

Raman Spectra of Silicon

Experiment #6

Characterization of Materials (96.445/545)

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Objective

The purpose of this lab is to measure the atomic mass of a sample of natural silicon.

Experimental Equipment

The experimental equipment used for this lab included:

- Isotopically pure flake of silicon, and a flake of natural silicon
- The RSI Raman spectroscopy system
- The X Powder software on the laboratory computer (used for determining the position and FWHM of Raman lines)

The BTX system and X Powder software were described in detail in previous reports.

Procedure

1. Sample Preparation

The samples were already prepared by the instructor.

2. Loading the Raman Platform

We carefully layed the silicon wafers onto the sample holder. We didn't rotate the samples. A few exposures were made to find the correct settings, and the optimum height for the laser and position on the sample for the laser focus point. For both samples, the settings that worked were 10 second exposure times at about half the peak laser intensity. The samples were positioned about a quarter of an inch below the spot aperture. The spot size was completely on the sample with very little diffuse scattering – the specular part of the isotopically pure silicon wafer was the optimal position for good signal to noise.

3. Acquire exposures.

We acquired about 10 exposures of 10 second integration time each. Visually, we decided that the signal to noise for a 'good' sample was about 3 to 1.

4. Save Exposures and Data Preprocessing

We saved the data to disk and copied it from the Raman computer to the laboratory computer. We used the Perl script to convert the csv file format to a text format compatible with the X Powder software.

5. X Powder Processing

The data sets were loaded into X Powder and then the "STACK" and "TOOLS | ADD" options were used to average the data sets. The interactive cursor tool was used to find the positions of the line center, and the half max point to the right and left of the line center. The plot offset was set from 3.01 to 0.01 (a requirement of using X Powder in this hacked way). To get the values in wavenumbers, the values X Powder interprets as 2Theta are multiplied by 10 and 200 is added.

Results and Discussion

Peak Position and FWHM

The measured positions and FWHM are given in Table 1. Plots for the Isotopically pure sample and for the Natural Silicon sample are given in Figures 1 and 2. The stacked spectra are appended at the end of the laboratory report.

Table 1: Measured Raman Frequency and FWHM

Sample	Si ²⁸ (Isotopically Pure)	Si ^x (Natural)
Center Position (cm ⁻¹)	499	517
FWHM (cm ⁻¹)	22	19

Figure 1: Raman Spectra of Isotopically Pure Silicon.

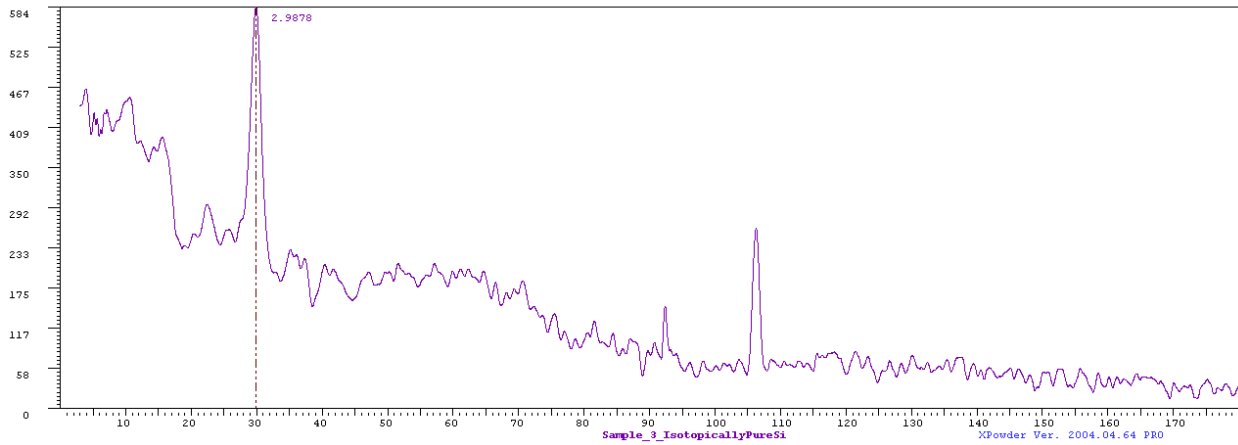
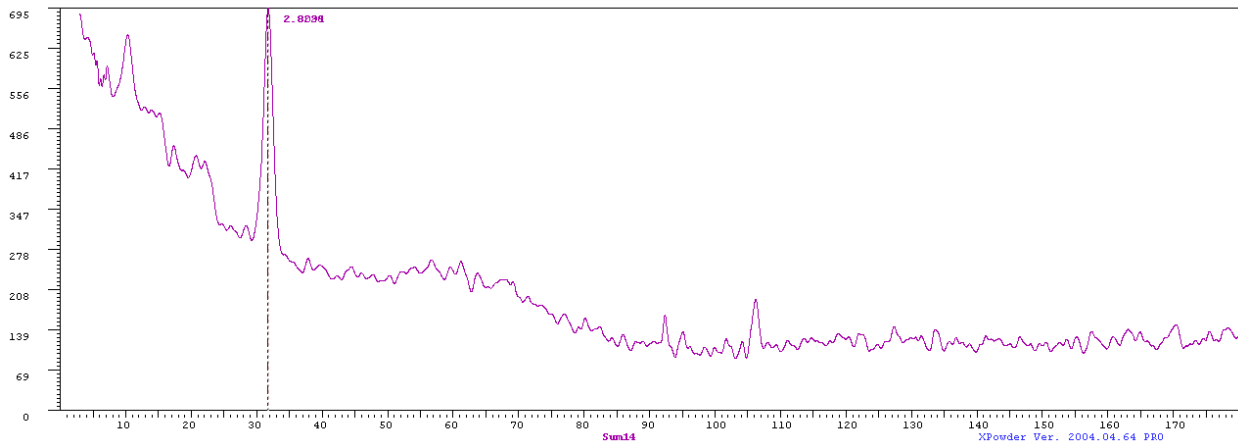


Figure 2: Raman Spectra of Natural Silicon



Conclusions

Natural silicon has a diamond crystal structure and is mostly Si^{28} with the Gamma Point Raman line around 519 cm^{-1} (Simets, 2009). Materials that crystallize in the diamond structure follow a simple scaling relation:

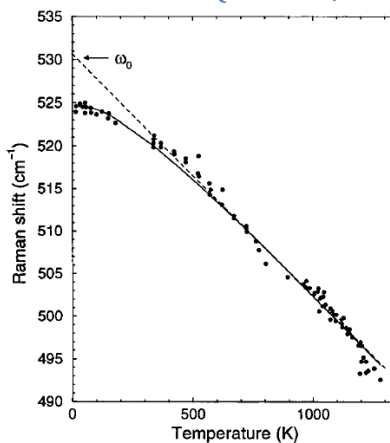
$$\omega \propto (\bar{m})^{-\frac{1}{2}}$$

This is called the trivial isotope effect, and accounts for most of the shift in Raman spectra of Silicon.

$$m = \frac{\omega_0^2 m_0}{\omega^2} = \frac{k^2 m_0}{k_0^2} = \frac{517^2 \cdot 27.982 \text{ amu}}{499^2} = 30.0372 \text{ amu}$$

Temperature also causes a Raman shift, but in the laboratory at room temperature it is expected to be only about 2 cm^{-1} and both the samples would be shifted (Figure 3). If both are shifted 2 cm^{-1} , the mass of the natural silicon is found to be 30.0456 amu.

Figure 3: Anticipated Temperature Effects on Raman Shift (Widulle, 2001)

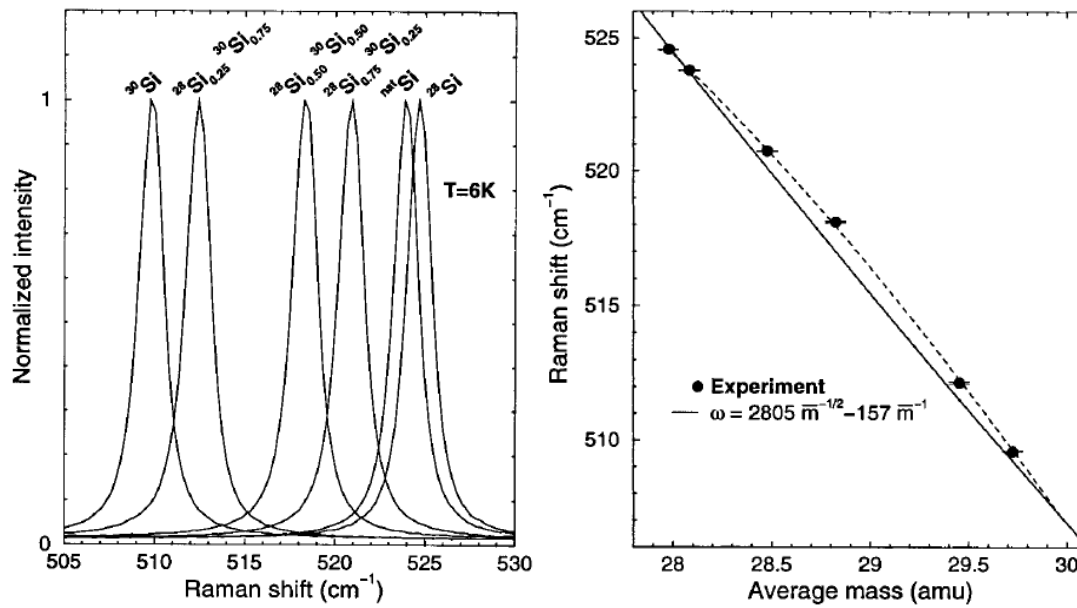


The value of natural silicon is higher than that found in the literature in the literature (Table 3, Figure 6). The values in Table 3 were determined by secondary-ion mass spectrometry (SIMS) and thermogravimetric mass spectrometry (TGMS) (Widulle, 2001). Furthermore, extrapolating from that experimental data for our found atomic mass, the Raman peak should have been closer to 505 cm^{-1} instead of at 499 cm^{-1} . Perhaps the sample had some contamination. We didn't wash it prior to making Raman measurements.

Table 3: Isotopes of Silicon and measured atomic mass (Widulle 2001)

Nominal isotopic composition	Actual isotopic composition $m_{28}/m_{29}/m_{30}$ (%)	\bar{m} (amu)	g_2 (10^{-5})
^{28}Si	99.7/0.1/0.2	27.982	1
$^{\text{nat}}\text{Si}$	92.23/4.67/3.10	28.086	20
$^{28}\text{Si}_{0.75}^{30}\text{Si}_{0.25}$	74.7/0.3/25.0	28.479	92
$^{28}\text{Si}_{0.50}^{30}\text{Si}_{0.50}$	56.3/2.4/41.3	28.826	114
$^{28}\text{Si}_{0.25}^{30}\text{Si}_{0.75}$	25.09/0.56/74.31	29.453	88
^{30}Si	11.9/1.2/86.9	29.724	48

Figure 6: Measured Raman Shifts in Literature (Widulle, 2001).



References

Stimets (Private Communication), 2009.

Widulle, et. al., Isotope Effects in Elemental Semiconductors: A Raman Study of Silicon, Solid State Communications 118, 2001

Extra Figure 1: Stacked Raman Spectra of Isotopically Pure Silicon



Extra Figure 2: Stacked Raman Spectra of Natural Silicon

