Optimizing the slicing pattern of stress-relief crystal analyzers for X-ray Raman scattering

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X-ray Raman scattering (XRS) spectroscopy is the non-resonant inelastic scattering technique used to measure local electronic structure and chemical bonding around low-Z atoms with hard X-rays. This technique is useful in environments where traditional soft X-ray techniques are not applicable. However, the small cross section of XRS requires that the spectrometer must simultaneously achieve large solid angles and good energy resolution. A large XRS spectrometer named ‘Qian Kun’ is currently under construction at the High Energy Photon Source (HEPS) in China, which can hold up to 100 analyzers with an energy resolution in the range 0.4–1.0 eV. Here, the batch production and performance evaluation of the spherically bent crystal analyzers fabricated for this spectrometer are reported. The stress-relief effect of various dicing patterns and their impact on the reflectivity properties of crystal analyzers to achieve good energy resolution when studying the near-edge features of carbon and oxygen K edges were investigated. It was discovered that radially dicing the thin silicon wafers is more effective in relieving stress than conventional strip cuts in the case that the total number of divided blocks is roughly the same.

1. Introduction

The development of fourth-generation synchrotron light sources has significantly increased the available X-ray beam flux and brightness, triggering wide employment of photon-hungry techniques such as X-ray emission spectroscopy and inelastic X-ray scattering (IXS) (Liu et al., 2014; Gallo & Glatzel, 2014; Rueff & Shukla, 2010; Sokaras et al., 2013). X-ray Raman scattering (XRS) is the non-resonant inelastic X-ray scattering from core or semi-core electrons and has a similar energy dependence to X-ray absorption, albeit with a much smaller overall cross section (Fister, 2017; Ketenoglu, 2021). This hard X-ray photon-in/photon-out technique combines the advantages of a hard X-ray probe with the sensitivity of soft X-ray absorption edges, and can measure the core-electron excitations and enable electron orbital imaging and chemical bond imaging (Amorese et al., 2021; Yavaş et al., 2019; Leedahl et al., 2019). In particular, it enables bulk property investigation of low-Z systems under many conditions including extreme pressure/temperature environments, liquids, in situ cells etc. (Li et al., 2021; Mao et al., 2010). In the past two decades, XRS has contributed to numerous science fields, including, notably, spectroscopic studies of water under high pressure (Cai et al., 2005; Mao et al., 2006), graphite electrodes for lithium-ion batteries (Nonaka et al., 2019) and SiO2 glass up to 1.6 Mbar (Lee et al., 2019).
The small cross section for XRS requires the incident flux to be sufficiently strong. However, continuous efforts to develop high-brightness beamlines lead to serious radiation damage issues. Thus, using a large-solid-angle XRS spectrometer to improve the collection efficiency becomes a feasible route (Fister et al., 2006). XRS spectrometers are often based on spherically bent crystal analyzers (SBCAs) that act as focusing monochromators after the sample and offer an energy resolution in the sub-electronvolt range for photon energies of around 10 keV (Collart et al., 2005; Jahrman et al., 2019; Ni et al., 2018; Liu et al., 2022). Several modern IXS beamlines provide large-solid-angle XRS spectrometers by utilizing dozens of such crystal analyzers (Huotari et al., 2017; Sokaras et al., 2012). A large XRS spectrometer (named 'Qian Kun') is under construction at the hard X-ray high-energy-resolution spectroscopy beamline of the High Energy Photon Source (HEPS) in China. It can hold up to 100 analyzers (six 1 m XRS modules with each containing 15 crystals, one 2 m XRS module and one resonant inelastic X-ray scattering module with a variable radius) with an energy resolution in the range 0.4–1 eV. The quality and consistency of the crystals are crucial for recording and superimposing the scattering signal. Batch manufacture and performance evaluation for these SBCAs are also necessary.

To obtain good XRS spectra, it is extremely important to reduce the strain at the front of the crystal to improve the energy resolution, since the energy resolution can be degraded by bending-induced strain that deforms the silicon structure. Typically, ~1 eV energy resolution is sufficient for most applications, but some XRS near-edge features (such as the O K edge) require ~0.4 eV or higher energy resolution. Practical approaches of masking the analyzer edges or increasing the bending radius have been applied to improve the energy resolution. However, these approaches sacrifice the detection solid angle. Alternatively, the ‘strip-bent’ method is an effective approach to release the bending strain by cutting the crystal wafer into strips prior to the bending and anodic bonding processes (Verbeni et al., 2009). The transverse strain in the crystal wafer can be partially released, and the gain in energy resolution is ~1.9 for 1 m SBCAs (Verbeni et al., 2009) and ~3.9 for 0.5 m SBCAs (Rovezzi et al., 2017). Equally spaced strips are one of the most common cutting patterns when using diamond dicing blades. The stress-relief effect of other cutting patterns has not been investigated so far.

Blade dicing is the most common wafer dicing method, which uses an abrasive blade rotating at high speed to cut along the dicing lanes (Yuan et al., 2023). It relies on the physical removal of material, which can cause chipping and cracking of the wafer. In addition to blade dicing, many new cutting strategies such as plasma dicing, laser dicing and deep silicon etching have been gradually employed for Si wafer dicing (Marks et al., 2022). Laser dicing has the potential to replace blade dicing as the next-generation ultrathin wafer singulation technology because it allows for faster cutting and a smaller kerf width. In particular, laser dicing combined with a two-dimensional motion mechanism can achieve arc dicing which cannot be achieved by traditional blade dicing. Some new dicing patterns can be realized using this method. Thus, the X-ray reflectivity and the stress-relief effect of analyzers adopting these new patterns are worth studying.

In this work, we batch-fabricated several traditional spherical-bent and strip-bent analyzers and evaluated their performance. We also designed several new types of stress-relief analyzers using the laser dicing method and investigated their energy resolution. Understanding the reflectivity curve and its behavior on various stress-relief patterns would be indispensable in the construction of fully optimized spectrometers with high performance.

2. Methods

2.1. Wafer dicing patterns and analyzer production

The in-house-developed analyzers are produced by the Platform of Advanced Photon Source Technology (PAPS) Research and Development, which provides technical support for construction, testing, and technological research and development for HEPS. Five types of HEPS Si(660) SBCAs with R = 1 m were designed and prepared for the XRS spectrometer as shown in Fig. 1. The first is the widely used SBCA, which is uniformly bent and obtained by anodic bonding techniques (Ketenoglu, 2021; Knowles & van Helvoort, 2006). It can be used for 2D and 3D XRS spectral imaging. The second is the strip-bent analyzer designed to minimize the influence of in-plane stress in one direction. The wafer is cut into ten strips by blade dicing before the anodic bonding process. The strip-bent analyzers as well as other stress-relief crystals are dedicated to XRS spectra application, although their focusing capabilities are degraded (Rovezzi et al., 2017). The first set of 15 spherically bent analyzers and 15 strip-bent analyzers were successively produced using the techniques reported in the literature (Rovezzi et al., 2017). In addition, three new types of crystals, named ‘radial-cut analyzer’, ‘cross-cut analyzer’ and ‘arc-cut analyzer’ in the present work, were also prepared by laser dicing techniques. It is desirable to achieve more efficient stress relief with the minimum number of blocks or the shortest dicing lengths. For the radial-cut analyzer, the thin wafer is sliced along the radius of the wafer, symmetrically dividing the circular wafer into eight sectors. For the cross-cut analyzer with large block sizes, the thin wafer is divided into nine parts through two horizontal cuts and two vertical cuts. For the arc-cut analyzer, the wafer was divided into 12 blocks by combining arc cutting and straight cutting. The purpose of dividing a wafer into individual blocks is to facilitate the release of transverse strain. In fact, there are many other ways to divide the wafer. The present work is only a preliminary attempt to find appropriate cutting patterns for stress-relief crystal analyzers.

All analyzers are of the spherical Johann type with a curvature radius R = 1000 mm. They are obtained from 4 inch Si(n60) wafers (float zone, resistivity > 3000 Ω cm, 300 μm-thick) and double-side polished to optical quality (λ = 632.8 nm), and the parallelism between the two faces is better than 10 μm. Borosilicate glass (Pyrex 7740) substrates with a
thickness of 12 mm are polished to a concave spherical surface with a surface shape error below \( \frac{1}{4}\lambda \). The silicon wafer and the spherical Pyrex substrate are cleaned in a class 1000 cleanroom with acetone and ethanol and then joined together through the anodic bonding procedure. For the laser dicing procedure, a fiber laser scribing machine (SFS30, Wuhan Sunic Photoelectricity Equipment Manufacture Co. Ltd) is employed to divide the thin wafer into individual blocks, where the dicing speed is about 5 mm s\(^{-1}\) and the power is about 30 W. The wafers are first diced through and then transferred to aluminium conductive tape. The tape holds the individual parts together and acts as an electrode during the anodic bonding process. Finally, the wafer was bonded to the spherical glass substrate. The stress-relief analyzers are made by an anodic bonding setup consisting of a heat source, a high-voltage power supply, electrodes and a brass base. The brass base can hold the concave glass, a convex spherical mold, whose role is to bend the silicon wafer to make it follow the surface shape of the concave substrate, and the Si wafer itself. These components are aligned and are tightened with screws. A void-free bonding interface was achieved for all crystals and can be clearly observed from the backside of the crystals.

2.2. X-ray characterization

The crystal analyzers are characterized by measuring X-ray reflectivity curves, which can also be referred to as the spectral resolution function or elastic peak. The intensity and full width at half-maximum (FWHM) of these curves are related to the diffraction efficiency and energy resolution of the crystal. These are measured by scanning the incident photon energy across the range of energies corresponding to the crystal analyzer reflection.

Two rounds of characterization experiments were performed. For the first round, 15 SBCAs were measured at the 1W2B beamline of the Beijing Synchrotron Radiation Facility (BSRF). The optical layout consisted of an Si(111) double-crystal monochromator followed by an Si(220) channel-cut crystal monochromator to decrease the bandwidth of the incident beam, and a polycapillary lens was used to focus the X-ray spot to 50 \( \mu \)m. The analyzers were mounted on a prototype three-element spectrometer to measure the elastic scattering signals from a plastic scatterer. A specially designed EPICS–bluesky control system was employed to synchronously scan the energy of the two monochromators. Using this setup, it is possible to perform a high-precision and highly efficient characterization of the SBCAs. The bandwidth of the incident beam was optimized to 0.8 eV at 9.7 keV (FWHM).

For the second round of experiments, two spherical bent analyzers, 15 strip-bent analyzers and three new types of stress-relief analyzers were characterized at BL13SSW of the Shanghai Synchrotron Radiation Facility (SSRF) with a seven-element point-to-point scanning spectrometer in the vertical Rowland circle geometry. The beamline was equipped with an Si(311) monochromator and its energy was calibrated using Zn foil. The incident bandwidth was measured by analyzing the incident beam with a perfect crystal Si(660) reflection in almost exact backscattering at 9686 eV, giving an energy spread of 290 meV FWHM. The beam was about 1 mm (horizontal) \times 0.5 mm (vertical) at the sample position, and thus the source size contribution to the total resolution was about 200 meV FWHM at the working energy. The analyzer was mounted on the spectrometer and a silver foil was used as a scatterer. The geometric pre-alignment is achieved by illuminating the silver foil with a laser, and then the laser diffusely scattered by the foil acts as a diverging optic. By tilting the

Figure 1
The five types of HEPS home-made Si(660) SBCAs with \( R = 1 \) m. The upper panel shows the designed patterns and the lower panel shows the real items. (a) Spherically bent analyzer by anodic bonding techniques. (b) Strip-bent crystal analyzer. (c) Radial-cut analyzer. (d) Cross-cut analyzer. (e) Arc-cut analyzer.
crystal analyzer (the pitch and the roll angle), the scattered laser can then be refocused onto a 2D detector (MiniPIX, 256 × 256 pixels, 55 μm in size). The focusing of the crystal is realized by angular alignment of the crystal to direct the light spot onto the detector, and then optimizing the position of the crystal along its normal direction to minimize the size of the spot. The reflectivity curves of spherical bent analyzers are fitted using a Gaussian function and the FWHM parameters are obtained automatically from the fitting. Since the reflectivity curve of the stress-relief analyzer has an asymmetrical shape, the exponentially modified Gaussian (EMG) function was found to be suitable for fitting them.

2.3. Elastic deformation and X-ray reflectivity curve simulations

In order to fully understand the experimental results, the elastic deformation of the wafer and the X-ray reflectivity curves were simulated using the Python packages pyTTE and tbcalc (Honkanen et al., 2014; Honkanen & Huotari, 2021). These codes used toroidal bending models to calculate the stretching stress and strain fields and their effect on the diffraction curves of the spherical-bent and strip-bent analyzers. This approach calculates the perpendicular strain field by integrating the one-dimensional Takagi–Taupin (TT) equations and the angular strain field via an analytical model (Honkanen et al., 2016.). The reflectivity curve was calculated using a circular Si(660) wafer with a diameter of 100 mm and a thickness of 300 μm. The wafer was spherically bent with a bending radius of 1 m. The incident bandwidth of an Si(311) monochromator was considered in the simulations, while the contributions of source size and pixel size of the detector to the energy resolution were ignored since the code lacks these features.

2.4. Effect of chemical etching on a strip-bent analyzer

To counter the chipping effect of mechanical cutting, chemical etching can be used to remove the damage and residual stress from the dicing process during the fabrication of strip-bent crystals. The strip-bent crystal analyzers were etched for 10 min at room temperature in a nitric acid (HNO₃) and hydrofluoric acid (HF) mixture (93:7 in volume). Comparing the energy resolution of etched and unetched strip-bent analyzers, an improvement of approximately 0.1 eV in energy resolution can be observed in the present experiments, although it depends on the etching time and mechanical parameters of the cutting operation.

3. Results and discussion

3.1. Evaluating the performance of HEPS-made spherical-bent analyzers

The current mass-scale production of spherically bent crystals at HEPS relies on the anodic bonding technique. With the current analyzer manufacturing technique, we found the Si(660) crystal quality to be highly reproducible and chose two individual crystals [denoted HEPS-Bent-Si(660)-No.1 and HEPS-Bent-Si(660)-No.2] as typical examples to compare with commercial products (from XRStech LLC) to evaluate their performance and validate the production method. The reflectivity curves were measured at BL13SSW of SSRF and are shown in Fig. 2. The reflectivity curves are fitted using a Gaussian function and the corresponding total FWHM values are 1.07, 1.04 and 1.20 eV. After deconvoluting the source size contribution of 200 meV and incident bandwidth contribution of 290 meV, the intrinsic resolutions of the HEPS-Bent-Si(660)-No.1, HEPS-Bent-Si(660)-No.2 and XRStech-Bent-Si(660) analyzers are approximately 1.01, 0.98 and 1.15 eV, respectively. Thus, the HEPS SBCAs have almost the same or even better energy resolution than the products from XRStech. In addition, the measured reflectance curve is in good agreement with the simulated calculation results based on the tbcalc code.

The first set of SBCAs was batch tested at the 1W2B beamline of BSRF to evaluate their focusing properties and consistency. Fig. 3 shows the focal conditions of the HEPS-

![Figure 2](image)

**Figure 2**
Elastic peak scans for the two HEPS-developed Si(660) SBCAs with \[ R = 1 \text{ m} \] and the XRStech product for reference, collected using the Si(311) incoming beam monochromator at BL13SSW of SSRF. The experimental data are fitted by Gaussian functions.

![Figure 3](image)

**Figure 3**
Focus spot images of the HEPS-Bent-Si(660)-No.1 crystal measured at the 1W2B beamline of BSRF with a position-sensitive detector as a function of photon energy. The center of the working energy is 9692 eV and the size of the spot is about 15 × 25 pixels with each pixel 55 μm in size. The detector was positioned at the focal spot of the SBCA. The color represents the recorded photon counts on a logarithmic scale. The left panel is the focus spot at the low-energy tail of the reflectivity curve. The middle panel is the focus spot when tuning the energy at the peak of the reflectivity curve. The right panel is the focus spot at 0.3 eV above the peak energy.
Bent-Si(660)-No.1 analyzer on the detector. The size of the focal spot is visually estimated to be approximately 825 × 1375 μm. This SBCA is measured in the energy domain using a position-sensitive detector; one can see the focal spot first appear as a faint hourglass-shaped figure at the low-energy tail of the resolution curve which then converges into a single spot as the energy is increased, as is considered to be characteristic of a high-quality crystal in previous work (Honkanen & Huotari, 2021). The qualities of the Si(660) crystals are highly reproducible and the average energy resolution is about 1.1 ± 0.1 eV (one standard deviation).

3.2. Stress distribution and energy resolution of strip-bent analyzers

Energy broadening of SBCAs mainly originates from the stress-induced energy shift and the TT curve without angular compression (Honkanen et al., 2014). The strip-bent strategy can relieve the stress of a bent wafer and thus reduce the energy shift caused by stress. For HEPS strip-bent analyzers, the wafers were cut into ten strips. The diffraction curve shifts and the contact forces before and after strip-cutting are compared and shown in Fig. 4. After the wafer is grooved, the energy shift attributed to transverse stretching becomes significantly smaller, and the energy offset is limited within ±15 meV. The reflectivity curves of the ten-strip Si(660) analyzer are shown in Fig. 5. The pronounced low-energy tail in the spherical-bent analyzer disappeared as expected. The green short-dashed line in Fig. 5 is the simulated results for the strip-bent analyzer with 10 mm strip width. The incident bandwidth of the Si(311) monochromator was considered in the simulations, while the contributions of pixel size of the detector to the energy resolution were ignored, and thus the simulated results seem slightly sharper than the experimental

Figure 4
(a) and (b) Comparison of the diffraction curve shifts attributed to the transverse stretching of spherical-bent and strip-bent analyzers. (c) and (d) Comparison of the contact forces between the wafer and substrate for the spherical-bent and strip-bent analyzers.
results. An EMG function is used for fitting the experimental data, and the total FWHM is about 0.6 eV. Thus the intrinsic resolution of the strip-bent analyzer is about 0.48 eV after deconvoluting other contributions. A total of 15 strip-bent analyzers were measured, and the average energy resolution was about $0.53 \pm 0.05$ eV (one standard deviation). By rotating the strip-bent analyzers by $90^\circ$, it was found that the orientation of the strips does not affect the energy resolution either theoretically or experimentally.

3.3. Comparison of three stress-relief crystal analyzers prepared by laser dicing

Lastly, the three stress-relief crystal analyzers, i.e. the radial-cut analyzer, cross-cut analyzer and arc-cut analyzer, were measured. The results are compared and shown in Fig. 6. The derived energy resolutions are approximately 0.463, 0.470 and 0.515 eV for the three types of analyzers. The first two have very similar energy resolutions while having an advantage over the third. The corresponding energy resolution gains using different cutting methods are summarized in Fig. 7. The gain ranges from 2.1 to 2.4 if the energy resolution before cutting is assumed to be 1.1 eV. The radial cutting through the center of the wafer has a small advantage over the others in the case that the total number of divided blocks is roughly the same. This may be due to the fact that radial cutting is more effective in relieving stress in the center of the wafer. But this observation needs further theoretical simulation support because it relates to many other factors including cutting length, surface figure errors of the substrate, wafer quality etc. Also, the sample size is 15 for strip-bent analyzers and only one for the other types of analyzers, and the actual performance may be influenced by the fabrication procedure as well as the quality of the substrate and the Si wafer used. Further improvement can be expected if the surface of an analyzer can be divided into finer segments. On the basis of the current results, an optimized stress-relief analyzer that combines finer radial and circular cutting can be designed and applied to higher-resolution XRS spectroscopy.

4. Conclusions

Spherically bent and strip-bent analyzers have been batch-fabricated for the XRS spectrometer at HEPS. These crystals have been characterized at BSRF and SSRF. The average energy resolution of the spherically bent analyzers and strip-bent analyzers reached approximately 1.1 and 0.53 eV at
9.7 keV (FWHM), which is close to the theoretically predicted value. To find a more effective way of reducing stress, three new cutting patterns were adopted for producing stress-relief crystal analyzers. It was found that the radial-cut analyzer has a slight advantage in energy resolution compared with analyzers with other cutting patterns. This could be attributed to the fact that radial cutting can release stress more effectively in the center of the wafer.

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