress is being made in ab-initio structural simulations, with methods based on DFT theory. The accuracy of these methods and the reliability of XAFS analysis is such that joint experimental-theoretical investigations are now possible [31,172]. Simulations of the local atomic structure can be useful as a starting point for XAFS analysis, as a guide in the analysis itself and as a very useful comparison with expected results. Further progress will certainly take place in both theory and experiment and this will concern both the EXAFS and the XANES regions.

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Figure captions

Fig. 1: Pictorial representation of the photoelectron scattering process. The solid lines represent the crests of the spherical wave fronts of the photoelectron wave function and their thickness is roughly proportional to the amplitude. The atom at the top of the figure is the photo-excited one (the central atom) while the two atoms at the bottom scatter the photoelectron. In the represented case scattering gives rise to an enhancement of the wave function at the site of the central atom and therefore to an increase of the cross section with respect to the isolated atom case.

Fig. 2: Ga K-edge X-ray absorption spectrum of GaAs. The top inset reports the EXAFS function, $\chi(k)$, while the bottom inset highlights the XANES spectral region.

Fig. 3. Pictorial representation of paths with (a) 2 and (b) 3 scattering legs. The excited atom is highlighted at the bottom left.

Fig. 4. Magnitude of the Fourier Transform of the Ga K-edge EXAFS spectrum shown in the top inset of Fig. 2 for GaAs.

Fig. 5. Spectrum of photons scattered by a sample consisting of $\sim 10^{16}$ Sn atoms/cm$^2$ implanted in SiO$_2$; elastic and inelastic (Compton) scattering and Sn fluorescence are identified.$^{52}$

Fig. 6. (a) Tetragonal distortion of the unit cell in pseudomorphic growth, in the case of compressive strain. (b) An elementary tetrahedron for an alloy in which one of the bonds (at the top right) is shorter than the other ones, under compressive strain.
Fig. 7. In-As bond length in InAs and InAs$_{0.6}$P$_{0.4}$ layers on InP(001) (both of which are compressively strained) as a function of thickness. Reprinted with permission from Y. Kuwahara, H. Oyanagi, R. Shioda, Y. Takeda, H. Yamaguchi, and M. Aono, Jpn. J. Appl. Phys. 33 (1994) 5631. Copyright (1994) by the Institute of Pure and Applied Physics.

Fig. 8: In-As and Ga-As bond lengths for In$_x$Ga$_{1-x}$As epilayers InP(001) in the range 0.25 < x < 0.75, reproducing the original results from reference [118]. Filled symbols are the results for the strained alloy layers while empty ones are for unstrained alloys. The dashed line is a fit to the data by Mikkelsen and Boyce while the continuous line is the result of the model as described in the text. Reprinted with permission from F. Boscherini, S. Pascarelli, C. Lamberti, S. Mobilio, F. Romanato, D. DeSalvador, M. Tormen, M. Natali and A. Drigo, J. Synchrotron Rad. 6 (1999) 506. Copyright (1999) by the International Union of Crystallography.

Fig. 9: Ge K-edge EXAFS spectra Ge for quantum dots on Si(001), illustrating intermixing of Si; adapted from Ref. [196].

Fig. 10: Fourier transforms of Ge K-edge EXAFS data for (a) polycrystalline and (b) nanocrystalline Ge embedded in silica upon Si ion irradiation (in units of ions/cm$^2$); note the factor of 10 difference in the doses between the two panels. Reprinted with permission from M.C. Ridgway, G. de M. Azevedo, R.G. Elliman, C.J. Glover, D.J. Llewellyn, R. Miller, W. Wesch, G.J. Foran, J. Hansen and A. Nylandsted-Larsen, Phys. Rev. B 71 (2005) 094107. Copyright (2005) by the American Physical Society.

Fig. 11: Fourier transforms of Ga K-edge EXAFS spectra for differently prepared GaN quantum dots and for bulk GaN. Samples S2 and Q1 are obtained by implantation of Ga and N in amorphous

Fig. 12: Magnitude (dashed line) and real part (solid line) of the Fourier Transforms of Cd K-edge EXAFS for CdS nanoparticles in glass. (a) as-received sample; (b) a sample annealed for 14 h at 700 °C; (c) bulk CdS; (d) CdO. Reprinted with permission from T.M. Hayes, L.B. Lurio, J. Pant, and P.D. Persans, Phys. Rev. B 63 (2001) 155417. Copyright (2001) by the American Physical Society.

Fig. 13: XANES (left) and FT of EXAFS (right) spectra for Sn nanoparticles implanted in amorphous SiO$_2$ (fluence $10^{16}$ cm$^{-2}$) and reference compounds. The samples differ in the annealing conditions; X1: as-implanted; X2: 800 °C, 120 s; X3: 900 °C, 30 s; 900 °C, 120 s. Reprinted with permission from S. Spiga, R. Mantovan, M. Fanciulli, N. Ferretti, F. Boscherini, and F. D’Acapito, Phys. Rev. B 68 (2003) 205419. Copyright (2003) by the American Physical Society.

Fig. 14: In the left panel, the photoluminescence spectra for two p-Si samples are reported; the higher current density sample has a higher porosity and its emission is blue shifted. In the right panel, the corresponding FT’s of the Si K-edge EXAFS spectra in the PLY mode are compared to those acquired in the TEY mode. Reprinted with permission from G. Dalba, N. Daldosso, D. Diop, P. Fornasini, R. Grisenti, and F. Rocca, J. Lumines. 80 (1999) 103. Copyright (1999) by Elsevier.

Fig. 15b: Polarization dependent N K-edge XANES spectra for GaN films deposited on Si(001) and (b) Al₂O₃(0001) substrates. Reprinted with permission from M. Katsikini, E.C. Paloura, and T.D. Moustakas, Jour. Appl. Phys. 83 (1998) 1437. Copyright (1998) by the American Institute of Physics.

Fig. 16a: Sketch of some of the hydrogen complexes in GaAsN predicted to be most stable by *ab initio* DFT simulations: the N-H₂⁺(a) and C₂ᵥ symmetric and asymmetric complexes hydrogen complexes in GaAsN. The N-H₂⁺(b) complex has an N-HBC-Ga-HAB configuration; similar “in line” configurations characterize the N-HBC and N-HAB mono-hydrogen complexes. Reprinted with permission from G. Ciatto, F. Boscherini, A. Amore Bonapasta, F. Filippone, A. Polimeni and M. Capizzi, Phys. Rev. B 71 (2005) 201301. Copyright (2005) by the American Physical Society.

Fig. 16b: Experimental N K-edge XANES for hydrogenated GaAsN (top) and corresponding FMS simulations based on the atomic coordinates calculated via DFT in presence of the most stable monohydrogen- and dihydrogen-nitrogen complexes, some of which are sketched in Fig. 15a. Reprinted with permission from G. Ciatto, F. Boscherini, A. Amore Bonapasta, F. Filippone, A. Polimeni and M. Capizzi, Phys. Rev. B 71 (2005) 201301. Copyright (2005) by the American Physical Society.

Fig. 17: Fourier transforms of Mn K-edge EXAFS data for a MnAs reference compound, a GaAs:Mn digital alloy and a (GaMn)As random alloy. The inset shows k-weighted EXAFS data.
References

26 Useful lists of XAFS software can be found on the wabe pages xafs.org, www.i-x-s.org, and www.esrf.fr/computing/scientific/exafs/xafs.html.
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