Structure and Characterization of Silicon Nanoparticles Produced Using a Vibratory Disc Mill

E. A. Odo¹, D. T. Britton², G. G. Gonfa³ and M. Harting² ¹Department of Physics, Federal University of Technology Akure, Akure, Ondo State, Nigeria ²Department of Physics, University of Cape Town, Rondebosch, Cape Town, South Africa

³Department of Physics, Haramaya University, Dire Dawa, Ethiopia

Nanocrystalline silicon powder was produced by using a vibratory disc mill in a top-down synthesis route from single crystalline silicon wafers and a polycrystalline bulk. The morphology and elemental composition of the produced silicon nanoparticles were investigated using microscopy (SEM and TEM) and energy dispersive x-ray spectroscopy (EDX) techniques. The particles consisted of a wide range of size distributions, ranging from a few faceted particles about $1-3\mu m$ in size to a large number of much rounder particles in the 100nm range. The EDX analysis reveals that the level of contaminants, which may have resulted from reactions with the milling medium, as well as with the atmospheric oxygen, remains insignificant for the duration of the milling process. The structural properties of the produced powder were investigated by means of X-ray diffraction (XRD), electron diffraction and Raman spectroscopy techniques. XRD reveals diffraction patterns with characteristic sharp peaks. It also shows a small broadening of the peaks widths, which may have arisen from a reduction in the powder's grain size and a possible buildup of lattice strain in the particles. Electron diffraction reveals patterns of continuous rings containing discrete reflections spots, which is indicative of a transformation from single crystalline to polycrystalline atomic structures in the case of powder milled from the wafer bulk. Raman spectroscopy study confirms that the milling process did not induce amorphous phases in the produced particle even after 5 hours of milling. This suggests that the milling of silicon from its bulk state with a laboratory disc mill is indeed a viable method of producing nanocrystalline silicon.

1. Introduction

Semiconductor nanoparticles have received much interest recently as a useful class of materials for future optical and electronic devices [1-4]. Their potential for industrial applications is due to their attributed unique properties to quantum confinement effects, which occur when the size of these particles becomes comparable to the excitonic diameter of electron-hole pairs in the bulk semiconductor material [1,5-7]. The realization of visible luminescence as the particles sizes is reduced to 100nm or less has fuelled interest in preparing silicon nanoparticles [4,8]. Free-standing silicon nanoparticles can be produced by either a bottom-up route (usually involving chemical reactions), or a top-down route (involving size reduction of their bulk material) [9, 10]. The route that has been most frequently applied and studied in the past is the former, which is usually achieved from gas-phase decomposition of silanes [1,11]. However, the complexity and the cost of this method of production makes it unprofitable for

commercial production of silicon nanoparticles. In contrast, the top-down synthesis route, usually involving mechanical attrition and chemical etching/lithography, is gaining popularity as a more practical method for the large-scale production of silicon nanoparticles [12-15]. The method most commonly applied in this category is milling, which requires a high energy mechanical impact on the bulk material in a controlled environment to prevent unwanted contaminations [10]. Many reports have suggested that mechanical milling of crystalline materials often results in particles that vary in size and structure, varying from isolated spherical particles to agglomerates of complex structures. Therefore, a major concern associated with this method is the control of resulting physical features, such as the average diameter and morphology of the particles. Another concern is the possible contamination of the processed materials by the milling medium [16,17]. Highenergy milling may also distort the crystalline lattice structure of the produced silicon nanoparticles, which is a problem particularly with the electronic charge transport. Many reported studies on milled silicon powder using electron diffraction and Raman spectroscopy have revealed

^{*}odoalawaye@gmail.com

grain refinement, lattice transformation and amorphorization of the final product [4]. Other possible effect of high energy milling on the produced nano-particles is the mechanical alloying of the primary content with the milling medium [18].

In this paper, we investigate the morphological, elemental and structural properties of two types of silicon nanocrystalline powders. Both types are fabricated by means of a laboratory vibratory disc mill, which produces fine powder of brittle materials by predominately grinding process. The structural properties of the silicon powder produced were studied using X-ray diffraction (XRD), electron diffraction and Raman spectroscopy techniques. The analysis of the results focuses on how the microstructures of the produced particles evolved with increasing milling time.

2. Experimental Procedure

2.1. Materials

Mechanical milling of bulk silicon was achieved by using a Siebtechnik 800W TS1000 laboratory vibratory disc mill equipped with a chrome steel pestle and mortar (Fig. 1) [19]. The mill consists of a vibratory disc unit powered by a three phase electric motor and a clamp placed on one side of the vibrating unit to hold the milling medium in place during the milling process. Two different sets of milling media were used for the milling of two types of bulk silicon. The first set of milling medium (set A) consists of a chrome steel 100ml milling vessel and a pestle (Fig. 1). The second medium (set **B**) consists of a larger 250ml chrome steel mortar with a ring in which the pestle sits (Fig. 1). The two types of milling vessel have a cover lid with a rubber seal to ensure that the milled content did not spill out. In our experiment, the actual milling occurred by predominantly horizontal vibration of the milling medium, which resulted in the material been ground to a fine powder, usually within minutes. For the arrangement in set A, milling occurred from the impact between the pestle and the inner wall of the mortar, crushing any materials trapped in between, while grinding the materials trapped underneath the pestle as the medium was shaken back and forth. In the case of set **B**, crushing occurred between the pestle and the ring's inner wall, and between the ring's outer wall and the mortar inner wall, while grinding of the material occurred underneath the pestle as well as underneath the ring as they move back and forth within the grinding medium.

Two main bulk silicon materials were milled using the laboratory disc mill. The first was a ptype single crystalline boron doped silicon wafers, and the second was a 2503 grade polycrystalline silicon metal provided by Silicon Smelters (PTY) Ltd. Polokwane, South Africa. Table 1 lists the silicon type, crystal orientation and tag names used to label the powders produced in this work.



Fig.1: A Siebtechnik 800W TS1000 laboratory vibratory disc mill, equipped with chrome steel pestle and mortar (set A) and including a milling ring (set B).

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Silicon Type	Dopant	Crystal Orientation	Resistivity	Mass Milled	Tag
Р	Boron	<111>	$2-5\Omega cm$	20g	P*
Metallurgical	Unknown	Polycrystalline	unknown	50g	Μ

2.2. Milling process

The milling of the p-type wafer was carried out using the milling medium set A under the normal laboratory conditions. Five wafers with a total mass of 20g, without any surface treatment, were placed in the mortar and broken into larger fragments by means of the pestle before milling. For the metallurgical grade silicon, 50g of the granules were poured between the pestle and the ring of set **B**. In both cases, the cover lid was then secured by means of the clamp attached to the vibratory disc mill. In the case of the p-type wafer, the milling was carried out for 5 hours and divided into1 hour periods. Each milling period was characterized by the generation of heat within the medium with temperatures reaching $120^{\circ}C$ To prevent excessive heat generation in the medium, each milling period was followed by a five hours period in which the mill was switched off and the milling medium was allowed to cool down to room temperature. A small quantity of the P* powders was taken from the mortar before the start of the next milling period. After the completion of five hours of milling in the case of the wafers and the three hours in the case of the metallurgical silicon, the remaining powder was scooped out of the mortar into different plastic containers and sealed. At a later time, a second batch of metallurgical silicon powder was milled for 5 hours using the same procedure. In this study, powders milled for 1-5 hours are labeled P*1 to P*5, while the metallurgical silicon powders are labeled M*3 and M*5, where the number indicates the milling time in hours.

2.3. Characterization of milled powder

The morphology and the elemental composition of these nanostructured sets of powdered silicon produced above were studied with a Leica Stereoscan S440i scanning electron microscope (SEM). For imaging, the operating beam energy used was 20keV with a probe current of 50-100pA, which gave an estimated resolution for images of about 10nm in secondary electron mode. SEM micrographs of each sample were taken from three different regions at magnifications ranging from relatively low (x10000) to high (x50000) levels. Different areas of the sample were then examined for their elemental compositions with a focus on silicon as the primary constituent, and oxygen, chromium and iron for a possible contamination from the atmosphere and the milling medium. This was achieved by using beam energy of 20keV and a

beam current of 1000pA with a working distance of 25.0mm.

To determine the structural characteristics of milled powders, an X-ray diffraction experiment was carried out on different powders with a Huber G670, Guinier, imaging plate X-ray diffractometer. The diffractometer had a 2θ range of 4-100° and a resolution of 0.05°. The X-ray wavelength used for this diffraction experiment was $\lambda = 1.5405$ Å. First, a background X-ray diffraction was carried out on an empty capillary tube for 15 minutes, after which another 15 minutes diffraction was carried out with similar capillary tubes from the same batch filled with the different powders P*1 to P*5 and M*3. The diffraction data was analyzed with the Origin data plotting and analysis software. First, the correction to X-ray intensity versus diffraction angle data for different powders was carried out by subtracting the background diffraction measurement from the sample measurement. Indexing of the different peaks was done using a lattice parameter constant of a = 0.543nm for silicon.

Transmission electron microscopy (TEM) was performed by means of a LEO 912 transmission electron microscope operating at 120*KeV*. Small quantities of different powders were dispersed in ethanol and sonicated in an ultrasonic bath for 1 hour. This ensured that the clustered lumps were properly broken down into free nanoparticles. Two drops, from each of the different dispersions, were placed with a pipette on holey (porous) carbon coated TEM grids. The electron diffraction study was carried out on selected areas of isolated particles or on clusters of particles suspended across the porous regions of the carbon coated grid.

The Raman spectroscopy measurement was carried out using a DeltaNu (Advantage 532) Raman spectrometer. The spectrometer uses a 532nm (green) solid state laser with a peak power of 200mW and a 35µm diameter focused beam. For this measurement, different powders were filled into small plastic cups which were supplied with the instrument. A multi-pixel CCD array detector with an attached microscope focused on the surface of the sample. The measurement time for both the background and sample measurement was set to 60 seconds, with the background measurement subsequently deducted internally from the real measurement by the instrument's software. Using the Origin software, a Gaussian function was fitted to the experimental data peak to obtain the individual peak centre and full width at half maximum (FWHM) used for performing other analysis similar to that reported in [18].

3.1. Morphology and elemental compositional characteristics

Figs. 2(a)-(e) are micrographs of the powder P*1 to P*5 milled for 1-5 hours. The morphology and size distribution of the particles in powder P*1, after an hour of milling as seen in Fig. 1(a), shows that the powder consisted of particles with a wide range of sizes and two main types of shapes. On the one end of size scale are large faceted particles cleaved along closely packed planes with sizes of $1-3\mu m$, whereas, on the other end are relatively smaller particles with sizes of 100-400nm and having an overall spherical shape. The size distribution, based on a random measurement of 150 particles having clearly defined boundaries along their longest axis, showed a typical log-normal distribution pattern. The smaller and more spherical particles appear to dominate the distribution, as can be seen in the distribution plot (inset of Fig. 1 (a)).

After 2 hours of milling, the resulting powder exhibited a similarly wide size distribution pattern like the powder after 1 hour of milling. A Comparison of the powder from the 2 hours milling with the 1 hour milled powder shows an observable increase in the proportion of the smaller particles in the range of 100-400nm with further milling from 1 - 2 hours (Fig. 2(b), see inset), with the average particle size now shifted towards lower numbers. Further milling of the powder up to 5 hours (Fig. 2(c)-(e)) shows a progressive increase in the proportion of relatively smaller particles resulting from a consistent reduction of the larger faceted particles due to further attrition with milling time. Also worth mentioning is the presence of agglomeration of the smaller particles into bigger clusters.

Fig. 2(f) is a micrograph of the metallurgical grade silicon after it has been milled for 3 hours (M*3). It has a similar size distribution as the P*3

powder produced from the wafer. Unlike the P*3 powder that has large faceted particles, however, the larger particles in this case appears to be more spherical with smoother surfaces.

Similar analysis using TEM confirms the characteristic morphology of the produced powder as described for the SEM study. A closer look up at a larger grain and higher magnification of Fig. 3 shows darker areas either overlaying or embedded in the particle (the areas indicated in the dotted circle). This may be the result of either the agglomeration and compacting of small particles into relatively bigger clusters due to the hammering process in the mill, or the result of deformation of particle, thus giving rise to stacks of crystallites with planes of orientation different from those of the initial material [19].

Fig. 4 shows the plot of the spectra intensity versus X-ray energy on a semi-log scale for the EDX analysis carried out for powder P*5. From the spectra, it can be seen that silicon at $K_{\alpha} = 1.739 KeV$ is clearly the dominant element in the powder at about 95a.t.%, with oxygen at $K_{\alpha} = 0.525 KeV$, iron at $K_{\alpha} = 6.398 KeV$ and chromium at $K_{\alpha} = 5.40 \text{KeV}$ constituting only of trace amounts in the powder. No clear peak was found at the different energy positions indicated by the arrows corresponding to the energy levels for the possible contaminants. Similar elemental characteristics were observed for other powders, P*1 to P*4, indicating that the contamination from the milling medium and possible atmospheric oxidation due to the milling process were minimal. The observed peaks for copper and aluminum may have resulted from the detector coil and the aluminum sample holder of the instrument, respectively, while the source of the calcium is not known.



Fig.2: SEM micrographs of milled wafer silicon powder after: (a) 1 hour; (b) 2 hours; (c) 3 hours (d); 4 hours; and (e) 5 hours milling consisting of larger faceted fragments and smaller more rounder particle appearing as clusters. The average cross-section size decreases with increasing milling time. Fig 2(f): A 3 hours milled metallurgical silicon shows a rounder shape d particle for both bigger and smaller clustered particles.



Fig.3: TEM micrograph of a single large grain showing either an agglomeration of smaller particles or a possible stacking of re-oriented crystallites.



Fig.4: EDX plot of spectra intensity versus X-ray energy for powder P*5 on semi-log scale, showing silicon at $K_{\alpha} = 1.739 KeV$ as the dominant element, with possible contaminants like oxygen, chromium and iron appearing in trace amount.

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3.2. X-ray diffraction powder characteristics

Fig. 5(a) shows the X-ray diffraction pattern for powder P*3 after background subtraction. Seven basic diffraction peaks, corresponding to reflections from the planes (111), (220), (311), (400), (331), (422) and (511) of a typical polycrystalline silicon can be identified, with the most intense peak being the (111) reflection. Other phases that may occur as a result of contaminating elements from the milling medium and oxidation from the atmosphere were below the detection limit of the instrument. Similar diffraction patterns were observed for powders P*1, P*2, P*4 and P*5. The diffraction patterns in all the P* powders are characterized by sharp peaks, which is an indication of the high crystallinity of the resulting milled powders. There is also a small broadening of the different peaks width, which may be due to the buildup of lattice strain, or due to the reduced grain sizes of the silicon particles in the powders [20]. A similar plot for the milled metallurgical grade powder M*3, as seen in Fig. 5(b), exhibited characteristics similar to those shown for the P*3 milled wafer.



Fig.5: X-ray diffraction patterns after background subtraction for (a) milled wafer P*3and (b) milled metallurgical silicon M*3 milled for 3 hours respectively, using the laboratory disc mill. The diffractions in both cases show 7 sharp peaks that are usually associated with polycrystalline silicon. These and the absence of a broad hump are indicative of high crystallinity of the two powders.

Figs. 6(a) and (b) are separate plots of (111) peak for P*5 and M*3 powders (the longest milled powders at the time of this experiment), respectively. From the plots, a characteristic small broadening of the peaks around the peak center $2\theta = 28.29^{\circ}$ is evident. There was no noticeable broad hump $(>2^{\circ})$, which is usually interpreted as an indication of the presence of an amorphous phase alongside the (111) peaks in both cases [21]. Similar broadening of the diffraction peaks widths has been reported by Diaz-Guerra et al. [8] for powder produced via mechanical milling of p-type silicon wafers in a Spex-8000 mixer-mill for up to 50 hours. The broadening of the Bragg peaks has been attributed to the refinement of the microstructure, resulting from plastic deformation of the lattice structure that is experienced during the processing of the nanoparticles [8]. In many cases, a structural transformation occurs from the single crystalline bulk to the polycrystalline silicon

nanoparticles. For a few other cases, there may be an amorphous surface with a crystalline core silicon resulting from such high energy milling and another phase [22]. The small broadening of the diffraction peaks for milling time up to 5 hours in the case of the milled wafers, and 3 hours for the metallurgical powder as observed in this study, may be attributed to a reduction in grain sizes or the results of induced lattice strain as mentioned above or both.

The Scherrer equation was used to determine the evolution of crystallites as measured by the average grain size of the powder with the progression of milling time. The Scherrer equation relates the peak broadening represented by the full width at half maximum in radian (β_{FWHM}) to the average grain size of a powder [23] as: The African Review of Physics (2012) 7:0007

$$t = \frac{K\lambda}{\beta\cos\theta_{\beta}} \tag{1}$$

Where, t is the coherent scattering length (crystallite size), θ_{β} is the Bragg angle, and K is a constant that depends on both apparatus and the sample studied. It is usually taken between 1.0 < K < 1.3 when an integral width is used and

K = 0.9 when a Gaussian function (rather than a triangle function) is used to describe the peak width. The application of the Scherrer equation in this work assumes that that the peak broadening is caused only due to size reduction with no strain contributions and that instrumental broadening has been corrected for [24, 25].



Fig.6: A Gaussian function fit to the (111) peak for (a) P*5 with a small peak width broadening, $\beta = 0.26^{\circ}$, and for (b) M*3, with $\beta = 0.33^{\circ}$ with no indication of a broad hump respectively, which is suggestive of the absence of an amorphous phase.

Taking K = 0.9 for a Gaussian function and $\lambda = 0.154nm$, the X-ray wavelength for this study, the values of the crystallite sizes were deduced from fitting a Gaussian function to the (111) peaks after correcting for instrumental broadening for P*1 to P*5 powders. The deduced crystallite sizes were observed to decrease in value as the milling progresses. Assuming that all broadening is due to

size effects, Table 2 shows the calculated crystallite sizes for powders P*1 to P*5 as well as for M*3 powders. The calculated crystallite size values are all lower than 100*nm* range for which Eqn. 1 is valid. The dependence of the crystallite size on milling time is shown in Fig. 7.

Table 2: Calculated crystallite sizes derived from fitting a Gaussian function to the (111) peak of the different powders using Sherrer's method after correction for instrumental broadening

Powder Type	P*1	P*2	P*3	P*4	P*5	M3
Sherrer's Crystallite size (nm)	39.66	37.59	36.11	36.27	34.64	25.68

The plot indicates a first order exponential reduction in crystallite sizes with milling time. The study of size distribution using SEM and TEM reported above indicated that the particles had an average particle size of 126*nm*. The crystallite sizes derived here indicated that these particles were indeed polycrystalline with two levels of

nanostructure; firstly as crystallites constituent in the nanometer range and secondly as whole grain nanoparticles. A Comparson of the average crystallites size of P*5 powder with that of M*3 powder shows that the calculated crystallite sizes for M*3 powder were much smaller. This suggests a difference in the manner in which grain or crystallite formation propagates in the two powders.



Fig.7: The dependence of the calculated crystallite size from the (111) peak using Sherrer's method on milling time for the milled wafer P*1 to P*5 showing a good fit to a first order exponential decay function.

3.3. Transmission electron diffraction powder characteristics

Figs. 8.(a)-(e) show the selected area electron diffractions for the regions indicated by circles as shown in the insets for P*1 to P*5 powders. The diffraction patterns for all powders consisted of continuous rings with discrete reflections spots. Since the diffraction was carried out on an isolated and clearly defined particle, it is reasonable that this diffraction pattern may have resulted from a polycrystalline particle. This suggests that particles derived originally from single crystalline wafers had been induced with crystallites oriented in different preferred directions. The electron diffraction pattern for M*3 silicon powder (not shown) exhibited a similar ring structure typical of polycrystalline silicon.

Fig. 9(a) shows the area isolated for diffraction on the sample from P*5 powder. As mentioned earlier, this image shows possible crystallite as embedded grains (marked with dashed boundaries), suggesting that the milling process had indeed refined the microstructure of the starting materials due to dislocation of grains in the particles induced by the high energy milling. This finding is in agreement with the X-ray experiment from which a crystallite size of $\approx 44nm$ was estimated.

Indexing of the diffraction patterns was carried out by using the JECP/PCED Polycrystalline Electron Diffraction software version 8.0 described in [26,27]. The first 7 rings of the diffraction pattern were compared with a simulated diffraction ring pattern of polycrystalline silicon in the software library. Fig. 9(b) shows the identification of major planes associated with the polycrystalline silicon for P*5 silicon powder, which is a proof that the final powder had indeed undergone significant transformation. The absence of a diffuse rings structure further strengthens the suggestion that amorphorization of the powder due to the milling process did not occur.



Fig.8: Electron diffraction pattern showing concentric rings in the zero order Laue zone with discrete spots indicative of a transformation from an initial single crystal of the feedstock to a polycrystalline material for the samples from P*1 to P*5. The inset shows the area where the selected area diffraction was carried out for (a) P*1, (b) P*2, (c) P*3, (d) P*4, (e) P*5.



Fig.9: (a) Magnified image of the area isolated for diffraction of P*5 powder showing a possible clustering or smaller grains or crystallite oriented in different directions. (b) Phase identification for the P*5 electron diffraction pattern using the JECP/PCED polycrystalline electron diffraction software.

3.4. Raman spectroscopy powder characteristics

Fig. 10 shows the plot of spectra intensities versus wave-number from Raman spectroscopy measurement for each powder from P*1 to P*5 and for the surface of a silicon wafer (topmost plot), taken from the same batch as those of the milled powders. Three main peaks, as indicated by the vertical lines, can be clearly identified from these plots. The first two prominent peaks at 520cm⁻¹ and $880-1000cm^{-1}$ may be associated with crystalline silicon, having a face centered cubic (fcc) diamond structure [18], and with the symmetric/antisymmetric vibrational modes of the oxide phase of silicon, respectively [28]. Similarly, the peak at about $1396-1414cm^{-1}$ can be attributed to the stretching vibrations of a double bond oxide phase [29]. It is interesting to note from these plots that almost all the peaks observed for different milled powders are also present for the silicon wafer (feedstock). This suggests that the milling process has not introduced a marked change in either the structure or the composition of the silicon.

Fig. 11 shows an extract from the Fig. 10 plots covering wave-number regions normally associated with the amorphous $(480cm^{-1})$, as well as the crystalline $(520cm^{-1})$ phases of the P*1 to P*5 powders. Also shown for the sake of comparison is the plot for feedstock (topmost plot). From these plots, the position of the peak center (a measure of the crystallinity of the silicon nanoparticles) is observed to shift toward the lower wave-number region, as milling time increases. By fitting a

Gaussian function to each of these peaks using Origin software, the peak centre and the FWHM could be determined. The peak center position for the wafer was $521.43cm^{-1}$ and it was taken as a reference for quantifying a different peak's left shift in this study. Fig. 12 shows the manner in which these center positions are shifted to lower wave-numbers with increasing milling time. The pattern fit fairly well with a first order exponential decay function.



Fig.10: Raman spectra from powder P*1 to P*5 as well as from a wafer sample taken from the same batch as those of the powder for comparison. The different spectra peaks present in the wafer sample can also be seen in all the milled powder, indicating that the milling process had not cause a severe change in structure or composition of the milled powder.

In a typical Raman plot for silicon, the amorphous silicon phase produced a broad peak centered

between $470-480cm^{-1}$ [18]; the presence of nanocrystalline silicon phase usually resulted in an asymmetric peak with centre at $520cm^{-1}$ [30]. From the spectra of the different P* powder shown, only the measured $521\pm10cm^{-1}$ peak associated with the optical-phonon frequency of silicon can be clearly identified. The absence of an amorphous peak shows that the milling process applied in this work introduced no amorphorization to the structure of produced nanoparticles. The increasing broadening of the observed peaks in the crystalline region with milling time and the asymmetry about the central peak position for each milling time was proof of the presence of nanometer size crystallite in the powder. A similar frequency down-shift and the broadening of $520\pm 2cm^{-1}$ peak for silicon, has been reported by many workers [31-34]. The Raman scattering line shift and the shape broadening has also been shown to be related with the crystallite size reduction by some workers. In particular, decreasing crystallite size of nanocrystalline silicon below 10nm has been explained in term of a phonon confinement model [35].



Fig.11: A comparison of the Raman spectra from the wafer sample with those from the powder P*1 to P*5 in the wave-number regions where the amorphous phase as well as the crystalline phase of silicon can be observed. With the center of the wafer taken as reference, the peak centers for the powder are observed to shift continuously to the lower wave-number (left) with increasing milling time.

An examination of the Raman plots of the bulk metallurgical silicon and of the M*5 siliconpowders shows a similar pattern as those reported for the p-type powders above. A comparison of these plots in the regions defined as the crystalline phase and the amorphous phase, as shown in Fig. 13, reveals a marked left shift in the central peak position of the M5 powder by $\approx 10cm^{-1}$, from the reference bulk metallurgical silicon. This shift here is comparable to the peak shift observed for the milled wafer.

By comparing the plots of the bulk metallurgical Silicon and the milled powder in the region $470-480cm^{-1}$ as shown in Fig. 13, a pronounced amorphous peak at about $475 cm^{-1}$ was observed for M*5 silicon powder, shown clearly in the re-plot in Fig. 14. An indication of such phase around the same region can also be seen upon a closer look at the plot for the bulk metallurgical silicon in Fig. 13. This shows that the metallurgical silicon bulk may contain an intrinsic fraction of the amorphous phase, which is further propagated by the induced plastic deformation resulting from the milling process. To estimate the crystalline fraction for the M*5 milled silicon powder from a Gaussian fit to the peak, the following equation was used [36].

$$X_{c} = \frac{I_{c}}{I_{c} = \gamma I_{a}}$$
(2)

In Eqn. (2), I_a and I_c are the amorphous and crystalline areas of the de-convoluted Raman spectra, and $\gamma = 0.8$ is a correction factor due to the different scattering cross-sections of the amorphous and crystalline phases [36]. The calculated crystalline fraction for M*5 silicon powder is $X_c = 96.6\%$. This level of crystallinity is very high and it suggests that the induced amorphorization of the metallurgical silicon powders as a result of the milling process after 5 hours is very small. The consequence of the structural transformation on the electrical property of this material may therefore be negligible.



Fig.12: The dependence of the crystalline center wavenumber $520 cm^{-1}$ left shift with increasing milling time is seen to fits fairly well to a first order exponential decay function.



Fig.13: A comparison of the Raman spectrum from the bulk metallurgical silicon and M*5 powder in the region of the amorphous $480cm^{-1}$ and crystalline $520cm^{-1}$ phases indicated with the broken lines suggests the presence of a small hump at about $475cm^{-1}$ in both the bulk and powder. This suggests an intrinsic level of amorphous phase present in the metallurgical silicon grade.



Fig. 14: Gaussian fit to the spectral region defined by the crystalline and the amorphous phase for the M*5 milled powder. The pronounced hump at wave-number $475 cm^{-1}$ indicates the presence of an amorphous phase and constitutes only about 4%.

4. Conclusion

In this study, a laboratory disc mill was used as a top-down production route for the fabrication of silicon nanoparticles from a single crystalline state as well as from a polycrystalline bulk state. The silicon nanoparticles powders produced showed a continuous reduction of particle size with milling time. In the case of powder from a single crystalline bulk (i.e. the wafers), the process started with cleavage along its main crystal orientation followed by attrition of the edges of the particles as they became smaller. In the case of powders from the polycrystalline bulk, the reduction process appeared to be due to attrition only. In general, the produced powders irrespective of the starting bulk materials were composed of an agglomeration of smaller particles resulting in bigger clusters. The effect of milling time on the contaminant level was negligible. Structural characterization using XRD revealed that the resulting powders from both bulk types had major structural change induced by heavy plastic deformation resulting from this process. While the resulting particles may themselves fall within the 100nm range, the broadening of the different peaks confirms the presence of crystallite of size $\approx 44nm$. A selected area electron diffraction study of these powders, and particularly of those from the milled wafer, confirms that structural transformation had indeed occurred from the single crystalline arrangement in the bulk material to polycrystalline structured silicon nanoparticles in the final powders.

Raman spectroscopy of the powders furthermore revealed a left shift in the peak positions towards a lower wave-number when compared with the peaks from the starting materials. A broadening of the FWHM of the crystalline peak region was also observed. These effects are the result of a continuous refinement of the microstructure with increasing milling time. The Raman spectroscopy analysis also shows that no amorphorization resulted in the case of milled P* powder and that a small fraction of an amorphous phase observed in the metallurgical powder was in fact intrinsic to the bulk.

It is, therefore, reasonable to conclude that the process of top-down milling of silicon using the vibratory disc mill is a viable method of producing silicon nanoparticles as theses remain highly crystalline for the entire milling period.

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