CONTRIBUTED POSTERS
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MATERIAL RESEARCH

Cross-sectional photoemission microscopy of semiconductor heterostructures

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Photoemission spectroscopy has been traditionally used to monitor chemical, structural and electronic changes upon interface formation [1]. Measurements are usually performed at different growth stages and the junction parameters are inferred from the coverage-dependence of the core emission. With the emergence of spectromicroscopy, a natural application of photoemission to the study of semiconductor interfaces is to directly determine the heterojunction parameters by measuring the device in cross section.

Initial test systems examined were GaAs p-n doping superlattices with different periods produced by molecular beam epitaxy (MBE). After growth, wafers were mechanically thinned-down to below 100 µm, pre-notched and transferred in vacuum to the photoemission spectrometer. *In-situ* cleaving was used to expose {110} cross-sections of the buried interfaces. Several efforts were devoted to obtaining flat bands conditions on both the p- and the n-side of the junction. Such conditions were inferred from an analysis of the Ga 3d core lineshape with energy and spatial resolution better than 0.15 eV and 0.5 µm, respectively, having reduced to a negligible spectral contribution the diffuse background typical of any Schwarzschild microscope.

The methods developed were then applied to Al/n-GaAs(001) Schottky junctions, also fabricated by MBE. Spatially-resolved studies of the core-level emission in cross-section were used to probe the semiconductor depletion layer near the metallurgical junction. Our data show that a systematic study of this system as a function of doping type and level can provide unique information of the static surface dielectric constant, which is relevant to many aspects of surface physics, including core-hole relaxation and electron/surface interactions [2].

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SPECTROSCOPIC CHARACTERIZATION OF ELECTRON AND X-RAY INDUCED DAMAGE IN SELF-ASSEMBLED MONOLAYERS

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An important practical issue in the research of thin organic films and in particular self-assembled monolayers (SAMs) is their response to irradiation by X-rays, UV-light, electrons or ions. On the one hand, irradiation-induced SAM modification can be used as a lithographic approach to pattern surfaces. On the other hand, a possible non-intentional irradiation-induced damage can occur during standard spectroscopic characterization of SAMs. Considering these aspects we have investigated the low-energy electron and X-ray induced damage in different aliphatic and aromatic thiol-derived SAMs on noble metal substrates by X-ray photoelectron spectroscopy (XPS), high resolution XPS, and angle resolved near edge X-ray absorption fine structure spectroscopy. It was found that both electron and X-ray irradiation causes the loss of the orientational and conformational order, partial dehydrogenation leading to the cross-linking and, in particular, to C=C double bond formation, desorption of the film fragments, reduction of the thiolate species, and the appearance of new sulfur species (see Figs. 1 and 2 for SAMs formed from $CH_3(CH_2)_{11}SH$ (C12) on Au). The chemical identity of this species have been identified. A possibility to modify the sensitivity of SAMs toward electron and X-ray irradiation and to control the balance between the irradiation induced cross-linking and desorption processes is analyzed in detail and practical recipes for SAM-based lithography are derived. It is demonstrated that this balance can be shifted both toward the quasi-polymerization of a SAM or an enhanced desorption of the molecular fragments by a proper design of the SAM constituents. This work has been supported by the German Bundesministerium für Bildung und Forschung through grants No. 05 SF8VHA 1 and 05 SL8VHA 2 and by DAAD (313/S-PPP-pz).

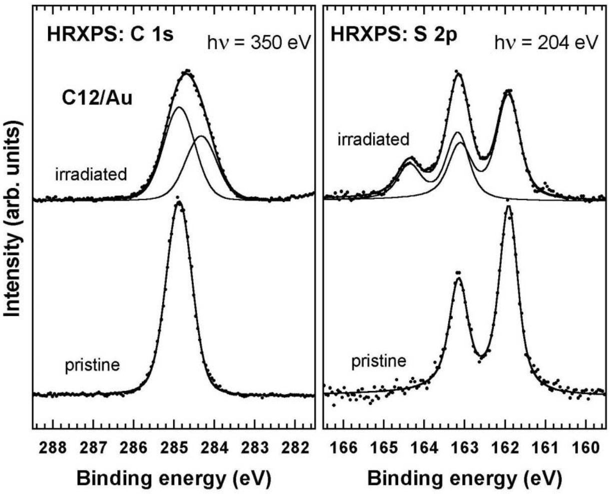

Figure 1. The C 1s and S 2p HRXPS spectra of the pristine and strongly irradiated C12/Au. The decomposition of the spectra into the components related to the pristine and irradiation-induced species is shown.

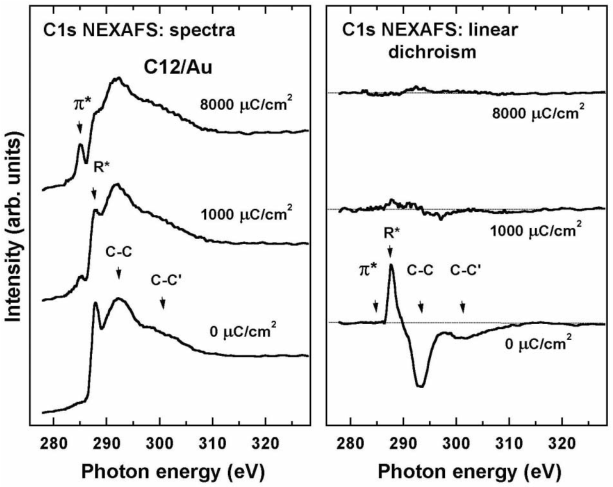

Figure 2. C1s NEXAFS spectra of pristine (bottom curves) and irradiated C12/Au as well as the respective differences of the spectra recorded at X-ray incident angles of 90° and 20°.

XPS AND NEXAFS SPECTROSCOPY STUDY OF THIOAROMATIC SELF-ASSEMBLED MONOLAYERS ON NOBLE METAL SUBSTRATES

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Self-assembled monolayers (SAMs) formed from thiophenol (TP), 1,1'-biphenyl-4-thiol (BPT), 1,1';4',1"-terphenyl-4-thiol (TPT), and anthracene-2-thiol (AnT) on polycrystalline Au and Ag (Fig. 1) were characterized by X-ray photoelectron spectroscopy and angle resolved near edge X-ray absorption fine structure spectroscopy. The measurements were performed at the German synchrotron radiation facility BESSY I in Berlin. With the exception of the poorly defined thiophenol film on Au, all thioaromatic molecules were found to form highly-oriented and densely packed SAMs on both substrates. The molecular orientation and orientational order of the adsorbed thioaromatic molecules depends on the number of aromatic rings, the substrate, and the rigidity of the aromatic system. The molecules, which in average are slightly inclined with respect to the surface normal, show a less tilted orientation with increasing length of the aromatic chain, and as observed for aliphatic SAMs, they exhibit smaller tilt angles on Ag than on Au. However, the difference in the tilt angles for aromatic SAMs on Au and Ag is smaller than that observed in the aliphatic films. A comparison of the monolayers formed from p-terphenylthiol and anthracenethiol films suggests that a higher molecular rigidity has only a slight effect on the final molecular orientation within the respective SAMs. Based both on the findings of this study and on the comparison of the thioaliphatic and thioaromatic films, we suppose that in the case of the latter systems the structure determining balance between the head group/substrate interactions and the intermolecular forces is shifted toward intermolecular forces. This work has been supported by the German Bundesministerium für Bildung und Forschung through grant No. 05 SF8VHA 1 and by the Fonds der Chemischen Industrie.

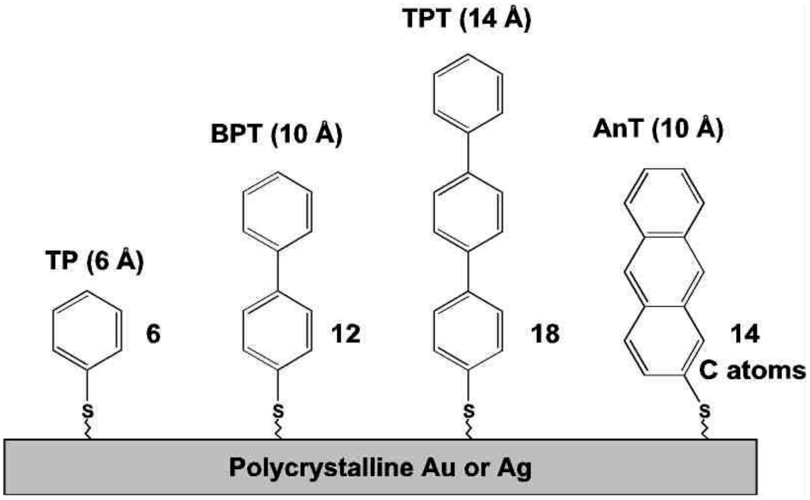

Figure 1. Schematic drawing of the thioaromatic molecules in an artificial upright adsorption geometry including the respective numbers of carbon atoms and the length of the aromatic chains (in closed brackets).

Cu contaminants removal using UV/O_3 and remote hydrogen plasma

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Removal of Cu contaminants from Si wafer surface was carried out using remote hydrogen plasma (RHP) and UV/O_3 cleaning techniques. The concentration of Cu impurities on the wafer surface was monitored by TXRF (total reflection x-ray fluorescence) and XPS (x-ray photoelectron spectroscopy). Our results show that metal impurities including Cu can be effectively removed by hydrogen plasma and UV/O_3 cleaning techniques, only if it is performed under optimum process conditions.

A two step cleaning process composed of remote hydrogen plasma cleaning, first and UV/O_3 cleaning, next has been found to be more effective than a single process of UV/O_3 or remote hydrogen plasma cleaning and a two step cleaning process composed of UV/O_3 cleaning, first and remote hydrogen plasma cleaning, next. The removal mechanism of Cu impurities in the two step cleaning seems to be as follows:

First, Si atoms react with atomic oxygen to form SiO^* during UV/O_3 cleaning. Next, metallic impurities including Cu are lifted off when SiO* is evaporated during remote plasma cleaning. The optimum process parameters for the remote hydrogen plasma cleaning are the rf power of 20W and the exposure time of 5 min. The optimum exposure time of the UV/O_3 cleaning for Cu impurity removal is 1 min. Cleaning efficiency is degraded with increasing the process parameters above the optimum values for both UV/O_3 and remote hydrogen plasma cleaning techniques.Body text

EFFECTS OF VUV IRRADIATION IN INSULATING CRYSTALS

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Effects of monochromatic VUV radiation on various insulating crystals were studied. We report here in particular on effects of monochromatic VUV radiation in the spectral region between 110 to 200nm on variously doped Fluorides such as LiF:Eu^{2+}, LiFMgTi , as well as on $CaSO_4$: Dy^{3+}, $CaWO_4$ and Carbon doped Al_2O_3 crystals. Some of these materials have recently been used as efficient radiation detectors and dosimeters for higher energy radiation. Optical absorption, optically stimulated luminescence (OSL), thermolumiscence (TL) and phototransferred thermoluminescence (PTTL) were measured. The irradiations were carried out at RT and at LNT and the thermal stability of some radiation-induced defects as well as temperature dependence was studied. In most of the materials TL could be excited by VUV irradiation in this spectral region and the TL excitation spectra showed maxima at the long wavelength tail of the exciton bands. This fits previously reported results in various alkali and earth-alkali crystals. The present results were also compared to those obtained in the same materials by beta, or x-rays. and indicated that the same defect levels are responsible for the TL induced by the VUV as by the higher energy radiation. Possible application of the materials as radiation detectors and TL dosimeters for the VUV region was also investigated.

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Study of P-type Photoluminescent Porous Silicon upon Annealing in Vacuum

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Photoluminescent porous silicon, fabricated by chemically anodizing boron-doped [100] Si wafer in 10% HF-ethanol solution, was annealed up to 650 ^{0}C in vacuum. After annealing, PL disappeared. We investigated the skeleton size using AFM before and after annealing, and chemical information of the PS surface in-situ using X-ray photoemission spectroscopy at the 2B1 SGM beamline at the Pohang Light Source. AFM data showed fine skeleton size of 5-10 nm before annealing, which is close to the size the quantum confinement model predicts the PL. After annealing, the fine skeleton structure became smoothened and the overall skeleton size increased to about 50-100 nm.

Fig. 1 shows photoemission spectra obtained with 130 eV photon energy of two different PS with the same thickness (same PL intensity and shape before annealing) but showing different suboxide states. The suboxide states, +3, +2, +1, were reported to be related with strong PL in PS layers [1]. As the annealing temperature increased, the suboxide state intensity increased. At 650 ^{0}C, where PL disappeared, the observed oxidation state is still in the range where the strong PL observed, indicating that the oxidation state change in this experimental condition is not a direct cause of the PL failure. The main cause of the PL disappearance in our study is attributed to the skeleton size increase.

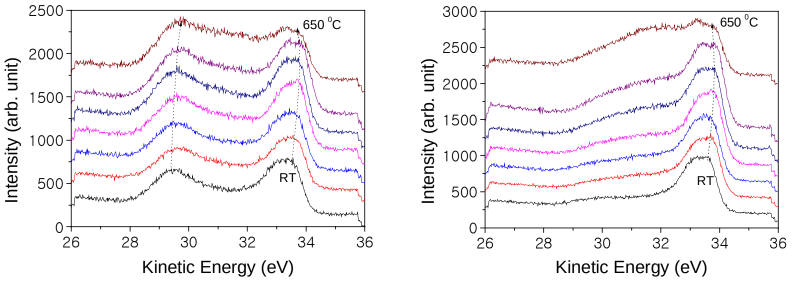

Fig.1. XPS scans near Si 2p for different annealing temperatures.
Left: 20mA/cm^2, 250s. Right: 5mA/cm^2, 1000s.

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O *K* X-Ray Absorption Spectra of Condensed Aromatic Compounds Having Various Oxygen Functional Groups

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Microporous carbon has been widely used for adsorbents and catalysts in many industrial fields. Its adsorption properties were thought likely to depend on the chemical states of the graphitic surface in the micropores. In order to analyze the oxidation states of the graphitic surface in microporous carbon, we measured O *K* x-ray absorption spectra of microporous carbon [1, 2] and condensed aromatic compounds having various oxygen functional groups such as -OH, -R-OH, -COOH, -C=O, -CH=O, and -C-O-C-. Total-electron-yield (TEY) x-ray absorption spectra of these compounds were measured in BL-6.3.2 at the Advanced Light Source, and fluorescence yield (FY) x-ray absorption spectrum of microporous carbon was in BL-8.0.1. Figure 1 shows the x-ray absorption spectra of the condensed aromatic compounds and microporous carbon in the O *K* regions. From the comparison in spectral features of microporous carbon with the condensed aromatic compounds, it can be suggested that -C=O or -COOH are the most probable chemical bonding states of oxygen in microporous carbon. Theoretical analysis of these x-ray absorption spectra is in progress to determine the chemical bonding states of oxygen on the graphitic surface in microporous carbon.

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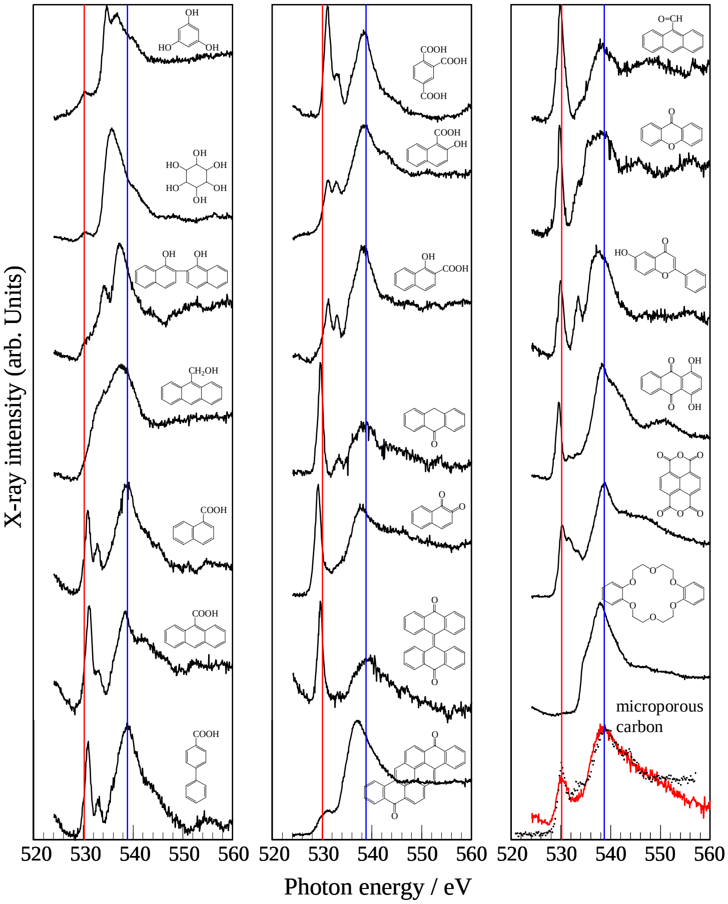

Figure 1. TEY x-ray absorption spectra of condensed aromatic compounds having various oxygen functional groups and microporous carbon. FY x-ray absorption spectrum of microporous carbon is shown by dotted line. Molecular structures of the condensed aromatic compounds are superimposed on the corresponding x-ray absorption spectra.

Deoxidization of a SiO_2 Layer by Irradiating Incoherent Vacuum Ultraviolet Excimer Emission

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Photochemical deoxidization of an oxidized layer on a silicon wafer has been demonstrated by use of an incoherent vacuum ultraviolet (VUV) light source.

Typical removal process of an oxidized layer on a silicon wafer utilizes chemicals such as hydrofluoric acid. Such a treatment would certainly influence the environment and residual chemicals may play a negative role in the semiconductor processing. We have been developing VUV light sources by use of rare gas excimers [1]. Rare gas excimer sources excited by a silent discharge make the highest emission power with wide varieties of emission geometry. We have chosen Ar_2* emission centered at 126 nm (9.8 eV), according to our previous silicon precipitation results using a high power Ar_2* excimer laser [2]. This deoxidizing process, however, has been realized with low power incoherent Ar_2* emission, resulting in pure photochemical process with absolutely no surface modification.

A silicon wafer with a SiO_2 layer was placed inside a vacuum chamber at pressure of 3×10^{-5} Torr. The thickness of the layer was controlled at 100 nm. The Ar_2* emission from a silent discharge pumped excimer lamp was irradiated onto the sample at an intensity of 0.3 mW/cm^2. An MgF_2 lens was used to increase the emission intensity. This lens also separated the vacuum chamber from the discharge lamp. The surface morphology was inspected by use of an AFM and the layer was monitored by ellipsometry. The atomic concentration of the surface was measured by use of XPS.

A ratio of atomic concentration of Si and SiO_2 as a function of irradiated time (i.e. number of deposited quanta) was measured. In XPS measurement, a peak at 103 eV was observed, which was caused by Si(2p) of SiO_2. Another peak at 99 eV originated from the atomic Si(2p). No other peaks appeared during the measurement. A ratio of these two peak intensities (I(99 eV)/I(103 eV)), i.e. the concentration of atomic Si in a layer, increased linearly with the irradiation time. AFM images of the sample showed no difference before and after the irradiation. The layer thickness was not changed, but the index of refraction decreased in 10^{-2} after the irradiation. Other measurement revealed that the precipitated atomic silicon concentration decreased exponentially with the sample depth. The characteristic depth was estimated to be 3 nm, which seems to be one order of magnitude smaller than the penetration depth of the 126-nm radiation into SiO_2. This photochemical deoxidization of SiO_2 layer would be connected with photochemical SiO_2 layer production process [3].

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LUMINESCENCE PROPERTIES OF Gd-BASED COMPLEX FLUORIDE CRYSTALS DOPED WITH Er^{3+} AND Tm^{3+} AS PROMISING MATERIALS FOR VUV-EXCITED PHOSPHORS

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The vacuum ultraviolet (VUV) spectroscopy of rare earth (RE) ions doped into wide band-gap crystal hosts has been attracting much attention for the past few years because of an industrial demand for efficient VUV-excited phosphors for mercury-free fluorescent lamps and plasma display panels where the VUV radiation from noble-gas discharge is used for excitation of phosphors [1]. In the present work spectroscopic properties of $CsGd_2F_7$ and $LiKGdF_5$ crystals doped with Er^{3+} or Tm^{3+} were studied from the viewpoint of their possible application as materials for VUV-excited phosphors based on the principle of so-called down-conversion [2]. The measurements were performed under excitation by both synchrotron radiation and VUV radiation from a pulsed molecular F_2-laser.

It has been found that VUV luminescence due to 5d – 4f transitions from Er^{3+} and Tm^{3+} doped in both $CsGd_2F_7$ and $LiKGdF_5$ is extremely weak. On the other hand, the emission spectra of both Er^{3+} and Tm^{3+} doped crystals contain intense lines in the UV/visible spectral range which correspond to 4f – 4f transitions in the doping ions and the Gd^{3+} ion. This means that the VUV energy absorbed by 4f – 5d transitions in the relevant RE ion is nearly completely converted into the UV/visible emission. Such a conversion of VUV energy to UV/visible light, i.e. down-conversion, is due to the energy transfer from the 5d state of the Er^{3+} or the Tm^{3+} ion to the neighbouring Gd^{3+} ion as a result of cross-relaxation giving rise to the emission of two UV/visible photons instead of one VUV quantum [2].

Both $CsGd_2F_7$ and $LiKGdF_5$ crystals doped with Er^{3+} or Tm^{3+} seem to be promising materials for efficient VUV-excited phosphors the luminescent properties of which could be better than those of the $LiGdF_4$ crystals studied in [2]. The strong absorption below 170 nm as a result of 4f - 5d transitions in the Er^{3+} or the Tm^{3+} ion matches well to the emission spectrum of the xenon monomer line or the krypton excimer discharge continuum with maximum at 147 nm. Besides, either the Er^{3+} - Gd^{3+} or the Tm^{3+} - Gd^{3+} combination offers efficient nonradiative energy transfer via cross-relaxation from the 5d level of Er^{3+} or Tm^{3+} to Gd^{3+} with nearly complete conversion of absorbed VUV radiation into the UV/visible emission.

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Electronic Structure and Reactivity of TM-doped $La_{1-x}Sr_xCoO_3$ (TM=Ni, Fe) Catalysts

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The catalytic properties of $LaCoO_3$ in aqueous oxidation are explored as a function of doping with both Sr substitution for La and with Fe and Ni substitution for Co. SR VUV photoemission is used to explore the surface reactivity of the ceramic catalysts in aqueous solution, using H_2O as a probe molecule. These measurements are complemented by EXAFS and XANES measurements designed to probe the local defect structure, XPS measurements of surface composition, and GC measurements of catalytic activity in the aqueous epoxidation of crotyl alcohol. We relate the observed catalytic activity to the defect structure of the doped materials. In Ni-doped materials, oxygen vacancies appear to be the predominant defect, whereas in Fe-doped samples, electron holes are stabilised on Fe, leading to very different behaviour in oxidation, and differing surface reactivity. The reactivity of theses perovskites is compared with that of related layered perovskites [1,2], and the possible mechanism for the epoxidation reaction is discussed.

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Luminescence properties of Gd_2SiO_5 doped with Eu^{3+} in the UV-VUV region

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Gadolinium oxyorthosilicate, Gd_2SiO_5 (GSO), is the host material of a useful scintillator, GSO:Ce^{3+}, for γ-ray detection. GSO doped with rare earth was also investigated as the potential high efficient luminescent material. To our knowledge, there was no report about GSO:Eu^{3+} in UV-VUV region up to date. From the viewpoint of the energy transfer mechanism, we investigated the UV-VUV excitation spectra and the emission spectra with UV-VUV excitation of GSO:Eu^{3+} (6%) crystal.

Excitation spectrum of GSO:Eu^{3+} crystal was measured at 614nm of Eu^{3+} emission (Fig. 1). The lines in the range 362nm~392nm are the transitions of $^7F_0 \rightarrow {}^5D_4$ in Eu^{3+} ions. While the lines at 306.5nm, 311.5nm and 3185nm relate to $^8S_{7/2} \rightarrow {}^6P_J$ of Gd^{3+} ions. The broad band from 200nm to 300nm is composed of two subbands. The subband peaked at 250nm is a charge-transfer (C.T.) transition in the Eu^{3+}–O^{2-} bond, while the subband peaked at 275nm relates to $^8S_{7/2} \rightarrow {}^6I_J$ of Gd^{3+} ions. The band gap of GSO is 6.1eV, so the broad band centered at 180nm relates to the transition from valence band (VB) to conduct band (CB). The excitation of $4f^6 \rightarrow 4f^5 5d^1$ (Eu^{3+}) is peaked at 120nm, and the excitation of $4f^7 \rightarrow 4f^6 5d^1$ (Gd^{3+}) is peaked at 75nm. The excitation peaks of Gd^{3+} ions around 311.5, 275 and 75nm in the excitation spectrum imply the presence of energy transfer from Gd^{3+} to Eu^{3+}. The excitation (180nm) from VB to CB indicates the energy transfer from the host to Eu^{3+}. The emission of Eu^{3+} (614nm) also can be excited by itself from ground state to some higher excitation states (>400nm).

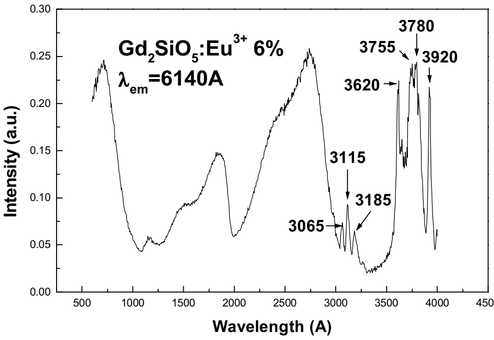

Fig. 1 Excitation spectrum of GSO:Eu^{3+} crystal. λ_{em}=6140Å

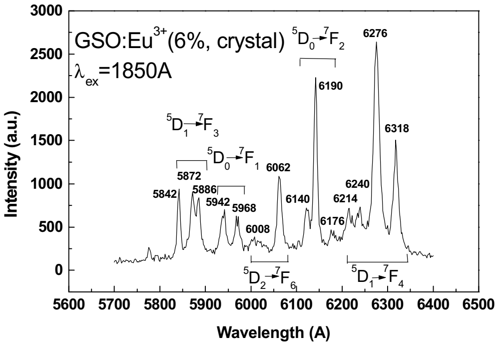

Fig. 2 Emission spectrum of GSO:Eu^{3+} crystal. λ_{ex}=1850Å

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Initial stage of nitridation on Si(100) surface using low-energy nitrogen ion

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The combination of the electronic and the mechanical properties of Si_3N_4 [1] makes it the extremely attractive materials for a wide variety of potential applications. Zhao *et al.* [2] obtained the information on the electronic structure, charge distribution, and charge transfer for the Si_3N_4/Si(111) system by using the linear combination of atomic orbital (LCAO) method. A number of techniques have been used to fabricate Si_3N_4 using chemical vapor deposition (CVD), pulsed laser deposition (PLD) and ion implantation. Especially, the nitridation of Si by low energy ion implantation offers several advantages. The most important thing of this method is the absence of undesirable impurities and the possibilities of controlling the film composition and thickness. The goal of our present work is to achieve a better understanding of the processes that occur during the thin film growth of Si_3N_4 caused by the nitrogen ion and Si surface reaction. The initial stage of the nitridation on Si(100) surface with the low energy nitrogen ion was studied by photoemission spectroscopy (PES) and low energy electron diffraction (LEED) at the 2B1 spherical grating monochromator (SGM) beamline in Pohang Light Source (PLS) [3, 4]. Depending on the temperature of nitridation, disordered surface changes to ordered surface with 2 x 1 LEED periodicity.

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The optimal formation condition of chromium oxide thin film on stainless-steel surface

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We investigated the various oxidation conditions of stainless-steel surfaces using synchrotron radiation photoemission spectroscopy. Stainless-steel samples are oxidized at 450 ~ 550℃ in various oxygen partial pressures. Increasing the annealing temperature from 450℃ to 550℃, the trivalent chromium concentration in the surface increased and iron oxides decreased. The PES spectra from stainless-steels oxidized at 550℃ show that there exists the critical oxygen partial pressure, $p'_c \sim 5\times10^{-7}$ Torr. Below this critical pressure, the oxide formed mainly consists of chromium oxide, while the oxide formed mainly consists of iron oxide above the critical pressure. The oxidation behavior is in good agreement with the Ellingham diagram(a free-energy/temperature diagram).

X-ray absorption spectroscopy studies of $CeAl_2$ thin films

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We report results of x-ray absorption on near edge structure (XANES) on Ce L_3-edge, $M_{4,5}$-edge and Al K-edge for thin films of $CeAl_2$ with thickness from 400 Å to 1200 Å. The intensity of near edge features at the Ce L_3-edge decreased and the line width increased as the film becomes thicker. On the other hand, we observed the intensity at $M_{4,5}$-edge increases with the film thickness. The differences among these spectral are attributed to surface effects. The valency of Ce in these films, as suggested by the spectral results, is mainly trivalent. In a more detailed analysis, we observed the Ce^{4+} feature ($4f^0$ configuration) increased in comparison with the thicker ones. We have also performed the temperature dependent study on bulk $CeAl_2$ at Ce L_3-edge spectrum from 35K to 300K. The small variations in the spectral shape between different temperatures indicate that a small amount of Ce^{4+} appear in low temperature.

Polarized XANES Studies in Zn-Doped GaN Thin Films

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The significant anisotropic nature of the nitrogen conduction bands in GaN are due to Ga *d* electrons energy coupling with N 2*s* states. X-ray absorption near edge structure (XANES) *K*-edge of Ga and N provides the information on the conduction band structure, we report the polarized X-ray absorption measurements on as-grown, *n* and *p* types of GaN performed at Synchrotron Radiation Research Center, Taiwan. A strong polarization dependence of the absorption spectra was observed in all the samples as grown, *n*-type and *p*-type. The shape and energy of the characteristic spectral features differ considerably in N *K*- and Ga *K*-edges spectra strongly with respect to polarization angle. The significant features points to microstructural modification with localized distortion. Our analysis of polarized XANES and quantitative estimation of dislocations/defects in GaN pointed mainly that defects/dislocations are confined in major way to Ga site with little distribution on N Sites. The other significant aspect of polarized XANES results is that as polarization angle varying, the number of defects/dislocations is changing pointing that most of the defects are distributed along the direction of substrate basal plane. In this presentation, we shall make an attempt to relate the polarization dependence, the nature of defects/dislocations distribution, anisotropy of the conduction band and the modification of electronic structure with filled Zn 3*d* shell.

The electronic and atomic structures of the exchange-biased NiFe-FeMn bilayers

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We measured the Ni, Fe, and Mn $L_{2,3}$-edge x-ray absorption near edge structure (XANES) and K-edge extended x-ray absorption fine structure (EXAFS) of the ferromagnetic (FM) NiFe and antiferromagnetic (AFM) FeMn bilayers prepared with various annealing temperatures. The branching ratios of white-line intensities in the Ni, Fe, and Mn L_3-edges XANES spectra of these bilayers depend strongly on the annealing temperature. This dependency indicates that the annealing temperature significantly influences the Ni, Fe, and Mn 3*d* local electronic structures and alters the magnetic properties of the exchange-biased FM NiFe-AFM FeMn bilayers. On the other hand, the similarity in the Ni, Fe, and Mn K-edge EXAFS Fourier transform spectra suggests that the Ni, Fe, and Mn atoms essentially have similar local atomic structure in the FM NiFe/AFM FeMn bilayers independent of the annealing temperature.

CONTROL OF EXCITONIC AND ELECTRON-HOLE PROCESSES IN WIDE-GAP CRYSTALS BY MEANS OF ELASTIC UNIAXIAL STRESS

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In recent years synchrotron radiation (SR) of 4-40 eV has been widely used for the investigation of the optical effects connected with the multiplication of electronic excitations (MEEs, i.e. the creation of secondary excitons or electron-hole (e-h) pairs by hot photoelectrons) in luminescent wide-gap crystals (WGCs). In WGCs, an elastic uniaxial stress (EUS) has been applied for the separation and thorough study of the elementary stages of MEEs [1]. Initially, the method of EUS was elaborated for the investigation of impurity luminescence centres in WGCs [2] and later used for the study of luminescence excitation processes near the edge of the fundamental absorption in alkali iodides [3]. We have continued investigations of the influence of EUS on the excitation processes of various impurity and intrinsic emissions in RbI, KI, KBr and NaCl crystals using the SR facilities of the HASYLAB at DESY, Hamburg, and MAX-Laboratory, Lund. The emission and excitation spectra for time-integrated signal as well as for the emission detected within a time window have been measured both for an unstressed and a stressed (~0.3-1.0 kg/mm^2) sample using SR of 5 to 35 eV.

Luminescence spectra for a time-integrated, fast (~3 ns) and a slow (~120 ns) component have been measured for stressed and unstressed samples of RbI, excited by photons of various energies in the region of fundamental absorption (5.7 to 35 eV) at 8 K. The time-resolved excitation spectra of 2.2 eV (π-STE emission), 3.9 eV (σ-STE emission), 2.6, 3.1 and 3.4 eV emissions have been measured for stressed and unstressed RbI samples at 8 K as well. The behaviour of the intensity ratio spectra for π and σ components of the self-trapped exciton (STE) emission (I_π/I_σ) and for the impurity emission and STE emission (I_{imp}/I_π or I_{imp}/I_σ) is quite different in the spectral region of 12-16 eV, where SR forms secondary anion excitons or secondary e-h pairs. It is shown that the applied EUS causes a lowering of the activation barrier between the energetic states of free excitons and STEs. At the same time the influence of EUS on primary and secondary e-h pairs, formed by SR, is more complicated. In particular, the EUS prevents the relaxation of hot holes to the top of a valence band, impedes their self-trapping and weakens the recombination emission. The micromechanisms of EUS influence on the self-trapping of secondary anion excitons and secondary valence holes, as well as on the decay of cation excitons in RbI will be discussed.

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Selective Cleavage of Functional Groups in the Substituted Organic Monolayers by Synchrotron Soft X-ray

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Aminosilylated surface was treated with nitro- and halide-substituted aromatic aldehydes, and the resulting molecular layers were examined with synchrotron X-ray photoelectron spectroscopy at 2B1 SGM and 4B1 microscopy beamline in Pohang Accelerator Laboratory. It is observed that nitro and halide group of the film diminished upon the irradiation, but the other bands were constant in terms of the intensity and the shape (Figure 1). This observation indicates that the functional groups of the organic monolayers are cleaved selectively by soft X-ray. The cleavage rate is measured as a function of photon energy and normalized with the photon flux. The cleavage is first-order to the concentration of the functional group. Its rate constant is sensitive to the molecular structure of the organic monolayers and the kind of substituents on aromatic ring.

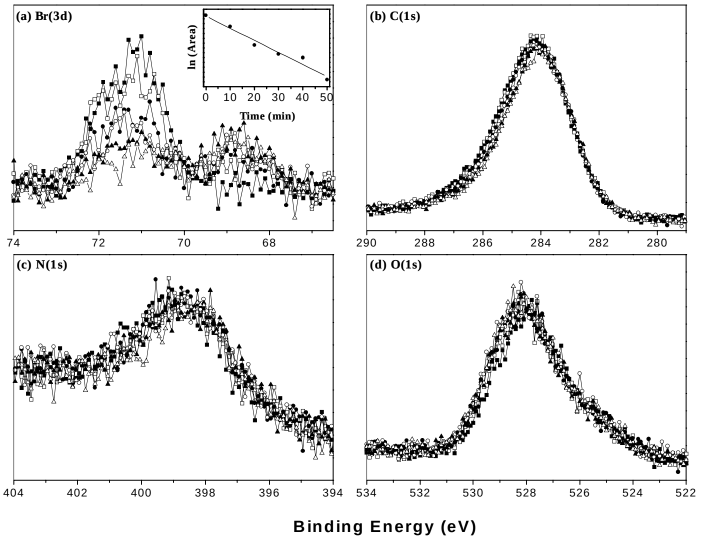

Figure 1. XPS spectra of the 4-bromobenzaldimine monolayer. (a) Br(3d); (b) C(1s); (c) N(1s); (d) O(1s) bands. Each spectrum was obtained after exposure to X-ray for 0 min (■), 10 min(□), 20 min(●), 30 min(○), 40 min (▲), and 50 min (△). Inset: A kinetic plot as a function of the irradiation time.

PEEM AND SXES CHARACTERIZATION ON SURFACE AND INTERFACE OF TRANSITION METALS/SiC SYSTEM

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Possessing extremely remarkable properties such as wide energy bandgap, high breakdown electric field, high thermal conductivity, and high- saturated-drift velocity, silicon carbide (SiC) is expected to be the material for high-power/high frequency, high-temperature, and radiation-resistant electronics devices. Among other polytypes, 3C-SiC, 4H-SiC, and 6H-SiC have been the objects of intense research especially on surface and interfacial reactions in nanostructures level in transition metal(film)/SiC(substrate) systems. The reactions in these systems have been classified either as Mode 1 (formation of silicides and graphite) or Mode 2 (formation of silicides and carbide) [1] with Ni/SiC and Ti/SiC as systems having Mode 1 and Mode 2 types, respectively.

With the introduction of ultra-high-vacuum technology in emission microscopy, photoemission electron microscopy (PEEM) became a high-resolution surface-sensitive technique for the study of surface structures. The image in the PEEM system is based on the lateral photoemission intensity distribution from a solid sample surface [2].

In this study, we have conducted a PEEM imaging on the formations of transition metals-nanostructures (Ti, Ni) on SiC surfaces. The contrast mechanisms of PEEM such as topographical, elemental, chemical, magnetic, and orientation contrasts allowed us a real-time view on the islanding and agglomeration of metals and its dynamics. We have observed during in-situ annealing the formation of island metal structures with diameter of ~2-3 microns as well as contrast in the surrounding of each island which is due to different work functions of surface reactants such as metal silicides and carbides/graphites. The PEEM system uses either Hg arc lamp or synchrotron radiation and is attached to BL-5 of Hiroshima Synchrotron Radiation Facility (HiSor), Hiroshima, Japan.

We have also complimented the PEEM images with SEM images and EDX profile of the surface structures.

The valence band density of states (VD-DOS) of the reacted layer in the interface of metal/SiC systems was studied by soft x-ray emission spectroscopy (SXES) utilizing either soft x-rays from synchrotron radiation source in Photon Factory, KEK, Japan or high-energy electron beam from an e-gun in a Shimadzu-type 0789 SXES device. The changes in the VD-DOS were due to the formations of combinations of silicides and carbide/graphite in the reacted interfacial region.

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Photo-induced phase transition of spin-crossover complex studied with the combination of SR and laser

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Combinational use of synchrotron radiation and laser is attractive and promising, since it is powerful to investigate the various photo-induced phenomena. Recently, some transition metal complex are attracting much interest, since they show drastic magnetic and chromic changes by the excitation with visible laser light. Up to now, these photo-induced phase transitions have been investigated mainly by optical and magnetic methods, but to our knowledge, there is no systematic work which highlights the electronic structure in the wide energy range. We have carried out a photoemission study on an organometal spin-crossover complex $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$, using a photoelectron micro-spectrometer system with the combination of synchrotron radiation and laser.

Experimental system has been constructed at BL6A2 of UVSOR facility. The photoelectron micro-spectrometer (FISIONS Instruments, ESCALAB 220i-XL) was installed at a focusing point from a PGM monochromator. The laser light was introduced through a quartz view-port of a main sample chamber. The crystalline sample was cooled with a liquid helium cryostat. The valence-band and core-level photoemission spectra were taken for high-spin (high temperature), low-spin (low temperature), and photo-induced phases. The Fe 3*d* and N 1*s* spectra showed remarkable changes due to the photo-induced phase transition, indicating that the electron charge was transferred from nitrogen to iron atoms on the phase transition. It was also found that valence-band structure of the photo-induced phase is very different from that of the high-spin phase caused by the thermally-induced phase transition. From these results, we discuss the photo-induced phase transition of spin-crossover complex.

Photoelectron spectroscopic study on core-exciton decay in Auger-free luminescence material BaF_2

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In recent decades, new luminescence, so-called Auger-free luminescence, was discovered by core-level excitations in the wide-band gap materials, where the band-gap energy (E_g) is larger than the energy difference (E_{vc}) between a valence band and an outer-most core level. The luminescence is attributed to the optical transition from the valence band to the core level. There is no Auger process when the condition $E_g > E_{vc}$ is satisfied, and therefore the Auger-free luminescence is so strong that it is useful for fast scintillation in the vacuum ultraviolet and soft x-ray regions. The Auger-free luminescence appears only with the excitation of core levels, but it is known that there is no exciton peak in the excitation spectrum. The present work has been conducted in order to understand why the core-exciton peak is missing in the excitation spectrum of Auger-free luminescence in BaF_2. The photoelectron and luminescence spectra were obtained on the same thin evaporated film under the same experimental conditions. It was found that the valence-band photoelectron intensity is enhanced with the excitation photon energy corresponding to the formation of the Ba-5p core-excitons, indicating the non-radiative decay of the core excitons. The probability of the non-radiative decay due to the direct-recombination process of an excited-electron and a hole which form the Ba-5p core-exciton can be estimated using the three-step model from the resonant enhancement of the photoelectrons. The probability is about 25%, indicating that other non-radiative decay processes of the core exciton exist in this material. It is also proposed that the core excitons in BaF_2 have the lattice relaxation of about 0.9 eV. The present result is in good agreement with that obtained in another Auger-free luminescence material CsCl.

Photoemission- spectromicroscopy of a-C and $C_{1-x}N_x$ hard disk coatings

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The protective coating of magnetic hard disks is an important application in the field of thin film technology. Thin films made of amorphous carbon (a-C) and $C_{1-x}N_x$ are used, where x denotes the fraction of nitrogen. These overcoats serve not only for mechanical wear protection but also for an increased corrosion resistance of the underlying magnetic film. One important contribution to increase the data storage capability is the thinning of the carbon coating to around 2 nm, which results in a decrease of the magnetic spacing and thus the storage density. XANES spectromicroscopy using a Photoemission Electron Microscope (FOCUS IS-PEEM) gives an insight into the bonding conditions and serves as a tool both for laterally resolved and chemically sensitive examination of these ultra- thin functional films. Especially for thin $C_{1-x}N_x$ films there is a discussion concerning the interpretation of XANES (and XPS) spectra with regard to microscopic bonding, because there exist sp, sp^2 and sp^3 bonding environments for the C and N atoms [1]. The arrangement of the atoms, the corresponding electronic structure and the features recorded in XANES spectra depends on the substrate temperature and nitrogen flux used for the preparation of the films. So, PEEM can be successfully applied for the laterally resolved investigation of the nucleation phase, the growth, the finished film and the head/ disk interaction during head crashes. The a-C and $C_{1-x}N_x$ thin films were deposited on silicon wafers and on hard discs using magnetron based and new cathodic arc reactors, both under experimental and production line conditions (UNAXIS M12 at IBM). The film thickness were around ≤ 5 nm, determined by ellipsometry. We present Micro- XANES spectra of a-C and $C_{1-x}N_x$ samples, prepared with different plasma reactors. The averaged intensity of predefined sample areas was recorded using a CCD- Camera (LaVision), triggered by the monochromator at the synchrotron source BESSY II (Berlin). Between hν= 283 eV and hν= 290 eV, the spectra reveal four clearly separated peaks. The first one at hν= 284.5 eV can be attributed to sp^2 bonded carbon atoms. The lateral distribution of these atoms is mapped. So, the most important information of these spectroscopic PEEM images is that the homogeneity of the local bonding conditions can be checked [2]. At hν= 289 eV C-H* bonds contribute to the spectrum. In addition, the distribution of the sp^2 atoms seems to be structured on a micrometer scale. By doping the a-C films with nitrogen, the local arrangement of the atoms changes. The results show the complex chemistry of the samples and the variation of the bonding structure at the surface of the carbon thin films. Due to the fact that XANES features are determined by the initial and final states, we compare the results with XPS and Raman studies.

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PHOTOEMISSION STUDY OF NOVEL HALF-METAL; ZINC BLENDE CrAs

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Half-metallic ferromagnets such as CrO_2 and Heusler alloys have attracted a great deal of attention due to its application to spin-dependent devices[1]. We have predicted that zinc blende(zb) type CrAs, which normally exists as the MnP type, shows a half-metallic band structure by *ab initio* calculations, and succeeded in fabrication of zb-CrAs[2]. Here, we show photoemission study of zb-CrAs.

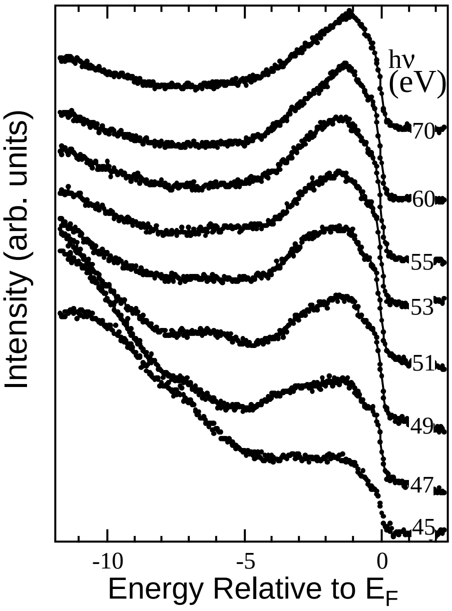

Figure 1: Valence band spectra of a zinc-blende type CrAs thin film measured with different photon energies.

The photoemission experiments were performed at BL-1C of the Photon Factory, and BL-8A1 of the Pohang Light Source. The angle-resolved photoemission, *3p*-*3d* resonant photoemission, Cr *2p* photoemission, and Cr *2p* X-ray absorption were obtained. Zb-CrAs were grown on clean GaAs (001) surfaces in an MBE chamber linked with a high-resolution photoemission end station. Figure 1 shows the valence band spectra of thin films measured with different photon energies. Distinct Fermi edges were observed for all the photon energies, which suggests the metallic characteristics. A flat band which corresponds to Cr *3d* was also observed around 1 eV which agrees well with band calculations. The change in the electronic structure depending on the crystallographic structure of CrAs will be presented in detail.

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Photodegradation of poly(tetrafluoroethylene) and poly(vinylidene fluoride) thin films by inner shell excitation

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Photodegradation by inner shell excitation for poly(tetrafluoroethylene) (PTFE, $-(CF_2)_n-$) and poly(vinylidene fluoride) (PVDF, $-(CH_2-CF_2)_n-$) thin films was investigated by partial ion yield (PIY) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopies.

Thin films of PTFE and PVDF with thickness of 250Å were prepared by vacuum evaporation on Cu plates. PTFE films were rubbed at room temperature. Experiments were performed at the beamline BL13C at the Photon Factory of the High Energy Accelerator Research Organization. PIY spectra were measured using a time-of-fight (TOF) mass spectrometer. NEXAFS spectra were obtained by the total electron yield method. At the measurements of PIY and NEXAFS spectra, the incidence angle of photon was about 55° (magic angle) from the surface normal.

Figure 1 shows ion TOF spectra of PTFE and PVDF thin films obtained at hν=723eV. For the PTFE thin film, peaks corresponding to F^+, CF^+ and CF_3^+ were observed, while for the PVDF thin film, H^+ and F^+ peaks were mainly observed. These indicate that for PTFE the polymer chain (C-C bonds) as well as C-F bonds are broken by irradiation of photons above fluorine K-edge, while for PVDF the bond scission occurs mainly at the C-F and C-H bonds.

Figure 2 shows NEXAFS and PIY spectra of F^+, CF^+ and CF_3^+ for PTFE thin film near fluorine K-edge. It is noted that the intensity of F^+ ion increases strongly at hν=689eV corresponding to the transition of $F1s \rightarrow \sigma^*(C-F)$, although the intensities of CF^+ and CF_3^+ ions do not. It indicates that the bond scission of PTFE by inner shell excitation depends on the electronic configuration of the excited states.

At the conference, PIY spectra for PTFE will be shown and compared with those of PVDF.

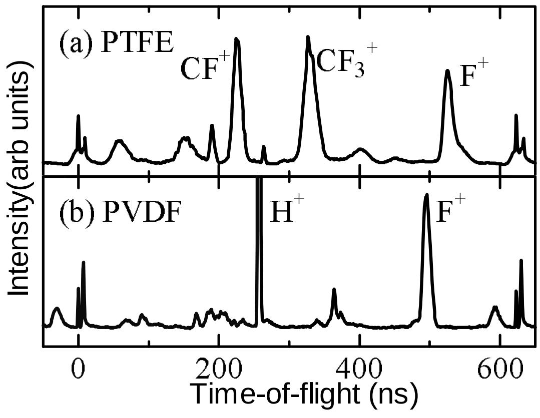

Figure 1 Ion TOF mass spectra of PTFE (a) and PVDF (b) obtained at hν=723eV.

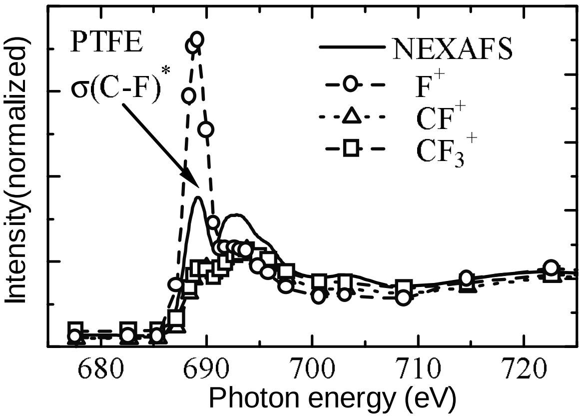

Figure 2 NEXAFS and PIY spectra of F^+, CF^+ and CF_3^+ for PTFE thin film near fluorine K-edge. Intensities of PIY spectra are normalized at hν=715eV.

Mn 3p-3d Resonant Inverse-Photoemission Spectroscopy of NiAs-type MnTe

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Recently, a number of Ce 3d-4f and Ce 4d-4f resonant inverse-photoemission spectroscopy (RIPES) for Ce compounds has been carried out [1] and the RIPES is demonstrated to be a powerful technique to investigate the unoccupied Ce 4f states. On the other hand, the RIPES for the 3d transition-metal (TM) compounds in the TM 2p-3d or 3p-3d excitation region has not been reported so much. In this study, we have measured the Mn 3p-3d RIPES spectra of antiferromagnetic semiconductor NiAs-type MnTe. The RIPES experiments were carried out using the low-energy electron gun with a BaO cathode, and a dispersive photon detector with a non-periodic spherical grating and a multi-channel plate [2]. Total energy resolution was ~0.5 eV with a kinetic energy of incidence electrons (E_k) of 50 eV. The polycrystalline sample used in the present experiments was grown by quenching an equal amount of Mn and Te from 1000˚C to room temperature. Clean surfaces were obtained by scraping with a diamond file every two hours and all measurements were performed at room temperature.

Figure 1 shows a series of the Mn 3p-3d RIPES spectra of NiAs-type MnTe. Energy is referred to the valence-band maximum, which is determined from the photoemission spectrum measured at an excitation photon energy of 21.2 eV for the same sample surface. With the increase of E_k from 40 eV, the intensity of a peak at 2.9 eV becomes minimum at E_k=46.5 eV and reaches maximum at E_k=50 eV. This is due to an interference effect between two processes; 1) $3d^5+e \rightarrow 3d^6+h\nu$ and 2) $3p^6 3d^5+e \rightarrow 3p^5 3d^7 \rightarrow 3p^6 3d^6+h\nu$, where $h\nu$ stands for the emitted photons. The resonance enhancement indicates that the peak at 2.9 eV is due to the d^6 final states, which supports the previous assignment of the IPES spectrum of NiAs-type MnTe obtained by monitoring the emitted photons centered at 9.4 eV [3]. In the RIPES spectrum at E_k=46.5 eV, the broad structure indicated by an arrow in the figure is observed around 12 eV, which is not shown in the previous IPES spectrum. In comparison with the theoretical analysis [3], this structure is assigned to be $d^7\underline{L}$ final states, where $\underline{L}$ represents a ligand hole. The broad structures a and b originate from the Mn 3d-3p and Te 5p-4d fluorescence emissions, respectively.

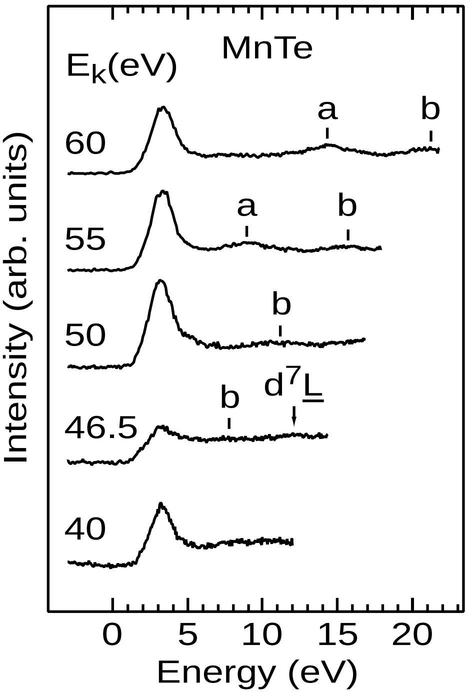

Figure 1: Mn 3p-3d RIPES spectra of NiAs-type MnTe.

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ELECTRONIC PROPERTIES OF TIN DIOXIDE SEMICONDUCTOR NANOPARTICLES STUDIED BY PHOTOELECTRON SPECTROSCOPY

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Thin layers of n-type SnO_2 nanoparticles, 60 Å in diameter, were studied using Photoelectron Spectroscopy with Synchrotron Radiation. The effect of Sb doping on the size of the bulk band gap was measured and results are compared to those found for bulk material [1]. Dopant induced changes in the band gap are discussed in terms of many body interactions. Particles were highly doped with Sb (16.7 atomic percent) and the dopant atom distribution was found using the depth sensitivity of Photoemission with Synchrotron Radiation. There is a high density of conduction band electrons giving rise to plasmon satellite peaks in the core level photoemission spectra. These peaks are more intense for spectra recorded at the higher photon energies showing that the conduction band electrons are confined to the central region of the nanoparticles.

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Total Electron Yield of Multilayers — Extension of Pepper's Method —

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Formula of total electron yield (TEY) of single layers derived by S. V. Pepper [1] (single-layer model) is extended to that of multilayers (multilayer model). The total electron emission process is divided into three steps. The first step is photo-absorption and photoemission processes, of which probabilities are assumed to be proportional to the divergence of the time-averaged Poynting vector depending on optical constants. The second one is travelling, scattering, and electron multiplication processes of the photoelectrons in the medium characterized by the escape depth. The third one is the passing process of the photoelectrons across the interfaces and the surface of the multilayer. The TEY formula of the multilayer model was obtained by combining the formula of TEY for single layers [1] and that of reflection and transmission for multilayers [2]. Schematic diagram of the multilayer is shown in Fig. 1. The *j*-th layer of a thickness d_j has the optical constant, $N_j=n_j+ik_j$, and the escape depth, L_j. The passing probability across the interface between the *j*-th and the *j+1*-th layers is defined as c_j. In the figure, the angle of incidence of θ, the amplitude reflectance of the *j*-th layer as for the vacuum, r_j, and the amplitude reflectance of the *j* layers, R_j, are given.

The obtained formula is applied to the analysis of TEY spectra around the Si-L edge of LiF/Si/LiF multilayers measured for different angles of incidence from 0° to 75°, which were not explained sufficiently by the single-layer model [3]. In the calculations, escape depths of Si and LiF are adopted as 8Å [4] and 70Å [5], respectively. When the ratio of the passing probability from the Si layer to LiF layer and that from the LiF layer to Si layer was 0.1, the calculations explained well the spectral shapes of the TEY spectra. This difference between the two passing probabilities may be related to the difference of the energy positions of the lowest conduction-band bottoms between LiF and Si. The details will be discussed in the session.

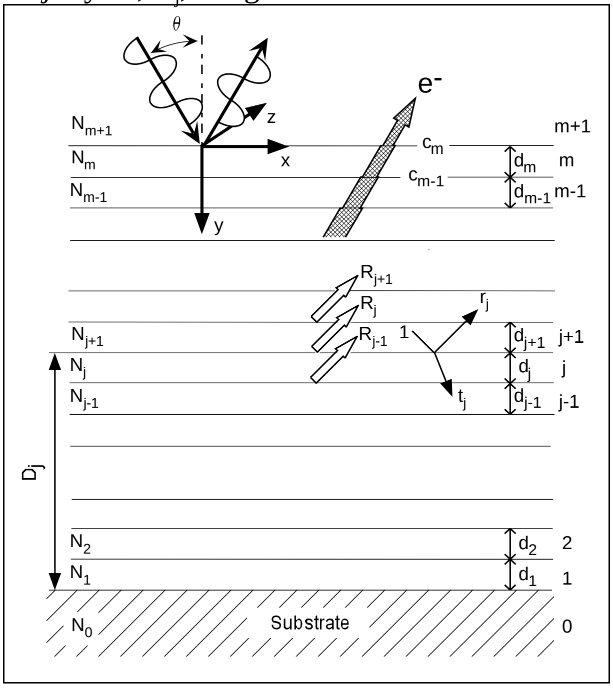

Figure 1: Schematic diagram of multilayer.

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ANGLE-RESOLVED PHOTOELECTRON SPECTROSCOPY AT HIGH PHOTON ENERGIES

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Tuneable light sources have emerged as an essential tool for investigating the electronic structure of solids and their surfaces. Employing angle-resolved photoelectron spectroscopy (ARPES) with synchrotron radiation in the ultraviolet regime large portions of **k** space are accessible, an achievement almost impossible with other spectroscopic techniques. For example, the recently developed photoemission mapping technique [1], in which one records two-dimensional photoelectron angular distributions patterns from a large piece of solid angle, directly provides constant-energy cuts through the band structure $E(\mathbf{k}_{\parallel})$ at $k_{\perp}$ values determined by the photon energy selected.

Going far beyond the ultraviolet regime, modern storage rings routinely supply synchrotron radiation in the 6 – 1500 eV range. Hence, it has become possible to bridge the entire gap between lower VUV ($h\nu < 41$ eV) and X-ray ($h\nu > 1254$ eV) energies available from laboratory sources. So far, however, only a few valence band photoemission studies have been done in the interesting transition region from sharply structured direct-transition features at ultraviolet energies to density-of-states-like spectra at X-ray energies. Importantly, the available high-intensity continuum of synchrotron radiation provides a means of probing both the bulk and the surface electronic states in solid materials, a technique that is based on the increase of the photoelectron inelastic mean free path at higher photon energies [2].

Here we present ARPES measurements on the layered model compound 1T-$TiTe_2$ at photon energies in the 10 - 400 eV range. We study matrix element effects in higher Brillouin zones, determine the photon energy limit up to which ARPES spectra can be understood in terms of the direct-transition model, and we investigate if there are any significant differences in the band dispersions at low ($h\nu < 30$ eV) and higher ($h\nu \geq 200$ eV) photon energies, which might indicate a possible surface effect in a layered material as suggested by Ref. [3]. All measurements were carried out at the beamlines W3.2 and BW3 at the Hamburger Synchrotronstrahlungslabor using our recently developed spectrometer ASPHERE [4].

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ABLATION OF POLYMETHYLMETHACRYLATE BY A SINGLE PULSE OF SOFT X-RAYS EMITTED FROM Z-PINCH AND LASER-PRODUCED PLASMAS

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The efficiency of ablation of polymethylmethacrylate (PMMA) by single pulses of soft X-ray radiation emitted from a Z-pinch and from laser-produced plasma was investigated. The Z-pinch was driven by the S-300 pulsed-power machine (Kurchatov Institute, Moscow; for more details see [1]). Sample irradiation by the Z-pinch results in comparatively softer radiation (maximum of emitted photons have energy about 120eV), higher total XUV pulse energy (~kJ), longer pulse duration (~40ns), and leads to ablation of a 350 nm thick layer of PMMA. The plasma formed by focusing the near-infrared beam from the Asterix IV high-power iodine laser system (Czech Academy of Sciences, Prague; for details see [2]) on the surface of a tantalum slab target in a vacuum interaction chamber was of higher temperature. Comparatively, the radiation pulse emitted by the laser-produced plasma contains much less energy (<100J), most of its radiation is significantly harder (~keV), the pulse duration is much shorter (<400ps), and only several nanometers of PMMA are ablated. Small bubbles were seen at the surface of the PMMA irradiated by the laser-driven X-ray source. Radiation-induced coloration of the material below the ablated layer was observed in both cases. The role of nonthermal processes in soft X-ray ablation will be discussed. Although polymer ablation by intense soft X-rays was first reported almost twenty years ago [3], the experiments were only performed with polymers which are extremely sensitive to ionizing radiation: Poly(butene-1 sulfone) [3] and teflon (PTFE) [4,5]. To the best of our knowledge, this is the first report of efficient pulsed soft X-ray ablation of an organic polymer which does not exhibit ultrahigh radiation sensitivity. The shortest wavelength previously used for ablation of PMMA was 125 nm (photon energy ~10eV) [6]. We expect that soft X-ray ablation can be used for fast and efficient nanostructuring.

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THERMALLY ASSISTED EMISSION OF ELECTRONS AND VUV PHOTONS FROM IRRADIATED RARE GAS SOLIDS

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Interaction of ionizing radiation with insulators turns them into metastable solids containing localized charge carriers, guest atoms, radicals and defects of structure. Energy absorbed during the irradiation and stored by these centers can be triggered by heating of samples resulting in a complex series of reactions followed by energy conversion and transfer processes. Understanding thermally assisted physical and chemical processes in irradiated solids is of considerable interest both from the point of view of fundamental solid state physics, and a number of important applications in dosimetry, photochemistry, material and surface sciences. Thermally stimulated luminescence (TSL) is a valuable tool for studying recombination and relaxation paths in metastable solids as well as for trap-level analysis [1]. However, an interpretation of TSL data is complicated by the fact that it can stem both from charge carrier recombination and from thermally driven chemical reactions of neutral fragments [2].

Here we present the results obtained combining the techniques of spectrally resolved TSL and thermally stimulated exoelectron emission (TSEE) applied to rare gas solids (RGS). These model insulators are the widest band gap solids and most of the optical spectroscopy of recombination processes must be done in the VUV range. The samples of pure and doped Ne, Ar, Kr and Xe solids were grown by pulsed deposition on a cooled substrate under a 200 eV electron beam or irradiated after deposition. Total and spectrally resolved yields of photons were studied upon controlled heating of preirradiated samples. Charge recombination reactions were examined both for intrinsic (self-trapped holes) and extrinsic positively charged centers. In addition we measured optical absorption of the samples subjected to stepwise annealing. The yield of TSEE was measured as a function of temperature in an external electric field of 20V/cm. Comparison of the yields of electrons and photons in VUV and visible ranges made it possible for the first time (i) to discriminate between reactions of neutral species and charge carriers, (ii) to find their interconnection, (iii) to identify the charge of mobile charge carriers and (iv) to differentiate between bulk and surface traps. The fading effect was studied and conditions of charge center stability were found. New information on the charge trap levels in the bulk and on the surface was obtained. TSEE and the recombination of positively charged centers (intrinsic and extrinsic) with electrons, induced by chemical reactions were found in doped RGS.

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X-ray absorption evidence for the back-donation in iron cyanide complexes.

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The nature of the electronic structure and chemical bonding in iron compounds is of fundamental and technological interest. The $3d\pi$-$2\pi(\pi^*)$ charge transfer (π-back-donation) between the 3d atom and ligands (CN^-, CO, NO, etc.) with low-lying unfilled antibonding $2\pi(\pi^*)$ molecular orbitals (MOs) is a characteristic feature of chemical bonding in these and similar compounds. Our recent X-ray absorption study of hexacyano complexes of 3d atoms has shown that this feature can be successfully probed by the ligand N 1s absorption [1]. In this work we present high-resolution Fe 2p absorption spectra of various Fe(II) and Fe(III) compounds with the metal atom coordinated octahedrally (or nearly octahedrally) to ligands (F, O, S, CN) expecting changes in the absorption spectra due to differences in the formal valence state and in the character of the chemical bond. The X-ray absorption measurements on iron compounds FeF_2, FeS, FeO, $FeCO_3$, $K_4Fe(CN)_6$, FeF_3, Fe_2O_3, $K_3Fe(CN)_6$, $Na_2Fe(CN)_5NO$ were performed at the VLS-PGM beamline at BESSY II in the total electron yield detection mode. The spectra are aligned energetically using the absorption peaks of a reference compound recorded simultaneously.

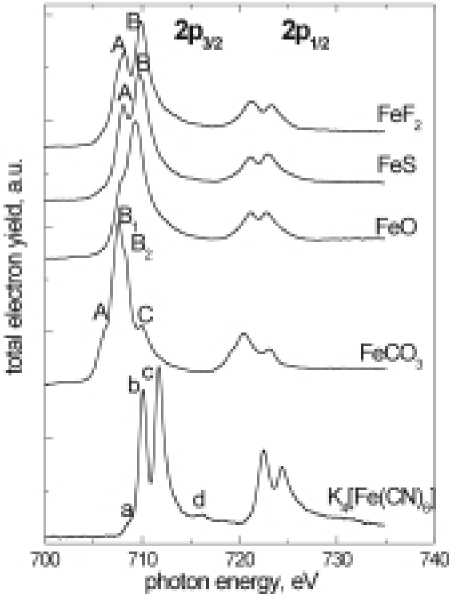

Fig. 1 Fe 2p absorption spectra of Fe(II) compounds

While the graduate low-energy shift of the absorption edge in the series FeF_2 – FeS – FeO – $FeCO_3$ can be explained by the growing 4s screening of the initial and final states, the large high-energy shift of the Fe $2p_{3/2}$ absorption (~ 3 eV for the center of gravity) in going from the more ionic $FeCO_3$ to the covalent $[Fe(CN)_6]^{4-}$ complex (Fig. 1) is quite surprising, because this most covalent Fe(II) compound of the investigated series should give a low-energy shift of the absorption spectrum. This fact may indicate a decrease of screening of the absorption transition because of a decreased number of the 3d electrons localized on the Fe(II) atom in the complex due to the mixing of the highest occupied Fe $2t_{2g}$ with the 2π-orbitals of ligands (π-back-donation). The shape of the spectrum (Fig. 1, bottom) also cannot be understood without taking of such molecular effects into account. That is why the Fe 2p spectra of both $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ can be hardly explained within the atomic multiplet approach for the transition metal compounds [2].

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ELECTRONIC STRUCTURES OF CARBON MATERIALS CONTAINING MULTIWALL CARBON NANOTUBES STUDIED BY PHOTOELECTRON SPECTROSCOPY

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Multiwall carbon nanotubes (MWNTs) are prepared by arc dc discharge method using graphite electrodes in helium atmosphere, and produced abundantly inside a deposit on a cathode. Electronic structures of one MWNT, which may depend on its structures such as multiplicity, chirality and so on, are researched with scanning tunneling microscopy (STS), while photoelectron spectroscopic experiments for electronic structures of MWNT-aggregates are carried [1,2]. Here ultraviolet and x-ray photoelectron spectra (UPS and XPS) of carbon materials before/after separating from the electrode, containing MWNTs with high concentration, have been measured and compared with other carbon allotropes.

The deposit appears like a hard crater at the center of the cathode. Following specimens are measured: (a) the deposit on the cathode, (b) powder material (obtained from the deposit) purified in ethanol, and (c) residue after separating the powder from the deposit. Specimens of (d) graphite and (e) C_{60} have been prepared for comparison. Each specimen is mounted on a gold substrate, especially powder (c) and (e) are applied in the same way [3].

UPS (Figure 1) of (b) MWNTs has several peaks and resembles that of (d) graphite, indicating that the difference between (a) and (b) is induced by the condition of arrangement and the direction of each MWNT. Details will be discussed with the results of XPS (Figure 2).

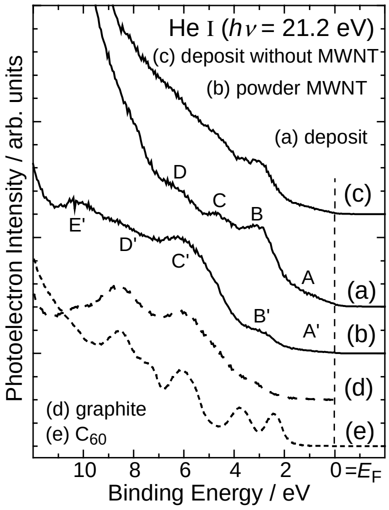

Figure 1. UPS of deposits and powder MWNTs.

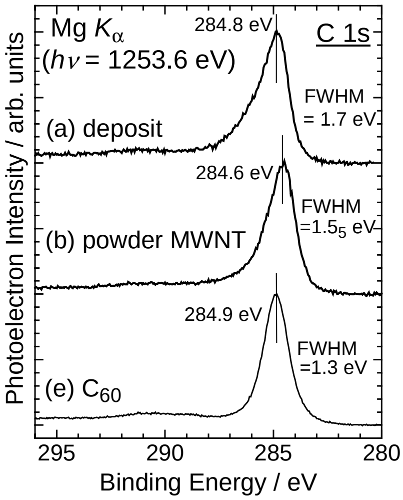

Figure 2. C 1s XPS of deposits and powder MWNTs.

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High resolution photoemission study of nitrogen chemical bonding in ultrathin Si oxynitride on Si(100)

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In current ULSI technology, oxynitride (SiO_xN_y) film is widely used as a specific dielectric material. The oxynitride gate dielectrics act as a boron diffusion barrier and reduce the damage from hot-carrier electron. This advantage is achieved by the crucial role of incorporated nitrogen at SiO_2/Si interface. However, the chemical and depth structure of nitrogen incorporated in the oxynitride film is unclear.

The chemical bonding structure of nitrogen within thin oxynitride films on Si(100) was investigated by high resolution photoemission spectroscopy for systematic comparison of NO and N_2O-nitrided species. Two N 1*s* peaks are resolved with separation energy of ~0.63 eV, which correspond to N atoms at interface and in SiO_2. The lowest binding component has the similar chemical environment as that in Si_3N_4. The higher binding components have electronegative O atoms as second nearest neighbors and is shifted more by core-hole screening effect. The different behavior of N_2O-treated film with NO-treated one is explained using the second-nearest-neighbor effect induced by lower nitrogen concentration in N_2O-treated oxynitride.

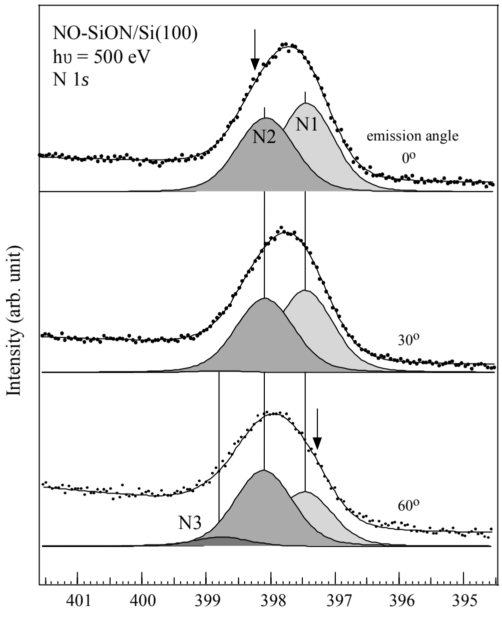

Figure 1: N 1s core level spectra and fitting results of NO-SiON film made by RTP at hυ = 500 eV. As the emission angle varies from surface normal, the intensity ratio of each component (N1 and N2) changes.

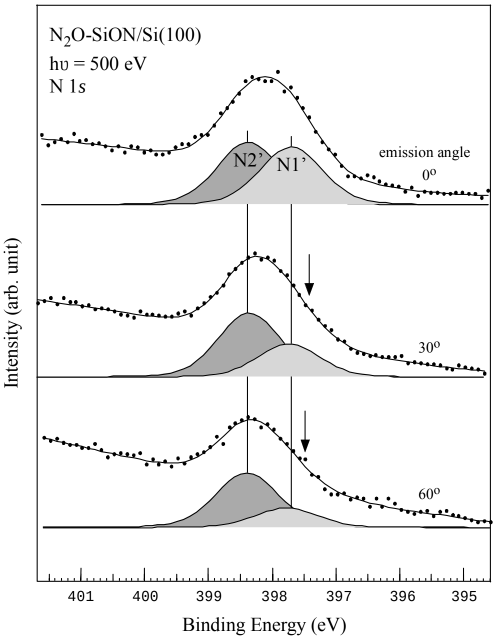

Figure 2: N 1s core level spectra and fitting results of N_2O-SiON film made by RTP at hυ = 500 eV with the same experimental geometry as in figure 1. To enhance the core level intensity, we etched the sample for 8min. in 0.1%-HF solution.

DOMAIN IMAGING OF SMALL MAGNETIC DOTS ARRAY BY PHOTOELECTRON EMISSION MICROSCOPE

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It is now well known that the combination method of MCD (magnetic circular dichroism) effect and photoelectron emission microscope (PEEM) enable us to make magnetic domain imaging [1]. We report here the results of magnetic domain imaging of small dots array. A variety of sizes, shapes of the Ni dots were produced onto a Si wafer covered with a gold film. These patterns were made by electron beam lithography combined with a chemical lift-off method. The thickness of the Ni dots is 40nm. The PEEM equipment (Staib inc. PM350) is attached to the home made spherical chamber. The experiments were performed at the bending magnet beamline BL11A and the helical undulator beamline BL28A at the Photon Factory. Circularly polarized light of the photon energy around the Ni *L* edge region is used at the BL11A by using the upper part light of the electron orbit. Circularly polarized light around the Ni *M* edge region is provided at the BL28A.

Figure shows an image obtained for hexagonal Ni dots arrays, in which the MCD effect around the Ni *L* edge is used. The sizes (diameters) of dots are 10μm, 5μm and 2μm, respectively. Magnetic domain is clearly observed. There seems to be no interaction between each dots. As the size of dots becomes smaller than 5μm, probably due to the effect of edge force of domain, the magnetization direction of the each domain is aligned to the edge of each dot, whereas the direction of magnetization for larger dots (10μm) is almost random.

The observed domain images can be simulated based on the Landau-Lifshitz-Gilbert equation [2]. The domain observation for other types of the magnetic dots array such as squares, circles, and triangles will also be reported. The results will be discussed by comparing with the simulation and the results of the observation by magnetic force microscope (MFM).

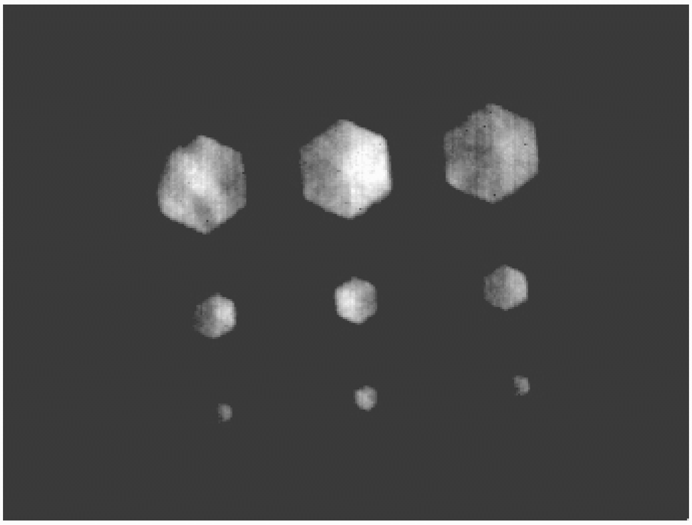

Figure : Magnetic domain images of Ni hexagonal dots. The sizes of dots are 10μm, 5μm and 2μm, respectively.

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The dynamics properties on luminescence of CeF_3 crystals

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CeF_3 is one of the excellent scintillator with fast decay time[1-4]. It was investigated broadly as a promising detector material used for future colliders (i. e. LHC). Meanwhile, it is also one of the excellent scintillators used in nuclear medicine such as positron emission tomography (PET). But its luminescent mechanism is still under discussion.

In present paper, We discussed the dynamics properties on luminescence of CeF_3 crystals, including the temperature dependence of emission spectra and excitation spectra in UV-VUV region, and the temperature dependence of decay time. The main results are shown as following:

1. At 5.5K, under VUV (61, 157, 191nm) excitation, the emission spectrum of CeF_3 crystal consists of a strong band with double peaks at 286 and 304nm, which originate from the "spin-orbit" splitting of 4f ground states ($2F_{5/2}$,$2F_{7/2}$) in the transition of Ce^{3+}:5d→4f. When excited under UV (270nm) region, there is only one emission band peaked at 342nm, which is ascribed to some defect centers. As the temperature increase, the double peaks decrease; however, the emission of the defect centers increases noticeably.
2. At 5K, the excitation spectrum of the 342nm emission includes a strong band peaked at 266nm and two weak bands (56nm, 120nm), two weak bands are corresponding to the intrinsic excitation of the host. While the excitation spectrum of the intrinsic emission (286nm, 304nm) has a broad band from 150nm to 260nm, this broad band caused by crystal field splitting. The excitation spectra of the Ce^{3+} and the defect centers only overlap around 260nm at 5K, but excitation spectra of Ce^{3+} and the defect centers are similar when excited at 360K.
3. The decay times of the 286nm and 304nm emissions are 4ns and about 30ns respectively, which are invariant from 5K to 360K. While the decay time of the 342nm emission increases from 20ns to 40ns when temperature rises from 5K to 360K.

From all above, it is suggested that the energy transfer from Ce^{3+} to defect centers exist in CeF_3 crystals. The probability of energy transfer will increase accompany with the increasing of temperature.

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HIGH-RESOLUTION SURFACE CORE-LEVELS OF InAs ON GaAs(001) SUBSTRATES

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Low-dimensional semiconductor heterostructures are one of the main research topics in electronics as well as solid-state physics. Semiconductor heterostructure and/or nanostructures are widely used in the field of opto-electronic devices and high-speed devices. Among them, InAs/GaAs is one of the most typical highly lattice-mismatched heterostructures in which Stranski-Krastanow growth mode is observed that leads to the formation of self-assembled quantum dots (QDs). To control the growth and a bandgap of self-assembled QDs, the information on the atomic structure and chemical composition of the 2D wetting layer as well as the intermixing effect is essential.

In this contribution, we have performed synchrotron radiation high-resolution photoemission for molecular beam epitaxy (MBE)-grown InAs/GaAs(001) and determined the surface structure and surface chemical composition of InGaAs wetting layers. The experiments were performed at the newly built MBE-*in situ* photoemission beamline BL-1C of the Photon Factory. The photoemission spectra of As 3*d*, In 4*d* and Ga 3*d* core-levels with 0˚ and 60˚ emission angles were shown in Fig.1. From the surface core-level shift (SCLS) analysis, we have observed that In atom has 2 components, Ga atom has 1 surface and 1 bulk components, and As atom has 3 surface and 1 bulk components. The above results are explained by our proposed surface structure model (Fig. 1), which considers the surface region up to the 4th layer. We have also quantitatively estimated the chemical composition of the top layer from the spectrum weight of each component and revealed the intermixing effect.

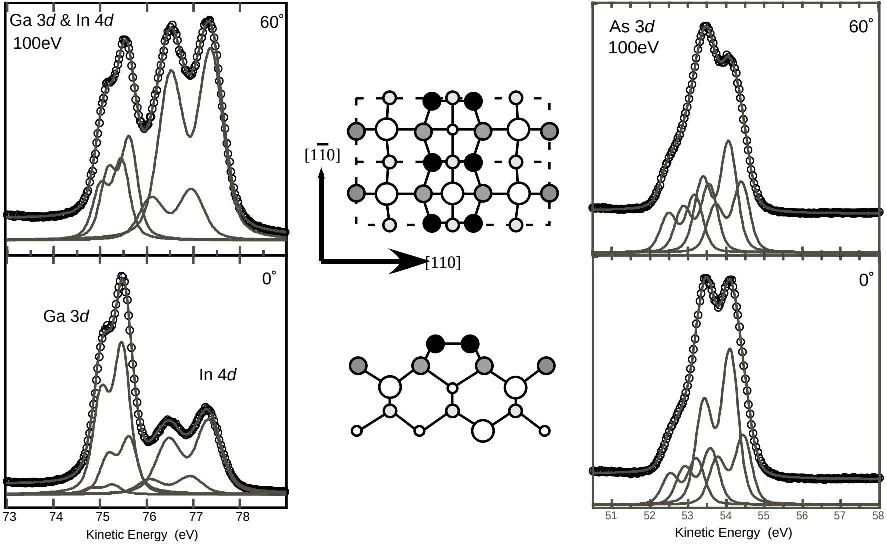

Figure 1: In, Ga, and As 3*d* photoemission spectra for the 1 monolayer InAs on GaAs(001) substrate with 0˚ and 60˚ emission angles.

X-RAY PHOTOELECTRON DIFFRACTION STUDY ON EPITAXIAL GROWTH OF SULFIDE FILMS AND SELF-ASSEMBLED DOTS

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The growth of II-VI films on III-V semiconductor substrates has attracted much attention for several years. Both epitaxial film growth and strain-induced island formation have been observed depending on the combination of materials. We have investigated the interface formation and growth of the CdS and PbS compound semiconductors on well lattice-matched InP(110) and (001) surfaces. While the originally wurtzite-type CdS adopts the zincblende structure of the substrate during initial film growth, the PbS keeps its rocksalt structure independent on the substrate face. We have investigated the growth and lattice matching of PbS using XPD experiments in the angle-scanned mode and multiple scattering cluster calculations accompanying LEED, ARUPS, and AFM studies on this interface.

The epitaxial relations of substrate and film were derived by comparison of angular distribution curves (ADC) of core levels. In agreement with LEED and ARUPS data we find that at substrate temperatures up to 200°C PbS films grow with the (001) face parallel to the substrate (001) or (110) surfaces. This results in a well lattice matched, commensurate film on InP(001), while the PbS films on (110) substrates are partially incommensurable. However, ADC recorded in both the commensurate and incommensurate orientations on InP(110) were in accordance with each other and comparable directions on PbS/InP(001) and PbS single crystals, indicating that the incommensurable matching does not significantly affect the film structure. The ADC could be explained well by single scattering cluster calculations based on the bulk PbS structure. Volcano-type modifications of the forward scattering peak features of the S2p peaks could be clearly traced back to complex interference patterns including Pb scatterers off the sulfur forward scattering direction by the simulations. In agreement with theoretical prediction, volcano-type peak shapes are not observed for ultrathin PbS films (<1nm), indicating a possible application of this feature as fingerprint for evaluation of the effective film thickness.

A more complex growth pattern of PbS was observed on InP(110) at temperatures of 250-300°C, indicated by a rigid shift of the ADC in polar angle. A tilt in the growth direction by 20° was revealed from these XPD and confirmed by both LEED and AFM. This could be interpreted by achievement of a completely commensurate matching to the substrate at these growth conditions, leading to appearance self- assembled PbS islands of rather narrow size distribution as determined from AFM [1].

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XMCD on paramagnetic V-compounds and metalloproteins

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X-ray magnetic circular dichroism (XMCD) spectroscopy provides a unique opportunity to study spin and oxidation states of concentrated and dilute transition metals in organic and inorganic complexes. Advantages of the technique include element selectivity and high sensitivity. The XMCD signal is given by the difference in absorption between right and left circular polarized X-rays [1]. Applying the sum rules to the measured spectra allows determining the spin and the orbital angular momentum of the metal centers. Sample current measurements have been performed on the concentrated model compounds. Similarly, the XMCD effect was measured on proteins. In this case the absorption spectra have been measured via fluorescence [2] utilizing a commercial 30-element Ge detector. With our current setup located at the elliptically polarized undulator beamline of the ALS we can study systems with a metal concentration of 500 ppm and below [3]. This gives us the ability to address widely discussed questions of oxidation and spin states of transition metals in active sites of certain proteins.

XMCD probes the population of the magnetically split levels. Since in paramagnetic systems this population is given by Boltzmann statistics, XMCD requires high fields and low temperatures. Our endstation hosts a 6 Tesla superconducting magnet cooled with liquid helium. The sample holder is located in the bore of the magnet and is attached to a separate pumped ^{4}He cryostat with a base temperature of 1.5 K.

We have studied a wide range of air sensitive sulfur ligated vanadium complexes. This approach gives a chance to study the influence of different ligands, oxidation and spin states. It is especially interesting since these complexes serve as models for biological systems like metalloproteins. The active sites of these proteins also have been studied with this technique. In this paper we will give an overview of the results achieved so far.

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ELECTRONIC STRUCTURES OF SYSTEMS FORMED FROM C AND F STUDIED BY UPS, VUV OPTICAL SPECTROSCOPY, AND NEXAFS: POLY(HEXAFLUORO-1,3-BUTADIENE) $[C(CF_3)=C(CF_3)]_n$, FLUORINATED GRAPHITES(CF, C_2F AND C_6F), PERFLUOROALKANES n-C_nF_{2n+2}, POLY(TETRAFLUOROETHYLENE) $(CF_2)_n$, AND FLUORINATED FULLERENES ($C_{60}F_x$ AND $C_{70}F_x$)

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Various types of compounds can be formed from C and F. In this work [1], the electronic structure of 4 such groups were systematically studied, based on the new and reported data of UV photoelectron (UPS), vacuum-UV (VUV) optical, and near-edge X-ray absorption fine structure (NEXAFS) spectroscopies. New data were measured for (1) UPS, VUV reflection, and NEXAFS (C- & F-K) spectra of poly(hexafluoro-1,3-butadiene), whose actual structure is $[C(CF_3)=C(CF_3)]_n$ [2], and (2) NEXAFS (C- & F-K) spectra of fluorinated graphites CF, C_2F, and C_6F. These data were analyzed together with the data for n-C_nF_{2n+2} + poly(tetrafluoroethylene) $(CF_2)_n$ [3-7] and fluorinated fullerenes $C_{60}F_x$ and $C_{70}F$ $[8]_x$. The UPS data and MO calculations indicated upper valence electronic states consisting of (1) C2p +F2p sigma-delocalized states, (2) the F2p lone pair orbitals at the middle of these levels, and (3) localizd pi states in unsaturated compounds. The details can be explained in terms of the degree of delocalization, inductive effects of F and CF_3, and steric hindrance. The energies of the lowest electronic excitations obtained by optical spectra could also be analyzed with these factors. The ionization threshold of PHFBD (10.3 eV) is the largest among unsaturated systems, due to electron localization in the twisted chain and the inductive effect of CF_3 groups. CF and C_2F gave well polarized NEXAFS spectra, which could be analyzed in comparison with the spectra of n-$C_{24}F_{50}$ etc. The NEXAFS of C_6F showed that the F atoms are neither in molecular form nor covalently bonded to C atoms, in consistency with the reported ionic or semi-ionic nature.

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HIGH-RESOLUTION PHOTOEMISSION STUDIES ON InAs(001)-c(4x4) SURFACE RECONSTRUCTIONS

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The III-V compound semiconductors are widely used for high-speed and opto-electronic devices. The morphology of surfaces and interfaces can significantly affect the performance of semiconductor devices. To control the physical properties of future quantum nano-devices, atomic scale accurate control of surfaces and interfaces is indispensable. In this contribution, we focus on the surface structure and chemical bonding of an InAs (001)-c(4x4) surface, which is observed under the most As-rich condition in the molecular beam epitaxy (MBE)-growth [1].

An n^+-InAs(001) substrate was used. After removing a surface oxide, a 1000Å buffer layer was grown. The surface structures were monitored by RHEED during the growth. The MBE-growth and photoemission experiments were performed at the newly built MBE + *in situ* photoemission beamline BL-1C of the Photon Factory [2]. The photon energy was set at 100 eV. The photoemission spectra of As 3*d* (shown in Fig. 1) and In 4*d* with 0˚ and 60˚ emission angles were measured. The surface structures were checked by LEED before and after each measurement. We have observed surface core-level shifts (SCLSs) from chemically inequivalent surface sites, while we have observed three surface components and one bulk component in the As 3*d* spectra. Whereas we have observed only one component in the In 4*d* spectra. Based on these SCLS results, we have successfully determine the surface structures and chemical bondings for the InAs(001) surface.

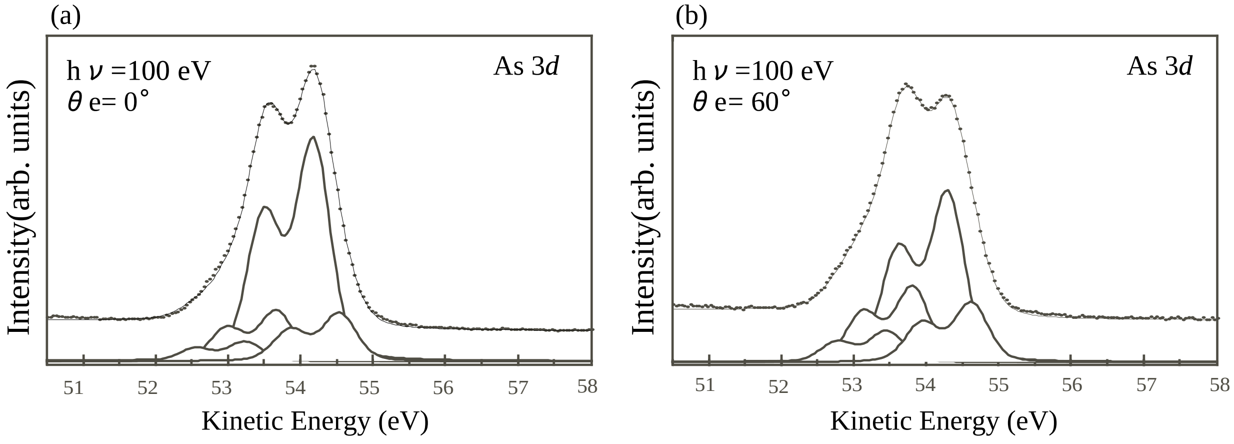

Figure 1:As 3*d* core-level spectra taken at (a) 0˚ and (b) 60˚.

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HIGH SPATIAL RESOLUTION SOFT X-RAY PHOTOEMISSION STUDY OF WO_3 THIN FILMS.

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Tungsten trioxide (WO_3) is a wide gap n-type semiconductor and it is the subject of an intense both theoretical and experimental studies because of its interesting applications, such as gas sensors towards different gases, like NO_2 and H_2S, and as electrochromic film. Many of these possible applications are mainly due to the oxygen vacancies. For example, in the sensing mechanism, the gas species are adsorbed on the surface changing the concentration of the free electrons on the surface. These electrons are present on the surface because of the oxygen vacancies. The variation of this concentration modifies the electrical conductivity of the film. Similarly, the presence of substoichiometric WO_{3-x} compounds, determines the optical properties of these films. An important parameter in the preparation of WO_3 thin films is the thermal treatment following the sample growth. For example it has been shown that the gas sensitivity and response time are strongly influenced by the annealing procedure, because of the phase transitions induced by the annealing. In this work the WO_3 surface chemical composition has been studied by means of high spatial resolution soft X-ray photoemission spectroscopy at the Elettra Synchrotron Radiation Center, Trieste, using the Spectromicroscopy beamline. We have studied the surface properties of both as deposited samples and samples after annealing in air at high temperatures. Valence band and W 4f core levels have been analysed on different samples positions and high spatial resolution maps have been acquired. The valence band spectra have shown W 5d density of state at the Fermi level, indicating the presence of metallic tungsten on the surface. This has been confirmed by the W 4f signal, which present both metallic and oxidized phases. The high resolution maps, obtained following both valence and core states, have clearly evidenced the presence non stoichiometric areas and of some metallic islands.

STRUCTURE OF AMORPHOUS SILICON INVESTIGATED BY EXAFS

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The local structure of amorphous Si (a-Si) has been investigated at the Si-K edge with extended X-ray absorption fine structure spectroscopy (EXAFS). Crystalline Si wafers were self implanted with a multi-energy Si implantation sequence, performed at -196 °C, to render an approximately constant level of energy deposited in vacancy production in the near surface region. For low ion doses, the residual disorder was characterised with Rutherford Backscattering Spectrometry (RBS), and the critical dose for amorphisation was determined. EXAFS measurements were performed at beamline 11C of the Photon Factory, Japan. The incident photon flux to the sample was measured from the photocurrent of a Gold mesh, and the Si absorption signal by total electron yield (TEY) by simultaneous electron detection and sample drain current. EXAFS measurements as a function of ion-dose were performed to characterise: a. the crystalline-to-amorphous transformation and b. any structural dependence within the amorphous phase; with ion doses exceeding that of the amorphous threshold by approximately two orders of magnitude. Data analysis by convention methods was hampered by the presence of the Si *KL* double electron excitation at ~ 124 eV past the Si K-edge [1]. Thus the background was modelled to include an additional step to account for this jump in absorption.

The EXAFS-determined structural parameters compared favourably to previous EXAFS investigations of a-Si [1]. Comparisons are also made to recent X-ray diffraction measurements of a-Si [2] and also the ion-dose dependent structure of another Group IV semiconductor: a-Ge [3].

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X-RAY ABSORPTION NEAR EDGE STRUCTURE AND PHOTOEMISSION INVESTIGATIONS OF NITRIDED AIII-BV SEMICONDUCTOR SURFACES

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The nitridation of AIII-BV semiconductors surfaces has attracted much attention because of the importance of nitride growth on established substrates and of semiconductor surface passivation [1,2]. In this work we have investigated the surface nitridation by a bombardment with low-energy N_2^+ ions at room temperature using X-ray absorption and photoemission.

GaAs, InAs and InSb(100) wafers were nitrided in situ using 300-1000 eV N_2^+ ions. XANES measurements were performed at the nitrogen (and oxygen) K-edge in total electron yield (TEY) mode in order to probe the chemical bonding of the implanted nitrogen species. Core level photoemission spectra were recorded using conventional excitation sources. Evident similarity of the principal features of XANES taken at α-GaN and the N_2^+ ion-bombarded GaAs indicates the formation of a nitrided surface layer on the N_2^+ bombarded GaAs, mostly consisting of GaN as confirmed by core level photoemission. In striking contrast to the typical brodening of all the other spectral features from nitrided GaAs compared to GaN, a rather sharp peak appears at 401.0 eV. Extending our X-ray absorption studies also to In-based III-V compounds we have observed similar indications for surface nitridation on InAs and InSb, too. But in contrast to the N_2^+ bombarded GaAs and GaN surfaces the XANES shown in Fig. 1 are now strongly dominated by an intense and sharp peak near the onset of absorption. The identical position of the sharp spectral features at 401.0 eV for the nitrided GaAs, InAs, and InSb suggests a common origin. We assign this characteristic feature to a π*-resonance related to interstitial nitrogen [3]. The good agreement with the 1s-π* transition energy of molecular nitrogen let us suggest that the peak is due to N_2 molecules. Extended photoemission studies permit us to propose a model that describes the surface nitridation steps.

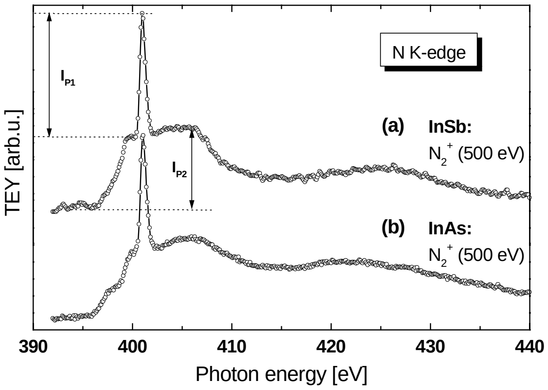

Fig. 1:
TEY spectra of the N K edge energy region recorded on InAs and InSb following N_2^+ ion beam bombardment

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Crystallinity dependence of the high resolution near edge X-ray absorption fine structure spectra of polyethylene

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The mechanical and electronic properties of polymers strongly depend on the intermolecular interaction. Using high-resolution near-edge X-ray absorption fine structure (NEXAFS) (recorded by scanning transmission x-ray microspectroscopy at NSLS Brookhaven) the influence of different branch lengths and branching ratios has been investigated for polyethylene in detail. Systematic changes in the C 1s NEXAFS spectra and the results of annealing experiments provide unambiguous evidence for different fractions of crystalline and amorphous phases. Ab-initio calculations [1] reflect the relatively strong influence of matrix effects on the electronic structure and reproduce the behaviour of the distinct C-H σ^*/Rydberg resonances observed between 287 and 289 eV. An explanation for the experimental observations is given on the basis of the different nearest neighbour distributions in the crystalline and amorphous phases.

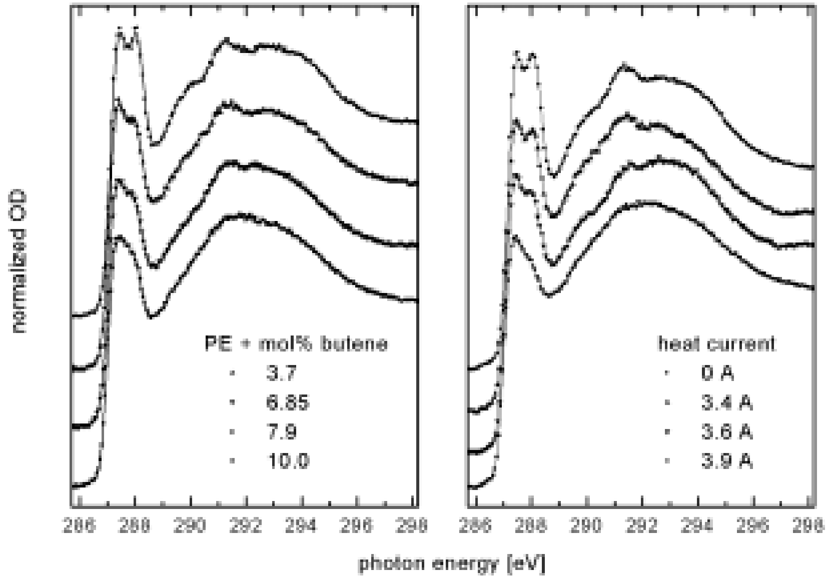

Fig. 1: C-K NEXAFS spectra of polyethylene with different butene comonomer content (left) and of a polyethylene sample with low comonomer content after annealing (right). The given values represent the current through the sample holder reflecting the "annealing temperature".

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ELECTRONIC STRUCTURE AND METAL-INSULATOR TRANSITION OF LaNiO$_{3\text{-d}}$

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The purpose of this work is to study the electronic structure of LaNiO$_{3-\delta}$ as a function of the oxygen concentration. This compound presents a metal-insulator transition for a critical oxygen concentration of around 2.75 ($\delta = 0.25$). The main experimental technique used in this study was O 1*s* X-ray Absorption Spectroscopy (XAS). The experimental results were analyzed using a cluster model solved by the configuration interaction method. The analysis of the results shows that the metal-insulator transition is related to the concentration of charge carriers in LaNiO$_{3-\delta}$. Furthermore, both the results and the calculation suggest that these charge carriers contain considerable oxygen character.

Stoichiometric LaNiO$_3$ is metallic, but a metal-insulator transition can be induced by controlling the oxygen concentration. In particular, LaNiO$_{3.00}$ is metallic ($\partial\sigma/\partial T < 0$) and exhibits Pauli paramagnetism, whereas LaNiO$_{2.50}$ is insulating ($\partial\sigma/\partial T > 0$) and antiferromagnetic ($T_N = 320$ K) [1]. The intermediate LaNiO$_{2.75}$ presents a subtle metal-insulator transition around $T_C = 75$ K, as well as spin localization and magnetic frustration [1]. The Ni ions in LaNiO$_{3.00}$ are all occupying octahedral sites, whereas in LaNiO$_{2.50}$ they equally occupy octahedral and square planar sites [1]. Finally, the Ni ions in the intermediate LaNiO$_{2.75}$ occupy both octahedral (66 %) and square planar sites (33 %) [1].

The O 1*s* XAS spectrum of LaNiO$_{3.00}$ presents a sharp peak at threshold which corresponds to $3d^8\underline{L} \rightarrow \underline{c}3d^8$ transitions [2]. The analysis of this peak suggests that the charge carriers in LaNiO$_{3.00}$ contain considerable oxygen character. This peak disappears almost completely in the spectrum of LaNiO$_{2.50}$ (a small intensity still remains due to a slight oxygen excess in LaNiO$_{2.50}$). This shows that the metal-insulator transition is related to the disappearance of the charge carriers and the ensuing band gap opening. The spectrum of LaNiO$_{2.75}$ presents an intermediate situation with the peak at threshold split by crystal field effects. The metal-insulator transition in this compound is attributed to potential disorder between the octahedral and square planar sites.

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ELECTRONIC STRUCTURE OF MGS, MNS, FES, AND CAS: SOFT X-RAY ABSORPTION STUDY

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The sulfur *s*-, *p*- and *d*- unoccupied states are investigated using S $L_{2,3}$- edge XANES and S *K*-edge XANES in MgS, MnS, FeS, CaS. The spectra were collected at the Canadian Synchrotron Radiation Facility (Aladdin storage ring; University of Wisconsin at Madison, Wisconsin) using a double crystal monochromator beamline in both total electron yield (surface sensitive) and fluorescence yield (bulk sensitive).

Theoretical analysis of experimental data has been done on the basis of full multiple scattering theory. This approach made it possible to study the origin of XANES peculiarities, including the role of the atoms, around sulfur atom and the influence of the symmetry of metal surrounds. The results show that a cluster of 3 shells (radius about 4.5 Å) could describe the features of the whole sulfides solids.

A special kind of hybridization has been found. It has been shown that as a result of the interaction between sulfur *p* states and metal *d* states, sulfur *p* states are "squeezed out" of the energy region of the metal d electronic states.

Soft-x-ray spectroscopic study of solvent-ligand exchange in Fe^{3+} water solutions

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Metal-ion transport in both aqueous- and polymer-solvent media involves continual solvent-ligand exchange. Metal-ion coordination chemistry is therefore fundamental to these phenomena where a dramatic exchange of ligands occurs. The application of soft x-ray absorption (SXAS) and emission spectroscopy (SXES) to study wet systems has been hampered by the experimental difficulties of handling the wet samples under high-vacuum conditions. Experimental solutions to these problems have been developed and recently such experiments: soft x-ray absorption and emission spectroscopic studies of liquid water and solutions have been carried out at BL7.0 at Advanced Light Source. The ligand field interactions and charge transfer effects have been observed in water, $FeCl_3$, and $K_3[Fe(CN)_6]$ solutions.

VIBRATIONALLY RESOLVED NEXAFS SPECTRA OF LONG-RANGE ORDERED ORGANIC THIN FILMS

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Organic thin films have recently attracted considerable interest in applied and fundamental research. Films of high structural quality can be prepared by vacuum sublimation under UHV conditions when high-quality single crystal (e.g., metals) surfaces are used. The additional degrees of freedom of large molecules even allow the preparation of metastable structures [1].

We have investigated two molecular model systems (NTCDA and PTCDA multilayers adsorbed on Ag(111)) using high-resolution near-edge x-ray absorption fine structure (NEXAFS). The experiments were performed using the total yield mode at the BESSY U49/1-PGM undulator beamline (E/ΔE > 10.000 at 400 eV) *with unprecedented accuracy for such large molecular systems*. The manifold NEXAFS resonances (see fig. 1) are unambiguously interpreted as coupling of core-electronic transitions to vibronic excitations. The peak fitting analysis yields various vibrational progressions, i.e. peaks with equal distances, and additional electronic transitions and thus enables a more detailed interpretation of the complex NEXAFS spectra of such large π-conjugated molecules. In addition, we find that the fine structure (inhomogeneous broadening, vibronic modes) strongly depends on the molecular structure and on the degree of structural order (see fig. 1) in the film underlining the influence of the intermolecular coupling in these weakly interacting (van-der-Waals) systems. We will compare the different vibronic excitations coupled to core-excited electrons with those from the electronic ground state derived from HREELS. (funded by the BMBF, contract 05 SF8WWA 7)

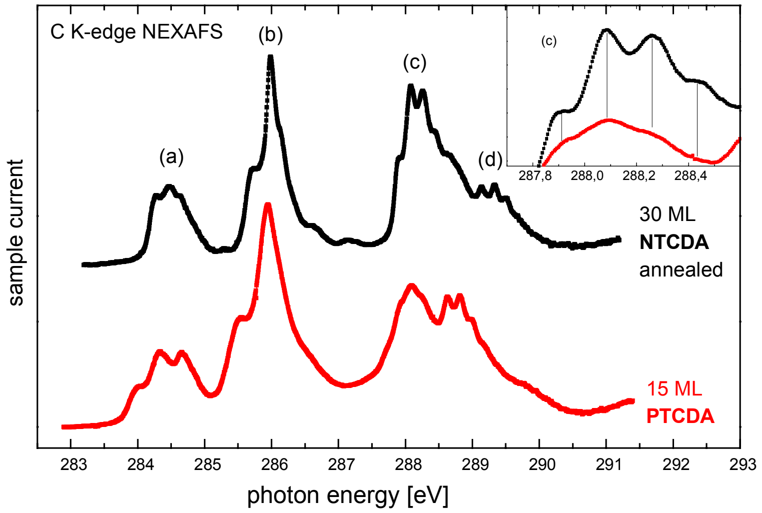

Figure 1:
Comparison of high-resolution C K-NEXAFS data of NTCDA (top) and PTCDA multilayers (bottom). The observed fine structure is due to the coupling of core-electronic transitions to vibronic excitations in the molecules. The inset shows the third resonance (c) on an enlarged scale reflecting the identical vibronic fine structure for molecular orbitals localized on the anhydride group, which is identical for both molecules.

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Photoemission and Photoabsorption Investigation of the Electronic Structure of Ytterbium Doped Strontium Fluoroapatite

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X-ray photoemission and x-ray photoabsorption were used to study the surface versus bulk composition and the electronic structure of ytterbium doped strontium fluoroapatite (Yb:S-FAP). High resolution photoemission measurements on the valence band electronic structure and Sr 3d, P 2p and 2s, Yb 4d and 4p, F 1s and O 1s core lines were used to evaluate the surface and near surface chemistry of this fluoroapatite. Enhancement of the photoemission signal from the partially filled Yb 4f orbitals in the valence band was accomplished by resonant excitation of the 4d–4f transition since there is an overlap between the 4f orbitals and the O and F p states in the valence band. Element specific density of unoccupied electronic states in Yb:S-FAP were probed by x-ray absorption spectroscopy (XAS) at the Yb 4d ($N_{4,5}$-edge), Sr 3d ($M_{4,5}$-edge), P 2p ($L_{2,3}$-edge), F 1s and O 1s (K-edges) absorption edges. These results provide the first measurements of the electronic structure and surface chemistry of this material.

STRUCTURAL AND ELECTRONIC PROPERTIES OF COPPER AND COBALT m-CRYSTALLITES IN A CONDUCTING POLYMER.

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Conducting polymer films may be used as host matrices for metal clusters and aggregates. Promising applications of such metal doped polymers may be envisaged in different areas as catalysis [1], environmental science [2] and magnetism.

In this work the electrochemical growth of copper and cobalt in polypyrrole $(C_4H_3N)_n$ films was followed by in-situ X-ray absorption spectroscopy (XAS) [3] at the LNLS XAS beam line (Cu and Co K edge). Thin polymeric films were grown and the copper insertion was carried out at selected potentials chosen from the electrochemical response of the system. XANES and EXAFS results showed that the initial stages of the copper and the cobalt insertion in polypyrrole took place in an ionic form, like $Cu^{+n}(OSO_3^-)_n$, with posterior reduction to a metallic form (Fig. 1). In addition, absorption measurements at the O and N K edges were performed in the LNLS SGM beam line for the same set of samples. These measurements allowed us to confirm the formation of an ionic form in the beginning of the process and to understand the final stability of the metal clusters inside the polymer matrix. A correlation between structural and chemical environment of the metal clusters will be discussed. (Support from LNLS, FAPESP, CNPq are gratefully acknowledged.)

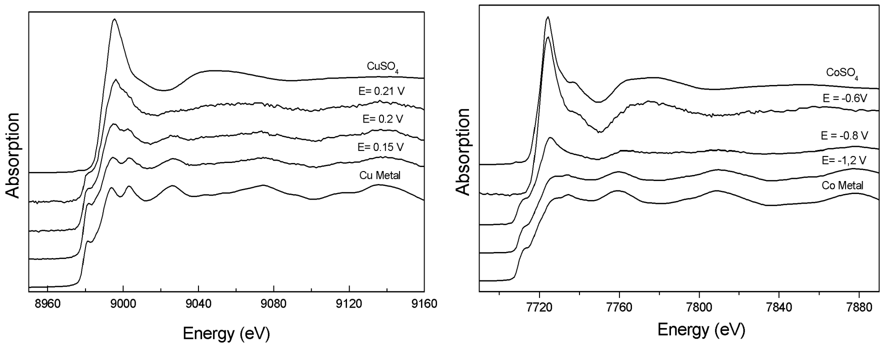

Figure 1: XANES spectra obtained at the Cu and Co K edges .

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SURFACE AND INTERFACE INVESTIGATION IN NANOMETRIC DIELECTRIC FILMS ON Si AND ON SiC

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The search for an alternative to SiO_2 as the gate dielectric material to be used in advanced Si-based MOS devices constitutes a new and very lively research area [1]. Many materials have been suggested, as Al_2O_3, Ta_2O_5, TiO_2, and many double (e.g. zirconium silicate) and triple (e.g. barium strontium titanate - BST) oxides. A major requirement is stability — specially at the interface with Si — upon thermal annealing, which is inherent to processing steps following gate dielectric deposition. We studied atomic transport and chemical stability in Al_2O_3, $ZrSiO_4$, $ZrAl_xO_y$, and Gd_2O_3 films less than 10 nm-thick on crystalline Si substrates, submitted to thermal annealing in vacuum or in O_2. The use of isotopically enriched oxygen ($^{18}O_2$) allowed to distinguish oxygen eventually incorporated during annealing from that originally existing in the films.

Single-crystalline SiC is a wide-bandgap semiconductor in current use to fabricate devices capable of operating at higher temperatures and higher frequencies than Si-based devices. Increased resistance to radiation is also observed. As observed for Si, thermal oxidation of SiC in O_2 leads to the formation of an amorphous SiO_2 film. The electrical characteristics of the interface between SiO2 and SiC are degraded by the formation of an intermediate layer of silicon oxicarbide of variable composition at the initial stages of oxidation. We studied the formation of this oxycarbide layer, starting with a clean SiC surface and performing in-situ layer-by-layer thermal oxidation and analysis.

In this work, we will report on recent investigations of the thermal stability of insulating films for advanced Si-based microelectronic devices and of the initial stages of oxidation of SiC. Surface compositions were determined by low-energy ion scattering. Elemental concentration profiles were accessed at sub-nanometric depth resolution using narrow nuclear resonance profiling. Near-surface, bulk, and near-interface chemical environments of various elements was determined by means of angle-resolved x-ray photoelectron spectroscopy. Atomic transport and compound formation were modeled based on diffusion-reaction equations.

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Burst Reaction of Thin Films Excited by High-Flux Soft-X-Rays

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Recently, high-flux soft X-rays from undulator can be available at the third generation facilities such as SPring-8. However, the changes or reactions of thin films owing to the effects of such strong light are not well known. The evaporation of thin films by irradiation with soft X-rays from bending magnet has been reported[1], but this rate is slow. So, heat or etching gases were used to assist the evaporation, drastic reaction have not been observed. In this report, we have observed a burst reaction when high-flux soft X-rays from the undulator of BL27 beamline [2,3,4] is directly irradiated with thin films such as amorphous-Si.

Amorphous-Si:H (*a*-Si:H) and micro-crystal-Si:H (μc-Si:H) were irradiated with soft X-rays. These samples were prepared by LP-CVD (low-pressure chemical vapor deposition) on the glass substrates at around 200^{o}C. Film thickness varies from 400 nm to 8200 nm. The high-flux soft X-ray irradiation was carried out under the following conditions. The samples were held in vacuum chamber and did not heated. The chamber is directly connected the SR-ring without any windows and filters. Fundamental emitted light energy is 1.1 keV and total photon number is 10^{15} photons/sec (calculated value). Typical irradiation time is 30 minutes, and the storage ring current is 90-100 mA. A mask is placed in front of the sample to characterize the difference between irradiated and unirradiated areas.

In the case of *a*-Si:H film of 8200 nm thickness on silica-glass, vigorous reaction is seen owing to soft X-ray irradiation. The film is crashed and its broken fragments fly off only for a several seconds. After the irradiation, the film was completely removed from substrate. On the other hand, such behavior does not observed in μc-Si:H and 400 nm *a*-Si:H. The evaporation was seen in the irradiated area, the mask pattern is transcribed to the surface on the samples. This unique reaction is strongly may depend on crystallinity and film thickness of the thin films, and never seen in the case of low density soft X-ray irradiation. The other remarkable irradiation changes of the thin films with high-flux soft X-rays will be discussed.

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Electronic Structure of MoS_2 clusters using X-ray Absorption and Emission Spectroscopes

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Molybdenum disulfide (MoS_2) nanoclusters have demonstrated to be effective photocatalysts for the detoxification of chemical waste. In such an application the cluster would absorb light creating electron-hole pairs and thus catalyze specific chemical reactions. For these applications the cluster must have a band gap that is matched to the visible spectrum and the valence and conduction band edges must be compatible with the redox potentials for the reactions involved. To tailor these properties for a specific application we measure the valence and conduction band edges of well-defined MoS2 clusters using x-ray absorption and emission spectroscopes. MoS2 clusters from 1-10nm in diameter were formed using the inverse micelle synthetic process at room temperature in inert oil. The cluster size and distribution could be precisely controlled using a high-pressure liquid chromatography system. By measuring the S 2p absorption were are able to measure the change in the conduction band edge of the MoS2 clusters as a function of particle size. We found that the conduction band edge was blue shifted with decreasing clusters size with shifts up to 1.2 eV measured for clusters 2nm in diameter. These results agree with earlier predictions of the conduction band shifts as a function of particle size. The valence band density of states was determined by measuring the soft x-ray emission from the S 2p core hole. A shift in the valence band edge together with a dramatic change in the density of states was observed with decreasing cluster size. For 2nm clusters a valence band shift of approximately 1.0 eV was measured. This does not agree with effective mass calculations, which predict little or no shift in the valence band edge. We compare these results to recent optical measurements.

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Intramolecular energy-band dispersion in oriented thin film of *n*-$CF_3(CF_2)_{22}CF_3$ observed by angle-resolved UV photoemission and its theoretical simulation

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Poly(tetrafluoroethylene) (PTFE) $(CF_2)_n$ is one of the most fundamental polymers, which is the perfluorinated analogue of polyethylene $(CH_2)_n$ with a simple repeating CF_2 unit. PTFE has been widely used due to its excellent properties, such as chemical stability, good electrical insulation and so on. Many of the interesting chemical and physical properties of PTFE are related to its valence electronic structures, and its elucidation is important from the viewpoints of both basic science and practical applications. For such a one-dimensional polymer, we can also expect the formation of intramolecular energy-bands, and the energy-band structures of PTFE have been studied theoretically.[1] Unfortunately, however, there were no experimental results to be compared with such calculated energy-band structure.

In the present work, we report on angle-resolved UV photoemission studies of oriented thin films of perfluorotetracosane (*n*-$CF_3(CF_2)_{22}CF_3$; PFT),[2] which is one of the oligomer of PTFE, prepared by in-situ vacuum evaporation. The use of oligomers is based on the theoretical and experimental findings that oligomers more than ten repeating units have very similar electronic structures with infinite polymers. The incident photon energy dependence of the normal-emission spectra of the PFT thin film at $22 \leq h\nu \leq 60$ eV is shown in Fig. 1. The emission intensities of these spectra are normalized by the photon flux of the incident photon energy. The main features show continuous and significant changes in both peak positions and intensities. We attribute the peak shifts to the intramolecular energy-band dispersion. We also performed the theoretical simulation of the spectra by using independent-atomic-center (IAC) approximation combined with *ab initio* MO calculations, which have been successfully applied to the analysis of the photoelectron angular distribution for oriented organic films and the energy-band dispersion of solid surface.[3]

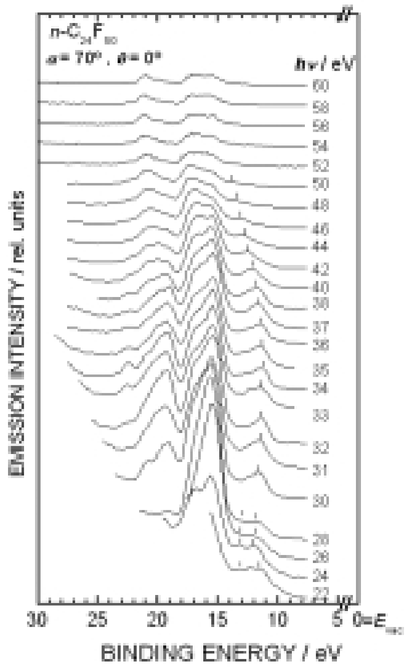

Fig. 1 $h\nu$-depencence of ARUPS spectra for oriented PFT film.

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XAFS AND PHOTOELECTRON DIFFRACTION STUDIES OF ALKANETHIOL SELF-ASSEMBLED MONOLAYER FILMS ON NOBLE METALS

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Self-assembled monolayers (SAMs) such as alkanethiols on noble metal surfaces have been investigated due to their unique properties and technological availability. How SAM films form chemical bonding with noble metal surfaces is of fundamental importance. The structure of the SAM films depend strongly on the kind of substrate metal, the face of the surface and the surface coverage. A number of structural studies have been conducted on SAM films on Au, Ag and Cu crystal surfaces as a function of coverage by use of IRAS, LEED, STM, LEAD, GIXD and C-K NEXAFS. S-K XAFS is a very suitable method for the study of chemical bonding of a thiolate and the metal substrate since it provides information of the local structure around the thiolate S atom.

Recently, we have studied the structures of several alkanethiol SAM films prepared by vacuum vapor deposition on Cu(100) and Ag(100) with C-K NEXAFS, S-K NEXAFS and EXAFS measurements. All the experiments have been carried out at the Photon Factory. In both cases, S atom is located at the fourfold hollow site without reconstruction. These results are compared with previous results on thiolates on Ag(111)[1] and Cu(111)[2]. On the other hand, the structures of alkanethiols on Au(111) cannot be studied by S-K XAFS experiment due to large background from the gold substrate. Instead, we found that S 2p photoelectron diffraction (PED) experiments are very promising to determine the adsorbed structures on gold. Polar and azimuthal dependences of the S 2p peak intensity relative to C 1s were obtained for methyl thiolate on Au(111). S2p energy scanning PED spectra were also obtained for the same system. The analyzed results will be discussed by comparing with other experimental and theoretical studies on the structures of thiolates on Au(111).

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TEST MEASUREMENTS ON THE SOFT-X-RAY EMISSION AT THE Fe *L*-EDGE OF MYOGLOBIN SOLUTION

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Iron-Porphyrin complexes are known as the basis of heme proteins. The electronic structure of the center irons in the complexes may be responsible for the basic biological function of them. Soft-x-ray emission spectroscopy(SXES) is one of the most applicable methods to know the electronic states of center irons because it follows dipole transition and projects Fe3*d* valence states as partial density of states by Fe2*p* core excitation. Moreover, polarization dependence of the soft-x-ray Raman scattering(PSXRS) at resonant core excitation is a noble tool to find non-degenerate states[1,2], so that it is even feasible to detect spin configurations by PSXRS at Fe2*p* resonant excitation. What is more interesting is the bulk sensitivity of SXES, which may allow us to do experiments on liquids as a physiological solution. Myoglobin is appropriate for the test measurements of solution because it has an equivalent heme site.

The experiments were perfonrmed at KEK-PF(Photon Factory, JAPAN) BL2C and BL19B. First, we tried SXES of a powdered Myoglobin that we could easily treat in ultra-high vacuum. SXES intensity of the Myoglobin powder was about 5% of that of Iron-Porphyrin powder even for only about 0.4% of the density ratio of iron ions as shown in the figure. Next, SXES of a frozen solution(8mmol/l) was measured with a liquid cell that holds a liquid in high vacuum below 1x10^{-7}Torr. A 150nm thick polyimide window was used where the transparency throughout the photon-in and the photon-out process was about 20%. Again the SXES intensity of the solution is almost the same as that of the powder even for only about 0.4% of the density ratio of iron ions. This means protein chains composed of light elements are quite transparent to the soft-x-ray above Fe2*p* resonance, which results in the quite effective emission from buried iron ions.

We have also experienced SXES of Myoglobin solutions of various spin and valency states, which will be discussed in the conference.

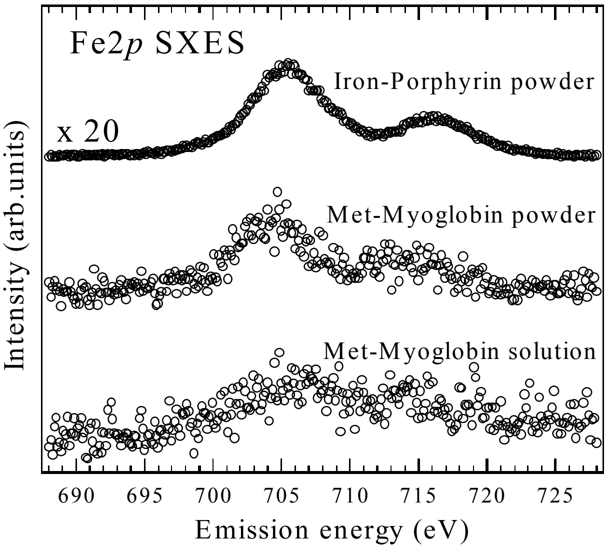

Figure : Fe2*p* SXES of heme samples. The intensity of the solution is calibrated by the window attenuation.

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MORPHOLOGY AND CHEMISTRY OF S-TREATED GaAs(001) SURFACES

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Most as-grown III-V semiconductor surfaces possess a very high surface state density, which leads to Fermi-level pinning near-midgap. Many studies addressed the problem of GaAs surface states since the pioneering work of C.J. Sandroff who passivated the GaAs surface by dipping it in a solution of $(NH_4)_2S$ [1]. Optical and topographic inhomogeneities on passivated surfaces were demostrated by scanning near-field optical microscopy [2], scanning tunneling microscopy [3], and atomic force microscopy [4]. However, no spatially-resolved information is presently available on the chemistry of the S-treated GaAs surface. We addressed this important issue by scanning photoemission microscopy (SPEM) on S-treated GaAs. The measurements were performed at the ESCA microscopy beamline at ELETTRA. The S-treatment consisted of a preliminary removal of the native oxide with a 1 min dip in a 1% $HF:H_2O$ solution, followed by a 30 s water rinse. Then the samples were soaked for a 5 min period in a $(NH_4)_2S$ solution, enriched by adding 8% by volume of S powder, at a temperature of 65-70°C. The treatment was stopped in two different ways. Sample A was removed from the solution and directly blown dry with N_2. Sample B instead was rinsed by flowing DI water in the same beaker for 10 min, thus avoiding drying of the surface before rinsing, and finally blown dry with N_2.

SPEM images of sample A show lateral inhomogeneities at the Ga 3d, As 3d, S 2p, and O 1s core levels. Two distinct regions with higher and lower intensity are observed, and a contrast inversion is observed between the image obtained at the O 1s core level and the images from the Ga 3d, As 3d, and S 2p core levels. On the other hand, SPEM images from sample B show that this sample is laterally homogeneous on the 100-nm scale. The nature of the inhomogeneities on sample A was identified by laterally resolved photoelectron spectroscopy. The spectra from the Ga 3d, As 3d, and S 2p core levels show that the intensity variation observed in the corresponding SPEM images is caused by an inhomogeneous attenuation of the signal from the S/GaAs interface. In comparison, the spectra from sample B indicate the loss of S from the sample surface during the water rinse. An analysis of the spectra from the O 1s core level, taken from samples A and B, shows that this peak is composed of two components. One is identified as corresponding to Ga-O and As-O bonds, while the other is assigned to S-O bonds. The relative contribution of the S-O component differs strongly from sample to sample, and in the case of sample A even from region to region on the sample surface. On sample B, it is much reduced as compared to sample A. Finally, on sample A a lateral variation in the intensity of this component is observed which can be explained by a monolayer-variation of the local O coverage.

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Analysis of phase composition of surface oxides using X-ray photoelectron spectral line shapes

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X-ray photoelectron spectroscopy (XPS) is a powerful method of surface phase composition analysis on the basis of spectral line deconvolution. Nowadays XPS is widely used for the investigation of surface phase composition of high-technology materials and phase transitions on the modified solid surfaces after the physical and chemical treatment.

In this work the influence of low-energy oxygen ion bombardment on the phase composition of surface layers of metals (Mo, W, Nb, Ta) was investigated by XPS. The in situ experiments including surface cleaning by argon ion bombardment, surface oxidation by low-energy (E=1-5 keV) oxygen ion bombardment, analysis of phase composition by XPS were carried out in an UHV chamber ($p=10^{-10}$ mbar) of a Leybold LHS-10 electron spectrometer. The XP-spectra were measured in the constant transmission energy mode of hemispherical energy analyzer (50 eV) with use of Mg K_α-radiation (1253.6 eV) as a primary excitation. The instrumental resolution - 0.9 eV (Au $4f_{7/2}$ spectral line). The accuracy of measurement of binding energies of core level electrons - 0.1 eV. The spectral line deconvolution was fulfilled using a Leybold software product.

Analysis of X-ray photoelectron spectral line shapes of Mo 3d-, W 4f-, Nb 3d- and Ta 4f-core level shown that the oxides are formed in metal surface layers during the low-energy oxygen ion bombardment at room temperature. The oxides with composition MO_2, MO_x, MO_3 (M=Mo, W) and MO, MO_2, M_2O_5 (M=Nb, Ta) were revealed. The oxidation degree of surface layers is a complex function of energy and fluence of oxygen ions and chemical reactivity of metal.

In Rabalais approximation the absolute values of fundamental parameters of low-energy oxygen ion interaction with metal surfaces (reaction and sputtering cross-sections) were calculated. The mechanisms of phase transformations in surface layers of irradiated metals are discussed.

THE EFFECT OF LiF LAYER ON AL/LiF/ALQ$_3$ INTREFACES STUDIED WITH ELECTRON SPECTROSCOPIES

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Organic electroluminescent(EL) devices have been extensively studied for possible application to flat panel display. The device structure is sandwiched organic layers between two metal electrodes, and the study of the organic/organic and metal/organic interfaces are important for understanding and improving the performance of organic EL devices. The enhancement of device efficiency at the insertion of LiF layer between tris(8-hydroxyquinolino) aluminum (Alq$_3$) and Al electrode was reported[1], and, interface energy level alignment was found to be changed by inserting the LiF layer[2]. For clarifying more details of this phenomenon, we have investigated Al/LiF/Alq$_3$ interface using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and metastable atom electron spectroscopy (MAES). Figure1 shows the observed UP spectra of Alq$_3$(0.5nm) film on Al substrate with inserted LiF layer of increasing thickness. When LiF layer is absent, an extra state(X) appears above the HOMO(A) of Alq$_3$, and the increase in LiF thickness leads to the decrease of the peak intensity of X. Thus this peak results from the interaction between Al and Alq$_3$. Figure2 depicts observed energy offset of the interfaces. The vacuum level shift occurs at the interfaces. The electron injection barrier, obtained as the difference of LUMO of Alq$_3$ and Fermi level of Al substrate, is decreased with increasing LiF thickness. We can suppose two possible origin of device efficiency enhancement. Thus, i.e. (1) suppressed of Alq$_3$/Al interaction and (2) reduction of the electron injection barrier.

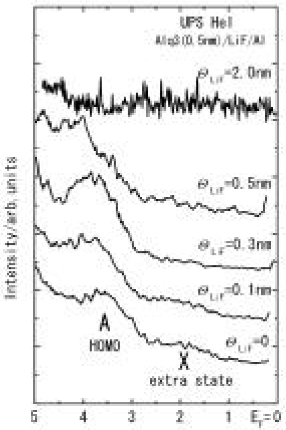

Figure1 The UP spectra of Alq$_3$(0.5nm)/LiF/Al interfaces. LiF layer thickness (q_{LiF}) is shown for each spectrum.

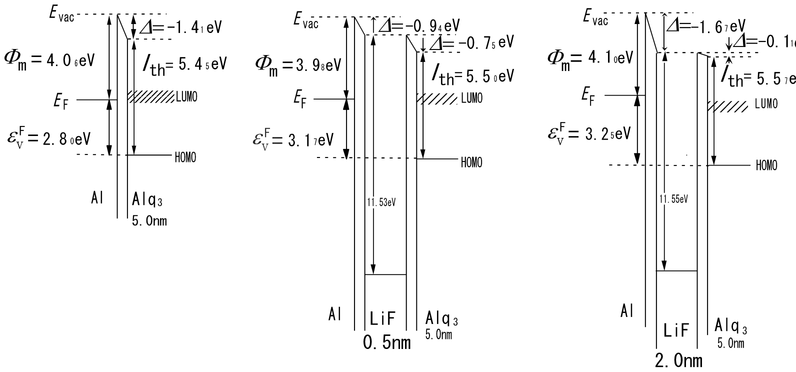

Figure2 The energy diagram of Alq$_3$/Al, Alq$_3$/LiF(0.5nm)/Al, and Alq$_3$/LiF(2.0nm)/Al interfaces. (F_m:work function of metal, E_{vac}: vacuum level, E_F: Fermi level, ε_v^F:difference between E_F and HOMO of organic layer, D:vacuum level shift, I_{th}: ionization potential)

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STRUCTURAL CHANGES IN ANNEALED, HYDROGEN IMPLANTED MONOCRYSTALLINE SILICON

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The grazing incidence small angle X-ray scattering (SAXS) technique was used to investigate monocrystalline silicon samples, prepared from Czochralski grown monocrystalline silicon, implanted with $H2^+$ (beam current density 1mA/cm^2) impinging on the sample at an energy of 31 keV, and annealed isochronally at different temperatures in the range from 100°C to 900°C.

Although the H depth distribution was expected to be smooth initially, nanosized features, like agglomerates of defects, have been detected (minor correlation peak, indicated by arrow, at 0.265nm^{-1} for implanted, but unannealed sample in Figure 1.). After annealing this features are destroyed due to the relaxing of the defect structure, controlled by hydrogen captured in intersticials, as well as in produced vacancies. Above 300 °C a well defined film with highly correlated borders is formed on the edge of the layer rich in defects (presumably due to the migration of vacancies and hydrogen), whose thickness is slowly decreasing from 17 to 12 nm with increasing annealing temperature. This is attributed to vacancies and bubbles agglomeration, and the size decreases due to hydrogen abandoning the vacancies in the region. With increasing annealing temperature, defects as well as hydrogen are migrating towards the surface, as it is indicated by the increase of the surface roughness. We will present a model for the film structure changes obtained by data evaluation using distorted wave Born approximation.

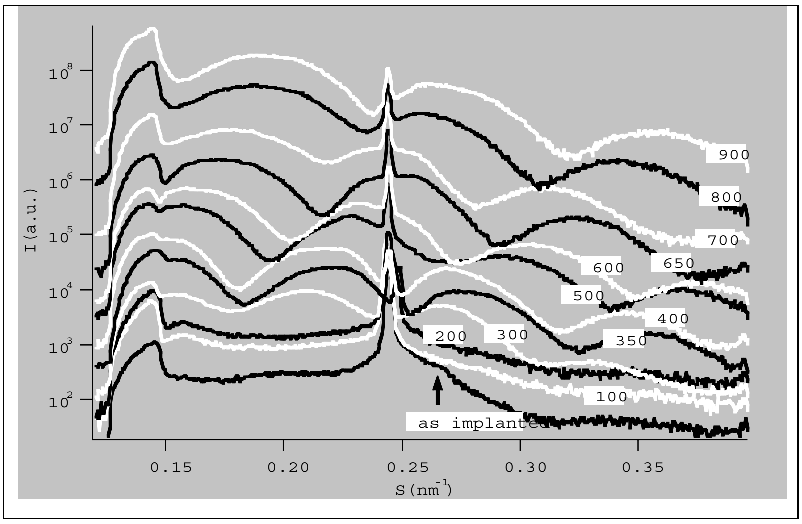

Figure 1: GISAXS intensities for H implanted silicon vs. scattering angle, for diverse annealing temperatures (in centigrades, as indicated)

SiC(100) ORDERED FILMS GROWTH BY C_{60} DECOMPOSITION ON Si(100) SURFACES

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Fullerene (C_{60}) was deposited on Si(100) 2x1 double domain reconstructed substrate. The interface has been treated with annealing procedure in order to induce covalent Si-C bond formation and to obtain carbidization. In this way 3C-SiC(100) can be obtained. The different stages of growth have been checked by in situ low energy electron diffraction (LEED), Auger and Inverse Photoemission techniques. We found that differences in the morphology and electronic properties can be detected depending on the growth procedure. In particular a SiC(100) 2x1 ordered sample have been obtained with a thickness of about 2000 Å. *Ex situ* we verified surface order by means of LEED technique, observing the recovering of the 2x1 double domain reconstruction.

We characterized electronic properties collecting valence band and core level photoemission spectra employing synchrotron radiation source. ARUPS measurements showed evident electronic surface states in valence band similar to those revealed on 3C-SiC(100) (2x1) surfaces grown by different techniques.

LOCAL GEOMETRY AND ELECTRONIC STRUCTURE OF BOROSILICATE GLASSES: X-RAY ABSORPTION FINE STRUCTURE ANALYSIS

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The Si $L_{2,3}$, and B K- edge XANES spectra of two types of borosilicate glasses (“white” and “black”) have been measured at the Canadian Synchrotron Radiation Facility (Aladdin storage ring; University of Wisconsin-Madison). These glasses correspond to two stages of micro-channel plate manufacturing. The TEY (surface sensitive) and FY (bulk sensitive) detection modes were used to study the distribution of Si and B atoms in the glasses. Theoretical analysis of XANES data has been done on the basis of “ab initio” full multiple-scattering theory. An agreement between theory and experiment has been obtained. The distribution of the unoccupied projected silicon *s* and *d* electronic states and boron *p* electronic states has been established. The interactions between these states in the bottom part of the conduction band of borosilicate glasses have been studied.

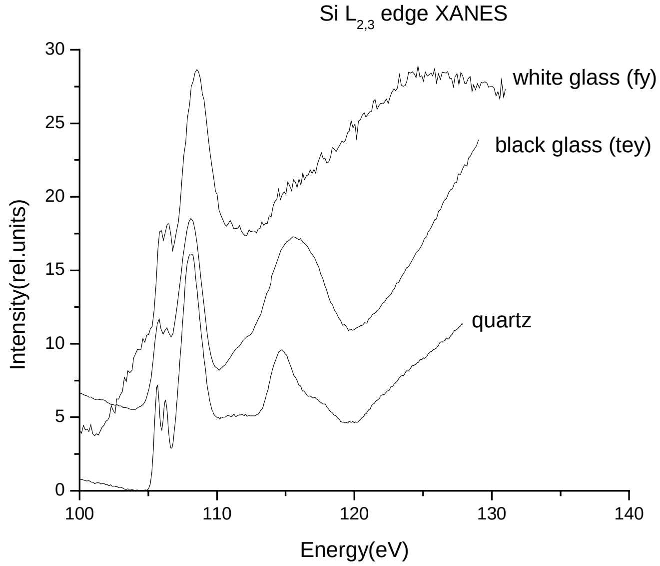

Figure 1: Si L2,3 edge XANES spectra in two types of borosilicate glasses compared with the spectrum of quartz..

SOFT X-RAY PHOTOEMISSION STUDY OF Ni, Pd AND Pt

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We report valence band photoemission spectra of Ni, Pd, and Pt metals measured with soft x-ray synchrotron radiation. Pd is interesting for its nearly ferromagnetic behavior. For example, spin alignment in Pd thin films is realized by a contact with ferromagnetic Ni [1]. In comparison with ferromagnetic Ni, Pd metal has the same crystal structure and comparable number of valence electrons. According to Kanamori's theory [2], the achievement of the ferromagnetism in Ni is related to the shape of the density of states (DOS) in the valence band, namely, the properly wide valence band DOS with a narrow and high DOS peak at the Fermi level (E_F). It is expected that Pd metal also has such a feature of the valence band DOS because of its nearly ferromagnetic behavior.

The measurements were performed at the soft x-ray undulator beamline BL25SU at SPring-8. The grazing incidence monochromator of BL25SU with varied-line-spacing plane gratings covers a photon energy (hν) range from 220 to 2000 eV [3]. The photoemission spectra were taken with a GAMMADATA-SCIENTA SES-200 analyzer. The sample temperatures were set at 100 K. The polycrystalline samples were cleaned by repeated filing under the ultra high vacuum (~ 4×10^{-8} Pa).

Figure 1 shows the valence band photoemission spectra of Ni, Pd and Pt metals taken at hν = 955eV with a total energy resolution of about 270meV. The valence band width becomes wider on going from Ni to Pt. A narrow peak close to E_F is recognized in the Pd spectrum indicating a high DOS at E_F. It is considered that this narrow peak of DOS is responsible for the nearly ferromagnetic nature of Pd metal.

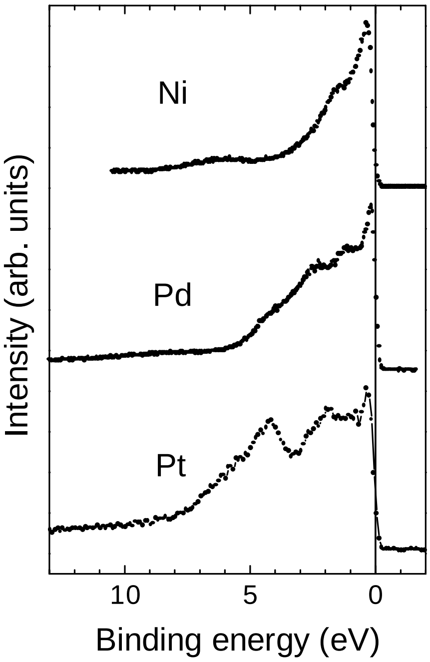

Fig. 1: Valence band photoemission spectra of Ni, Pd and Pt taken at hν = 955eV.

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Effects of Air-Exposure and Cs-Deposition on the Electronic Structure of Multi-Walled Carbon Nanotubes

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The field emission (FE) current from carbon nanotubes has been found to be significantly enhanced by adsorbates [1] and by Cs deposition [2]. We studied the electronic structural change of multi-walled carbon nanotubes (MWNTs) induced by air-exposure and by Cs-deposition using photoemission spectroscopy.

Figure 1 shows the secondary electron threshold spectra of as-received (before an anneal) and annealed aligned MWNT samples. This figure shows the work function of as-received sample which is covered by adsorbates is slightly larger than that of the annealed sample. The valence band measurement revealed that the work function increase was mainly due to a surface dipole moment induced by the adsorbates rather than to a Fermi level shift. Whereas, Cs deposition on the clean sample caused a Fermi level shift and a large enhancement of the density of states at the Fermi level, indicative of an intercalation reaction. Furthermore, in strong contrast to the air-exposure, Cs deposition drastically decreased the work function of the MWNTs. These results reveal that the FE current enhancements caused by adsorbates and Cs deposition are based on essentially different mechanisms.

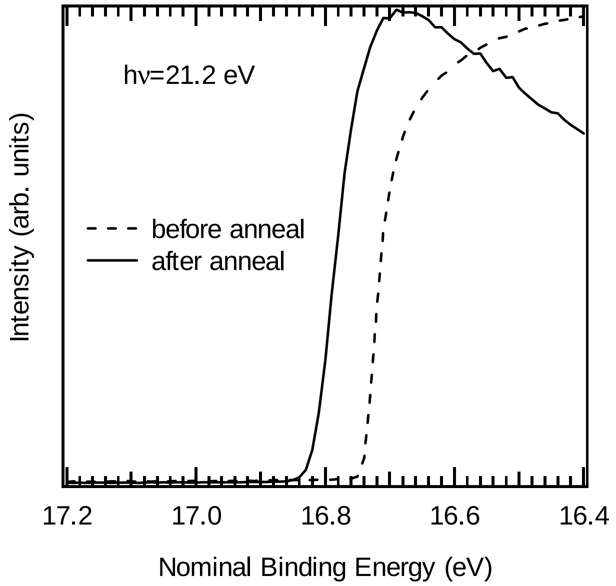

Figure 1: Secondary electron threshold spectra of the as-received and annealed aligned MWNTs.

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SOFT X-RAY ABSORPTION SPECTROSCOPY OF *SINGLE* NANOCRYSTALS

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The development of the electronic structure of nanocrystals and the investigation of size dependent scaling laws is an active research area of academic and technological relevance [1,2]. In general, experiments are performed on ensembles of nanocrystals which, even in the best samples, still exhibit a distribution with respect to particle size and shape, crystallinity and defect structure etc. In consequence, scaling laws derived from such experiments represent an ensemble average with an inherent uncertainty with respect to intrinsic properties of individual nanocrystals. To overcome these limitations, single particle experiments have been developed and performed in recent years [3-5]. For instance, in optical fluorescence spectroscopy of ensembles of semiconductor nanocrystals one observes typically rather broad fluorescence lines (FWHM ~0.1-0.2 eV at 10 K). However, experiments on individual nanocrystals yield not only extremely sharp emission lines (FWHM ~200 µeV at 10 K) but also allow the observation of effects like spectral diffusion and blinking of single nanocrystals which is inherently not possible with ensemble techniques [3].

While the size dependence of the optical excitation gap can be investigated with optical spectroscopy, detailed information about the electronic structure can be obtained by X-ray absorption spectroscopy (XAS) [6]. In addition, insight into the chemical composition, structural properties, and even the magnetic properties of nanostructures can be obtained. Here we report the first experiments to explore the feasibility of spectromicroscopy to record the X-ray absorption spectra of a *single* nanocrystal using photoelectron emission microscopy (PEEM). The experiment was carried out with the PEEM2 instrument of the Advanced Light Source at beamline 7.3.1.1 [7].

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Soft X-ray absorption spectra of lithium phthalocyanine radical

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Lithium phthalocyanine (LiPc) is a stable neutral radical and one of the few intrinsic molecular semiconductors with energy gap of nearly 0.2 eV and conductivity of 2×10^{-3} S/cm at room temperature [1]. These semiconducting properties imply many potential applications for molecular electronic devices such as light emitting diodes, laser diodes, solar cells, sensors, etc. To realize these electronic devices and improve the device properties, it is very important to understand the electronic structure of LiPc in detail. The valence band structure of LiPc was studied using ultraviolet photoelectron spectroscopy, which showed that LiPc had similar electronic structure with that of H_2Pc and ZnPc except for the weak intensity of the highest occupied molecular orbital (HOMO) peak [2]. This weak intensity corresponds to the single-electron occupation of the HOMO, in contrast to the double occupation in other Pcs. In this study, the unoccupied electronic structure of LiPc was studied by near edge X-ray absorption fine structure (NEXAFS) spectroscopy. The carbon (C) and nitrogen (N) K-edge NEXAFS spectra were measured in the total electron yield mode at BL-11A of Photon Factory.

Figure shows the C K-edge NEXAFS spectra at low photon energy region of (a) LiPc and some phthalocyanine compounds ((b) CuPc, (c) ZnPc, and (d) H_2Pc) at an X-ray incidence angle of $\theta \sim 55°$ (magic angle). The spectra except for LiPc have similar features. The slight difference between the spectra of H_2Pc and Cu- and Zn-Pc can be ascribed to the different symmetries of these molecule (H_2Pc : D_{2h}, CuPc and ZnPc : D_{4h}). The spectrum of LiPc is different from these spectra. In particular, a peak around 283.5 eV indicated by an arrow in figure appears only in the spectrum of LiPc. On the other hand, the general appearance of the spectra of these Pcs in N K-edge region is similar in spite of the difference in the central element. Molecular orbital calculations show that the singly occupied HOMO of LiPc mainly consists of the atomic orbitals of carbons rather than those of nitrogens. These results indicate that the peak around 283.5 eV observed in LiPc is attributed to the excitation to the HOMO. Based on these results, the unoccupied electronic structure of LiPc radical will be discussed.

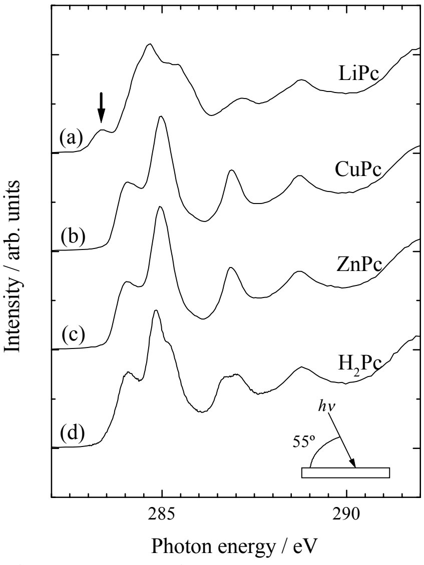

Figure : C K-edge NEXAFS spectra of LiPc, CuPc, ZnPc, and H_2Pc.

This work has been performed under the approval of Photon Factory Advisory Committee (99G180 and 2000G282).

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VUV Photoelectron Dynamics in Pure Cesium Halides and Impurity(Tl and Na) doped CsI; Absolute Photoemission Total Yield, Auger Free Luminescence, and STE Luminescence.

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In last decade, large band gap and shallow innershell substances have been attracted interest in their VUV photoelectron dynamics for the usefulness to photoelectric devices and scintillator[1-3]. Absolute photoemissin total yield (APTY) spectra in cesium halides of CsCl, CsBr, and CsI, as well as in Tl-doped and Na-doped cesium iodide, were studied at several temperatures from 400K to 80K in VUV region (5 〜 30eV). SOR-RING(Tokyo University) BL-1 site was used for the total yield measurements. The measurments of the APTY were explained in detail elsewhere[1]. Luminescence measurements were performed at UV-SOR (Okazaki-IMS) BL-8 site and also at the SOR-RING BL-1 site at room temperature and several low temperatures down to 20K.

APTY spectra are appeared to exceed unity in the photon energy region exciting Cs^+ 5p core electron in all of these halides. This phenomenon was explained in terms of Auger enhancement due to the Auger effect associated with the decay process of the Cs^+ 5p core hole[2,3]. Decrease of APTY at the core excited photon energy region for decreasing temperature was attributed to increase of Auger free luminescence (AFL) in CsCl and CsBr. As the results of detail analysis, a strong complementary relation between APTY and AFL was revealed[1], and the temperature dependence of energy level diagram of CsBr including the valence band and the Cs^+5p core level was proposed [1]. In pure CsI, APTY indicate as large as 1.5 or more at the high temperature as shown in Figure 1 and the APTY due to valence primary coincides very well with the results of DiStefano et al[4] in intensity at the photon energy of 12 eV. Decrease of APTY in these cesium iodides for decreasing temperature can be commonly explained in termes of complementary relation with STE luminescence.

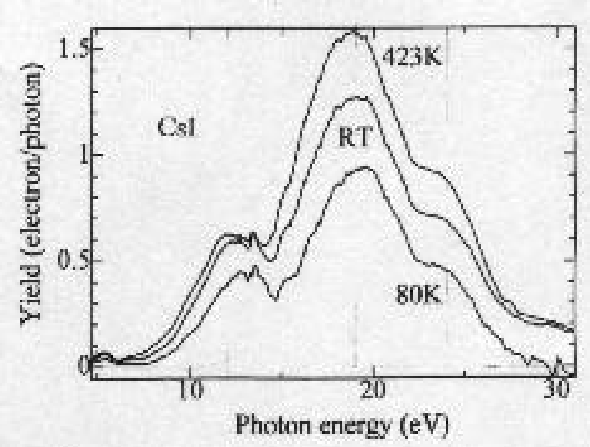

Fig. 1. Absolute photoemission total yield and its temperature dependence in CsI.

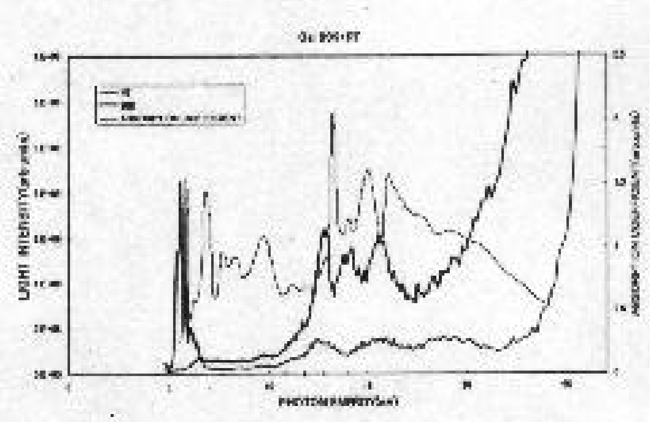

Fig. 2. Excitation spectra of STE luminescence (400nm) at 90K and room temperature in CsI.

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Electronic Structure of Transition Metal Oxochlorides

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Transition metal compounds (TMC) have been extensively investigated by SR spectroscopy (photoemission and absorption) in the solid state due to the fundamental importance of these materials in catalysis, sensors and a range of other applications. On the other hand SR spectroscopy of free molecule TMC's in the gas phase is a barely touched subject. This is certainly due to additional experimental difficulties in dealing with not stable, often not volatile and rather aggressive compounds, which are however routinely manipulated in chemistry laboratories.

Here we present some results of a XAS study on $TiCl_4$, $VOCl_3$ and CrO_2Cl_2.spectra at chlorine, titanium, vanadium and cromium L-edges and oxygen K-edge [1].

Moreover their electronic structure of the first two compounds has been analysed by PES through a complete mapping of all the electronic states accessible with photons in the energy range 20÷1000 eV [2].

The absorption measurements were carried out on the undulator-based Gas Phase Photoemission beamline at Elettra [3], Trieste.

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GISAXS STUDY OF CADMIUM SULFIDE QUANTUM DOTS

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The traditional method of preparing quantum dots in optical semiconductor devices is adding semiconductor components into glass melt. During the solidification process however, one has not sufficient control over the growth proces, which results in non-ideal sample properties (defects, semiconductor surface states, dopant size fluctuations). Most of these drawbacks are overcome in a newly proposed technique of ion implantation into solid substrates.

In order to investigate the structure of films prepared by this new method, the grazing incidence small angle X-ray scattering (GISAXS) technique was applied on the films of CdS nanocrystals synthesized in SiO_2 by implanting separately constituent Cd and S atoms with a dose of $10^{17}/cm^2$ each and subsequently annealed at $700^{O}C$. Due to the high concentration of nanocrystalline CdS, the scattered intensity is not following the distorted wave Born approximation. The inherent Gaussian variation of implanted ions concentration with depth results in a similar profile of nanocrystals sizes. Changing the grazing incidence angle controls the depth of X-ray penetration, and detects this size distribution to be varying from 15 to 35 nm. When the surface roughness contribution is deconvoluted numerically, inplane correlation contribution to scattering is obtained (see Figure 1.). We will show that numerical analysis of this contribution can be a powerful tool to determine the depth variation of the nanocrystals sizes and their inplane size distribution. The results are to be used for further improvements of semiconductor quantum dots preparation.

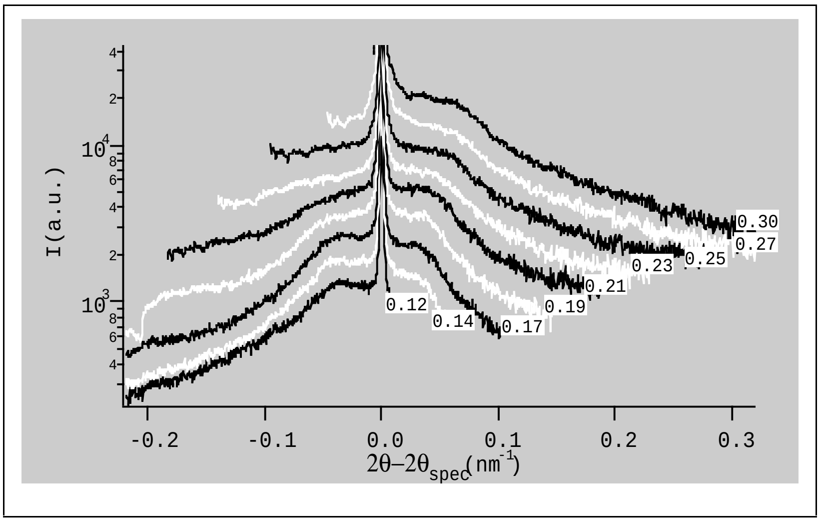

Figure 1: Inplane correlation part of GISAXS from ion (Cd and S) impanted glass vs. offset from specular angle, for diverse grazing incidence angles (in nm^{-1}, as indicated)

VUV Optical Investigations of Carbon-Deuterium Films Produced in Tokamak-10 Plasma.

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The Tokamak-10 instrument for the thermonuclear investigations has the graphite entities working in immediate proximity to the hot plasma. Under the impact of plasma on these entities the carbon is deposited on the cold walls of Tokamak along with elements of plasma, i.e. deuterium. The deuterieum-carbon (D/C) ration in developed carbon films could reach the value of 0.8 [1],[2]. Note that the fullerenes, nanotubes etc are usually produced in the related conditions.

The investigations of the C-D films are technologically stimulated by the thermonuclear synthesis problem. Particularly, the investigation is directed towards the increase of plasma confinement quality, because the process eliminates the deuterium from plasma to the C-D films.

We have studied the C-D films using the optical methods. The luminescence spectra were measured using nitrogen (3.68 eV) and synchrotron (3.5-12 eV) excitation. The possible explanations of the observed features and their connection with deuterium confinement in films are discussed.

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Investigation of scintillators for medical and high energy physics applications using VUV and XUV synchrotron radiation

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A large variety of gamma and X-ray photon detectors is based on scintillators. Scintillation of a crystal is the result of several consecutive processes:

- Absorption
- Inelastic electron-electron scattering and Auger decay processes (hot relaxation stage)
- Emission of phonons (cooling)
- Capture of charge carriers by radiative and non-radiative centres (trapping)
- Photon emission.

Hot relaxation stage results in the creation of secondary electronic excitations of intermediate energies, similar to those created after the absorption of VUV-XUV photons. Thus synchrotron radiation in this energy range provides a unique tool for their direct “imaging” and investigation.

As an example the role of synchrotron radiation in the study of lead tungstate, a new heavy scintillator for high energy physics, is discussed. The results on other scintillators based on rare earth elements are provided as well.

Reflectivity and luminescence excitation of barium fluoro-halides doped with Eu in the fundamental absorption region.

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Barium fluorobromide doped with Eu is a well known phosphor for X-Ray storage screens. Its luminescence properties were extensively studied by several experimental groups, however most of the measurements have been performed either on powder or thin film samples. Here we present the results of the study of single crystals of BaFBr:Eu and BaFCl:Eu grown by Shteber technique in Vinogradov Institute of Geochemistry, Irkutsk. Reflectivity and luminescence excitation and emission spectra were measured using synchrotron radiation of DORIS storage ring (HASYLAB, Hamburg) at the stations SUPERLUMI (excitation energy range 4 – 30 eV) and BW3 (energy range 50 – 600 eV) special attention was paid to the region of core levels as well as to temperature dependence of self-trapped exciton luminescence.

Depth resolved soft X-ray emission spectroscopy of Si-based materials

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It is well recognized by now that the variation of the primary electron beam energy (E_0) is an excellent method for the non-destructive depth-resolved study of the electronic structure and spatial distribution of atoms in the surface region of solids by means of the characteristic soft X-ray emission (SXE). The main goal of the work presented here were:

1) To obtain an estimate for the sensitivity of the SXE for the top surface atomic layer (surface sensitivity) and its dependence on E_0 and the experimental geometry.
2) To apply this method to the investigation of materials with non-uniform depth distribution;
3) To modify the electron scattering and X-ray excitation model to describe non-isotropic solids and to verify it.

As samples Si-based materials have been used. For the study of surface sensitivity we have used Si(100) wafers covered with natural SiO_2 films of 1.5 and 0.6 nm thickness. It was found that the contribution of the characteristic Si $L_{2,3}$ emission from the surface (SiO_2) to the total signal (Si + SiO_2) even from 0.6 nm SiO_2 / c-Si sample is more than 50% for primary beam energies E_0 exceeding the Si 2p ionization threshold up to 150 eV. The experimental data are in a good agreement with the theoretical calculation. Due to the isotropic character of the low energy electron scattering in the surface region a grazing incidence of the primary electrons does not increase surface sensitivity considerably. One can conclude in general that for any SXE spectra a relatively wide E_0 range up to more than hundred eV above threshold may be used for measurements with high surface sensitivity.

As a system with a non-uniform depth distribution Si(100) implanted with Al ions before and after heat treatment has been investigated. The analysis of the Al $L_{2,3}$ band shape clearly demonstrates that only a short heat treatment at 1000K for 100 sec initiates a fast Al impurity redistribution. The metallic-like chemical bonding structure in the ”as-implanted” sample where Al atoms form metallic conglomerates or clusters in a highly damaged Si matrix, changes to a semiconductor-like structure. Here the chemical bonding of the Al-Si type dominates and impurities are mainly in substitutional, interstitial or point defect positions. The dependence of the SXE intensity on E_0 allows to resolve the Al impurity depth profiles before and after annealing in the depth range up to 50 nm. These profiles were reconstructed by means of developed modified theory, they prove that during heat treatment Al moves not only inside the matrix but also form prominent concentration peak at surface.

This work clearly demonstrates that SXE with variable energy electron excitation can be very fruitful for the investigations of surfaces, ultrathin films and materials with a non-uniform depth distribution.

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Polarization properties of synchrotron radiation in the study of anisotropic insulating crystals

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Application of lead tungstate as a scintillator for high energy physics stimulated extensive studies of its optical properties. However, a substantial controversy in the reflectivity and luminescence excitation spectra measured by different groups, especially in the low energy part of the fundamental absorption region, was observed. Our studies revealed that to a large extend these ambiguities can be accounted for by anisotropic properties of lead tungstate, which is a representative of a group of crystals with scheelite structure, characterised by a substantial anisotropy. New developments in crystal growth techniques in VNIISIMS allowed to grow large size, good optical quality crystals of several compounds of this class, namely $CaWO_4$, $BaWO_4$, $BaMoO_4$, $PbMoO_4$ and $PbWO_4$. Notwithstanding similar crystal structure, these compounds have substantially different luminescent properties. Thus, $CaWO_4$ is a well-known X-ray phosphor, while $PbWO_4$, due to its nanosecond luminescence at room temperature, is used as a scintillator. Samples oriented along different crystallographic axes were studied using linearly polarised synchrotron radiation in the range 4 – 30 eV at temperatures 7 to 300 K at the SUPERLUMI station of HASYLAB, DESY. Luminescence emission and excitation spectra as well as reflectivity and luminescence decay kinetics were measured and the results are presented. Orientation of the crystals affected luminescence excitation and reflectivity spectra up to ~ 20 eV, though the most prominent differences were observed, as expected, at the fundamental absorption threshold. Features of the reflectivity and excitation spectra attributed to cation core excitons are analysed. The contribution of electronic states of cations to the formation of the bottom of the conduction band and the top of the valence band for the series of the crystals studied is discussed. Its relation with the dominant mechanisms of the energy transfer to the emission centres and the formation of these centres is demonstrated. These investigations were also extended to other types of anisotropic crystals: berlinite ($AlPO_4$, a highly transparent crystal up to ~ 8 eV, suitable as a material for optical windows, radiation hard) and calcite ($CaCO_3$, a birefringent material used for manufacturing prisms) of improved optical quality. Recent advances in DFT of complex oxides allows to compare experimental results with calculations when available.

OPTICAL PROPERTIES OF HEAT TREATED GLASSY CARBON

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Glassy Carbon is one of the important synthetic materials with a wide range of industrial applications. Like some other products of pyrolysis of organic compounds, glassy carbon is considered to be resistant to three-dimensional ordering of bulk graphite [1].

In this paper the optical properties of turbostratic glassy carbon samples subjected to a heat treatment from 1000 to 3000 °C are reported. From the Raman spectra measurements it was concluded, that the ordering and perfection of graphitic regions in this material increases with increasing of the heat treating temperature [2].

The optical constants and dielectric functions are evaluated by Kramers-Kronig analysis, combining the method of the spectroscopic ellipsometry (1.5 to 5 eV) and theVUV reflectivity (4 to 14 eV). The reflectivity vs angle-of-incidence method [3] is also used for testing.

The results are discussed in analogy with graphite in terms of single-electron transitions and π-electron plasma oscillations. Spectra are compared with those, reported by Williams and Arakawa [4]. A systematic shift of σ-electron transitions to lower energies with increasing heat treating temperature is observed. It indicates only fine changes of ordered regions, but not a bulk graphitization. These results are supported by the density and microhardness measurements.

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X-Ray Photoelectron Spectroscopy and Ultra Soft X-Ray Spectroscopy of the Multilayer X-Ray Mirrors

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The multilayer Si-Mo and Mo-Si with different layer thickness obtained by magnetron sputtering were investigated by x-ray photoelectron spectroscopy (XPS) and ultra soft x-ray spectroscopy (USXS). The chemical composition,in-depth profiling,and stoichiometry of the multilayer structure were determined by using of these methods. Identification of chemical compounds were carried out by using of photoelectron lines Si2s,Si2p,Mo3d$_{5/2}$,O1s,N1s and ratio of atomic concentrations (XPS method). Emission band SiL$_{2,3}$,which reflects the distribution of valence 3s-electrons in silicon,was obtained by USXS method. Using this spectral data,the formation of chemical compounds of Si with different elements (C,O,N,Mo) were studied. The presence and concentration of Mo were determined by measurement of MoM$_{\xi}$-line. The data of USXS analysis were treated by programme of phase analysis using x-ray emission bands. The samples produced without preliminary cleaning of Ar in magnetron installation showed the presence of silicon oxynitride through all the analysed depth.There were no molybdenum silicide (MoSi$_2$) and amorphous silicon (a-Si). Preliminary cleaning of Ar leads to the a-Si layers pure enough, with MoSi$_2$ at the Mo interfaces.

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Intermetallic Alloys surface studied by spectromicroscopy

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We focussed our attention on the surface chemical and electronic features of a metal hydride alloy, Zr0.33V0.25Ni0.42. The use of these alloys as active materials in rechargeable battery electrodes depends on the properties of the surface (both elemental composition and spatial distribution of elements). Freshly produced metal hydride electrodes consist of alloy grains with a high surface oxidation. The results obtained at the Spectromicroscopy beamline, show a non-uniform oxide distribution on the surface resulting in three different surface composition separated by clear borders. Moreover, the oxidation process seems to be related to the segregation of Ni. Removing the few surface layers by Ar sputtering, we studied the pristine material in the same surface region. The spectroscopic features changed remarkably revealing the 'substrate' elemental distribution. Finally, comparing the spectroscopic maps of the same region we can point out an interesting correlation between substrate and surface oxidation and segregation processes.

Time-resolved luminescence spectroscopy of some Hf compounds in the VUV range

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The search for new inorganic scintillators often concentrates on dense, high atomic number materials. Their obvious advantage is a short attenuation length, hence smaller volumes of the crystals are required and the price is reduced; it can affect also such characteristics of scintillator-based detectors as resolution (in positron emission tomography, for example). Hf compounds are quite attractive in this respect, however none of them is acknowledged as a scintillator. Here we present the results of the study of optical and luminescence properties of some Hf-compounds: single crystals of solid solutions HfO_2-Yb_2O_3 with different ratios of the components and fluoro-hafnate glasses of the system HfF_4-BaF_2-RF_3-AlF_3-NaF-InF_3, where R=La, Ce. Attractive feature of the former material is a high concentration of Yb (up to 40 %), which makes it suitable for the neutrino detection based on recently discovered reaction [1] when the capture of ν_e is accompanied by a prompt emission of an electron followed by a delayed by 50 ns emission of a γ-quantum or of another electron. At present there are no industrial scintillators available with large Yb concentration, however research is underway. In [2] ytterbium containing aluminium garnets were shown to posses a set of attractive properties. Solid solutions of hafnium and ytterbium oxides for such application were studied the first time and encouraging results are presented. Fast (characterised by 20-30 nanoseconds decay time) emission peaking at ~ 290 nm was observed. It was investigated in a wide region of excitation from 4 to 600 eV and in the temperature range 6 to 300 K at the SUPERLUMI and BW3 stations of HASYLAB, DESY, Germany. The origin of this luminescence, the possibilities to increase its yield and to eliminate slow luminescence component are discussed.

Glasses are a cheaper alternative of single crystal scintillators. However, low yield and insufficient radiation hardness prevent from their wide applications. Here the results of the study of the effect of synthesis conditions on the luminescence properties and radiation hardness of cerium-containing fluoro-hafnate glasses are presented.

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X-RAY EMISSION SPECTROSCOPY OF A LIQUID-SOLID INTERFACE: WATER AND THE CU(IN,GA)(S,SE)$_2$ SURFACE

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We present a spectroscopic investigation of the interface between liquid water and Cu(In,Ga)(S,Se)$_2$ (CIGSSe) thin film solar cell absorbers using soft X-ray emission spectroscopy (XES). The photon-in-photon-out nature of XES, combined with the high photon flux of third-generation synchrotron sources, allows to investigate the electronic and chemical structure of buried interfaces and "under-water" surfaces with atomic and chemical sensitivity as well as high spectral resolution. In the present approach, we have used a thin (1 μm) polyimide vacuum window and a custom-designed stainless steel frame to create a 1.3 μm-thick water layer under ambient conditions. The complete sample assembly is transferred into a UHV chamber, and experiments are performed in a 45°-in-45°-out geometry with a conventional XES spectrometer in the SXF endstation at ALS beamline 8.0.

CIGSSe-based solar cells represent one of the most promising classes of materials for thin film solar cells, with record efficiencies of 18.8 % on a laboratory scale [1] and around 15 % for modules [2]. There are two areas of interest for which investigations of liquid/CIGSSe interfaces are of particular importance. First, a commercial success will heavily rely on a detailed understanding of the influence of humidity on the solar cell performance. Hence insight into the chemical reactions to be expected during the life of a solar cell is very important. Secondly, a more detailed understanding of the interfaces involved in CIGSSe solar cells is widely regarded as a prerequisite for further optimization. Currently, the common preparation procedure is to coat the CIGSSe film with a thin CdS buffer layer in a chemical bath deposition process. XES and FY-XAS promise to be uniquely suited methods to study such an interface formation in-situ, provided that the general problems of investigating a liquid-solid interface can be solved.

In our presentation we will demonstrate that such experiments can be readily performed, and that chemical reactions at the liquid/solid interface can even be locally stimulated by the exciting X-ray beam as well as monitored in XES spectra. In particular, we will show that the CIGSSe "surface" is oxidized by H_2O via a sulfate formation. At the same time, sodium impurities – which are generally beneficial for the solar cell performance - are attracted to the CIGSSe surface, allowing insight into the complicated mechanism of oxygen-sodium correlation in these materials. The results will be discussed in view of the applicability to study the electronic structure of liquid/solid interfaces and liquid solutions in general.

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EMPLOYMENT OF XPS METHOD FOR STUDYING THE CARBON CLUSTER SYSTEMS OBTAINED BY THE METHOD OF LOW-ENERGY SYNTHESIS

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The method of X-ray photoelectron spectroscopy (XPS) is well applied for study of systems in amorphous and liquid states, alloys, powders. It's undestructive method and has a good resolution of 0,1eV. The investigations were carried out on X-ray photoelectron magnetic spectrometer with AlKα-radiation. The studying systems are nonconducting samples. It is known that the positive electric charge, accumulated on the sample during the process of radiation owing to electrons emission, can shift the atomic levels by some electron-volts. To avoid the influence of these effects on XPS data obtaining the aluminum grid was applicated. The absence of the charging was controlled by C1s, O1s lines. The spectra shift was not observed.

In this paper the carbon cluster systems containing different transition metals of the third period (Mn, Co, Ni), nano- and mezoscopy sizes were investigated. These cluster systems were obtained by the method of low-energy synthesis of aromatic hydrocarbons in active media. Anthracene was mixed with the powders of metal chlorides (Mn, Co, Ni) in a molar ratio (anthracene : metal chloride). The dependence of graphite-like bonds forming from the ratio of initial substances (the anthracene and metal chlorides) was investigated.

Due to the obtained results it's discovered that:

1. The contents increase of metal chloride (transitional metal of third period) to definite composition in each type of the sample in mixture leads to quantity increase of graphite-like bonds.
2. Depending on the degree of d-electron shell filling of transitional metals saturation occurs at different metal chlorides contents. The less d-shell of metal filling, the more metal chlorides is necessary in the mixture for nanostructures forming.

The obtained results are confirmed by data of electron microscopy.

Cu3Au(001) surface relaxation probed by Surface Core Level Shift X-Ray Photoelectron Diffraction

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The Cu3Au compound has attracted much interest for its order-disorder phase transition at 665 K, moreover its (001) surface is being used as a template for the growth of thin Fe films with strained fcc and bcc structure, i.e. different magnetic properties from the Fe bulk ones. However only a few theoretical[1] and experimental[2] studies have been devoted to the determination of the clean Cu3Au(001) surface structure, with only a rough agreement on a buckling of the topmost Au (up) and Cu (down) atoms. High resolution photoemission spectra of the Au 4f core level allow to resolve the surface component from the bulk one. The surface core level shift measured at the ALOISA beamline at ELETTRA (540 ± 10 meV) is in good agreement with the theoretical calculations[3] (630 meV) and refines previous experimental determinations[4]. Polar scans along the main symmetry axis have been also taken for both the bulk and surface component to investigate the structural relaxation of the outermost layer.

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