Diamond Coated Wire Cutting of Solar Si Ingots: New Insights Using Raman Microspectroscopy

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Diamond Coated Wire Cutting of Solar Si Ingots: New Insights Using Raman Microspectroscopy

by

Junting Yang

A thesis presented to the School of Engineering of Washington University in St. Louis in partial fulfillment of the requirements for the degree of Master of Science

August 2015

Saint Louis, Missouri
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List of Abbreviations

DCW = Diamond Coated Wire

Id/Ig = Height intensity ratio of D band and G band

FWHM = Full-width half max

Depth of focus = D.O.F
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Juting Yang

Washington University in St. Louis

August 2015
Dedicated to my parents.

Love you forever. I want to dedicate this thesis to my lovely parents (Sen Yang and Qi Sun) for believing, supporting, and always being there for me.
ABSTRACT
Diamond Coated Wire Cutting of Solar Si Ingots: New Insights Using Raman Microspectroscopy
by
Junting Yang
Master of Science in Materials Science
Washington University in St. Louis, 2015
Research Advisor: Professor Parag Banerjee

Diamond embedded abrasive wire (henceforth called diamond wire) sawing process of Si is a highly efficient technique for rapid wafering of solar Si ingots. However, the root causes for cutting efficiency losses are unknown. One approach to understanding this complex process is to study 1) diamond particles on diamond coated wire (DCW) and 2) Si swarf collected during cutting process. In this thesis, we use confocal, micro Raman spectroscopy to unravel loss mechanisms of wafer sawing efficiency.

In the first part, we analyze the diamond microparticles which perform the sawing. By analyzing the phase transformation and stress distribution on single diamond particle, graphitization (i.e. softening of diamond) and residual stresses are observed.

By studying the individual Si particles (swarf), correlations between particle shape and phase is established. Fibrillar Si particles are found to be amorphous – indicative of a ductile cut; while spherical Si articles are crystalline – indicative of a brittle cut. This important find helps to quantify the rates of cutting efficiency by simply measuring the entire Si swarf cluster; its phase distribution and stress change, as a function of Si swarf extraction time during the cutting process.
Chapter 1

Introduction

1.1 Motivation

Solar cell manufacturing industry has grown since the early 1980s as crystalline silicon modules have become economically cheaper to fabricate. The solar silicon manufacturing process is shown in Figure 1.1. To obtain ever lower costs on a panel, researchers are trying to improve several processes, such as crystal growth, wafer slicing, and module manufacturing. [1]

In wafer slicing process, cost reduction is obtained by both the cutting losses (kerf loss), and by minimizing the damage of wafer after slicing. In the 1990s, slurry wire sawing was first applied on slicing Si ingot into wafers. In the slurry wire sawing process, slurry contains liquid and abrasive particles, with steel wires as cutting tools. [2, 3] To enhance the cutting efficiency and optimize the performance of wafer, fixed diamond wire cutting process was invented, which is a highly efficient technique for rapid wafering of solar Si ingots. [4] In the fixed diamond cutting, micro-size diamonds, which are fixed on cutting wire, were substituted for loose abrasive particles in slurry, while cooling liquid was used instead of slurry liquid. Compared with slurry wire sawing, there are several advantages in fixed diamond cutting wire such as lower wear of steel wire, higher cutting speed, and lower kerf loss when slicing wafers. [3, 5, 6]

However, there are several problems occurring in diamond coated wire (DCW) slicing process, such as losses of abrasive diamonds, change in property and structure of diamonds after cutting, and
nonuniform quality of wafers. This thesis will address these unknowns. Before understanding the reason of efficiency reduction on DCW, wafer machining mechanism will be introduced in the following section.

Figure 1.1 Silicon manufacturing process in solar industry. [I]
1.2 Wafer Machining Mechanism

The process of diamond coated wire sawing is shown in Figure 1.2. Figure 1.2 a), a spool of DCWs is interlaced through the cutting grooves, while the silicon ingot moves down as the DCW moves at velocities ~ 10 m/sec in and out of the plane of the figure. An optical micrograph of the DCW is also shown. Figure 1.2 b) shows the cross section of the cutting groove between two would-be wafers. There are two types of machining modes, brittle and ductile mode. Brittle machining mode occurred rapidly in Region ‘A’ in Figure 1.2 a), while ductile mode of machining occurred in Region ‘B’, leading to a smoother surface finish of the final wafer. Based on the analysis, the stochastic nature of the process can be appreciated by recognizing that every diamond micro particle spends some time 1) removing material along the cut direction within the ingot slot (Region ‘A’, 2) scratching the surface of the would-be wafer (Region ‘B’ or 3) not participating in the cutting process at all. Depending on the state of the diamond, brittle fractures may result in removal of Si particle or ductile shavings may be produced. Brittle fractures are preferable for faster cutting, while ductile removal of material will provide smoother Si wafer surfaces. The effect of additional tool and machining parameters such as diamond tool shape, crystalline orientation, temperature and pressure on the cutting of Si also have influence on cutting process.[7-9]

Based on the above analysis, to understand the reason of slicing efficiency loss, both the sawing tool input (i.e. DCW) and materials output (i.e. kerf loss or Si swarf) should be studied. Raman spectroscopy is suitable to study DCW and Si swarf. The reason and mechanism of Raman spectroscopy will be illustrated in the next section.
Figure 1.2 (a) Diamond wire sawing set up shows a spool of diamond wire interlaced through the cutting grooves. (b) Cross section of the cutting groove between two would-be wafers. The single diamond wire is moving inside the plane of the paper (defined by symbol ‘⊗’).

1.3 Mechanism of Raman Spectroscopy

Raman spectroscopy is non-destructive, and does not require sample preparation or a vacuum chamber for analysis. Furthermore, with higher resolution (i.e. small laser spot size and depth of focus (D.O.F)), Raman spectroscopy is suitable to study the slight property and structure change of materials. Si and the allotropes of carbon – diamond (sp$^3$ bonded) and graphite (sp$^2$ bonded), are the classic examples of materials studied using Raman spectroscopy. Any changes to the bonding environment (sp$^3$ → sp$^2$) can easily be detected by Raman.

The mechanism of Raman spectroscopy is based on Raman scattering of monochromatic light, such as a laser source. When applying radiation, photons are scattered from molecule, with two types of scattering. One is Rayleigh scattering, and the other is Raman scattering. As shown in Figure 1.3, most of the molecules are scattered with the same frequency as the incident ones, which is defined
as Rayleigh scattering. A very small fraction of the scattered molecules shows a different frequency, which is defined as Raman scattering. By detecting the Raman scattering light, Raman spectroscopy can be used as a technique to monitor bond vibrations in a material [10].

Raman spectroscopy contains four parts, excitation source, sample illumination system, filter, and detector. Figure 1.4 shows the schematic of Raman spectroscopy. The laser with wavelength range from 532 nm to 785 nm is used in Raman spectroscopy. [12]. Detector is used to record the intensity of Raman scattering, and the intensity will be normalized by Raman peak. Materials have their own Raman peak positions, which means that Raman peak position can be defined as fingerprint of a specific material. To focus the laser source, convex lens are applied, with depth of focus (D.O.F) and laser spot size changing with different excitation source. D.O.F and laser spot size can be calculated by Equation 1.1 and 1.2, respectively.[13]
\[ D.O.F \approx \frac{4\lambda}{N.A^2} \]  \hspace{1cm} (1.1)

\[ d_0 \approx \frac{1.22\lambda}{N.A} \]  \hspace{1cm} (1.2)

Where, \( \lambda \) is wavelength of excitation source, and N.A. is numerical aperture of the microscope objective being used.

![Figure 1.4 Schematic of Raman spectroscopy. [14]](image)

In this thesis, Renishaw InVia micro-Raman confocal spectrometer was used, as shown in Figure 1.5.
The thesis contains the following three parts. **Chapter Two** introduces the materials and methods. By using Raman spectroscopy, materials, including diamond particles on DCW and Si swarf collected from kerf loss, are studied. In **Chapter Three**, phase transformation and stress distribution of the single diamond particles are analyzed by Raman spectroscopy. In **Chapter Four**, both the individual Si particles and Si swarf clusters are studied using Raman spectroscopy. In the study of individual Si particles, the relation between Si morphology and Si phase is analyzed. Furthermore, stress distribution and wafer machining mechanism are also illustrated. In the study of Si swarf cluster, we focus on Si phase and stress distribution at different cutting periods (beginning and end of the cut process), which can be used to predict the gradual change (i.e., rates) in Si phase and stress as a function of time.
Chapter 2

Materials and Experiment

2.1 Diamond Coated Wires (DCWs)

2.1.1 Materials

Fresh and used DCWs were obtained from SunEdison Inc. The cutting wires were made of stainless steel 100 µm in diameter, with micro-size diamonds at high density covering the surface. Diamond particles were embedded using a Ni electroplating process [15]. Diamond particles on a fresh wire were initially coated under the Ni film and then exposed during the cutting process. The DCWs are tens of kilometers long, rolled into large spools (Figure 1.2 a). Therefore, to define samples from the cutting spool, the position on the cutting wire measured as the wire length from the start of the spool to the cutting position on the wire was used. 2 km cutting wires were studied.

2.1.2 Experimental Section

Due to its sensitivity to carbon materials and high spatial resolution, micro-Raman spectrometry is particularly suited in analyzing the property and structure of the individual diamonds[16]. A Renishaw InVia micro-Raman confocal spectrometer was used, as shown in Figure 1.5. Laser excitation at 514 nm (power = 1.175 mW/cm²) and 785 nm (power = 2.467 mW/cm²) were applied, with laser spot size of 0.83 µm and 1.3 µm in diameter, respectively. An objective of 50X was used to collect data resulting in a numerical aperture (NA) of 0.75. Scans were conducted from 100 cm⁻¹
to 3200 cm\(^{-1}\). The exposure time for every scan was 10 seconds. Every scan was integrated once. The grating used was 1800 lines/mm and 1200 lines/mm for 514 and 785 nm laser sources, respectively.

2.2 Si Swarf

2.2.1 Materials

Si swarf solution was obtained from SunEdison Inc. Both Si wafers and swarf were produced by DCWs after wafer cutting process. Si swarf was mixed in cooling liquid, which contained water and surfactant.

2.2.2 Experimental Section

To separate Si swarf from cooling liquid, the mixed solution was centrifuged at 8000 rpm for 10 min.

1. Individual Si particles

In order to obtain the individual Si particles, 0.0010 g Si swarf was dispersed into 10 mL ethanol. After sonicating for 5 min, 10\(\mu\)L of this diluted solution was drop-casted on glass, which has been covered with Al foil.

Scanning electron microscope (SEM) was used to study the morphology of individual Si particles. To further understand the property and structure of Si swarf, a Renishaw InVia micro-Raman confocal spectrometer was carried out with laser excitation at 514 nm (power = 1.175 mW/cm\(^2\)). An objective of 50X was used to collect data, resulting in a numerical aperture (NA) of 0.75, with the laser spot size of 0.83 \(\mu\)m. Scans were conducted from 100 cm\(^{-1}\) to 600 cm\(^{-1}\). The exposure time for every scan was 10 min. Every scan was integrated once, with grating of 1800 lines/mm.
2. Si swarf cluster

Si swarf produced by diamond coated wire (DCW) sawing at the beginning and end of the cutting process was collected, respectively. The beginning process (beginning) is defined as when diamond wire moves into Si ingot 20 mm, while the end process (end) is cutting into the ingot with a depth of 150 mm. Si swarf powder was tested at room temperature with a Renishaw InVia Raman spectrometer, with 514-nm excitation source. An objective of 20X was used to collect data, with exposure time 20s. To further detect signal from diamond, map scanning of Raman spectrometer was applied. Area map with 48 scans was conducted on each cutting process, including the beginning and end.
Chapter 3

Raman Study on Single Diamond Particles

In this chapter, we focused on single diamond particles used for Si wafering. Raman spectroscopy was carried out to study phase transformation on the cutting face of a diamond particle. Further, diamond Raman peak shifts were also observed and studied on the diamond particles, which maintained their diamond crystal structure. Based on the Raman peak shift, stress distribution was analyzed during wafer machining process.

3.1 Nature of the Graphitic Phase in Diamond Particles

3.1.1 Raman spectra of diamond on DCWs

Figure 3.1 a) shows Scanning Electron Microscope (SEM) image of diamond particles on DCW. Diamond particles are observed in red circles in Figure 3.1 a), while diamonds are dislodged from DCW or embedded in unexposed shell in green circles. Figure 3.1 b) shows the cross section of DCW.

Figure 3.2 a) shows a confocal image of the diamond particle obtained from the cutting wire at 2 km length under the InVia Raman microscope at a magnification of 50X. The particle is ~ 20 µm in diameter. For taking the spectra, the tip of the diamond is in focus while the region below the tip is out of focus. Later, we will describe confocal Raman measurements, which profile the diamond along the vertical z-direction.
Figure 3.1 (a) SEM image of diamond particles. (b) Optical micrograph of cross section of DCW (courtesy Flores Lab).

Figure 3.2 b) shows the Raman spectra obtained from spot ‘1’. The laser used is 514 nm unless otherwise stated. A clear diamond peak is shown, centered at 1332 cm\(^{-1}\). This is related to the T\(_{2g}\) symmetric vibration of the sp\(^3\) carbon bond.[17] The peak at 2060 cm\(^{-1}\) is ascribed to the N\(_2\) photoluminescence (from air). Another broad peak at 2450 cm\(^{-1}\) is also noticeable and is attributed to the second-order Raman of diamond which is 250 times weaker than its primary, 1332 cm\(^{-1}\) peak.[18].

The full-width half max (FWHM) of the diamond micro particle was found to be 7 cm\(^{-1}\). Single crystal diamonds have been shown to have a FWHM of 3 cm\(^{-1}\). Chemical vapor deposited diamond films are known to show larger FWHM (9 cm\(^{-1}\)) [19]. Increase in FWHM is speculated to occur due to internal strains or polycrystallinity in diamond.
Figure 3.2 (a) Image of diamond focused on the tip of the particle through the confocal microscope (b) Raman spectra taken from spot ‘1’. ⊙ = diamond $T_{2g}$ peak and $\nabla$ = N$_2$ photoluminescence peak, ♦ = second-order peak for diamond (c) Raman spectra taken from spot 2 showing the graphitic nature of the localized region.

Raman spectra measured from spot ‘2’, however, is completely different. Figure 3.2 c) shows the presence of two broad peaks. The primary peaks are centered at 1350 cm$^{-1}$ and 1597 cm$^{-1}$. These are assigned the classic D band [20] and G band [21] for graphitic carbon, respectively.

The D band is induced by defects in graphite, while the G band in graphitic materials is due to the $E_{2g}$ Raman active mode for sp$^2$ carbon [22]. The D band can be influenced by the remnant diamond
phase (located at 1332 cm$^{-1}$) physically present around the graphitic phase. Further, we note that the G band is blue shifted from 1580 cm$^{-1}$ to 1597 cm$^{-1}$ and is attributed to the nanocrystalline graphite as will be discussed in the next section [16, 23]. Additional peaks noted are the G’ peak at 2700 cm$^{-1}$ and the D+G combination mode near 2945 cm$^{-1}$, both of which are attributed to defects. [24]

Interestingly from Figure 3.2 c), a Si TO peak at 520 cm$^{-1}$ was also observed. We note that the presence of Si was not found on fresh, uncut diamond particles (data not shown in this thesis). This shows that the graphitic phase is a result of the cutting process and not inherently present in the uncut diamond micro particle. Further, the Si tends to stick to the soft graphitic phase during the cutting process. No evidence of SiC was found in any of the Raman tests conducted.

### 3.1.2 Phase transformation of diamond on DCWs

We propose that the graphitic phase observed in diamond micro particles is nanocrystalline in nature. Several pieces of evidence support this claim. First, evidence of formation of the nanocrystalline graphite is obtained by observing the full width at half maximum (FWHM) of the D band. It is noted that FWHM of D band for amorphous carbon materials is between 200 and 300 cm$^{-1}$. [25, 26] On the other hand, single crystal graphite has a FWHM of 15 cm$^{-1}$. [27] In our experimental results (Figure 3.2 c)), the FWHMs of D band is 107.4 cm$^{-1}$, which is in between the FWHM of amorphous and single crystalline states.

Second, the dispersion of the D and G bands are studied as a function of two laser wavelengths – 514 nm and 785 nm. This information is provided in Figure 3.3 and Table 1. The peak positions are obtained by fitting two Lorentzian peak fitting functions to the D and G bands. As stated previously, the 514 nm laser results in the D and G bands to be positioned 1350 cm$^{-1}$ and 1597 cm$^{-1}$, respectively. For the 785 nm laser, the D and G bands are observed to be at 1314 cm$^{-1}$ and 1597 cm$^{-1}$, respectively.
Thus, the D band red-shifts by 36 cm\(^{-1}\). The behavior of D band red-shifting is in accord with the observation by several researchers, who predict dispersion behavior in nanocrystalline graphite of the D band at the rate of 40 to 50 cm\(^{-1}\)/eV. [16, 21, 28, 29] In our case, the energy difference between the two lasers (514 and 785 nm) is 0.83 eV. Accordingly, one should expect a D band downshift of 33 to 41 cm\(^{-1}\). This is in excellent agreement with the experimental observation of 36 cm\(^{-1}\).

![Raman spectra](image)

Figure 3.3 Raman spectra with 514 nm laser source (a) and 785 nm laser source (b) fitted with two Lorentzian fitting functions; Raman spectra with 514 nm laser source (c) and 785 nm laser source (d) fitted with three Lorentzian fitting functions.
No dispersion is observed for the G band. From the experimental results of Ferrari et al.,[30] the G band position does not change with different laser wavelengths in crystalline graphite. However, the G band shows dispersion in amorphous carbon and the dispersion increases with increasing degree of disorder.[30, 31] Based on these evidences, we conclude that diamond on the cutting wire transforms into nanocrystalline graphite instead of amorphous carbon material.

<table>
<thead>
<tr>
<th>Laser Wavelength</th>
<th>I_d Peak position (cm⁻¹)</th>
<th>I_g Peak position (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>514 nm</td>
<td>1350</td>
<td>1597</td>
</tr>
<tr>
<td>785 nm</td>
<td>1314</td>
<td>1597</td>
</tr>
</tbody>
</table>

### 3.2 Size of Nanocrystalline Graphite on Diamonds

#### 3.2.1 Raman depth profile study on diamond

In order to understand the extent of graphitization in diamond, we conducted confocal Raman spectroscopy at spot ‘2’ of the diamond particle in Figure 3.2. This series of spectra obtained are shown in Figure 3.4 a). The spectra are separated by 2 μm in the vertical z-direction. The start of the confocal measurement occurs at the tip surface of the diamond micro particle and results in the spectrum labeled as ‘1’ in Figure 3.2 a)). Subsequent spectra clearly show the presence of the D and G graphitic bands (labeled 2 and 3). Additionally for spectra ‘3’, the diamond T₂g at 1332 cm⁻¹ is observed emerging from the graphitic D band (broad and centered at 1350 cm⁻¹). We note that the Raman scattering intensity of diamond as compared to graphite is 50 times weaker. Thus, the
appearance of a strong diamond peak with graphitic peaks indicates largely, the presence of diamond rather than graphite. Further, the depth of focus of the Raman microscope is 4.2 µm. This implies that the diamond and graphitic phases could co-exist within this length scale. Probing deeper into the micro particle reduces the D and G bands while the T\textsubscript{2g} diamond peak increases in peak intensity. At 14 µm laser penetration, the G band of the graphitic phase completely disappears and only the T\textsubscript{2g} peak from the diamond remains. This sequence of Raman spectra captures the phase transformation of the diamond to the graphitic phase during Si wafering.

Since the confocal measurement takes images of the diamond micro particle (as shown in Figure 3.2 a)) for every z-height, it is possible to reconstruct the shape of the diamond by stacking the individual images of the focused regions together in a 3D contour map. The result of such 3D reconstruction is shown in Figure 3.4 b) for a stack of 74 images (z-height difference of 0.2 µm, the lowest achieved by the microscope stage).

The arrow in Figure 3.4 b) shows the region where the graphitic phase was detected. Thus, a complete chemical and physical picture of the phase transformation process is obtained with our analysis. While the diamond micro particle reported in Figures 3.1 and 3.2 shows the diamond to graphite phase transformation, more often than not, the micro particles retained their diamond phase while only subtly changing Raman features. These minute shifts can be a source of valuable information providing insights to the diamond cutting process of Si.
Figure 3.4(a) Confocal Raman spectroscopy of the graphitic region. Red curve (1) is 2 µm above sample surface. With increasing the number from 1 to 9 of the curve, the laser spot moves from surface to inner part of the sample with a step distance is 2 µm. (b) 3D reconstruction of the diamond particle as obtained from the confocal data using the focused region as a single slice at a specific z-height. The black arrow shows where the graphitic region exists.
3.2.2 Calculation of size of nanocrystalline graphite

Knowing the intensities of the D and G bands allows us to calculate the size of the nanocrystalline graphite. The relationship between crystallite size and ratio of the integrated area between of $I_d$ to $I_g$ is given as[32]:

$$L_a = 2.4\times10^{-10} \lambda^4 \left(\frac{I_d}{I_g}\right)^{-1}$$

(1.3)

Where, $L_a$ is the crystallite size (nm), $\lambda$ is the laser wavelength used in nm (i.e., 514) and $I_d$ and $I_g$ are the integrated area under the D and G bands, respectively. The estimated nanocrystallite size of the graphite on the diamond micro particle as a function of depth is shown in Figure 3.5. The crystallite size varies from 10 nm near the surface to 52 nm near the interface of graphite and diamond. Thus, with increasing vertical distance inside the sample, the crystallite size appears to increase.

![Graph showing nanocrystallite size as a function of depth](image)

**Figure 3.5** The variation of graphitic nanocrystal size $L_a$ as a function of depth inside the diamond micro particle shown in Figure 3b. Here, depth = 0 $\mu$m is the surface and depth > 0 $\mu$m is inside the diamond micro particle.
3.3 State of Stress of the Diamond Micro Particles

3.3.1 Raman linescan on diamond surface

In Figure 3.6 a), two diamonds are noted in the micrograph. The arrow on top of the image indicates the drawing direction of the spool as the diamond wire performed the cutting. A line spectra was obtained across both the diamonds, starting from X = 42938 µm to X = 42991 µm. The diamond T\textsubscript{2g} peak was plotted in its peak intensity (left axis) and its peak position (right axis) in Figure 3.6 b). The peak intensity simply shows the presence of the diamond phase. However, the peak position shifts indicate the presence of built-in stresses.[33] It was confirmed separately (not shown) that fresh wires not subjected to cutting always showed the T\textsubscript{2g} peak centered at 1332 cm\textsuperscript{-1}. Thus, any shift in the T\textsubscript{2g} peak would be a result of the cutting process.

The T\textsubscript{2g} peak shifts on the left diamond by 3.6 cm\textsuperscript{-1}. For the right diamond, the peak shifts by 2.0 cm\textsuperscript{-1}. Most remarkably, these shifts occur on the left side of both diamonds only and along the drawing direction of the wire. Clearly, the peaks are related to the cutting process and show the highly directional nature of the cut as the diamond particle presses against the Si ingot. From the peak shifts it is possible to estimate the stresses in the diamond as will be shown in Section 3.3.2.

3.3.2 Relationship between stress and Si Raman peak position

It has been shown previously that hydrostatic stresses alone cannot induce graphitization of diamond. In order for phase transformation to occur, a combination of hydrostatic and shear stresses must be present.[34] These stresses must manifest themselves in some form in the diamond that can be detected by Raman. Indeed, compressive stresses cause blue-shifts, while tensile stresses lead to red-shifts in the Raman spectra.[33]
Data from Figure 3.6 b) shows that blue-shifts / compressive stress are produced in the diamond during Si cutting. The wavenumber shift is 3.6 cm\(^{-1}\) for the left diamond and 2.0 cm\(^{-1}\) for the right diamond. We have used the empirical model proposed by Hemley et al.,[35] for 4 \(\mu\)m diamond powders under non-hydrostatic conditions and obtained 2.9 GPa and 1.7 GPa for the two diamonds, respectively. These stresses are concentrated on the left face of the diamond particles and along the direction of the wire drawing – as is to be expected.

Compared to the stresses required to induce phase transformation in diamond, it is clear that these stresses are quite low. For example, theoretical investigations show that under uniaxial stresses on diamonds, a pressure of at least 285 GPa is required for metallization.[36] During wear, shear stresses on diamonds have to reach 95 GPa for graphitization to occur. [37] Finally, it has been suggested that plasticity in diamond can be induced at pressures \(~\) 150 GPa.[38] These stresses are much higher than the one uncovered on the stressed diamond in Figure 3.6 b). Thus, for graphitization to occur in diamond wires, we propose that 1) either the micro particles have to undergo a series of cutting events in which the stresses accumulate over time or, 2) the diamonds encounter a single cutting event where the pressure on the diamond increases catastrophically causing it to convert to nanocrystalline graphite. The fact that a systematic trend in graphitic nanocrystalline grain sizes is found on the surface of diamond implies that the former mechanism (i.e., multiple stress events) is the likely scenario. With each cutting event, grain refinement (i.e., breaking of larger grains into smaller sizes) of the topmost graphite layer occurs and leaves the sub-surface graphite untouched. Since graphite is extremely soft compared to diamond, the stresses during the cutting events continue to drive the conversion of diamond to graphite at the sub-surface interface.
Figure 3.6 (a) Micrograph of two diamond particles which were subjected to Raman linescan measurements. The arrow points towards the movement of the wire as it slid through the cutting groove. The start and end points show the beginning and ending of the Raman linescan. (b) Intensity (left axis in log scale for clarity, and black) and peak position (right axis and red) as a function of laser position during the line scan. Both diamonds show a shift of the peak position on their left faces – a sign of compressive stresses.
This conclusion is in line with the known mechanisms of diamond to graphite phase transformation proposed in literature. Zerda et al.,[39] have suggested that the transformation occurs via either 1) direct ‘peeling’ of the C atoms at the interface between (111) diamond and (002) oriented graphite or 2) via groups of C atoms which detach from the interface and bond as sp² in tiny clusters. In case of disoriented nanocrystallites of graphite and therefore to a larger D band signal. In case of mechanism ‘1’, the G bands dominate the Raman signal for graphitization. Mechanism ‘2’ leads to disoriented nanocrystallites of graphite and therefore to a larger D band signal.

Alternately, between these two extreme events, the micro particles while being subjected to cutting events can also be dislodged from their positions due to failure of the Ni film. Recall that the Ni film binds the diamonds to the stainless steel wire. Therefore, the compressive stresses obtained by our analysis provide a minimum estimate of the shear modulus of Ni films required to maintain embedded diamond micro particles on the Ni surface. Finally, the role of temperature during the cutting process needs to be addressed. Since a coolant is used during diamond wire sawing, large temperature increases (> tens of degrees) are not expected to occur.[2, 40]

### 3.4 Statistics of Diamond Particles

Twenty diamonds are tested with Raman spectroscopy. Among those diamonds, three of the diamonds show graphitization. By observation of the diamond particles, it is noted that all of these three diamonds have larger sizes. The observation indicates that bigger diamonds are more likely to show the phenomenon of graphitization. Thus, statistics of diamond particles can show a guidance of future on diamond property change. It seems that more uniform size of diamonds will result in higher quality of wire cutting.


3.5 Conclusion

First, phase transformation from diamond to nanocrystalline graphite occurred in some of the diamonds. The size of the nanocrystalline graphitic phase can be calculated, varying from 10 nm near the surface to 52 nm at the graphite-diamond interface.

Second, on the fresh diamonds, no stress is detected, while on used diamonds, compressive stress is observed.

Based on these two observations, one of the reasons for the efficiency reduction could be the graphitization of diamond during the diamond coated wire sawing process. The graphitization can be a multi-step event where with each cutting, an increment in the local compressive stress state occurs. When the stress reaches a critical threshold, graphitization spontaneously occurs in a localized and confined volume within the diamond particle.

Statistics of diamond particles shows that bigger diamonds are more likely to have graphitization. More uniform size of the diamond particles may result in a higher efficiency of cutting process.
Chapter 4

Raman Study on Si Swarf

This chapter contains Raman study on both individual Si particles and Si swarf cluster. In “Raman study of individual Si particle” section, the crystallinity of individual Si swarf particles, is studied. Furthermore, relationship of stress and wafer machining mode is elaborated. In “Raman Study of Si swarf cluster” section, comparisons of phase and stress distribution are made between samples collected at the beginning and end of the cutting process.

4.1 Raman Study on Individual Si Particle

4.1.1 Morphology of individual Si swarf

As shown in Figure 1.2 (b) in Chapter 1, when cutting Si ingots with DCW, there are two types of machining mode, brittle mode and ductile mode, respectively. More ductile mode of machining occurred in the region A in Figure 1.2 (b), which was on the top of Si ingot pressing direction. For brittle mode of machining, it is more likely to occur on the two sides of DCW, as shown in region B in Figure 1.2 (b).

SEM image of the individual Si particle is shown in Figure 4.1, with two different types of Si morphology observed. Curved Si particles are produced from ductile machining mode (marked with red circle in Figure 4.1), while blocky-shaped Si particles are from brittle machining mode (marked with green circle in Figure 4.1). The morphology of Si swarf is in agreement with the Si machining mechanism. Hence, both ductile mode of machining and brittle mode of machining occurred during...
the cutting process, leading to two types of Si morphology. To better understand the property of Si particles produced by different machining mode, Raman spectroscopy is carried out.

Figure 4.1 SEM image of individual Si particles. (Brittle Si particle was marked with green circle, while ductile Si particle marked with red circle.)

4.1.2 Phase analysis of different morphologies of Si swarf

As mentioned in Section 4.1.1, two different morphologies of Si particles were observed by SEM. Raman spectrum of ductile Si (spot 1 in Figure 4.2 a)) and brittle Si (spot 2 in Figure 4.2 a)) are shown in Figure 4.2 b). After deconvolution of the ductile Si Raman spectrum (in Figure 4.3) with Lorentzian fitting function, amorphous Si, Si – I, Si – XII and Si – III formed during ductile machining mode.[41] As shown in Figure 4.3, peaks at 286.0 cm\(^{-1}\) and 518.6 cm\(^{-1}\) belong to Si – I. The peaks at 480.4 cm\(^{-1}\) and 150 cm\(^{-1}\) are ascribed to amorphous Si. Si – III shows peaks at 350.7 cm\(^{-1}\) and 435.2 cm\(^{-1}\), while peak at 422.2 cm\(^{-1}\) is ascribed to Si – XII. This observation indicates that phase transformation is more likely to occur during ductile mode of machining.
Figure 4.2 (a) Optical micrograph of Si particles through the confocal microscope; (b) Raman spectra taken from spot ‘1’. ⊙ = Si-I (cubic diamond structure), ▽ = a – Si (amorphous Si), and ◦ = Si – XII or Si – III. (c) Raman spectra taken from spot ‘2’. ⊙ = Si-I (cubic diamond structure).
It can be explained by the following theory. Before the cutting process, phase of Si ingot is made of Si – I (cubic diamond structure), which is brittle. When DCW moves towards Si ingot, higher stress is applied on Si ingot. With the increasing pressure, plastic deformation occurred, leading to the formation of new metallic Si phases (Si – II). After cutting, with faster stress unloading rate, Si – II transformed into amorphous Si. With slower unloading rate, Si – III and Si – XII formed instead. Thus, both amorphous Si, Si – III, and must occurred during ductile machining mode.[42] Hence, it can be concluded that more amorphous Si phase, Si – III, and Si – XII form during ductile mode of machining, while more cubic Si remain as the original Si – I phase in brittle machining mode.

Figure 4.3 Deconvolution of ductile Si Raman spectrum. ⊙ = Si-I (cubic diamond structure), ▽ = a – Si (amorphous Si), and ◇ = Si – XII or Si – III.
4.1.3 Relationship between stress and Si swarf morphology

Nine Si individual particles with different morphologies were studied by Renishaw InVia micro-Raman confocal spectrometer (Si particle morphologies shown in Appendix B). Five of the nine Si particles were produced by brittle machining mode, and four samples were formed by ductile machining mode. Raman spectrum were fitted with Lorentzian fitting function.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Si–I Raman Peak Position (cm$^{-1}$)</th>
<th>$I_{\text{cubic}}/I_{\text{amorphous}}$</th>
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<tr>
<td>1</td>
<td>520.91</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>522.3</td>
<td>3.85</td>
</tr>
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<td>3</td>
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<td>12.85</td>
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</tr>
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<td>6</td>
<td>N/A</td>
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<tr>
<td>7</td>
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<td>0</td>
</tr>
<tr>
<td>8</td>
<td>517.89</td>
<td>0.36</td>
</tr>
<tr>
<td>9</td>
<td>517.01</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 2 Relationship between machining mode and Si – I Raman peak position
Stress can be calculated by analyzing Raman peak shift of Si – I, which is originally at 520 cm\(^{-1}\). Si – I Raman peak positions of nine Si samples are shown in Table 2. For Si particles (Si sample number 1 to 5) produced by brittle machining mode, upshifts of Si – I Raman peak occur. Downshifts of Si – I Raman peak occur with Si particles (Si sample number from 6 to 9), which are produced by ductile mode of machining. It is noted that tensile stress leads to the downshift of Raman peak, while compressive stress results in the upshift of Si – I peak, which has been mentioned in Chapter 3.[33] The relationship between stress distribution and Si machining mode can be explained by wafer machining mechanism. As mentioned in Chapter 1, DCW moves towards region A, leading to the formation of compressive stress. In the meanwhile, region A contains more brittle mode of machining. Hence, it can be concluded that compressive stress forms during brittle machining mode. Likewise, region B is predominated by ductile machining mode. Since the moving direction of DCW is parallel to the surface of region B, it is more likely for tensile stress to form on region B. Thus, tensile stress exists during ductile mode of machining.

Figure 4.4 shows the mechanism of wafer machining mechanism in a more clear way. More brittle Si formed with higher I\(_{\text{cubic}}\) / I\(_{\text{amorphous}}\), while more ductile mode of Si occurred with lower I\(_{\text{cubic}}\) / I\(_{\text{amorphous}}\), which indicates that more amorphous Si forms during the brittle machining mode. This analysis further proved the conclusion that mentioned in Section 4.2.1.
4.2 Raman Study on Si Swarf Cluster

The preparation of Si swarf cluster has been introduced in Chapter Two. In this section, Si swarf cluster produced at the beginning and end of the cutting process was collected, respectively. The beginning process (defined as beginning) is defined as when diamond wire moves into Si ingot 20 mm, while the end process (defined as end) is cutting into the ingot with a depth of 150 mm. Using Raman spectroscopy, Si swarf cluster is studied by comparing the difference of the Si phase distribution and stress distribution during the beginning and end of the cutting process. Furthermore, trend of Si phase transformation and stress change can be understood as a function of cutting process time.
4.2.1 Raman spectrum of Si swarf cluster

Figure 4.5 shows a confocal image of the Si swarf cluster under the Raman microscope with a magnification of 20X. Laser of Raman spectroscopy is focused on the position marked in Figure 4.5. Raman spectrum is shown in Figure 4.6, with peaks at around 140 cm\(^{-1}\), 300 cm\(^{-1}\), 470 cm\(^{-1}\), and 518 cm\(^{-1}\) fitted with Lorentzian fitting function. Amorphous Si has peak positions at 150 cm\(^{-1}\) and 470 cm\(^{-1}\), which is in agreement with our fitting peaks. Peaks at 300 cm\(^{-1}\) and 520 cm\(^{-1}\) belong to Si-I (cubic diamond structure Si). [42] Raman spectra of Si swarf cluster is similar as the one of individual Si particles, which better indicates that Si swarf cluster is a mixture of individual brittle and ductile Si particles.

![Figure 4.5 Optical micrograph of Si swarf cluster.](image)
4.2.2 Si phase distribution of Si swarf cluster

To further understand the Si phase distribution in a more statistical way, map scanning of Raman spectroscopy is conducted. Area map with 48 scans is conducted on each cutting processes, which are the beginning and the end, respectively. Raman spectrum of each scanning is fitted with Lorentzian function. The intensity ratio of cubic Si and amorphous Si ($I_{\text{cubic}}/ I_{\text{amorphous}}$) can be used for describing the Si composition. The ratio could be calculated, using the peak height intensity of 520 cm$^{-1}$ and 470 cm$^{-1}$. The intensity of these peaks can be fitted with Lorentzian fitting function. The Weibull distribution is widely used to model time to failure data. Hereby, Weibull plot is applied for analysis of Si phase distribution. The reason of using Weibull distribution is that it is a more clear way to compare the difference of data statistics.
Weibull probability distribution can be calculated in Eq. 1.4.

\[ F(t) = P(T \leq t) = 1 - e^{-(\frac{t}{\theta})^\beta} \quad (t < 0) \]  

(1.4)

Where, \( \beta \) is the shape parameter, \( \theta \) is the scale parameter. When \( \beta = 1 \), the Weibull becomes the exponential distribution.

Eq. 1.4 can be derived as

\[ y = ax + b \]  

(1.5)

Where,

\[ y = \ln \left[ -\ln (1 - F(x)) \right] \]  

(1.6)

\[ a = \beta, \quad b = -\beta \ln \theta, \quad x = \ln t \]  

(1.7)

Eq. 1.5 is expressed as a linear function. Based on Eq. 1.6 and 1.7, vertical axis of Weibull plot is Weibull cumulative probability expressed as a percentage, while horizontal axis is log 10 scale of the parameter, which we plan to compare.[43] The slope of linear curve is equal to the shape parameter of Weibull distribution. \( F(x) \) is usually taken as 63.2%, which corresponds to the extreme value occurring in Weibull distribution. By using Eq. 1.6, \( y \) is calculated to be 0 when \( F(x) \) is equal to 63.2%. It is noted that with higher shape parameter, the distribution spreads more widely. Hence, difference in data distribution can be analyzed in a more visualized way, simply by comparing the slope and \( x \) value when \( y \) is equal to 0.

Based on statistics of map profile, \( I_{\text{cubic}} / I_{\text{amorphous}} \) is analyzed by Weibull distribution. As shown in Figure 4.7, \( \ln \left( I_{\text{cubic}} / I_{\text{amorphous}} \right) \) is defined as \( x \), while \( y \) is defined as Eq. 1.6, which is Weibull cumulative probability. Weibull distribution of the slope of beginning and end of the process is similar, which indicated they have the similar distribution trend. However, when \( y \), Weibull cumulative probability, is equal to 0, \( \ln \left( I_{\text{cubic}} / I_{\text{amorphous}} \right) \) of beginning and end is different, which indicates that the extreme value of distribution in the beginning and end is different. The extreme
value of \( I_{\text{cubic}} / I_{\text{amorphous}} \) is lower during the end of the cutting process, which shows that more amorphous Si phase form with longer-lasting cutting process. Hence, we can conclude that during the beginning and end of cutting process, more cubic Si phase transform into amorphous Si with longer time of cutting.

![Weibull plot for \( I_{\text{cubic}} / I_{\text{amorphous}} \). Red curve is end of process, while black curve is beginning of process.](image)

**Figure 4.7** Weibull plot for \( I_{\text{cubic}} / I_{\text{amorphous}} \). Red curve is end of process, while black curve is beginning of process.

### 4.2.3 Stress distribution of Si swarf cluster

Comparison of stress distribution of beginning and end of process can also be studied by Weibull distribution. As mentioned before, by comparing Si – I peak position at 520 cm\(^{-1}\), type of stress can be illustrated.

The implication of Weibull plot is very significant. By using Weibull plot, the extreme value can be analyzed. The extreme value changes with time, which can be used to predict the quality of cutting wire changes over time. For example, with Si swarf obtained from different date of cutting process,
changes in quality of cutting wires and Si phase can be detected. Hence, it is of great importance to use Weibull plot to study the Si swarf.

Figure 4.8 shows Weibull distribution plotted as a function of ln (stress). The slope of beginning is almost 2 times larger than end of the process, which indicates that the stress distribution in the beginning of the process is much narrow than the one at the end of cutting. The extreme value of beginning and end (when y is equal to 0) is similar.

![Weibull plot for stress. Red curve is end of process, while black curve is beginning of process.](image)

Furthermore, in our measurement (i.e., begin and end), the cubic Si peak in all the scanning data shows a downshift with a minimal peak at 515.7 cm\(^{-1}\). For the cubic Si with no residual stress, peak position should be around 520 cm\(^{-1}\). It is noted that stress is a major cause of shift of Si. Hence, we can conclude that residual stress, which causes the downshift of cubic Si peak, also has influence on the brittle-to-ductile transition. Furthermore, this residual stress might be the critical stress to trigger the brittle-to-ductile transition, which would be significant.
Hence, we can conclude that the extreme value of stress distribution is similar for the beginning and the end of the cutting process, while stress distribution in begin is more concentrated than the end.

4.3 Conclusion

By analyzing the morphology of individual Si particles, and Raman spectra of the individual Si particles, it can be concluded that more amorphous Si form in ductile machining mode, while more cubic phase Si form in brittle machining mode. Furthermore, tensile stress predominates in ductile mode of machining, while compressive stress occurs in brittle machining mode.

By comparing the Weibull statistics of phase and stresses at the beginning and end of the cutting process, it can be concluded that more cubic Si phase transform into amorphous Si with longer time of cutting. Also, the stress distribution in beginning is more concentrated than the end.
Chapter 5

Conclusions

By studying on diamond particles on DCW, two conclusions can be drawn from our investigations. First, some of the diamonds showed presence of nanocrystalline graphite co-existing with the diamond phase in the same particle. Using the model proposed by Cancado et al., we predict the size of the nanocrystalline graphitic phase varied from 10 nm near the surface to 52 nm at the graphite-diamond interface. On other diamonds, the presence of compressive stress could be detected. The stress was localized on regions, which faced the Si ingot during the cutting process. Compressive stresses as high as 2.9 GPa were detected.

Based on these two observations, there appears to be a possibility that one of the reasons for the loss in efficiency during diamond coated wire sawing could be the graphitization of the diamond particles. The graphitization can be a multi-step event where with each cutting, an increment in the local compressive stress state occurs. When the stress reaches a critical threshold, graphitization spontaneously occurs in a localized and confined volume within the diamond particle.

By analyzing the morphology of Si swarf, and Raman spectra of the individual Si particles, two conclusions can be drawn. First, Morphology difference of Si particles leads to two different types of wafer machining modes. Based on the analysis of Raman spectra, amorphous Si phase, Si – III, and Si – XII are more likely to form during ductile mode of machining, while more cubic phase Si remain as the original Si – I phase in brittle machining mode.

Second, wafer mechanism is further understood that compressive stress is more likely to occur in brittle machining mode, with more Si particles remaining as their original cubic phase Si. In ductile
machining mode, tensile stress predominates, with more amorphous Si forming, which is in accordance with the previous study by other researchers.

By comparing the data statistics of begin and end cutting process with Weibull plot, it can be concluded that more cubic Si phase transform into amorphous Si with longer time of cutting. Also, the stress distribution in end is wider than the beginning of cutting process. The gradual transformation in Si phase and gradual change in stress distribution as a function of different cutting period give us a method to better understand the details of wafer sawing process.
Chapter 6

Future Work

Future effort can be focused on the statistical data analysis of the Si swarf cluster. In this thesis, the study on Si swarf phase change and stress distribution as a function of time is incomplete as only two pieces of data (beginning and end) are collected and analyzed. However, the methodology has been highlighted and this can pave way for future work.

Samples collected at longer time intervals will lead to better understanding of phase and stress change during the cutting process. The kinetic (i.e., rate) information obtained can then lead to prediction and reliability models of the DCW cutting process. The availability of such models will be very beneficial for the wafer sawing industry and will help improve process uptime and quality of the wafer sawing process.
Appendix A

Raman spectra data of nanocrystalline graphite size as a function of depth

\( \frac{I_d}{I_g} = \) Height intensity ratio of D band and G band

<table>
<thead>
<tr>
<th>Curve number</th>
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</thead>
<tbody>
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</tr>
<tr>
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</tr>
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<td>9</td>
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</tr>
</tbody>
</table>
Appendix B

Morphology of the nine Si swarf particles under optical microscope

The following images are the optical micrograph of Si swarf particles, which are used for Raman study in Table 2.
References


Vita

Junting (Sophie) Yang
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Summary
Thesis based M.S. in Materials Science with titled as “Diamond Coated Wire Cutting of Solar Si Ingots: New Insights Using Raman Microspectroscopy”. Advanced research focused on semiconductor design, wafer manufacturing, and their applications to industry. Seeking a position as an Engineer in semiconductor industry with strong hand-on and analytical skills. Willing to travel and relocate. Available in August 2015.

EDUCATION

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<th>Washington University in St. Louis</th>
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<td>Thesis based M.S. in Materials Science, August 2015</td>
<td>B.S. in Materials Science and Engineering, July 2013</td>
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SKILLS

• Cleanroom: Reactive Ion Etch (RIE) and Wet Etch, Photolithography, Ellipsometry, Profilometer, Spin Coater, Physical Vapor Deposition (PVD), Oxidation Tube Furnace
• Laboratory: Scanning Electron Microscopy (SEM), Energy-Dispersive X-Ray Spectroscopy (EDS), Sputtering, Thermal Evaporator, Optical Microscopy (OM), X-Ray Diffraction (XRD), Raman Spectroscopy, JANIS (Electrical property test probe station), Chemical Vapor Deposition (CVD), Gleeble-3500
• Software: C, Microsoft, Visual Basic, Origin

RELATED COURSES

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<th>Principles and Methods of Micro and Nanofabrication</th>
<th>Materials Characterization Techniques II</th>
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<td>Fundamentals of Materials Science</td>
<td>Quantitative Materials Science &amp; Engineering</td>
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<td>Mathematics of Modern Engineering</td>
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RESEARCH EXPERIENCE

Study on transformation behavior of diamond wires for cutting Si wafers  
**St. Louis, MO. 08/2014 – 01/2015**
• Industrial collaborated project with Sunedison
• Analyzed the properties of diamond cutting tools by Raman spectroscopy and EDS
• Determined reasons for gradual reduction in efficiency of the diamond cutting tools
• Became familiar with wafer manufacture process such as cutting, cleaning, and testing

Invention of flexible and transparent CuO nanowire solar cells  
**St. Louis, MO. 03/2014 – present**
• Became proficient with RIE, spin coater, and sputtering deposition
• Invented methods of transferring nanowires into flexible substrate, and optimized etching recipe
• Tested electrical properties and optical properties of device

TEACHING & PROJECT EXPERIENCE

**Teaching assistant (TA) for “Principles and Methods of Micro and Nanofabrication”**  
01/2015 – present
• Served as an instructor of the experimental procedure and facilities in cleanroom
• Supported ten students with their electrical device design

**Fabrication of enhanced ZnO UV sensor**  
**St. Louis, MO. 01/2014 – 05/2014**
• Mastered cleanroom techniques, such as photolithography, thin film deposition, and etch
• Enhanced UV sensor performance 1.3 times by adding PSS polymer
• Worked efficiently on a team of four graduate students

PUBLICATION


Yang, Junting, Banerjee, S., Wu, J., Myung, Y., Rezvanian, O., and Banerjee, Parag “Study Si swarf using Raman spectroscopy” (In preparation)