

X-ray Emission Collected in a Novel Energy Dispersive Approach

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Abstract. Novel methods & materials have been used to produce dynamically bent Bragg diffraction analyzer crystals in a modified von Hamos geometry. They are used to collect a wide energy range X-ray emission spectrum over a large solid angle with electron volt resolution. Crystals fabricated from silicon-on-insulator wafers by photolithography and deep reactive ion etching can bend to 10 cm radius without increased lattice strain. The design permits adjustment of energy dispersion for individual analyzers in an array. A multilayer mono, mono-capillary focusing, and multi-crystal spectrometer together collect signals at a bend magnet beamline comparable to those from an undulator. Preliminary measurements validate this new energy dispersive spectrometer.

1. Introduction

X-ray emission spectroscopy (XES) is one of several photon-in/photon-out methods to probe electronic structure with element selectivity [1]. Here we consider non-resonant emission where the incident energy is set well above the absorption edge and the emitted x-ray fluorescence is collected at eV resolution. The energy dispersive spectrometer we describe is appropriate for current XES studies and will help to enable time-dependent studies that require 4th generation, ultra-bright sources. Bragg reflection spectrometers, based on flat crystals, von Hamos analyzers [2], can simultaneously collect emission spectra over 100eV at 10KeV. A significant challenge with such analyzers is low signal rate since flat crystals intercept a small solid angle per unit energy interval and reflect a bandwidth typically a small fraction of this interval.

Under conditions in Figure 1, the spectrometer resolution is $dE/E|_{\text{spect}} = \cot\Theta_B (\delta/2R) \sin^2\Theta_B$, with detector pixel size δ , Bragg angle Θ , and bend radius R . Reflection bandwidth is $dE/E|_{\text{ana}} = \cot\Theta_B \Delta\Theta_{\text{Darwin}}$, and solid angle intercepted by a pixel is $d\Omega = \phi\delta\sin^3\Theta / 2R$ where $\phi=RS$ is the angle subtended bending analyzer of length S about the joining line. Signal increases with decreasing R and as $\phi \rightarrow 2\pi$. The spectrometer reported here significantly reduces R without increasing crystal strain, increases signal using multiple crystals adjusted to a common dispersion (energy vs. position) at the detector, and uses novel upstream optics to increase flux on the specimen.

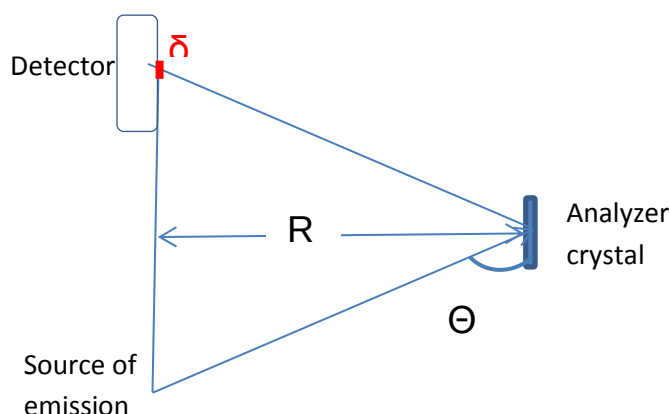


Figure. 1: The plane of diffraction of a von Hamos spectrometer with a point source of emission. The signal is increased by bending the analyzer around the “joining line” between source & detector.

2. Design & fabrication of bendable analyzer crystals

Deep reactive ion etching (dRIE) for fabricating bent silicon x-ray optics was first reported with a



sagittal focusing monochromator [3]. Etch depth varies 5% over the 100 mm wafer area and will distort curved optics, so we suggested using bonded (bilayer) wafers [4]. This was realized using silicon-on-insulator (SOI) [5] with a thick FZ silicon diffraction layer bonded to a thin CZ silicon bendable layer through a micron thick SiO_2 layer. The FZ surface is lithographically patterned to form the dRIE etch mask. The “bar analyzer” shown mounted in Figure 2, consists of narrow strips defined by trenches in the FZ layer; only the CZ layer bends. Strips have length (in diffraction plane) H and width w , trench width is g , and analyzer active width is S .



Figure 2: “Bar analyzer” bent in a simple bending apparatus. The diffraction plane contains the bend axis and is normal to crystal surface. Bending occurs when the pair of inner rods move down relative to outer rods. All 4 rods are free to rotate.

The energy band collected depends on Θ_B , R , H as $dE/E|_{\text{collected}} = H \sin(2\Theta_B)/2R$. Focus size (transverse to dispersion direction) at detector is $2w$. $S \approx Nw$, with N the number of strips across the bar. A simple beam bending model for trench width g , illustrated in Figure 3, assumes uniform bending confined to layer thickness t where local bend radius $r = Rg/(w+g) \geq 0.5Et/\sigma$. If silicon has elastic modulus $E = 190\text{GPa}$, and maximum stress $\sigma = 2\text{GPa}$, then $r = 6\text{mm}$ with safety factor 3 for $t = 40\mu\text{m}$. So analyzers with $w = 500\mu\text{m}$, $g = 32\mu\text{m}$ will bend to $R < 100\text{mm}$.

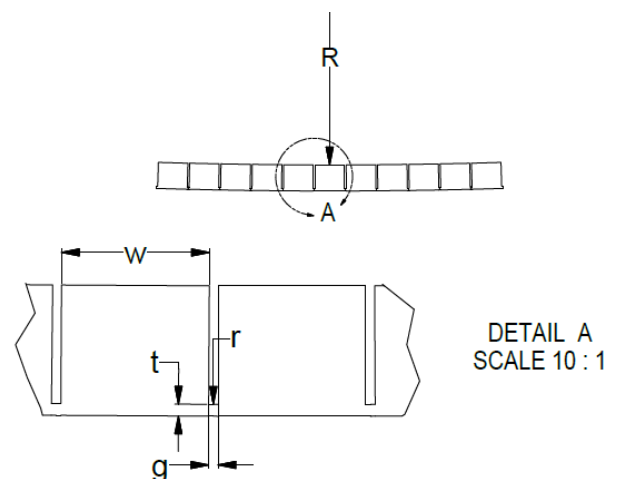
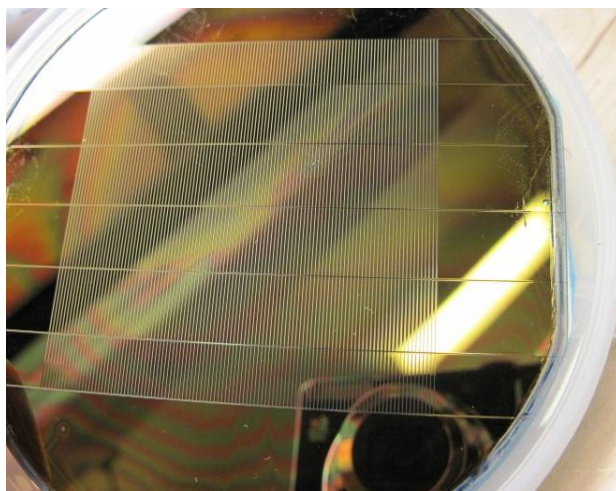


Figure 3: left) 100mm diameter silicon wafer, with bar analyzer pattern produced by deep-reactive ion etching. right) Model used to estimate “bar analyzer” design parameters: w , t , g .

3. Superimposing signals

The first measurements collected were copper K β emission using silicon (553) von Hamos analyzers. Collecting weak K β emission requires intercepting a large solid angle. This is done by increasing the number of analyzers and decreasing R. A multiplexing scheme to match dispersion of energy with position on the detector, for 3 analyzers, is illustrated in Figure 4. Analyzers are oriented so beam incidence angles match at corresponding points on each surface, and diffracted rays of common energy intersect on the detector. This occurs when distance from source to center of analyzer n is $L(\varphi_n) = R \sin(\Theta_0 + \varphi_n)/\sin^2\Theta_0$, and if the detector face is tilted away from joining line by $90 - \Theta_0$. Θ_0 is Bragg angle center and $\varphi_n > 0$ for crystals positioned above center crystal relative to source point. Figure is drawn for center plane where crystals are furthest from the joining line. To achieve best resolution analyzers should bend so $R_n = L_n \sin\Theta_0$ where each energy diffracts along circular arcs of length S. In this case analyzers with $\varphi \neq 0$ focus slightly off the detector plane, therefore focusing on this plane produces very slight dispersion errors.

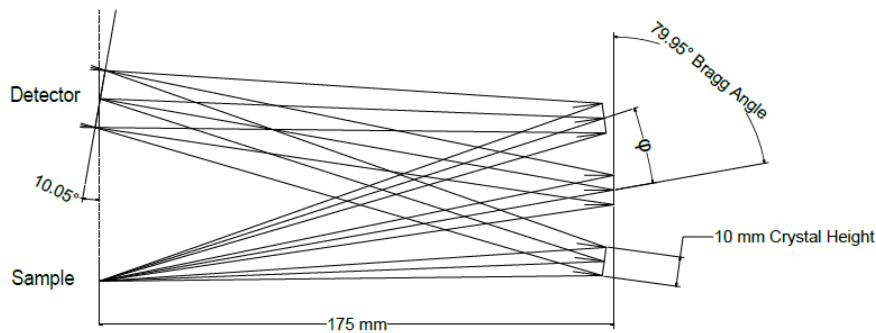


Figure 4: Configuration for collecting copper K β emission using silicon (553) reflection. Corresponding incident and diffracted rays shown for each crystal; center crystal is vertical.

4. Realized spectrometer

The spectrometer in Figure 5 was tested collecting copper K β emission with 3 Si(553) analyzers ($\Theta_B = 79.95^\circ$) with $R_{\text{center}} = 175\text{mm}$, $S \approx 55\text{mm}$, using Dectris100K detector with $172\mu\text{m}$ square pixels. For $H=1\text{cm}$, $dE|_{\text{collected}} = 87\text{ eV}$ with $d\Omega = 147\text{ }\mu\text{Srad/analyzer/1 eV}$. Each analyzer is: bent to adjust R, rotated to adjust energy, & translated to adjust dispersion. Translating the spectrometer parallel to incident beam changes Bragg angle Θ and 2Θ changes as the detector is also translated. The 10 KeV incident beam, with bandwidth 1.2%, was focused to $140\text{ }\mu\text{m}$ on a pressed powder sample using a 125 mm working distance monocapillary built at CHESS.

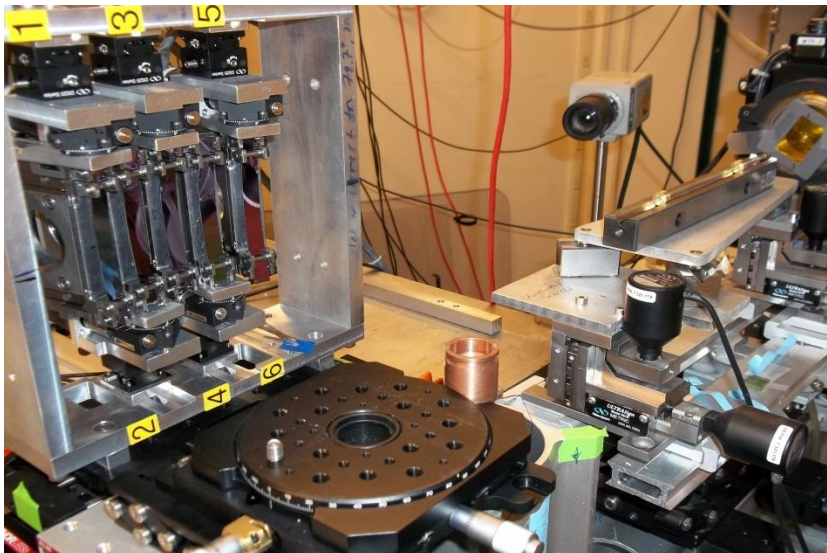


Figure 5: CHESS multi-crystal spectrometer with detector (on black rotation stage) and sample (on copper mount) removed for clarity. Downstream is to left. Center crystal (#3) is oriented parallel to line joining detector and sample centers. Focusing capillary is on alignment stage upstream of sample.

5. Results

This work demonstrates how novel, highly flexible analyzers can be combined to multiply signal collection rate and match energy dispersion to overlap spectra from multiple crystals without reducing resolution. The dispersion matching works, but our benders introduce displacement of spectra transverse to the dispersion direction. In practice this problem actually simplifies dispersion adjustment. Figure 6 shows the detector image and resultant spectrum from a single analyzer. Figure 7 (left) shows $K\beta_{1,3}$ peaks from three analyzers and (right) scaled to common intensity, one sees agreement in line shape and centroid resulting from dispersion match. These spectra would be summed to increase statistical precision before further analysis.

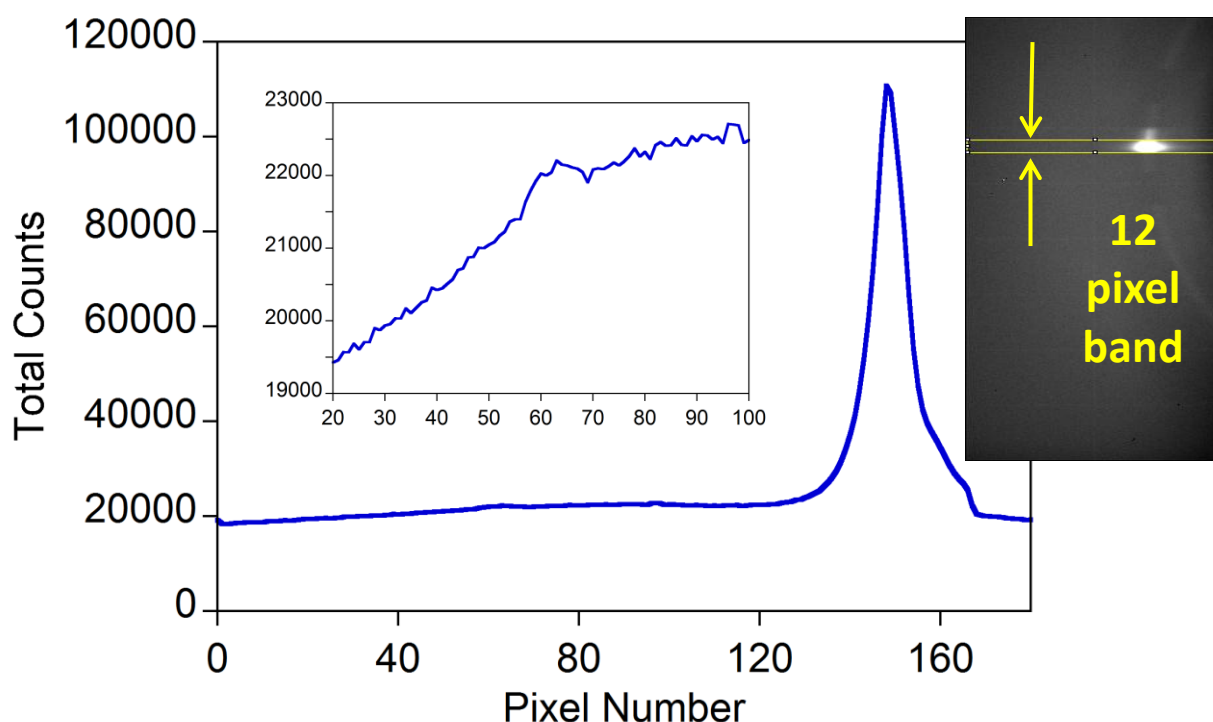


Figure 6: Copper $K\beta$ spectrum from CuO_2 collected by single analyzer; energy decreases with pixel number. Analyzer $R=175\text{mm}$, collection time 3000 sec. Inserts: (upper left) valence-to-core (V2C) region, (right) detector image. Spectrum is vertical sum over 12 pixels. Background subtracted peak count rate is 30Hz and $K\beta_{1,3}$ is 8.65 pixels wide, so line is collected at 277Hz. Known separation between V2C and $K\beta_{1,3}$ calibrates the horizontal axis at 0.82eV/pixel and yields $K\beta_{1,3}$ peak width 7.06eV, in agreement with Reference 6. The large background, from close proximity of sample, analyzer and detector, precludes quantitative analysis of V2C line shape.

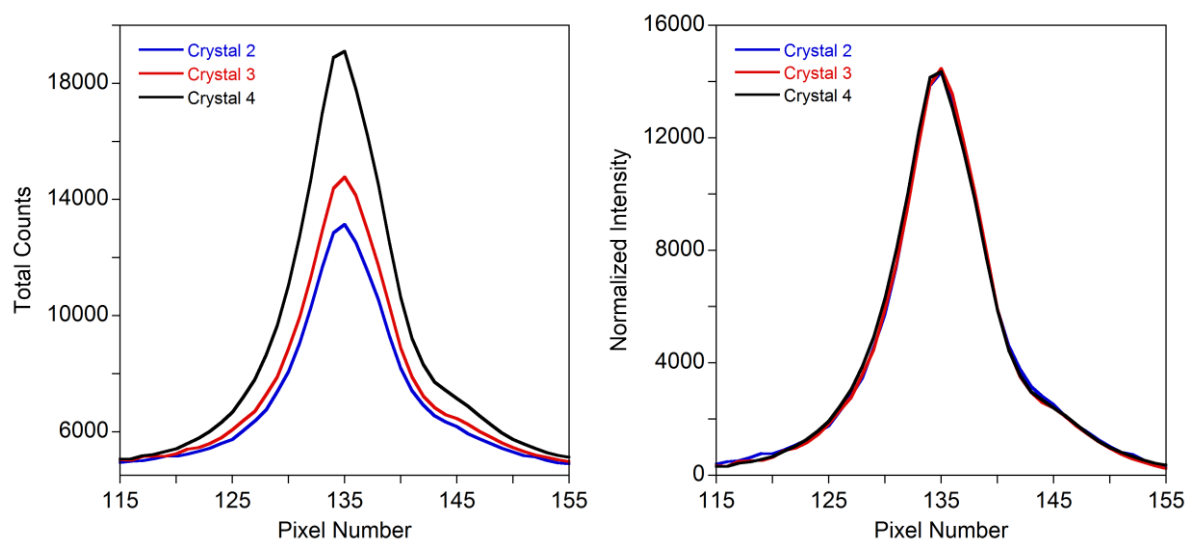


Figure 7: To adjust energy dispersion and peak position, analyzer crystals are translated in spectrometer center plane. Plot at left shows spectral peaks from 3 crystals. In the plot at right individual spectra have been background subtracted and peak intensities have been scaled to show agreement in line shape and position.

6. Conclusion and directions of continued development

Results are reported on the development of a multi-crystal von Hamos analyzer that multiplies rate of signal collection for x-ray emission with eV resolution. The novel method of analyzer fabrication produces highly flexible analyzers and the new arrangement of crystals demonstrates matching of energy dispersion at the detector. The prototype spectrometer produces dynamical bending using 4-pin benders with limited mechanical adjustment that produces image aberrations. We conclude that dynamic bending is very hard to realize in the compact size required to maximize collection solid angle/analyzer, so a 2nd generation spectrometer with fixed bend radius and optimum collection capability is now being developed.

References

- [1] Overview and references may be found in Synchrotron Radiation News Vol.22, 2, 12-16 (2009).
 - [2] J. Hoszowska, J.-Cl. Dousse, J. Kern and Ch. Rhême, *High resolution Von Hamos Crystal x-ray Spectrometer*, Nucl. Instrum. Meth. A **376**, 129 (1996).
 - [3] K.D.Finkelstein, S.Rosenblatt, P.Cottle, *Rev.of Sci.Instr.*,73,1464 (2002).
 - [4] K.D. Finkelstein, P. Abbamonte, V. Kostroun, Proceedings of SPIE 4783 (2002).
 - [5] Celler, G. K.; Cristoloveanu, S. (2003). "[Frontiers of silicon-on-insulator](#)". *J Appl Phys* **93** (9): 4955.
- We use SOI made by Ultrasil Corporation in Hayward, Calif. USA <http://www.ultrasil.com/>
- [6] J.Szlachetko, M.Nachtegaal, E.de Boni, M.Willmann, O.Safonova, J.Sa, G.Smolentsev, M.Szlachetko, J.A.van Bokhoven,J.-Cl.Dousse,J.Hoszowska,Y.Kayser,P.Jagodzinski,A.Bergamaschi,B.Schmitt,C.David, and A.Lücke; REVIEW OF SCIENTIFIC INSTRUMENTS **83**, 103105 (2012).