Investigation of group IVA elements combined with HAXPES and first-principles calculations

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Abstract. The core level and valence band spectra of group IVA elements were investigated with hard x-ray photoemission spectroscopy (HAXPES) photon energy of 7.939 keV by bulk sensitive manner. The survey and valance band spectra were presented, relative peaks intensity are discussed by thinking about inelastic mean free path (IMFP) and photoionization cross section of photoelectrons (PICS). In order to understand bulk band structures, valence bands are compared with the calculated ones by considering PICS, IMFP and total energy resolution. The calculated results by GGA, HSE06 and GW0 methods are simply discussed by comparing with experiment spectra.

1. Introduction
The group IVA elements of the periodic table (C, Si, Ge, Sn and Pb) were shown great interest in past years not only due to the important applications on semiconductor industries, but also their crystal structure changes against pressures and atomic numbers. Such as in group IVA above Sn, the elements C, Si, and Ge tend to form a diamond structure with strong covalent bonds, while below Sn the stable phase for Pb is metallic and fcc. It turns out that Sn is border line between covalent and metallic bonding, below 286 K, Sn crystallizes into a grey material with a diamond cubic structure and with a zero band gap and a metallic and tetragonal crystal structure (β-Sn) above this temperature. Even though, there are so many works have been done about the investigation of electronic states by means of photoemission spectroscopy (PES). But due to the much surface sensitive of UPS and XPS, the electronic states for true bulk information are still untouched so far. The newly developed high-energy, high-resolution HAXPES at third generation synchrotron light sources, improves greatly the photoelectron IMFP (~3 nm for lab XPS at hv ~ 1486 eV, and 10 ~ 20 nm for HAXPES at hv ~ 7.939 keV) [1]. It indicates that HAXPES can be used to detect the bulk information, interface or buried phases, even for the samples without surface treatment [2], which usually has to be done for XPS or UPS methods.

In this work, by combination of HAXPES and first-principles calculations, the bulk electronic states of group IVA elements (except C) were investigated to deepen our understanding of real bulk information for these elements and their compounds.
2. Experimental and method of calculation

Hard x-ray photoemission measurements were carried out at the undulator beamline BL46XU of SPring-8. The excitation energy used for HAXPES was monochromatized with Si (111) double crystal and Si (444) channel-cut monochromators, which provides an x-ray energy resolution of 40 meV at around 7939 eV, a focal spot size of 0.02 mm (vertical) × 0.2 mm (horizontal), and a photon flux of 2×10^{11} photons/s. A VG Scienta R4000 electron analyser for high electron kinetic energies of up to 10 keV was used. The electrons emitted at direction of 80 degree respect to the sample surface were detected with an acceptance angle of ±8°. The curved slit with the width of 0.5 mm is used and pass energy is fixed to 200 eV for sufficient counting rates, which result in a total energy resolution of 230 meV at room temperature evaluated by Au Fermi edge. The experiment was carried out at room temperature with the vacuum better than ~5×10^{-6} Pa in the analyser chamber. The single crystal samples for Si and Ge, as well as high purity polycrystalline samples for Sn and Pb are used. Si samples (111 and 100 plane, n and p type doping) were measured without surface cleaning. Ge, Sn and Pb samples were cleaved or scraped to get clean surface before measurements.

The calculations are done using the projector-augmented wave method as implemented in the Vienna Ab Initio Simulation Package (VASP) [3, 4] with the Perdew, Bourke and Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional [5]. For the hybrid functional calculations, the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional is used [6]. For the GW0 calculations [7], the initial wave functions and eigenvalues in G were determined using the HSE06 functional. Enough bands have to be included, and for the update of G and W, four steps are necessary to find band gap energies converged up to 10^{-3} eV. The valence configurations are treated as s^2p^2 for Si, Ge, Sn, and Pb. The cut-off energy for plane-wave basis functions is 400 eV. The experimental structural parameters are taken for the elemental materials. For all the calculations, energy convergence and k-point grids are carefully checked.

For our analyser set-up, the photoelectron intensity can be described as (after refs. [8, 9]):

\[ I(E) = F \frac{\sigma_i}{4\pi} (1 + \beta_i) \DeltaQA_D T f \rho \lambda_s \sin \theta \]

Where, \( F \) is the average flux of x-ray on the sample, \( \Delta Q \) is the acceptance solid angle of the analyzer, \( A_0 \) is the area of the sample irradiated by x-rays that is viewed by the analyzer for photoemission normal to the surface, \( D \) is the efficiency of the detector, \( T \) is the transmission function of analyzer, \( f \) is the fraction of photoemitted electrons that appears in the main or no loss peak, \( \rho \) is the total atomic density of the sample, \( \lambda_s \) is the IMFP for the photoelectrons in the sample with certain kinetic energy, \( \sigma_i \) is the photoionization cross section [10], \( \beta_i \) is the dipole angular distribution [10]; \( i \) is the index of subshell, \( \theta \) is the mean emission direction of photoelectron with respect to the sample surface. Eq. (1), will be used for both the quantitative analysis of core levels and the comparison of theoretically calculated results and experimental ones.

3. Results and discussion

The survey spectra of Si, Ge, Sn, and Pb samples were presented in figure 1. Strong plasmon peaks can be found in Si, Ge, Sn samples, and relative weak one in Pb sample. The inset of figure 1 shows the comparison of the standard spectra of lab XPS (by Al Kα monochromatic x-ray) and that of HAXPES for Sn metal sample. The relative peak intensity is much different for lab XPS and HAXPES due to the change of PICS against excitation photon energy [10] as well as variation of IMFP with kinetic energy of photelectrons [1], since the photoelectron intensity is strongly dependent with PICS and IMFP with respect to Eq. (1). For example, the intensity of Sn 3d is much larger than that of 3p for spectra by Al Kα, while the intensity is opposite for HAXPES (hv~7939 eV). Also, some deep core levels such as Si 1s, Sn 2p, and Pb 3d, etc. can be probed by HAXPES. Additionally, in HAXPES spectra, the Sn MNN Auger spectra move out of the low binding energy regions where they appear in lab XPS, owing to the changes of photoelectrons in kinetic energy.

The O and C 1s core levels are checked for all samples, their contribution is too weak to be seen except Si sample, since Si sample is measured without surface cleaning, while other samples are cleaved or scraped to get clean surface before measurements. It is confirmed that Si valance band
spectra obtained by x-ray of 7939 eV show negligible difference with and without thin natural oxidized layer, due to the small contribution (<5%, by fitting the Si 2p core levels), which can also be easily understood since the thickness of natural oxidized layer (~1nm) is so thin comparing with the total probing depth of HAXPES (~39 nm) [11].

Figure 1 Survey spectra of group IVA elements with hard x-ray (hv ~ 7939 eV). The inset shows the comparison of survey spectra of Sn metal with Al Kα (dotted line) and hard (solid line) x-rays. Arrows mark the position of plasmons.

Figure 2 The valence band structures and the calculated density of states after consideration of photoionization cross section, Fermi-Dirac distribution and convolution with the experimental total energy resolution determined Gaussian function.

The valence band structures of Si, Ge, Sn and Pb measured with HAXPES at room temperature are shown in Figure 2. The occupied states of Si and Ge show 3 dominated structures due to the strong sp3 hybridization in diamond crystal structure. Sn, and Pb show different electronic structures, since Sn shows the tetragonal crystal structure (β-Sn) and Pb is a fcc crystal structure at room temperature. In
order to understand the experimental structures, the calculated spectra by GGA, HSE06 and GW0 were presented in Figure 2 after consideration of photoionization cross section (basing on Eq. (1)), Fermi-Dirac distribution and convolution with the experimental total energy resolution determined Gaussian function. The calculated band gaps and occupied band widths are listed in Table 1. The different calculation methods give the same band shapes and relative intensities except some differences in some peak positions in other words band gaps and band widths. By comparing the experimental and calculated results, one finds that the GGA and GW0 give proper band widths for all of samples and show nearly the same peak position as experimental ones, while the HSE06 provides the relative large band widths than that of experiment. If considering the bang gaps of Si, Ge and α-Sn (1.11 eV, 0.67 eV and 0.08 eV respectively) from experiments [12, 13], the HSE06 and GW0 provide the reasonable band gaps value relative to that of experiment, while the GGA seems under evaluation of the band gap values. Basing on the discussion above, the GW0 is the best method to give proper band structures and band gap of group IVA elements. If just the band width is cared, the GGA can give reasonable results for much reduction of calculation time comparing with that of GW0.

**Table 1** The calculated band gaps $E_g$ (occupied band widths $E_w$) of Si, Ge, Sn, Pb (in eV)

|       | Si     | Ge     | α-Sn   | β-Sn   | Pb     |
|-------|--------|--------|--------|--------|--------|
| GGA   | 0.58 (11.96) | 0.07 (12.78) | 0.00 (10.64) | (11.15) | (11.80) |
| HSE06 | 1.21 (13.28) | 0.75 (14.07) | 0.01 (11.79) | (12.54) | (12.54) |
| GW0   | 1.28 (11.91) | 0.80 (12.62) | 0.05 (11.02) | (11.30) | (11.30) |

4. Conclusions
In conclusion, the group IVA elements Si, Ge, Sn, Pb were investigated with HAXPES by bulk sensitive manner. The relative peaks intensity is discussed by thinking about IMFP and PICS, which will provide the principles to quantitative analysis of these elements with HAXPES. Calculated valence bands are combined well with the experimental ones by considering PICS, IMFP and total energy resolution. Amount of calculated results, GW0 method is the best one by comparing with experiment spectra and band gaps.

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