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Sub-micron imaging of sub-surface nanocrystalline structure in silicon

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This work reports on a surprising and abnormal increase of the Raman intensity when the probing area is moved to the edge of a mechanically cleaved Si wafer. Our detailed surface structure study based on atomic force microscope and scanning electron microscope rules out any effect from surface morphology. Systematic study of the Raman system focusing effect with a range of μm finds no focusing effect involved in our observed phenomenon. The linewidth, wavenumber, and intensity of the 521 cm^{-1} peak are obtained and evaluated quantitatively when the testing region is moved from the center to the cleaved edge. When the grain size of crystalline silicon varies from 20 to 10 nm, the Raman intensity of the 521 cm^{-1} peak is increasing abnormally, by about 100%. Meanwhile, both the linewidth and wavenumber change by about 2 cm^{-1} and 4 cm^{-1}, respectively. If instrument and surface factors are well controlled/defined, the change of Raman intensity could provide a sensitive and complementary method for grain size characterization in addition to the Raman wavenumber and linewidth methods. Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: raman intensity; nanocrystaline silicon; imaging; cleaving

Introduction

Nanocrystalline silicon, a material composed of nano-size silicon crystalline grains,[1] is widely used in microelectronics and optoelectronic devices such as gates, load resistors, and solar cells, because of its high performance. Compared with single crystalline silicon, nanocrystalline silicon can be easily recognized with visible grains and produced through various methods in different sizes, shape, and purity.[2] Although amorphous silicon also has the aforementioned advantages, nanocrystalline silicon has a larger quantity of mobile charge carriers and is more stable under electric field and light-induced stresses.

In engineering applications of nanocrystalline silicon, it is important to characterize the crystalline structure and relate such information to the desired functionality. Among different techniques, Raman spectroscopy is an effective way to characterize structure of crystals. In Raman spectrum, the lattice vibration mode in single crystalline silicon is observed as a sharp peak around 521 cm^{-1}, while a broad peak centered at 480 cm^{-1} represents the amorphous state because the breakdown of lattice periodicity relaxes the symmetry restrictions and permits scattering from all other vibrational modes. Nanocrystalline silicon is the intermediate state between these two forms, so it is easily recognizable by fitting these two peaks in the spectrum.[1] After fitting, the basic information, such as peak intensity, linewidth, and wavenumber, can be extracted from the original data, which has a close and direct relationship with the structure of crystals. In the work of Tong *et al.*, the crystalline perfection can be detected from the intensity of the Raman peak by analyzing the ratio of intensity between the peaks at 521 cm^{-1} and 480 cm^{-1}. From the linewidth of the peak, the amount of lattice perturbation and residual internal strain can be investigated. Furthermore, there are many models to calculate the actual size of the nanograin from the peak shift.[3] However, the Raman peak intensity is rarely used to characterize the profile of the nanocrystalline structure due to the fact that the intensity can be influenced by many factors, such as the excitation laser level, optical alignment and material surface roughness.

The information from the Raman spectrum aforementioned has also been used to measure temperature, and characterize strains and stresses in crystalline materials. The relationship between temperature and Raman shift was calculated by Balkanski[4] and was also verified by many other researchers.[5,6] Through Raman scanning near-field optical microscopy, Webster[7] and his group found that the degree of shift depended on the nature of stresses. The residual stress decreased with the positive shifts of the wavenumber of the Si Raman peak at 521 cm^{-1} as a function of the distance when approaching the scratch in their silicon sample.

This work is to explore the very sensitive change of the Raman intensity with various grain sizes of nanocrystalline silicon on the cleaving edge of a silicon wafer. Raman spectroscopy is utilized to assess the grain size of nanocrystalline silicon in the sub-surface region with a formula in ref. [3]. The analyzed Raman results are used to exclude other factors that could cause the change of the spectroscopy and prove the very high sensitivity of Raman intensity in terms of grain size characterization.

Experimental details

A 270 μm silicon (100) wafer (University Wafer) and a 7 μm silicon wafer are cleaved by using a conventional method. The silicon

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wafer is placed on a desk and cut on its edge with a knife to make a sharp notch. Then a small needle is placed under the notch, and forces are applied on both sides of the notch to break the wafer. The sample edge is finally formed when the silicon naturally cleaves along its crystal face. The cleaved silicon edge is cleaned with ethanol before all tests. A confocal Raman spectrometer (Voyage, B&W Tek, Inc.) installed with a 532 nm excitation laser, and a microscope (Olymoys BX51) is employed to focus the laser. The spectral resolution is 1.05 ~ 1.99 cm^{-1}. During the experiment, a 100× microscope objective lens (NA = 0.80) is used to focus the laser beam and collect the scattering signals. The laser is focused on the surface of the cleaved silicon wafer, and the scattering signal and Rayleigh scattering signal are both collected by the same objective lens in the backscattering mode. The focal spot size is about 0.5 μm in diameter. Considering the optical absorption depth of Si at 532 nm wavelength is around 0.82 μm, the confocal volume in Si will be around 0.4 μm^3. Because the 100× microscope objective lens is the only lens used in our experiment, the focal spot will not change when the sample is fixed in the *z* direction during the experiment.

The experiment setup is shown in Fig. 1(a). The sample is mounted on a combined two-dimensional stage. One is in the *x* direction (ThorLabs NFL5DP20S) and the other is in the *z* direction (ThorLabs MT1-Z8). The movement ranges of those two stages are 20 μm in the *x* direction with a resolution of 20 nm and 13 mm in the *z* direction with a resolution of 0.2 μm. The combined stage is located under the focal spot of the laser beam and can move around the focal spot in the *z* direction. When mounting the sample wafer, the optical trace is perpendicular to the cleaved edge of the wafer which is along the *y* direction. During the experiment, the stage makes the laser point move from the center of the cleaved silicon wafer to the edge with a step of 266 nm at the beginning and then the step length is changed to 133 nm after the intensity starts increasing. The step is controlled by adjusting the voltage on an electronic control box, and 1 V adjustment is for 266 nm movement. One second integral time is used in this measurement to obtain a strong Raman signal from silicon. The whole measuring system is placed in open air. Because of the resolution limit of the spectrometer, Raman signals are processed to calculate the linewidth, maximum intensity, and the precise peak wavenumber after all of the spectra data obtained. The fitting procedure can be simply described as picking up a segment of Raman data (from 492.11 to 552.45 cm^{-1}), choosing eight points on both tails of the peak by fixing the *x* coordinate as the baseline (four on each side), subtracting the baseline from the original data, and finally using Gaussian function to fit the peak to get the information we need.

Results and discussion

Raman imaging for 270 μm thick silicon wafer

By changing the position of the laser spot on the surface of the cleaved silicon wafer sample, a series of Raman spectra are obtained and analyzed. Figure 1(b) shows three typical results with fitting curves near 521 cm^{-1} at selected points marked as A, B, and C in Fig. 1(a). These three points are located from farthest to nearest to the edge. The black line is from point A,

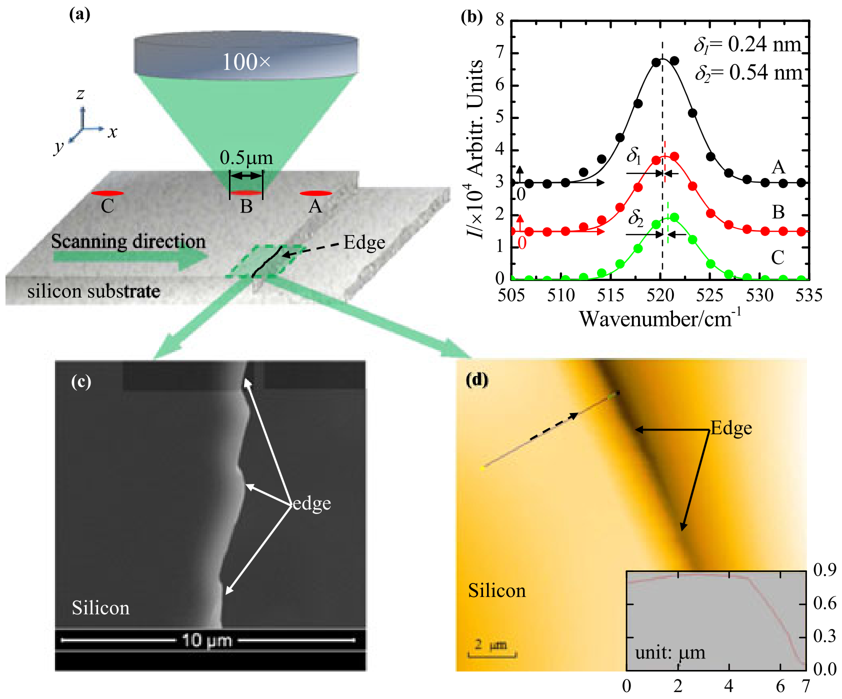

Figure 1. (a) A schematic of the experimental setup for Raman experiment with a 100× objective lens (not to scale). The relative location of the laser spot moves along the *x* direction shown by green arrow. Red dots show the approximate positions of A, B, and C spots. A is mostly near the edge, then B and C is farthest from the edge. (b) The three Raman spectra of silicon near 521 cm^{-1} at selected spots A, B, and C. The dots represent the raw data, and curves are from Gaussian fitting, and both of them have the baseline subtracted. For clear comparison, the curves A and B are shifted up, and 0 points of their *y* coordinates are shown in the plot. (c) Scanning electron micrograph (SEM) shows a smooth surface. The right half of the image is the area, which is out of focus and shown black, while the left half is the silicon wafer surface. The boundary of the silicon wafer is indicated by white arrows. (d) Atomic force microscopy image of the silicon wafer surface is also taken in the same place like that in SEM. The inset plot is the profile of the cross section measured along the direction of black dash arrow in upper right side of Fig. (d) The boundary of the silicon wafer is indicated by black arrows.

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which is the nearest location to the edge; the red line is from B, which is in the middle of A and C, and finally C, shown as a green line, is the farthest point away from the edge. It is obvious that the intensity, linewidth, and Raman wavenumber of these peaks vary with the position from which the signal originates. The peak from point A has the strongest intensity in Raman spectrum, while the peak intensity from point B is weaker, and point C's intensity is the weakest. This variation of the intensity is very large and surprising, by 100% from position C to position A. Meanwhile, the linewidth and wavenumber of the Raman peak also change, but the changes are relatively small to observe compared with the change of the intensity. Furthermore, no 480 cm^{-1} broad peak appears in the spectrum, which means no amorphous silicon formed during cleaving.

In the Raman experiment, the intensity of the Raman signal will be affected by the profile of the tested area. A rough surface will enhance the Raman intensity largely because it can increase the absorption of the incident light on the surface. The sample has a flat surface until the edge. This is proven by the results of scanning electron microscope (SEM) and atomic force microscope (AFM) characterization. The SEM measurement is taken under 10 kV in a vacuum. In Fig. 1(c), the image shows that the surface of the area is very smooth in 2–3 μm abutting on the edge. Furthermore, contact-AFM is also employed to measure the detailed structure in a $15 \times 15\ \mu m^2$ area. In Fig. 1(d), the right hand side of the dark line indicates the silicon surface and the edge, and the left hand side is caused by the system adjustment because the difference in height is too steep to track. The inset graph in Fig. 1(d) is the profile of the cross section of the straight line drawn in the figure. Both SEM and AFM results in Figs 1(c) and (d) illustrate that the surface roughness is very small, and there is no special structure, which could increase the roughness. Therefore, the enhanced intensity is not caused by the roughness in the testing area.

There should be another factor leading to this sensitive change in Raman intensity. Gaussian fitting[8] is applied to all of these measurement results to obtain more accurate data to analyze. Gaussian curve fitting is more suitable for solid materials. In solid materials, when a molecule is excited, the relaxation is much longer than dephasing, and Gaussian profile is a better shape to depict this process. Furthermore, in our Raman spectra of silicon, Lorentzian curve fitting has been tried as well, and gives very close results to the fitting result from Gaussian curve fitting. Thus, Gaussian fitting is chosen in this paper. Figure 2(a–c) shows changes of the intensity (I), linewidth (Γ), and wavenumber (ω) against the location in the x direction, when the focused laser spot is moving to the edge of the silicon. The red dash line indicates the edge position. In Fig. 2(a), the point having the maximum intensity indicates that the whole laser spot is focused on the silicon immediately next to the edge. Part of the laser will irradiate other places lower than the silicon surface when the laser spot keeps moving toward the silicon wafer edge, and thus the Raman intensity decreases quickly. Ninety percent change of the maximum intensity is used for spot size evaluation and it is about 0.5 μm.

During the whole process, the decrease of the Raman wavenumber can be observed, while the linewidth of the peak is broadening. After passing the edge, continuing changes of the wavenumber and the linewidth are out-of-focus effects, which will be detailed later in this paper. However, the intensity changes in a quite different manner. It first increases quickly from the beginning till the edge and then immediately declines caused by decreased power when the laser spot gradually moves away from the edge. The location of the focal spot is measured by using a CCD camera, and this phenomenon is repeated three times to ensure the reliability. In Fig. 2, the range of the change is 4 cm^{-1} for Raman wavenumber and 2 cm^{-1} for the linewidth. In contrast, the intensity increases by almost 100% from the beginning to the edge, and it is extremely obvious and sensitive with the location of the focal spot.

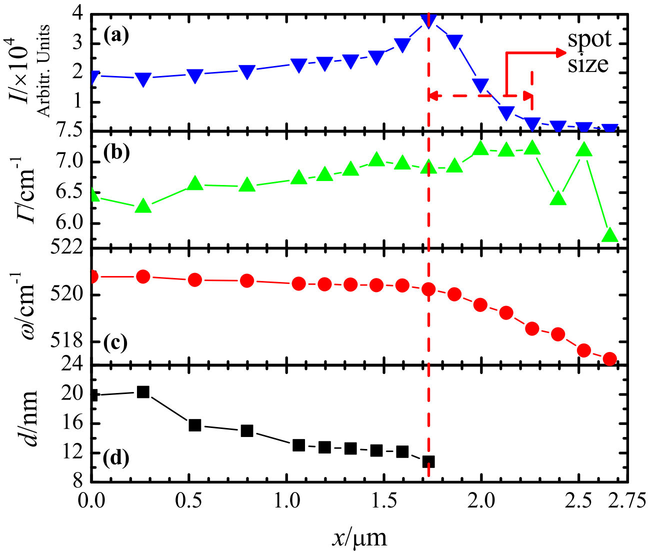

Figure 2. Raman imaging results from the center to the edge of 270 μm thick silicon wafer. (a) Peak intensity (I). The laser spot size is calculated from the highest intensity to 10% of maximum intensity in this plot, (b) width (Γ), (c) 521 cm^{-1} peak wavenumber (ω), and (d) size of nanocrystalline silicon grain (d) change with focal spot from the center to the edge, calculated from $d = 2\pi\sqrt{B/\Delta\omega}$ in ref.3. The red line in this plot shows the actual position of the edge.

In Raman experiments, many other factors will affect the spectrum. The most important one is the focal level, because it can cause many other effects. The out-of-focus effect will lower the density of the incident light and therefore lead to a decreasing effect of heating and stress in the sample surface. Both the heat and stress effects will cause the change of the wavenumber and Raman linewidth. Also the out-of-focus effect will change the incident angle of the backscattered Raman signal into the spectrometer, which may cause some Raman signal change. In this experiment, the stage in the z direction is locked mechanically. However, it may still have a little shift due to vibrations from its surroundings, which will finally cause the sample to be out of focus. To study the out-of-focus effect in our results, a group of Raman spectra are obtained from the surface of single crystalline silicon in the middle area of the same sample silicon wafer located at different distances to the focal level in the z direction. The sample surface level is adjusted near the focal level in a range smaller than 1 μm in order to analyze the out-of-focus effect on the silicon surface. The moving step is 50 nm. Raman spectra are recorded at each step with an integration time of 2 s, and the background noise is subtracted to obtain sound Raman signal.

Figure 3 shows how the Raman wavenumber, linewidth, and intensity change with the z location. Those solid legends represent the result from 270 μm Si wafer, and hollow legends are for 7 μm Si wafer, which is another sample that was used and will be discussed later. At the beginning, the focal level is below the sample surface. When the surface approaches the focal level from the upper side, both the laser spot size and the

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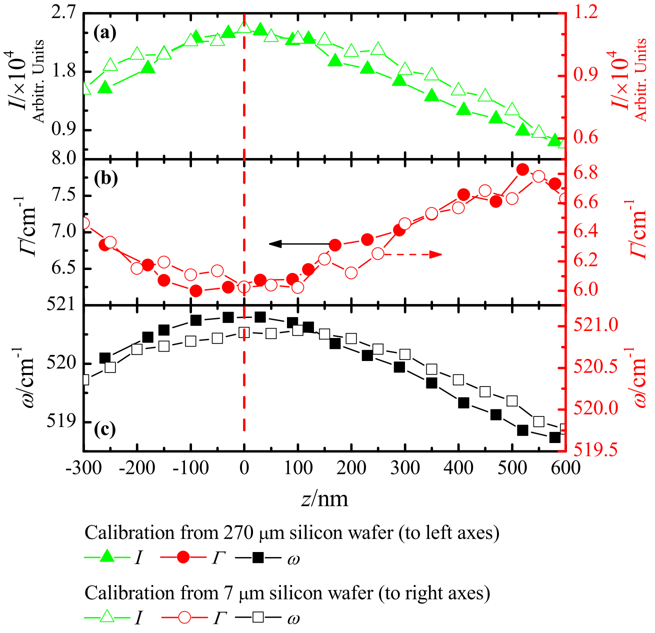

Figure 3. Variation of the Raman spectrum from different focal levels on two single crystalline silicon wafers. (a) Peak intensity (I), (b) width (Γ), and (c) 521 cm^{-1} peak wavenumber (ω) change with the distance to the focal point. The solid legends represent Raman information for the 270 μm thick Si wafer, and the hollow ones are for the 7 μm thick Si wafer. The red line in this plot shows the 0 nm position in the *z* direction, and the laser beam is well focused on this level.

linewidth are decreasing, while the peak wavenumber and intensity increase. After the surface passes the focal level to a lower position, it reverses the previous process: the laser spot and the linewidth become larger, but the Raman intensity and wavenumber decrease. Moreover, the maximum wavenumber, and Raman intensity, and the minimum Raman linewidth appear at the same focal level, which is marked as 0 nm with a red dash line in Fig. 3. The out-of-focus effect causes the continuing change in the wavenumber and linewidth in Fig 2(b–c) after the laser spot passes the edge. Some parts of the lower surface can be irradiated because the cleaving lateral edge is not perfectly perpendicular to the surface. This lower surface is located away from the focal plane ($z = 0$ nm in Fig. 3). As a result, the wavenumber decreases and the linewidth increase.

The variation of the wavenumber and linewidth are similar to the result in Fig. 2, but the trend of the intensity change is completely different for the out-of-focus effect. The linewidth broadens about 2.5 cm^{-1}, and the wavenumber shifts 2.5 cm^{-1} in the condition of 600 nm away from the focal point. These ranges are a little larger than those in Raman results mentioned in the previous paragraph. However, the moving distance in the *x* direction is about 2.6 μm in the whole measurement. If there were a difference in the *z* direction from the beginning to the end in our experiment, the tilt angle would be as large as 13°, which can be easily detected. Furthermore, the intensity increases and becomes abnormally large when the stage moves in the *x* direction. So if there is any movement in the *z* direction to make the sample shift from the focal plane, the intensity should become smaller instead of larger. Therefore, it is believed that the results observed in Fig. 2 are not induced by the out-of-focus effect due to stage shift.

Nanocrystalline grain size

Neither the surface roughness nor the out-of-focus effect has been proven to exist in our samples, and thus they are not the factors causing the abnormal increase of the Raman intensity of the 521 cm^{-1} peak. Moreover, the previous work by Webster *et al.*[7] has mentioned that the residual stress was preserved in and affected the Raman spectrum. They found that a positive shift of the wavenumber of 521 cm^{-1} peak when approaching a mechanical scratch in a single crystalline silicon wafer, which indicates a compressive stress in the silicon surface. However, based on their results, the residual stress will cause different changes in Raman spectrum from ours. One more factor that will change the Raman spectrum of Si is the formation of nanocrystals. Nanocrystals from mechanical machining waste were first discovered and reported by researchers at Purdue University.[9] Some works showed that sub-micron structures,[10] and nano-fine and ultra-fine grained structures[11] in metals and alloys could be formed by machining, such as cutting and large deformation. There might be the formation of nanocrystals in our sample and cause the change of Raman spectra. Furthermore, theoretical studies on the electronic structure of Si nanospheres, assuming spherical confinement of phonons, have been reported, and its results showed the wavenumber would increase when the diameter became larger.[12–15] This shift was explained to be a result of the localization of phonons at the quasi-isolated crystallites.[16]

Our results on the Raman linewidth and wavenumber are similar to the results in previous studies of polycrystalline silicon,[16] and such similarity indicates that there are nanocrystals formed in the area next to the edge in our sample. The formula $d = 2\pi\sqrt{B/\Delta\omega}$ in ref. [3] is used to determine the size of silicon nanocrystalline grains. B is 2.24 cm^{-1} nm^2 for Si, and $\Delta\omega$ is the value of Raman wavenumber with respect to single crystalline Si peak at 521 cm^{-1}. From this formula, the nanograin size can be calculated, and results are plotted in Fig. 2(d). The dash line in Fig. 2 indicates the edge location. From the calculation, the size of Si nanocrystalline grains changes from 20 to 10 nm in silicon surface. Meanwhile, the Raman linewidth increases from 6.5 to 7.0 cm^{-1}, and the wavenumber down shifts from 521 to 520 cm^{-1}. However, the intensity of the Raman peak increased by about 100% because of the variation of grain size.

The change of Raman intensity with the crystalline size was rarely studied in previous works because in Raman spectroscopy the intensity is affected by many factors such as the surface roughness, optical alignment, integration time, and excitation level of Raman equipment. In our experiment, we exclude those possibilities first before further analysis of nanocrystalline effects. The intensity of the incident light remains constant in all measurements, and the surface was proven to be very smooth using the SEM and AFM studies.

Veprek *et al.*[16] and his group used a chemical transport method to produce a thin layer of nanocrystalline silicon film, about several micrometers thick, and treated it in different temperatures to form nanocrystals of various sizes. They found the Raman intensity of Si 521 cm^{-1} peak varied as a parabolic function of grain size in thin film of nanocrystalline silicon. The maximum intensity appeared at the grain size of 18 nm and then became weaker when the grain size either increased or decreased. X-ray diffraction (XRD) was also employed in their works, and it showed a surface model of 'amorphous-like' Si in their samples with a 480 cm^{-1} 'shoulder' near 521 cm^{-1} peak in Raman spectra. This surface model was raised by either stretching or compression of the bond lengths in grain

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boundaries during the nanocrystalline formation, and the bonds dilatation would affect the absorption of incident energy and Raman scattering intensity. In nanocrystalline structures, both the optical absorption coefficient and Raman scattering are increased because of bond dilation in grain boundaries, which can cause fluctuating electric charge density and enhance the coupling of the electromagnetic field to the charge-density fluctuation.[16] It is observed in previous work that the absorption of nanocrystalline silicon is much higher than that of single crystalline silicon.[17]

Compared with their results, Fig. 4 shows the relationship between crystalline size and Raman intensity of 270 μm thick Si wafer in our experiment. From the beginning point to the edge on the silicon wafer, the size of nanocrystals declines while Raman intensity increases by 100% because of the increased density of both nanocrystals and grain boundaries. There is a rapid increase around the size of 12 nm, and on the other side of this curve, the intensity is gradually approaching that from single crystalline silicon when the grain size increases. We obtain a monotonic decreasing relationship between intensity and grain size. The differences between Veprek's work and our work may result from samples' preparation methods. Our sample is formed during mechanical cleaving without heating. Si breaks easily along its (100) face. Therefore, the tensile stress in Si surface next to the broken edge produces nanocrystals, which do not have the 480 cm^{-1} peak. In the past, effort has been taken to relate the Raman peak shape to the grain size as[12,14]

$$I(\omega)\cong\int\frac{d^3q|C(q_0,q)|^2}{(\omega-\omega(q))^2+(\Gamma_0/2)^2}\propto\int\frac{d^3q|C(q_0,q)|^2}{(q-q_0)^2+[1/(2\tau_0)]^2},\qquad(1)$$

where $|C(q_0,q)|^2\cong e^{-(q-q_0)^2d^2/4}$ is a Fourier coefficient, q_0 is the wave vector of optical phonon, $|q-q_0|\leq 1/(2d)$, $\omega(q)$ is the phonon dispersion curve, Γ_0 is the natural linewidth of Raman active mode $\Gamma_{25'}$ (521 cm^{-1} peak) in single crystalline silicon, and τ_0 is the mean free path of the excited optical phonons. Due to the good, long range order in single crystalline silicon, the restricted q-selection rule only allows phonons with wave vector $q_0 = 0$ and gives a narrow peak at 521 cm^{-1}. However, in nanocrystals, the restriction of q-selection is relaxed by the smaller crystalline grain size, and more phonons are optically allowed in Raman spectrum, so the linewidth of Raman peak of $\Gamma_{25'}$ mode broadens and the wavenumber decreases. For the nanocrystalline structure revealed by the Raman spectrum, the tested area of our sample is very small (around 1 μm). If XRD is used to characterize the grain size, micro XRD has to be employed to reveal how the nanograin size varies in space. Such work will be conducted in our near-future research.

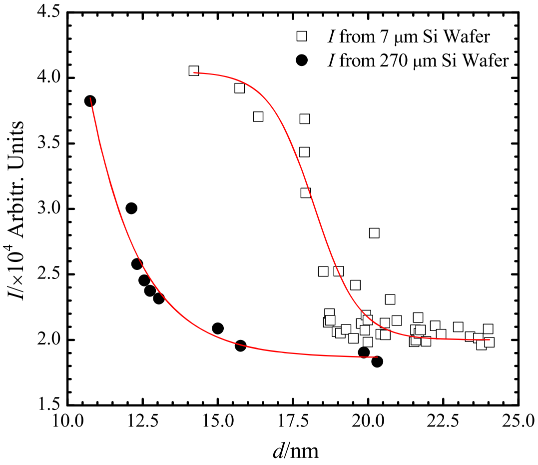

Figure 4. Relationship between Raman peak intensity (*I*) and nanocrystalline grain size (*d*) in the 270 and 7 μm thick silicon wafers. Peak intensity is decreasing with the grain size increasing. The solid line is used to guide the eyes for the data trend.

Raman imaging for 7 μm thick silicon wafer

A 7 μm ultrathin silicon wafer is cleaved in the same way as that in 270 μm Si wafer sample preparation, and the edge is used. We scan along a 1 μm long path perpendicular to the edge with a resolution of 20 nm and collect and analyze Raman information. Fitting results of intensity, linewidth, wavenumber, and crystal size are all shown in Fig 5(a–d). The changing trends of all four properties are similar to those of thick silicon sample. The intensity is gradually enhanced when the tested area approaches the edge, and the maximum intensity at the edge is twice of the intensity at the center. The Raman peak intensity variation against the grain size is also plotted in Fig. 4.

Differences exist between this thin Si sample and the previous thicker one. The point where the intensity starts increasing is 200 nm away from the edge and is much closer to the edge than

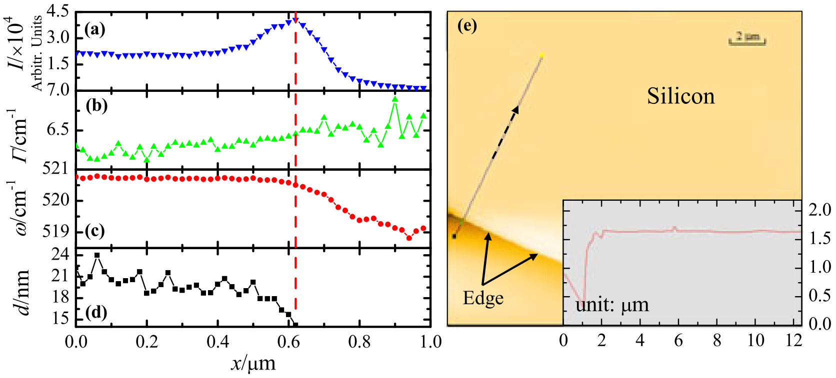

Figure 5. Raman imaging results from the center to the edge of 7 μm thick silicon wafer. (a) Peak intensity (*I*), (b) width (*Γ*), (c) 521 cm^{-1} peak wavenumber (*ω*), (d) size of nanocrystalline silicon (*d*) change with focal spot from the center to the edge. The red line in this plot shows the actual position of the edge. (e) Atomic force microscope image of the silicon wafer surface close to Raman testing area. The inset plot is the cross-sectional profile measured along the direction of black dash arrow in the left, and the edge of the wafer is located in the lower left (black area).

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that in the thick Si wafer sample (about 1 μm), which means that the area containing nanocrystals is smaller. Because of the ultrathin thickness, the wafer is easily and quickly divided, and so the stress caused by cleaving impacts a smaller region. To evaluate the smooth surface of the thin Si wafer near the cleaving edge, AFM study is conducted, and the result is shown in Fig. 5(e). The upper side of this image is the silicon wafer, and the edge is on the lower left side. The inside plot is the cross sectional profile along the black line on the left, and it indicates that the surface of the thin Si wafer is smooth at the edge and no roughness will affect the Raman intensity during testing.

Conclusion

In this work, Raman spectroscopy was conducted for mechanically cleaved Si wafers of 270 and 7 μm thicknesses. When the probe laser point was moved from the center to the cleaved edge by a distance of 1.75 μm, a very surprising phenomenon was observed: the intensity of 521 cm^{-1} peak increased abnormally, up to 100%. Our careful study of the surface morphology near the edge by using AFM and SEM did not reveal change on the Si surface to explain such an abnormal intensity increase. Also, the out-of-focus effect was ruled out based on the observed Raman shift change and linewidth broadening. According to the Raman wavenumber change, the crystalline size within the Si wafer was evaluated. It changes from 20 to 10 nm when the laser point is moved from the center to the cleaved edge. Meanwhile, both the linewidth and wavenumber changed by about 2 and 4 cm^{-1}, respectively. If instrument and surface effects are well defined, the change of Raman intensity could provide a sensitive and complementary way to characterize grain size.

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