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The Investigation of Chemical Shift of Silicon X-ray Energy in Different Stoichiometry or Structure with Microcalorimeter EDS

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The ultra-high X-ray energy resolution down to 3 eV full-width at half-maximum (FWHM) of the STAR Cryoelectronics MICA-1600 Microcalorimeter (μCal) Energy Dispersive X-ray Spectrometer (EDS) [1] provides more detailed spectral information than conventional semiconductor EDS, from 1st generation of Si(Li) detectors to current 2nd generation silicon drift detectors, which have typical energy resolutions around 125 eV. The modern μCal-EDS has sufficient resolution to investigate chemical shifts, which so far has only been available by soft X-ray[2], WDS (or EPMA)-in-SEM and (Electron) EELS-in-STEM. Now, the development of μCal-EDS is the 3rd generation of EDS [3], combining the speed and ease of use of EDS with resolution closer to WDS.

We have used the MICA-1600 [4,5] to investigate the chemical-dependent energy shift of the silicon (Si) K X-ray emission induced by different stoichiometry, such as SiO_2, Si_3N_4 and $CoSi_X$; or structure, like crystalline vs. poly-crystalline Si. The mechanism of the shifting of the X-ray peak energy [6] is the variable chemical bond energy of electrons in the single atom or molecule. The shift of peak position in the X-ray spectrum can reflect the crystal structure around the probed element or the process to make the materials. Figure 1 shows the normalized spectra for Si K_α (~1.740 keV) and Si K_β (~1.837 keV) lines of different sample states of Si. The K_α intensity of X-ray signal is more than 10 times the K_β and exhibits a more significant chemical shift. Table 1 summarizes the samples measured and the fitted peak shifts of the Si K_α and K_β peaks relative to crystalline Si. This makes it possible to establish a table of X-ray peak positions for different silicon states and then deduce the conditions of silicon compounds and structures made by different processes or from different starting materials. In the future, μCal-EDS application to SiGe made with different compositions of Ge or made with different process recipes might be valuable for in-line process monitoring and advanced technology development.

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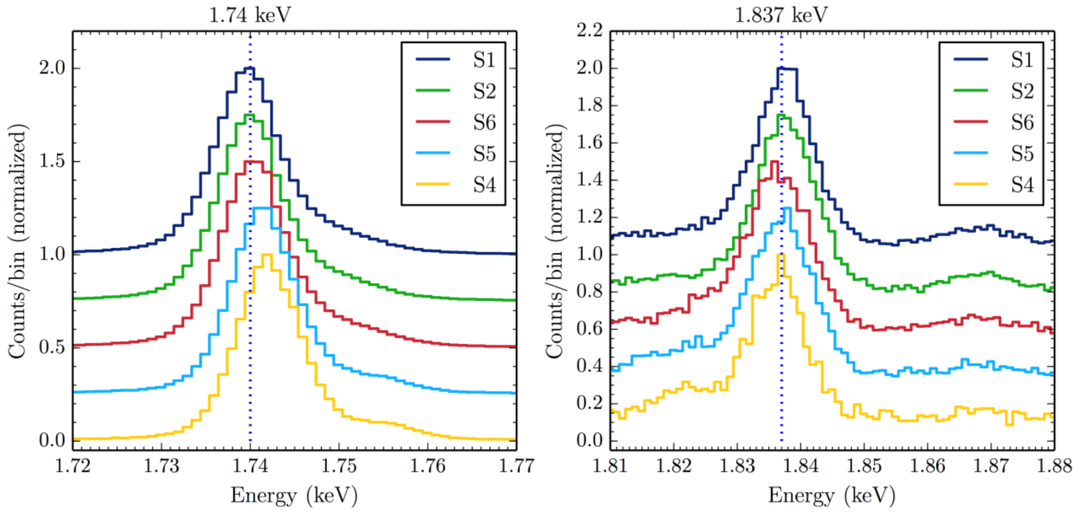

Figure 1. MICA-1600 shows chemical shifts of Si K_α (~1.740 keV, left panel) and K_β (~1.837 keV, right panel) emission lines at 5 kV SEM V_{acc}. Sample compositions are described in Table 1. Samples are arranged in order of Si K_α peak position.

Table 1. Comparison of Si peak shifts for several samples. The crystalline Si K_α peak is used as a calibration and reference at 1.740 keV. Peak positions are determined by fitting a Gaussian profile.

Label	Description	K_α (keV)	K_α Shift (eV)	K_β (keV)	K_β Shift (eV)
S1	Crystalline Si	1.74000		1.83767	
S2	Un-doped poly-crystalline Si, 2000 Å	1.74024	0.24	1.83780	0.13
S6	Si_3N_4 (400°C, PE-CVD process), 10000 Å	1.74063	0.63	1.83660	-1.08
S5	TEOS (680°C, SiO_2), 2000 Å	1.74151	1.51	1.83697	-0.70
S4	SiO_2 (400°C, PE-CVD process), 10000 Å	1.74210	2.10	1.83622	-1.45