

L-03

Extended abstract

Tue. 01. 09., 14²⁰-15⁰⁰

Elemental and orbital-selective characterization of semiconductor materials by X-ray spectroscopy - XAS, RIXS and XPS

I. N. Demchenko*

Institute of Physics PAS, al. Lotnikow 32/46, 02-668 Warsaw, Poland

Keywords: synchrotron radiation, XAS, XES, RIXS, XPS

*e-mail: demch@ifpan.edu.pl

The ability to control the physical properties of novel materials, by controlling crystallographic structure, arrangement of atoms inside sample's volume and along the surface taking into account point defects, is of crucial importance nowadays from both fundamental and applied research points of view. As electronic structure ultimately determines physical properties of matter, it is natural to anticipate that knowledge of it for existing systems together with the ability to describe and predict it for new systems will bring progress in science and technology to a new level. Among the ways to reach such information X-ray spectroscopy techniques stand considerably out due to their capabilities to provide detailed information on material electronic structure and thus helping us to construct the informational bridge between the structural and electronic properties of wide class of materials.

This communication focuses on just a few (out of plenty) techniques, namely X-ray absorption/emission spectroscopy, Resonant inelastic X-ray scattering, and X-ray photoelectron spectroscopy and their application to characterize semiconductor materials is presented with examples.

1. Application of X-ray spectroscopy to highly disordered systems.

Opposite to the very extensively studied As-rich GaNAs alloys much less work has been devoted to highly mismatched alloys (HMAs) on the N-rich side of this alloy system. In these studies a highly mismatched GaN_{1-x}As_x alloy system was successfully synthesized in the whole composition range using a nonequilibrium low temperature molecular beam epitaxy technique [1]. In addition to other techniques X-ray spectroscopy was utilized to determine the reorganization of electronic (around Fermi level) and atomic structure of novel GaN_{1-x}As_x system in the whole composition range. Examination of atomic structure by X-ray diffraction for the most part of samples was impossible since obtained films had no long ordering, i.e. had amorphous structure. It is an important fact that crystallinity is not required for X-ray spectroscopy measurements, making it one among a few structural probing techniques available for noncrystalline and highly disordered materials, including solutions.

The optical gaps of the GaN_{1-x}As_x alloys were measured by absorption using a LAMBDA-950 UV/vis/NIR spectrophotometer over the range of 190–

3300 nm. It was shown that the films in the composition range of 0.17 < x < 0.75 are amorphous while those outside this range are crystalline (either single crystalline or polycrystalline).

The composition dependence of the optical band gap energy for both crystalline and amorphous GaN_{1-x}As_x alloys were compared directly with calculated composition dependence of the band gap. It was shown that the band gap values for the amorphous GaN_{1-x}As_x alloys cannot be explained by the virtual crystal approximation (VCA) or the fitted curve using a single bowing parameter of 16.2 eV. Simultaneously, excellent agreement can be observed between the band gap values for the crystalline alloys and the band anticrossing (BAC) model [1-2]. The deviation of the experimental optical absorption results from the BAC calculations found for the amorphous alloys is not unexpected as the model has been developed for crystalline materials. Additional uncertainty is introduced by the fact that the band gap has been calculated as a composition weighted interpolation of the BAC model results and is less accurate for the alloys in the middle range of compositions.

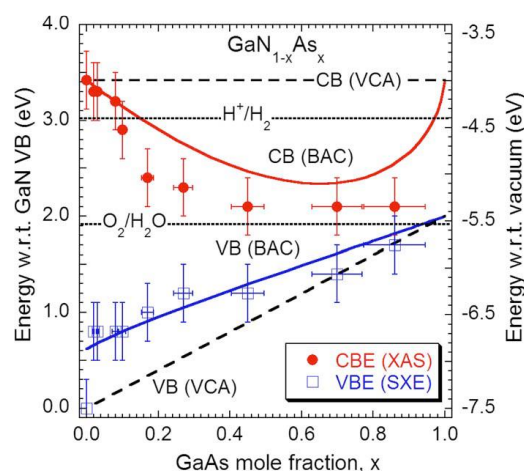


Figure 1. Composition dependence of the CBM and the VBM energies for GaN_{1-x}As_x alloys as measured by XAS and SXE, respectively, plotted together with the BAC predicted values. The linear interpolations of CB and VB between end point compounds (GaN and GaAs) are also shown. The positions of the H₂/O₂ redox potentials with respect to the VBM of GaN are also shown.

According to the BAC model the observed reduction in the band gap can be attributed to an upward shift of the valence band edge (VBE) and a downward movement for the conduction band edge (CBE) in the N-rich and As-rich GaN_{1-x}As_x alloys, respectively. However, the absolute movement of the conduction band (CB) and valence band (VB) of the GaN_{1-x}As_x alloys cannot be derived from conducted optical measurements. To examine electronic structure of investigated system around Fermi level the combination of soft X-ray emission (SXE) and X-ray absorption (XAS) spectroscopies with the following interpretation of obtained results were done. XAS and SXE directly probe the partial density of states (DOS) of the CB and VB, respectively [1]. Overlapping the SXE and XAS spectra

with reference to the core level provides a direct measurement of the energy positions of the VB and CB states in semiconductor materials. For this purpose, the nitrogen K-edge (around 400 eV) was investigated at room temperature at the Advanced Light Source (ALS) on beam line 8.0.1. XAS was detected by the total fluorescence yield detection mode with an energy resolution of about 0.2 eV, and SXE was measured using the Tennessee/Tulane grating spectrometer with a total energy resolution of 0.6 eV.

The absolute positions of the CBE and VBE are directly measured as a function of composition and compared to the results of conventional optical measurements [1]. The composition dependence of the CBE and the VBE energies at N sites of $\text{GaN}_{1-x}\text{As}_x$ alloy as measured by XAS and SXE were displayed together with the BAC predicted values (see Fig. 1). It should be pointed out here that the calculated band movements by an interpolation of the BAC model are included for comparison purposes only. Band movements in the amorphous alloys may vary dramatically from those of crystalline alloys. Both CBE and VBE are observed to shift as x increases. A jump in the VBE to higher energy for dilute As ($x \sim 0.10$) polycrystalline samples as compared to GaN is observed consistently with the BAC model. A second jump to lower energy is observed in the CBE upon entering into the amorphous phase ($x \sim 0.17$). For increasing x in the amorphous phase, both the VBE and CBE are only very weakly shifting to higher and lower energies, respectively. Finally a smaller jump in the VBE yet again to a higher energy is observed for the amorphous to As-rich polycrystalline transition ($x \sim 0.70$). Not unexpectedly the smooth interpolation of the BAC model from the dilute polycrystalline regions does not explain the discontinuous energy jumps into the amorphous phase. It should be also pointed out that the band gap energies measured by XAS and SXE are lower than the values obtained by optical absorption. This may be attributed to excitonic coupling between the screened core hole and conduction electron.

2. Potential of combined soft X-ray emission and absorption spectroscopies for estimation of direct and indirect bandgaps size in semiconductors.

With the arrival of high-brilliance third-generation synchrotron sources, a new approach to study the bulk band structure has been established, namely to utilize resonant inelastic X-ray scattering (RIXS). In RIXS, an electronic Raman scattering process is used to select specific excitations of valence electrons into unoccupied conduction band states. In other words, a core electron is resonantly excited into an unoccupied state at a certain k value, and the resonant fluorescence decay of a valence electron with the same k value into the core hole is detected. The observed RIXS spectrum thus contains momentum-resolved information about the occupied and unoccupied electronic states, which can be analyzed based on the Kramers-Heisenberg formalism [3]. Since the reachable information depth is typically of the order of a few hundred nanometers, study of systems with poorly defined surface properties or protective cap layers becomes possible.

In order to probe the bulk-sensitive occupied valence band electronic structure, near-threshold excitation X-ray emission spectra were recorded for CdO films for excitation energies at the O K absorption threshold [4]. Main idea of this research was to demonstrate that the XES experiments are unique since they can provide direct evidence to the band structure of a semiconductor, in particular whether a semiconductor has direct or indirect band gap, without further theoretical input.

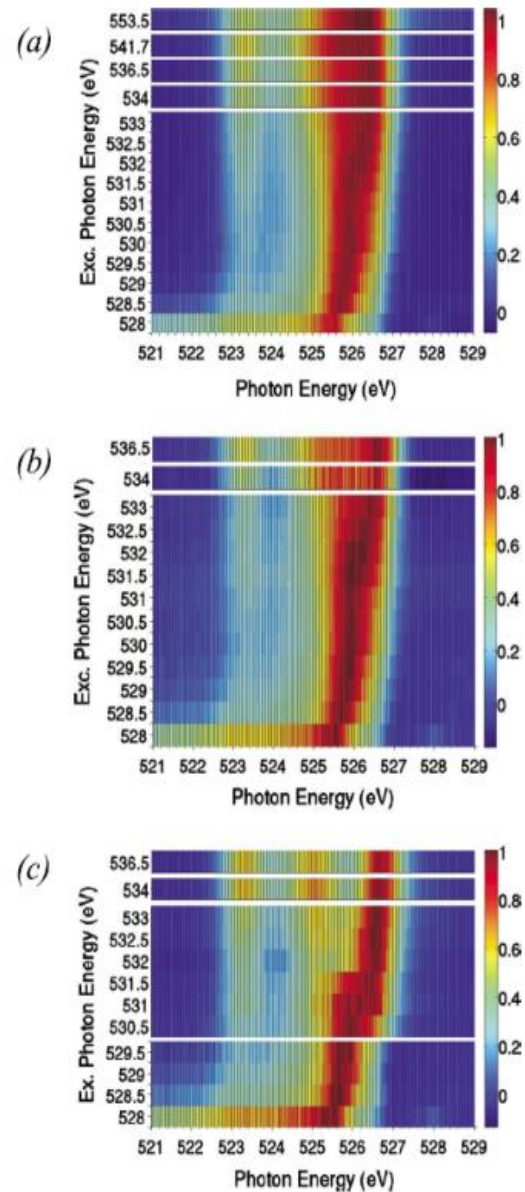


Figure 2. (a) Intensity maps of normalized RIXS and partially coherent fractions of XES corresponding to (b) standard and (c) intermediate approaches. Intermediate procedure works well for visualization of branching dispersion of occupied states. The details will be discussed during the presentation.

In a XES experiment the band-gap type can be determined by observing the emission spectra as a function of excitation energy. In case of a direct energy gap material, emission at the highest energy is expected for an excitation energy in the vicinity of the absorption threshold (into the conduction band minimum, CBM). As

the excitation energy increases the emission should shift to a lower energy. For indirect band-gap materials the opposite behavior is expected, i.e., a shift of the emission spectrum (namely, top of the valence band maximum, VBM) to higher energy with increasing excitation energy. In another words, as the excitation energy increases, the probing transitions get closer, in k space, to the top of the VB. Our XES/RIXS data, see Fig. 2 and [4], clearly show this tendency and will be discussed in details.

Based on RSMS theory we were able to interpret the experimental XAS spectra in terms of local geometrical and electronic structures. Calculated near-edge structure for cation and anion X-ray absorption edges represents a good coincidence with experimental one. Calculated PDOS describes well all features corresponding to unoccupied states of investigated films and allows to conclude that the orbital character of the lowest energy of the CB is mostly $Cd\ 5s-O\ 2p\ \sigma^*$. Presented RIXS CdO data set is showing a progressively varying partial k mixing of initial and final states near the threshold and thus a varying incoherent line shape. Overlapping of XAS spectrum with RIXS ones makes possible to estimate both direct ~ 2.4 eV and indirect ~ 0.9 eV bandgap values. The obtained results are consistent with the theoretical/experimental ones presented in the literature and our own optical absorption results.

3. The properties of ultrathin superconducting films by X-ray photoelectron spectroscopy.

One of the fundamental problems in nanoscience research is a question about the nature of the ground state in confined systems, particularly in the case of the superconducting (SC) materials. It is well established that the reduction of the thickness of SC films leads to the superconductor-insulator transition (SIT) [5-6]. The usual assumption is that the SIT is induced by disorder which reduces mean-free path. In [7] authors demonstrate an example of the SIT for which its origin may be even more complex. The structural and magnetotransport properties in a series of Si/Nb/Si trilayers grown by magnetron sputtering at room temperature are shown. The thickness of Nb, d , is varied from 20 nm down to 1.1 nm with a fixed Si thickness of 10 nm. The high-resolution TEM and the X-ray diffraction indicate that for $d > 6$ nm the films are polycrystalline, while they become amorphous for smaller d . The Hall effect measurements reveal that the positive Hall coefficient, characteristic for bulk Nb, starts to decrease for d below 6 nm, and eventually changes sign into negative for d below 2 nm. The slight nonlinearity of the Hall voltage versus magnetic field is observed in the thinnest samples (d about 1.3 nm), which may indicate the presence of two types of carriers. The possible origins of this effect may include the modification of the niobium band structure or the contribution of the Nb-Si interface to the conduction. Therefore, surface analysis studies by X-ray photoemission spectroscopy were conducted to investigate the electronic structure, the valence band, core levels of related components, and the relative positions of the energy levels involved in the interface of

Si/Nb/Si structures. By repeated ion etching and XPS measurements (i.e. depth profiling), the depth distribution of the elements in the investigated samples were determined (see, for example, Fig. 3). The obtained results for Nb layers with different thickness buried in Si matrix will be shown and discussed in details.

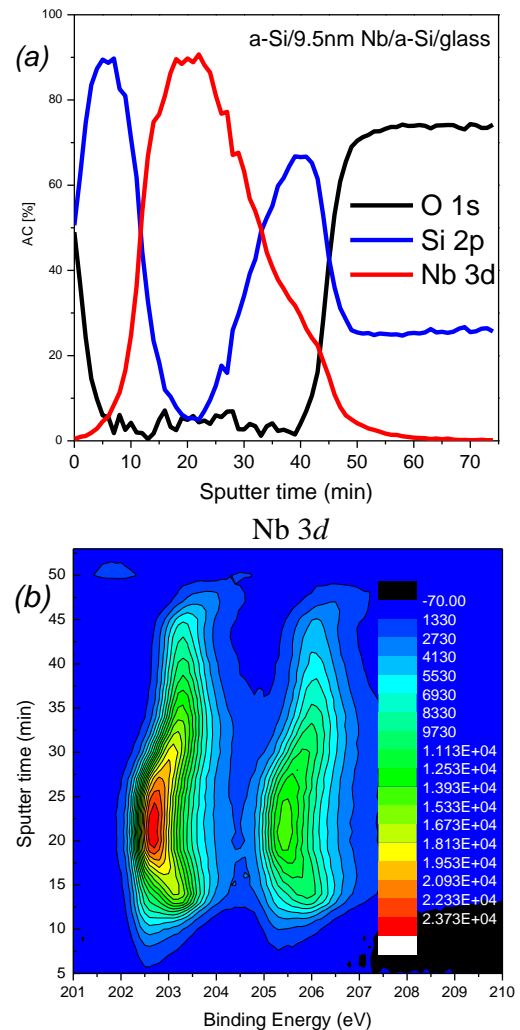


Figure 3. (a) Concentration–depth profile of the a-Si/9.5 nm Nb/a-Si trilayer at glass substrate. (b) Contour plot of Nb 3d spectra during a depth profiling experiment.

Acknowledgments: The author wishes to thank W. Lisowski (IPCh PAS) for experimental support and useful discussions.

- [1] K. M. Yu, S. V. Novikov, R. Broesler, I. N. Demchenko *et al*, *J. Appl. Phys.* **106** (2009) 103709.
- [2] W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller *et al*, *Phys. Rev. Lett.* **82** (1999) 1221.
- [3] M. Rovezzi, P. Glatzel, *Semicond. Sci. Technol.* **29** (2014) 023002.
- [4] I. N. Demchenko, J. Denlinger, M. Chernyshova, K. M. Yu *et al*, *Phys. Rev. B* **82** (2010) 075107.
- [5] C. A. Marrache-Kikuchi, H. Aubin, A. Pourret, K. Behnia *et al*, *Phys. Rev. B* **78** (2008) 144520.
- [6] T. I. Baturina, C. Strunk, M. R. Baklanov, A. Satta, *Phys. Rev. Lett.* **98** (2007) 127003.
- [7] I. Zaytseva, O. Abal'oshev, P. Dłuzewski, W. Paszkowicz, L. Y. Zhu, C. L. Chien, M. Konczykowski, M. Z. Cieplak, *Phys. Rev. B* **90** (2014) 060505(R).