

A probe of intrinsic valence band electronic structure: Hard x-ray photoemission

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Hard x-ray valence band photoemission spectroscopy (PES) is realized using high-energy and high-brilliance synchrotron radiation. High-energy (~ 6 keV) excitation results in larger probing depths of photoelectrons compared to conventional PES, and enables a study of intrinsic electronic property of materials in actual device structures much less influenced by surface condition. With this technique, requirements for surface preparation are greatly reduced, if not eliminated. It is a nondestructive tool to determine electronic structure from surface to genuine bulk as shown by a study on $\text{SiO}_2/\text{Si}(100)$. Electronic structure modification related to the ferromagnetism in the diluted magnetic semiconductor $\text{Ga}_{0.96}\text{Mn}_{0.04}\text{N}$ is also observed. © 2004 American Institute of Physics. [DOI: 10.1063/1.1756209]

Photoemission spectroscopy (PES) has been used extensively to experimentally determine valence band (VB) electronic structure.¹ However, conventional VB-PES is surface sensitive because of short inelastic-mean-free-paths (IMFPs)² due to low kinetic energy (KE). In order to attain larger probing depths than that in vacuum ultraviolet (VUV) spectroscopy, soft x-ray VB-PES using synchrotron radiation (SR) has recently become attractive.³ However, it is obvious that soft x-ray PES is still surface sensitive, because the IMFPs of a valence electron are only 1.3 and 2 nm for Au and Si at a KE of 1 keV, respectively.² It should be noted that if surface reconstruction occurs, which is often the case for semiconductors, the “depth of the surface” extends down to around 1 nm.

In contrast to the above-mentioned surface sensitive PES techniques, the IMFP values of a valence electron for Au and Si increase to 5.5 and 9.2 nm, respectively, at 6 keV², which lies in the range of hard x rays. The larger probing depth results in small, if not negligible contributions from the surface, e.g., for Au and Si, and a reconstructed surface of 1 nm thickness, the surface contributions to intensity would be $\sim 18\%$ and $\sim 10\%$. The first feasibility test of hard x-ray PES was done by Lindau *et al.*⁴ in 1974 using a first generation SR source, however, the feeble signal intensity even of the Au 4*f* core level excluded the possibility of studies of VBs. What has prevented hard x-ray VB-PES is the rapid decrease in subshell photo-ionization cross section (σ). The σ values

for Au 5*d* (1×10^{-5} Mb) and Si 3*p* (3×10^{-5} Mb) at 6 keV are only 1%–2% of those at 1 keV.⁵ Here, we report hard x-ray VB-PES with high throughput and resolution, realized for using third-generation high-energy SR at SPring-8. Unprecedentedly high photon flux and flux density from an undulator^{6,7} compensate for the decrease in cross section and make hard x-ray VB-PES possible. VB modification in a diluted magnetic semiconductor $\text{Ga}_{0.96}\text{Mn}_{0.04}\text{N}$, a material whose ideal clean surface cannot be prepared, is revealed.

Experiments were performed at an undulator beam line, BL29XU,^{6–8} of SPring-8. A schematic of the experimental setup including optics is shown in Fig. 1. The vacuum of the analyzer chamber was 10^{-4} – 10^{-5} Pa during measurements. No surface treatment was carried out and all the samples were investigated as they were inserted. A Gammatdata Scienta SES2002 electron analyzer was modified to measure

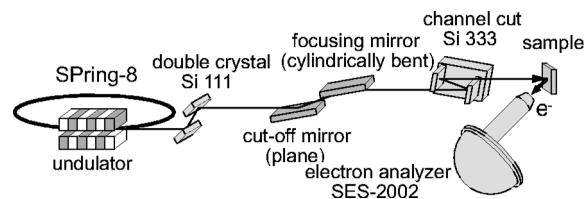


FIG. 1. Schematic of experimental setup including optics. X rays monochromatized at 5.95 keV with a Si 111 double-crystal monochromator were vertically focused with a cylindrically bent mirror onto samples mounted in an analyzer chamber. A channel-cut monochromator with Si 333 reflection bandwidth down to 70 meV. At the sample position, photon flux in a focal spot of 0.12 mm (vertical) \times 0.7 mm (horizontal) was measured to be 2×10^{11} counts/s.

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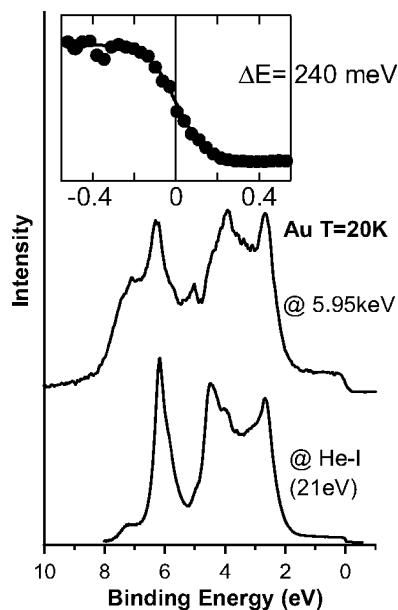


FIG. 2. VB-PES spectra (upper curve and inset) of a Au plate measured at 5.95 keV with the pass energy (E_p) of the analyzer being 200 eV, at a photoelectron take-off angle (measured from sample surface) of $\theta=70^\circ$. The sample temperature was 20 K. The spectrum (lower curve) of a Au film measured in UHV at 21 eV (He I) is also shown as a reference.

high kinetic energy photoelectrons up to 6 keV. Analyzer performance was tested by measuring VB spectra of an Au plate at 5.95 keV. Figure 2 shows the observed spectrum (upper curve) with an accumulation time of 50 min at an 80 mA ring current. The VUV spectrum (lower curve) of Au films deposited in ultrahigh vacuum (UHV) and measured with 21 eV (He I) photons, with an instrumental resolution of 30 meV, is also shown as a reference. In spite of the fact that no surface cleaning was carried out before and after introducing the Au plate into the analyzer chamber for hard x-ray PES, no trace of surface contamination from C or O was observed. The instrumental energy resolution including bandwidth of the incident photons at 5.95 keV is determined to be 240 meV from the Fermi edge profile (the inset in Fig. 2). In comparison with the high resolution VUV spectrum,⁹ all the features including fine structures spread over the VB are observed in the hard x-ray spectrum, although with different relative intensities. Hard x-ray PES will measure densities of states (DOSs) and in comparison, ultraviolet photoemission spectroscopy (UPS) measures k -conserving direct transitions.

Next, to confirm the capability of the present method to probe bulk states of reactive surfaces, the VB spectrum of a Si(100) surface with a thin-SiO₂ layer (0.58 nm) was measured. Si is a basic material in semiconductor technologies and is the most popular and important substrate in surface science and nanotechnologies. It is well known that this surface is easily oxidized even in UHV. Figure 3 shows the VB spectrum obtained at 5.95 keV with accumulation period of 30 min at room temperature. The VB spectrum measured at 0.85 keV using SR is also shown as a reference. Two peaks at around 11 and 14 eV in the spectrum at 0.85 keV are due to the surface thin layer of SiO₂. These peaks vanish in the hard x-ray spectrum indicating negligible contribution of surface oxide layer of 0.58 nm thickness. The “surface insensitivity” of this method is reasonable because IMFP values at 6

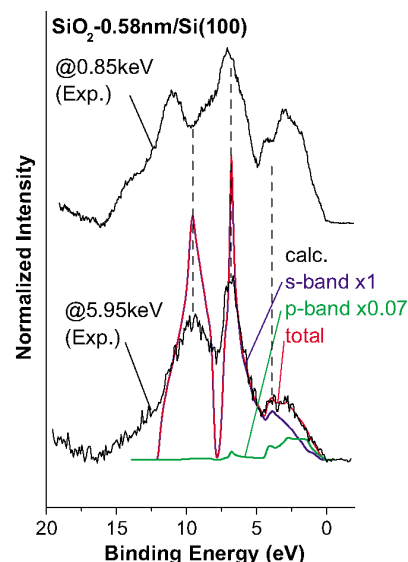


FIG. 3. (Color) VB-PES spectra of thin-SiO₂ layer (0.58 nm) on Si(100) measured at 5.95 (lower panel) and 0.85 keV (upper panel). The spectra are aligned at the valence band maxima set to the binding energy of 0 eV. E_p and θ are the same as those for Au spectrum at 5.95 keV in Fig. 2. The red curve shows weighted sum of the s -like (blue), and p -like (green) partial DOS obtained from first principles calculations.

keV are very high for SiO₂ (14 nm) and Si (9 nm).² From this result, we can expect to obtain “surface insensitive” spectra of many materials without resorting to surface treatment procedures. The Si total and partial DOSs obtained from first principles calculation are also shown in Fig. 3. The total curve (red line) obtained by summing the weighted s -like (blue: multiplied by 1) and the p -like (green: multiplied by 0.07) partial DOS reproduces nicely the experimental spectra at 5.95 keV especially in the range between 0 and 5 eV. Note that the s -partial DOS is dominantly observed in the hard x-ray spectra. The ratio $\sigma(p\text{-like})/\sigma(s\text{-like})$ is obtained as 0.07, and is comparable to the ratio $\sigma(3p)/\sigma(3s)$ of 0.05 known from atomic calculations.⁵

The “surface insensitivity” of hard x-ray VB-PES confirmed above enables us to investigate the intrinsic bulk state of a diluted magnetic semiconductor Ga_{1-x}Mn_xN. This class of materials is presently being intensively studied to develop spin electronic devices.¹⁰ An understanding of the VB modification induced by Mn doping is needed to understand the origin of ferromagnetism. However, this kind of material is grown as epitaxial thin films by molecular beam epitaxy (MBE), and is beyond the reach of “surface sensitive” VB-PES because of the lack of surface cleaning and preparation procedure. The samples were N₂ plasma-assisted MBE-grown Ga_{0.96}Mn_{0.04}N and GaN on a c -Al₂O₃ substrate. GaN is a reference and a key material for blue-violet light emitting diodes and lasers. VB and Ga 2 $p_{3/2}$ core-level spectra were measured at 5.95 keV after structural and magnetic characterization.¹¹ Figure 4(a) shows the VB spectra of GaN (black) and Ga_{0.96}Mn_{0.04}N (red). The VB spectra are very similar but weak broadening is induced by Mn doping. Judging from the σ of Ga and N derived states at 6 keV,⁵ the bands ranging between 0 and 8 eV, the peak at around 14 eV and the peak at 17 eV are attributed to Ga 4 s and 4 p , N 2 s , and Ga 3 d bands, respectively. Strong hybridization of Ga 3 d and N 2 s bands obscures spin-orbit splitting of Ga 3 d

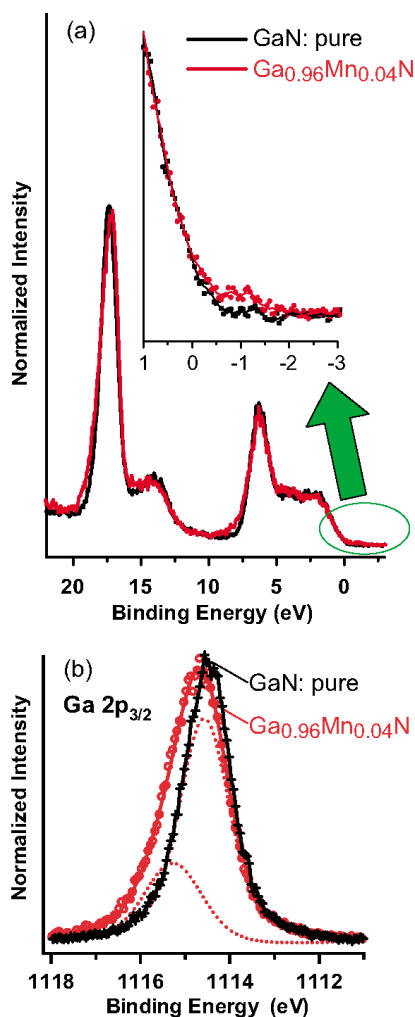


FIG. 4. (Color) (a) VB-PES spectra of MBE grown GaN (black) and Ga_{0.96}Mn_{0.04}N (red) measured at 5.95 keV. The spectra are aligned at the valence band maxima of GaN derive features set to the binding energy of 0 eV. (b) Ga 2p_{3/2} core spectra of GaN (black) and Ga_{0.96}Mn_{0.04}N (red) measured at 5.95 keV. Curve fit results with two components (dotted curves) are presented by solid curve in the Ga_{0.96}Mn_{0.04}N spectrum.

band in both samples. The remarkable difference in these spectra is the appearance of a new band in Ga_{0.96}Mn_{0.04}N above the VB maximum of GaN. This is clearly seen in the expanded spectra [the inset in Fig. 4(a)]. Atomic σ values of Mn 3d (6×10^{-6} Mb) and N 2p (2×10^{-6} Mb) are much smaller than that of Ga 4s (6×10^{-5} Mb) and the composition of Ga_{0.96}Mn_{0.04}N corresponds to a net concentration of Mn being only 2%. Therefore, the new band in Ga_{0.96}Mn_{0.04}N is unambiguously attributable to the Ga 4s-derived state. This result is very significant to understand the origin of the ferromagnetism. The Mn atom, which is substitutionally positioned at the Ga site, affects charge densities of the first neighbor N and even the second neighbor Ga atoms. The appearance of Ga 4s-derived state is evidence for the Mn 3d orbital being hybridized with the Ga 4s

orbital via the N 2p orbital. The interaction between the Ga and Mn atoms is confirmed by the Ga 2p_{3/2} core-level spectrum shown in Fig. 4(b). Compared to the GaN spectrum (black curve), the Ga_{0.96}Mn_{0.04}N spectrum (red curve) shows asymmetric tailing toward higher binding energy side, and is separated into a dominant component and a chemically shifted component as shown by red dotted curves. The binding energies of dominant components coincide with those of GaN. Furthermore, first principles local density approximation calculations clearly reproduce Ga 4s state hybridized with Mn 3d at the VB maximum.¹¹ It is emphasized that hard x-ray VB-PES has high enough sensitivity to detect small changes in VB structures induced by low density doping.

Hard x-ray VB-PES with high throughput and resolution is realized using very brilliant SR at SPring-8. The “surface insensitivity” at such high energies has enabled us to probe intrinsic bulk states without surface conditioning. New functional materials such as MBE-grown thin layers and various organic functional films, whose ideal surface cannot be prepared, are accessible even after structural, electric, and magnetic characterizations. In a previous study, we have reported additional capabilities of hard x-ray core level spectra by showing nondistractive chemical analysis at more than 30 nm depth for a high-dielectric material HfO₂/SiO₂/Si(100) is possible.¹² The combination of hard x-ray VB and core-level spectra can thus provide information on electronic properties and depth distributions of interest of various materials in the field of basic science and technologies.

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²The electron inelastic-mean-free-paths were estimated using NIST Standard Reference Database 71, “NIST Electron Inelastic-Mean-Free-Path Database: Ver. 1.1.” It is distributed via the web site <http://www.nist.gov/srd/nist71.htm>, and references therein.

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