X-ray diffraction in materials science

Goals:

- Use XRD spectra to determine the orientation of single crystals and preferred orientations in a thin film.
- Understand how grain size and strain affect the shape of XRD peaks.
- Use XRD as an analytical tool to determine the composition of a sample.

> ***In the XRD-1 lab you learned how the position and relative intensities of XRD peaks can be used to determine the crystal structure of a sample. In this lab you will learn how XRD can also be used to gain information about the microstructure of a material—e.g., grain size, grain orientation, distribution of strain, and composition.***

I. Background

In this lab you will study Si, Ge, and W. These materials are widely used in the microelectronics industry. Si and Ge are used as substrates and active materials in electronic devices. They display complete solid solubility, allowing the growth of alloy layers of any desired composition which, in turn, gives control over the lattice constant and electron mobility. W is widely used as a metal contact due to its low resistivity, but further thermal processing can result in its reaction with Si, forming tungsten silicides WSi_x which results in an undesirable reduction in electrical conductivity.

To study these effects, Si-Ge alloying and WSi_x formation, we will use XRD as an analytical technique (to detect the presence of newly formed phases) and we will have a closer look at the shape of the diffraction peaks to obtain information about the microstructure of our samples.

We begin with Bragg's law:

$$\lambda = 2d\sin(\theta). \tag{1}$$

If there is a *uniform* strain ε in the sample, the modified lattice constant produces a peak shift to a new position θ'

$$\sin(\theta') = \frac{\lambda}{2d'};\ \text{with}\ \varepsilon \equiv \frac{a'-a}{a} = \frac{d'-d}{d}. \tag{2}$$

If the sample contains a non-uniform strain field, the lattice constant will vary from region-to-region of the sample, resulting in peak broadening arising from the superposition of multiple shifted peaks. (For this to be true, the length scale over which the train varies must be larger than the coherence length of the diffraction.) The magnitude of this inhomogeneous broadening in terms of the microstrain η is

$$\mathrm{FWHM}_{\mathrm{strain}} = \eta \tan(\theta)\,. \tag{3}$$

Common sources of strain in the sample are defects (e.g., vacancies, dislocations, or stacking faults) and alloying. The lattice constant of an AB alloy typically follows Vegard's law

$$a(x) = (1-x)a_A + x a_B\,, \tag{4}$$

where x is the composition (atomic fraction of B) of the alloy. Usually, Vegard's law has a tendency to overestimate the lattice constant (bowing effect) and works better for alloys of compounds with similar electronic structure.

Another source of peak broadening is the finite crystallite size. The bigger the size of the diffracting crystal the more atoms contribute to the diffraction pattern and, just like in the case of an array of scattering centers, the sharper the peaks get. Conversely, small grains generate broad diffraction peaks

$$\mathrm{FWHM}_{\mathrm{size}} = \frac{0.9\lambda}{<L> \cos(\theta)}\,, \tag{5}$$

where <L> is the volume-weighted average grain size (diameter) in the sample.

The peak broadening arising from strain and size effects add to give the sample broadening

$$\mathrm{FWHM}_{\mathrm{size+strain}} = \frac{0.9\lambda}{<L> \cos(\theta)} + \eta \tan(\theta)\,. \tag{6}$$

The different θ-dependence of the strain and grain-size contributions to the peak broadening sometimes allows us to separate the two mechansisms. Multiplying eq. (6) by cos(θ) gives

$$\mathrm{FWHM}_{\mathrm{size+strain}} \cos(\theta) = \frac{0.9\lambda}{<L>} + \eta \sin(\theta)\,, \tag{7}$$

which means that <L> and η can be determined from a linear fit to the data plotted as FWHM cos(θ) vs. sin(θ).

However, a complication arises from the limited resolution of the x-ray diffractometer, which results in further peak broadening. The instrumental broadening can be characterized using a line width standard, e.g., a set of large, strain-free crystals. For Gaussian peak profiles, the instrumental broadening is described by

$$\mathrm{FWHM}_{\mathrm{inst}}^2 = \mathrm{u}\tan^2(\theta) + \mathrm{v}\tan(\theta) + \mathrm{w}\,. \tag{8}$$

Once the instrumental broadening is characterized (the value of the u,v,w parameters in Eq. 8), the instrumental broadening can be subtracted from the observed broadening to measure sample grain size and strain, using

$$\mathrm{FWHM}_{\mathrm{observed}}^2 = \mathrm{FWHM}_{\mathrm{inst}}^2 + \mathrm{FWHM}_{\mathrm{size+strain}}^2\,, \tag{9}$$

where $\mathrm{FWHM}_{\mathrm{observed}}$ is determined from a least squares fit of a Gaussian to the observed diffraction peak

$$I_{\mathrm{Gauss}}(x) = A\exp\left[\frac{(x - x_0)^2}{2\sigma^2}\right]; \quad \mathrm{FWHM} = 2(\ln 4)^2\,\sigma\,. \tag{10}$$

II. Experimental procedure

Note: Read trough this section and plan your experiments before you start acquiring data and making samples. You will not have time to complete your assignment unless you make efficient use of your lab time.

1. For each spectrum you measure, write down the conditions (range, step size, and scan speed) in your lab book.
2. Take a survey spectrum of a single crystal Si wafer and of a W thin film deposited on Si. Use the pdf charts for Si and W to index these patterns.
3. Take detailed spectra of each Si and W XRD peak in the above patterns. Pick adequate step size, 2θ range, and scan speed to obtain a detailed peak shape in a reasonable time. You will be using the data to characterize the resolution of your instrument (from the Si data) and the thin film microstructure (from the W data.)
4. Prepare a Si-W powder mixture and a Si-Ge powder mixture of known composition using the precision balance in the lab. Approximately 20%-30% (atomic percent) of W and 40%-60% (atomic percent) Ge is OK. You will be using these samples as standards and to prepare Si-Ge alloy and WSi_x samples.
5. Take survey spectra of both powder mixtures before annealing.

6. Anneal both powder mixtures in the vacuum oven using the provided program (2h at 1200 °C, slow ramp down to 1100 °C, hold for 1h, then cool down). The oven takes a long time to cool down, so you will be loading your crucibles at the end of the lab session and the TA will take them out and store them the next morning. Coordinate with the other group using the oven and keep track in your lab-book of which crucibles are yours and what are the contents.

7. Take survey spectra of both annealed samples and use the provided pdf charts to index them.

8. Take detailed spectra of as many peaks in the annealed Si-Ge sample as you have time. Ignore the (111) peak as you will not be able to deconvolve it because the d-spacing is large.

III. Data analysis

A. Instrumental broadening

9. Each of the Si peaks in the wafers shows a doublet arising from the $CuK_{\alpha 1}$-$CuK_{\alpha 2}$ split. Characterize the position (2θ) and width (FWHM) for both sub-peaks and use them to characterize the instrumental broadening of your diffractometer.

B. Preferred orientation

10. What reflections are present in the Si wafer? And in the W-coated Si wafer? What are the orientations of the wafers and the W thin film?

11. Fit a Gaussian curve to each of the detailed scans of the W peaks in the W/Si wafer and note down the peak position (2θ) and peak width (FWHM). Use this information to characterize the grain size and strain in the W film. Take into account the instrumental broadening corresponding to each W peak.

C. WSi_x formation

12. Use the provided pdf charts to index the XRD patterns of both the annealed and non-annealed W-Si powder samples. Include the labeled patterns in your report and compare them. What are the phases present in both of them?

13. Identify the strongest Si and W peaks in both patterns. Use the intensity ratios W/Si and the known composition of the non-annealed sample to estimate the W/Si at% ratio in the annealed sample. Assuming that only the majority WSi_x phase is formed, what fraction of the sample has reacted? Note that the peak intensities are also proportional to the acquisition time, i.e., (scan speed)$^{-1}$.

D. SiGe microstrcture

14. Use the provided pdf charts to index the XRD patterns of the annealed and non-annealed SiGe powder mixtures. How many phases are present on each sample? How does the pattern change upon annealing? Why? Does any preferred orientation develop?

15. Fit a Gaussian curve (or a sum of Gaussian curves, if needed) to each of the detailed XRD scans of the annealed SiGe sample. Identify which sub-peaks correspond to each phase and use the position (2θ) and width (FWHM) of the Gaussian fits to characterize the grain size and strain of each phase present in the sample.