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High-Index Facets in Gold Nanocrystals Elucidated by Coherent Electron Diffraction

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Abstract

Characterization of high index facets in noble metal nanocrystals for plasmonics and catalysis has been a challenge due to their small sizes and complex shapes. Here, we present an approach to determine the high index facets of nanocrystals using streaked Bragg reflections in coherent electron diffraction patterns, and provide a comparison of high index facets on unusual nanostructures such as trisoctahedra. We report new high index facets in trisoctahedra and previous unappreciated diversity in facet sharpness.

Keywords

Coherent Electron Diffraction; Au; Nanocrystallography; Atomic Structure

Recent developments in synthesizing noble metal nanoparticles of various shapes and sizes using wet chemistry^{1,2} have spurred a correspondingly significant interest in methods to characterize their 3D structure. Gold nanoparticles, in particular, have found applications in chemical sensing, nanomedicine and catalysis.³⁻⁵ Nanoparticle shape has been shown to affect the physiochemical⁶ and thermodynamic properties;⁷ in particular, particles enclosed

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Associated Content Additional diffraction, HRTEM images, and streak tracking methods are available in the Supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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by high index facets are thought to have higher catalytic activity.^{3, 8, 9} At present, researchers employ an array of structural characterization tools, including transmission electron microscopy (TEM),⁷ electron diffraction¹⁰, atomic force microscopy (AFM)¹¹ and x-ray diffraction (XRD).¹² These techniques provide a wealth of information regarding size, shape, crystallinity and structure,¹³ particularly when integrated with analytical methods such as electron energy loss spectroscopy (EELS),¹⁴ energy dispersive spectroscopy (EDS), and electron back scattering diffraction (EBSD).¹⁵

For face-centered cubic (FCC) metal nanocrystals (NCs) such as gold, silver and platinum, several unique geometries such as rhombic dodecahedron,¹⁶ tetrahexahedra,¹⁷ and trisoctahedra¹⁸ have recently been synthesized. Characterization of these nanostructures by TEM using selected area electron diffraction (SAED) suggest the existence of higher index facets not previously observed in metal nanoparticles.¹⁹ Typically the structures for these nanoparticles are obtained by measuring angles in SEM images of large NCs^{20, 21} or by examining the projected images recorded using high-resolution transmission electron microscopy (HRTEM). However, the intensity in a HRTEM image is sensitive to thickness and its resolution is limited by lens aberrations. Additionally, the projection of images hides inward facing facets in concave nanocrystals. Due to these limitations, only convex nanocrystals have been characterized in a few low index zone axis orientations, which limit the type of facets that can be observed. Complicated schemes have been used to address this limitation. For example, Zhang et al. cut a large concave gold nanocrystal with a focused ion beam so that the facets were edge-on;¹⁹ however this technique can damage the sample.

An alternative approach is to use tomography in a scanning transmission electron microscope (STEM). Here, the 3D shape of nanoparticles is obtained by projecting the nanoparticles at different angles and reconstructing a 3D image from different projections. However, the resolution of the reconstructed 3D image is limited to few nanometers; applications to nanoparticles often show rounded facets, which is insufficiently resolved for the determination of high index facets.²² The limitations of above methods show there is need to evaluate high index gold nanocrystals using a direct technique.

Here we utilize a technique known as coherent nanoarea electron diffraction (NED), where the structural information of a single nanoparticle can be recorded in reciprocal space for the study of its three-dimensional structure.²³ In small nanoparticles, the diffraction pattern recorded is the intersection of the Ewald sphere (radius of $1/\lambda_e$, nearly flat for high energy electrons) with the reciprocal lattice of the nanoparticle convoluted with the nanoparticle shape function. The reciprocal lattice rod of a nanoparticle facet intersects the Ewald sphere almost tangentially when the facet is normal to the incident electron beam. The reciprocal rod is characterized by its direction, width (w) and length (R). Measurement of recorded reciprocal rods, together with the electron diffraction pattern, allows a determination of nanoparticle crystal structure. For large nanoparticles of size greater than the mean free path of scattering, multiple scattering causes the redistribution of diffraction intensities, which does not affect the direction of reciprocal rods. Using coherent NED, we are able to determine multiple high-index facets parallel to the beam direction and measure the angles between these facets for NCs as large as ~100 nm. The use of diffraction patterns significantly improves the precision for determining the facet normal direction and for measuring angles between facets over the methods based on direct imaging. As results here show, coherent NED provides a quantitative measurement of the facet sharpness ($1/R$) and facet size ($1/w$) of high index facets.

Figure 1 illustrates the principle of NED. We set up a nanometer-sized parallel beam of electrons in the nanoarea electron diffraction (NED) mode²⁴ for this study. Small probe forming apertures are used to limit the beam size between 55 to 120 nm, which is

accelerated to 197 kV ($\lambda_e = 2.53$ pm). Diffraction produces reflections which satisfy the Laue condition in reciprocal space. In the limit of kinematical approximation, the diffraction intensity is proportional to the square of structure factor, which is a Fourier transform of the crystal potential:

$$F(\mathbf{s}) = FT\{V(\mathbf{r})\} = FT\{s(\mathbf{r})\} \otimes FT[V^{\text{Crystal}}(\mathbf{r})] \quad (\text{Eq.1})$$

The shape of the nanocrystal introduces an additional broadening function in the form of the shape function, $FT[s(\mathbf{r})]$. For faceted small crystals, reciprocal lattice points transform into shape functions consisting of reciprocal rods for each facet.^{10,25} The Ewald sphere intersects the reciprocal lattice rods and the diffraction pattern is a projection of that 2D slice of reciprocal space. Figure 1b shows an example of a rectangular crystal and its three dimensional reciprocal space shape. As the figure illustrates, each facet gives rise to a separate reciprocal rod. Its intensity oscillates with a period of one over the distance between the two opposite facets. The length of the rod in the normal direction (R) is inversely proportional to the sharpness of the facet, while the width of the rod (w) parallel to the facet is inversely proportional to the size of the facet. The direction of the rod can be used to determine the Miller indices of the facet, as shown by Ding et al. on platinum tetrahedral nanocrystals.¹⁰ The electron dose used for recording nanoarea electron diffraction patterns is also much smaller than in HRTEM or convergent beam modes²⁶, which reduces the electron beam induced damage to the nanoparticles.

Figure 2 displays a diffraction pattern from a $16 \text{ nm} \times 41 \text{ nm}$ Au nanorod oriented on the $[1\ 1\ 0]$ zone axis. The diffraction pattern shows a well ordered spot pattern indicating the nanorod is single crystalline. The weak diffuse rings in addition to sharp diffraction spots are due to diffraction from amorphous carbon, which is used to support nanorods. Each reflection has a streak pointed in the $(0\ 1\ -1)$ direction in reciprocal space. These $(0\ 1\ -1)$ streaks come from intersection of the Ewald sphere with reciprocal lattice rods of $(0\ 2\ -2)$ planes. The longer length of the streaks indicates a sharp facet. There is no intensity oscillation in the recorded diffraction streaks, which is often observed in coherent diffraction of small nanoparticles. The absence of intensity oscillation indicates that the facet is not atomically sharp. Streaks for $(0\ 0\ 2)$ planes in the $[0\ 0\ 1]$ direction are weakly observed; they are much shorter and broader than those in the $[0\ 1\ -1]$ direction. This indicates the $(0\ 2\ -2)$ facets are sharper than $(0\ 0\ 2)$ facets. The broader streak of $(0\ 0\ 2)$ is due to the small size of this facet. A further demonstration of the facet size effect can be found in the Supporting Information.

The above example demonstrates the principles of nanocrystal facet determination using electron diffraction. While in the simple case of a rod, this information is equivalent to information that would be obtained from a series of TEM images alone, since the shape of rod is convex and its facets can be simply observed by projecting the edges from several orientations. Coherent NED is very powerful for the case where not all the edges and faces can be easily observed.

Figure 3 displays a diffraction pattern from a 44 nm trisoctahedron (TOH) oriented on the $[1\ 1\ 0]$ zone axis, with an inset of $(00\text{-}4)$ to show the streaks more clearly. Around each of the Bragg reflections, we observe 8 strong streaks. In FCC crystals, the direction is normal to the plane of the same index. Therefore, the angle between directions is also the angle between planes. We measure the direction that the streaks were pointing towards by tracing a line from each streak until it intersects a Bragg reflection. In general, we select higher order reflections since the streaks typically point at reflections far from the origin. To determine the direction of these vectors from the origin, the angle between direction vectors is given by Equation 2:

$$\cos(\theta) = \frac{h_1 * h_2 + k_1 * k_2 + l_1 * l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \sqrt{h_2^2 + k_2^2 + l_2^2}} \quad (\text{Eq.2})$$

For example, using the reflection of (3 -3 -1), two streaks pointing to [-1 1 9] and [-6 6 -2] are observed; the directions of these streaks are determined to be [-4 4 10] and [-9 9 -1] by a vector difference, and the angle between these directions is 65.0° (see the Supporting Information for visual traces). Diffraction patterns such as Fig. 3 contains multiple reflections; several reflections may be used to index the complete array of streaks. Table 1 displays the measured angles in the [1 1 0] zone axis from the experimental diffraction pattern.

The 8 streaks observed in the diffraction pattern are normal to high index facets. Some of the angles between these facets cannot be measured from a TEM image, since a TEM image records a projection of atomic planes and only the outer edges can be observed.¹⁹ Figure 4 displays the angles between edge tangential (white text) and plane normals (black text) measured for the image of the TOH particle. The facet directions were measured by determining the angle between edge normal and fundamental directions in the Fourier transform of the image. The error of measuring angles directly from the image is 4% and is primarily due to the facet edges appearing curved in the TEM images. In comparison to the diffraction patterns, two facet indices match ((-4 4 10) and (1 -1 3)). Streak for the (1 -1 0) and (-2 2 -8) facets from the image are not observed in the diffraction pattern. We conclude that either these facets are small and not sharp or we are seeing a cliff like edge in the transmission image where the nanocrystal is concave and the facet is not normal to the beam. Thus the coherent electron diffraction pattern, combined with the image, reveals 3D information about the nanocrystal. The 44 nm TOH geometry is verified through comparison of measured angles (Figure 4) to a computer generated 3-D model with unit edge lengths 1 and $1 + 1/\sqrt{2}$. The corresponding tangential angles are expected to be 117° and the angles between plane normals are predicted at 62.8°.

A larger 101 nm TOH crystal oriented on the [110] zone axis is displayed in Figure 5. There are many more streaks visible in the NED pattern of the larger particle than the smaller particle, which indicates additional facets. We combine the streak directions from multiple reflections to measure additional angles shown in Table 2. The larger TOH crystal corresponds well to a computer generated 3-D model with unit edge lengths $1 + 1/\sqrt{2}$ and $1 + 1/\sqrt{42}$. Figure 6 shows the measurement of angles between normals from the TEM image. We confirm these measurements through comparison to the 3-D model. The outermost tangential angles are ideally 84.8° and the angles between plane normals are expected to be 95.3°. These angles are in close agreement to what we observed with coherent NED but with increased measurement error since the edge sharpness is reduced for larger particles in TEM images. The low index facets could also be measured by acquiring a series of high resolution images; however, in our experiments, the large thickness of the nanocrystal with-structure-directing surfactant on the surface prevented us from observing lattice fringes. The precision in measurement of high index facets is increased in coherent NED compared to TEM imaging.

The measurement of streak length yields additional structural information about each nanoparticle. We calculate the length of each streak in reciprocal space by solving for the camera constant in Equation 3, λL , where R is the number of pixels from a reflection to the origin, and d is a known d spacing for Au for the particular reflection. We then measure the length of the streak R and define 1/R as a facet sharpness parameter.

$$1/R=d/\lambda L \quad (\text{Eq.3})$$

For example, in the rod diffraction pattern of Figure 2, the streak facing $[0\ -2\ 2]$ measured from the reflection $(0\ 0\ -2)$ has a length of 119 pixels and the camera constant is 575 pixels*Å. The facet sharpness parameter is $0.21\ \text{\AA}^{-1}$ or $4.8\ \text{\AA}$.

In the small trisoctahedra in Figure 3, the $[-7\ 7\ 3]$ and $[-4\ 4\ 10]$ facet sharpness parameters are $0.065\ \text{\AA}^{-1}$ and $0.069\ \text{\AA}^{-1}$, respectively for $(0\ 0\ -2)$. The rod is ~3 times sharper than the small trisoctahedra. In comparison to the large trisoctahedra in Figure 5, facet directions of $[-3\ 3\ -1]$ and $[1\ -1\ 5]$ have facet sharpness parameters of $0.11\ \text{\AA}^{-1}$ and $0.054\ \text{\AA}^{-1}$, respectively. The large trisoctahedra shows significant differences in facet sharpness along different facets, which is not is not apparent from the TEM images.

We can also define a facet size parameter, which is the inversely proportional to the width (1/w) of each streak. Thin streaks indicate a larger facet size. For example, high order reflections in the Au rod show thin streaks in the $[0\ 1\ -1]$ direction and wide streaks in the $[0\ 0\ 1]$ direction. $[0\ 1\ -1]$ facets are larger than $[0\ 0\ 1]$ facets. Similarly in the small trisoctahedra in Figure 3, $[-4\ 4\ 10]$ facets are larger than $[-7\ 7\ 3]$ facets. The exact ratio of facet size is difficult to measure in our diffraction patterns due to the large background signal from the carbon substrate. However, the information is helpful for understanding facet sizes of concave nanocrystals. Thinner substrates and magnified diffraction patterns will allow for a more precise measurement.

The higher order reflections are expected to have a shorter streak length due to the small curvature of the Ewald sphere. Additionally, there can be errors in sample mistilt, beam tilt, and projector lens distortion, which affect the length of the streak. A correction factor can be expressed in Equation 4 that accounts for these errors.

$$1/R_{hkl}=c_{hkl} * \frac{d}{\lambda L} \quad (\text{Eq.4})$$

In our analysis, we avoided this correction factor by using the same (002) and equivalent reflections across different diffraction patterns assuming the sample and beam mistilt are small. An accurate measurement of beam tilt, nevertheless, will improve the precision of measurement.

In crystal growth, the fastest growing planes terminate during early stages of growth and slowly growing planes dominate the 3D shape. These slowly growing planes are the lowest energy facets. For macro sized crystals, these facets and their sharpness can be measured physically. For nanocrystals, however, there has not been a precise method to measure the lowest energy facets in nanocrystals with high index facets. The lowest energy facets can change with aging time or synthesis parameters. In the nanorod, the $(0\ 2\ -2)$ facet is the lowest energy due to its large size and large sharpness parameter and the $(0\ 2\ 0)$ facets has higher energy. However in the small trisoctahedra, the $(0\ 2\ -2)$ facet is not the lowest energy facet. The lowest energy facet must take into account the size and sharpness of the facet. The streaks in our diffraction results are nearly the same length; however, four streaks are thinner in width. The diffraction results of the larger trisoctahedra show very different high index facets. These facets are similar in size and sharpness. Our sharpness parameters show that initial TEM characterization of nanoparticles such as cubes and trisoctahedra may suggest relatively sharp corners. Further inspection by coherent electron diffraction, shows that atomic level surface roughness to be very different. These differences are most likely a direct consequence of the different synthetic parameters used for each structure. In the Supporting Information, we show the size dependent diffraction on trisoctahedra of

increasing size, as a result of increased synthesis time. The streaks in the diffraction pattern clearly change with nanocrystal size and shape. Thus, coherent electron diffraction can be used to determine the lowest energy facets of nanocrystals with high index facets.

In summary, coherent NED can measure high index facets and the angles between facets of complex Au nanoparticles. This approach is especially useful for large nanoparticles, in which lattice fringes are not observed in TEM images due to multiple scattering in thick crystals, directions cannot be determined from FFTs of images, and many facets are invisible due to the crystal concavity. We have defined a facet size and sharpness parameter to describe facet shape. This technique can be used to precisely determine the 3D shape of nanoparticles and is accessible in any field emission TEM. These developments enable progress in several fields. The sharpness of facets in nanoparticles plays an important role in molecular enhanced spectroscopies such as surface enhanced Raman scattering (SERS)²⁷ and plasmonic enhanced fluorescence.²² With the electromagnetic fields focused to sharper edges and corners researchers have moved towards utilizing nanoparticles with higher radii of curvature such as cubes and higher index polyhedral.²⁸ Molecules absorbed onto these sharper surfaces, within these focused electric fields could dramatically enhance the observed spectral response. Hence, characterization of the sharpness using the tools here is likely to spur better design and use of nanoparticles for SERS.

Additionally this technique can also be extended to characterize high index polyhedra platinum and palladium nanoparticles.^{29, 30} With great interest in their catalytic properties, many research groups have looked to explore how their surface energies vary with different shapes.³¹ Initial studies have proposed that these differences in surface energy for platinum and palladium nanoparticles are greater than that for gold and silver nanoparticles.³² Hence, a systematic investigation to compare the effect of surface structure on catalysis reactions is warranted and is now possible using NED.

Materials and Methods

Materials

Hydrogen tetrachloride (HAuCl_4 , > 99.999%), sodium borohydride (NaBH_4), and ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, > 99.0%) were obtained from Aldrich and used as received. Cetyltrimethylammonium bromide/chloride (CTAB, > 99%, CTAC > 98%) was obtained from Sigma and used without further purification. All glassware were cleaned using aqua regia and rinsed with Barnstead E-Pure 18 M Ω -cm water.

Instrumentation

Transmission electron micrographs (TEM) images were taken on a 197 kV JEOL JEM2010F Field Emission Microscope with a spherical aberration coefficient (C_s) of 1.0 mm. We used parallel probe sizes of 55 - 120 nm to acquire diffraction from individual nanoparticles. It is important to select a probe size slightly larger than the nanocrystal size so that all facets are sampled. In contrast to SAED, in NED, only the part of the specimen illuminated with the electron beam contributes to the observed diffraction pattern, leading to high signal to background diffraction patterns. Gold nanoparticles were tilted onto a low index zone axis such as [1 1 0] or [0 0 1]. Diffraction patterns were recorded onto image plates. The diffraction patterns were calibrated by collecting patterns of polycrystalline aluminum with known d-spacings using the same conditions as the gold nanoparticles for each experiment. We displayed a cropped section of the diffraction pattern for clarity. However for measurement we used the full diffraction pattern as many streaks pointed to high index reflections beyond the 4th Laue zone. For TEM sample preparation, 10 μL of

gold nanoparticle suspension was drop cast onto holey and lacey carbon TEM grids (Pacific Grid Tech).

Measurement of Diffraction Streaks

The diffraction streaks are traced until the traced lines intersect a Bragg reflection. An experimental error can arise from the precision in tracing the small streaks. Typically the error can be up to 1° to 2° . The experimental error is lower for smaller particles with fewer facets, as the streaks will appear longer and are easier to trace. Generally the diffraction pattern and image are rotated with respect to each other. Thus for large particles, the FFT of an image will not reveal the orientation as the lattice fringes cannot be resolved in thick specimens.

We use a Thermo Scientific Sorvall Legend X1 Centrifuge for purification as detailed in the synthesis below.

Synthesis of seeds for CTAB rods—The nanoparticle seeds were synthesized by modification the method of El Sayed et al.³³ CTAB solution (7.5 mL, 0.1 M) was mixed with 0.25 mL of 0.01 M HAuCl₄. To the stirred solution, 0.6 mL of ice cold newly made 0.01 M NaBH₄ was quickly added, which resulted in a light brown solution. After stirring the solution vigorously for 2 minutes, the solution was kept for 1 hour in room temperature before use.

Synthesis of CTAB seeds for trisoctahedra (TOH)—The nanoparticle seeds were synthesized by following the procedure by El Sayed. et al.³³ CTAB solution (7.0 mL, 75mM) was mixed with 46 μ L of 20 mM HAuCl₄. To the solution, 0.42 mL of ice cold newly made 0.01 M NaBH₄ was quickly added under vigorous mixing and to give a pale brown solution. The solution was used within 2-5 h after the preparation.

Synthesis of CTAB Gold Nanorods—Gold nanorods of aspect ratio 2.5 were synthesized as reported elsewhere.³⁴ To 95 mL of 0.1 M CTAB, 5 mL of HAuCl₄, 0.55 mL of ascorbic acid, and 0.4 mL of AgNO₃ 0.12 mL of seed was added and left overnight. The gold nanorods were purified twice by centrifugation at 8000 RPM for 20 mins.

Synthesis of TOH gold nanoparticles—Trisoctahedra (TOH) nanoparticles were synthesized by a seed mediated method used by Lee et al.²⁰ A 0.125 mL solution of 20 mM HAuCl₄ was mixed with 9 mL of 22 mM cetyltrimethylammonium chloride (CTAC). To this mixture, 3.06 mL of 38.8 mM ascorbic acid was added to make the concentration of ascorbic acid 9.5 mM and was thoroughly mixed. Then, seed) was diluted 100 fold with nanopure water, and 50 μ L of the diluted seed was added to the solution and left overnight. The gold nanoparticles were purified twice by centrifugation at 3381 RCF for 20 mins.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

(a) Schematic diagram of the TEM microscope in nanoarea electron diffraction mode (NED). A coherent, parallel beam of size 50 to 120 nm illuminates a 3D crystal. The beam must be larger than the crystal in order to include all facets. The resulting diffraction pattern is a slice of the Ewald sphere through the reciprocal lattice, producing a 2D diffraction pattern shown. Sharp facets of the reciprocal space which are perpendicular to the beam will appear as streaks in the diffraction pattern. (b) An example of a rectangular crystal with different sized facets showing the 3D reciprocal lattice and the resulting diffraction pattern. The diffraction pattern is used to measure the size of asymmetric facets.

Figure 2.

(a) NED pattern of a nanorod oriented on the $[110]$ zone axis. Well-defined streaks point in the $[0\ 1\ -1]$ direction. (b) Magnified view of $(0\ 2\ -2)$ reflection showing streaks pointing in the $[0\ 1\ -1]$ direction. (c) Image of the nanoprobe on the nanorod. (d) A computer generated image of the nanorod.

Figure 3.

(a) NED pattern of a 44 nm TOH crystal oriented on the $[110]$ zone axis. The streaks are normal to the planes. (b) Magnified view of $(00-4)$ reflection showing streaks measured from this and other reflections. (c) TEM image of the TOH crystal. (d) Computer generated image of the TOH crystal.

Figure 4.

TEM image of a 44 nm TOH gold nanoparticle. The tangents to the faces are drawn and the angles between tangents are shown in white text. The angles between plane normals are 180° minus this angle and are shown in black text. The measurement error arises in drawing lines tangent to the shape edges. The facets are determined by tracing normals to the edges and measuring the angle from fundamental directions in the fast Fourier transform of the image).

Figure 5.

NED pattern of a 101 nm TOH crystal oriented on the $[110]$ zone axis. There are many more streaks compared to the crystal in Figure 3, which indicates additional facets grow. (b) Magnified view of $(-2\ 2\ 0)$ reflection showing streaks measured from this and other reflections. (c) TEM image of the TOH crystal under the nanobeam. (d) Computer generated image of the TOH crystal.

Figure 6. TEM image of a 101 nm TOH gold nanoparticle. The tangents to the faces are drawn and the angles between tangents are shown in white text. The angles between plane normals are 180° minus this angle and are shown in black text.

Table 1

Direction and Angles of Diffraction Streaks for the Small TOH in Figure 3

Reflection	Points to Reflection	Facet Direction	Angle Between Planes	Angle from Image/Calculation	Facets Direction from Image
(3 -3 -1)	(-1 1 9)	[-4 4 10]	65.0°		
	(-6 6 -2)	[-9 9 -1]			
(3 -3 -1)	(-1 1 9)	[-4 4 10]	54.7°	55.4° (54.7°)	[-4 4 10]
	(4 -4 2)	[1 -1 3]			[1 -1 3]
(0 0 -4)	(1 -1 -1)	[1 -1 3]	53.2°		
	(-6 6 12)	[-6 6 16]			
(2 -2 -4)	(-3 3 -5)	[-5 5 -1]	24.9°		
	(-5 5 -1)	[-7 7 3]			
				61° (64.8°)	[1 -1 0]
					[1 -1 3]
				40° (43°)	[1 -1 -3]
					[-2 2 -8]

Table 2

Direction and Angles of Diffraction Streaks for Large TOH in Figure 4

Reflection	Points to Reflection	Facet Direction	Angle Between Planes	Angle from Image
(0 0 -2)	(-3 3 -1)	[-3 3 1]	9.7°	12°
	(-5 5 1)	[-5 5 3]		
(-2 2 0)	(-5 5 5)	[-3 3 5]	24.5°	23°, 27°, or 28°
	(-3 3 5)	[-1 1 5]		
(-2 2 0)	(2 -2 2)	[4 -4 2]	54.7°	
	(-1 1 5)	[1 -1 5]		
(-2 2 0)	(-3 3 5)	[-1 1 5]	31.5°	27°, 28°, 35°, or 36°
	(-1 1 5)	[1 -1 5]		
		[1 -1 5]	82.8°	83°
		[-5 5 3]		
		[-5 5 3]	82.5°	83°
		[-4 -4 2]		
		[-4 -4 2]	94.4°	92° or 96°
		[-3 3 -1]		