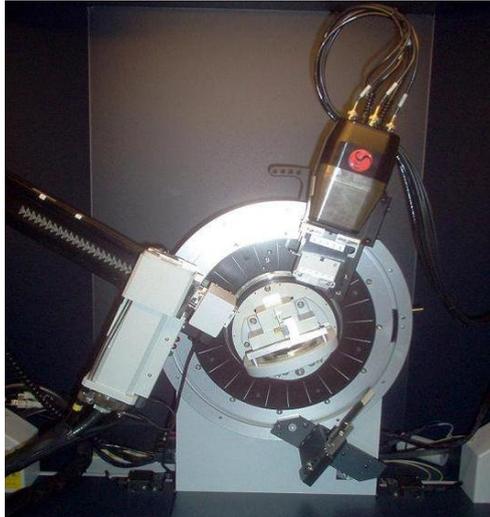


Basics in X-ray Diffraction and Special Application



Introduction:

X-ray Diffraction (XRD) helps one to reach the science at atomic scale in the analysis of crystal structure, chemical composition, and physical properties of bulk and thin film crystalline or polycrystalline materials. Semiconductor industries use XRD to know crystallite size, lattice strain, chemical composition, and crystal orientation. While biological samples such as DNA, vitamins, protein, drug synthesis, use XRD to identify its elements and their crystal structure. It can also be used to identify arrangement of atoms in minerals, alloys, organic and inorganic complex compounds. Thus it has become the back bone of material characterization.

XRD- Under the Hood

Crystals are periodic arrangement of atoms. A beam of x-ray which is directed towards the crystal interacts with its electrons, which undergoes elastic collision to make them oscillate and hence an electron cloud act as secondary source to release coherent source of Electromagnetic radiation of same frequency and phase as that of the incoming X-ray. The emission will undergo constructive or destructive interference with the radiations from other atoms. For constructive interference, the diffraction peaks are measured. The peaks are recorded and analysed to calculate the desired set of properties of the crystal.

Constructive interference as mentioned above follows Bragg's law, while destructive interference disobeys the same. As shown in Figure 1, the sample (thin film on a substrate) is exposed to x-ray beam of wavelength (λ) at an angle θ with the tangential surface which undergoes diffraction and is detected at a specular angle of 2θ . Bragg's law is used on the perpendicular spacing between two consecutive crystallographic planes parallel to the surface of a film.

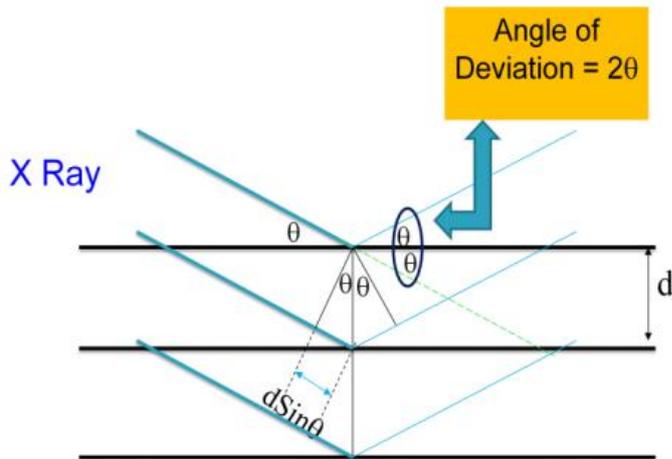


Figure 1: X-ray diffraction from different planes follow Bragg's Law

Other parameters such as texture measurement (i.e. to know about crystallographic orientation) can be recorded by diagnostic as shown in the figure 2. Here the angle of deviation (2θ angle) is kept fixed, while the sample is rotated over the polar (ψ) and the azimuth (ϕ) angle, and the intensity is recorded. Each angle of deviation has its own corresponding miller indices (h,k,l).

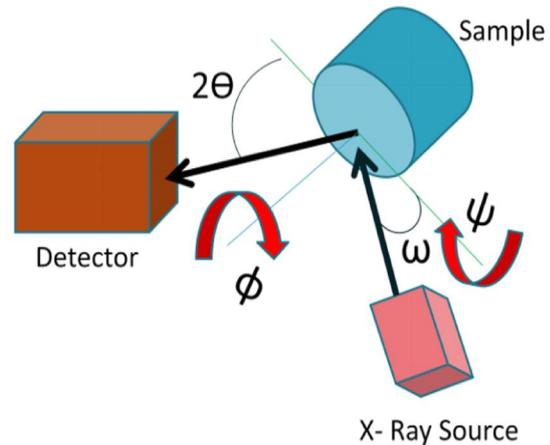


Figure 2: Schematic diagram of source, sample, detector with different measurement angle .

Analysis of measurement:

Commonly X-ray diffraction gives graph of Intensity versus 2θ . This scan result provides a signature peak of the phases present in the sample. By comparing this signature peak with standard reference patterns, the required properties can be identified of the subjected material. The unit cell crystal structure and its parameters can also be determined as follows.

For every intensity peak, its corresponding value of θ and $\sin^2\theta$ is calculated. The value of $\sin^2\theta$ not being an integer, should be converted to integer by scaling with any arbitrary factor. The obtained integers are equated to $h^2+k^2+l^2$, and then the probable values of h, k, l are to be evaluated.

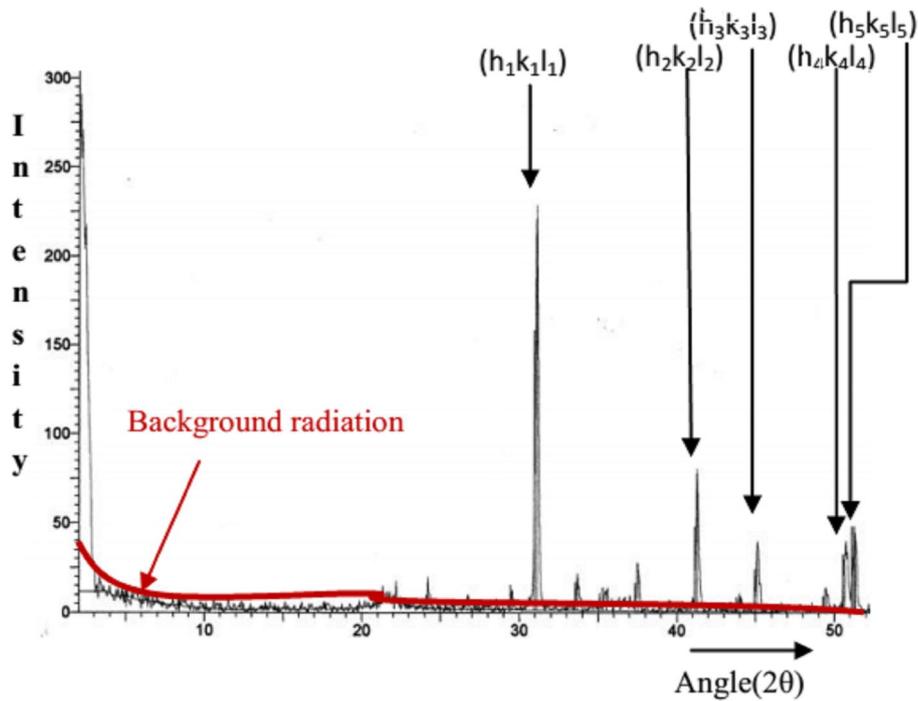


Figure 3: X-ray diffraction intensity versus angle pattern

By examining these set of values, the crystal structure can be interpreted. For instance all even or all odd values of h, k, l will result in FCC crystal structure. For each set of obtained h, k, l plane, the lattice parameter ' a ' can also be calculated. The lattice parameter ' a ' is used to know about the physical dimensions of crystal structure. The point worth mentioning is that the value of ' a ' obtained from each h, k, l plane as shown in figure 3 for different θ is approximately same.

Figure 4 (a) shows the broadening of the intensity peak defined by full width half maximum (FWHM). Instrumental errors such as a non monochromatic x-ray beam and imperfect focusing lead to broadening of intensity peak. It may also happen due to residual strain arising from dislocation of coherent precipitates. In principle every defect contributes to some broadening of peak which shown in figure 4 (b). The distortion in the result suggests that there are defects in the crystal structure, strain or stacking fault in the crystal. While the crystallite size and the FWHM of recorded data follows inverse proportionality.

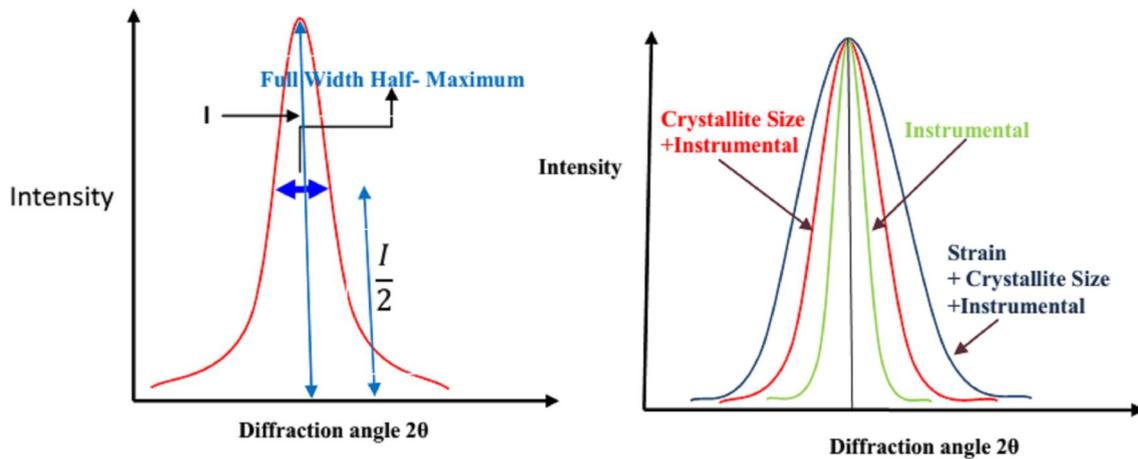


Figure 4: (a) Schematic diagram showing FWHM (b) broadening of intensity peak

If the analyzed crystals are free from micro-strain and defects, while considering the error factor of instrument to be negligible, the peak broadening would then only depend upon the crystallite size. In this case crystallite size (grain size) is determined from the Scherrer equation.

In Scherrer equation K (as shown in figure 5) is about 0.94, β_c and β_s is the broadening of intensity due to crystallite size and strain in the film at FWHM (in radians). The broadening of intensity peak due to crystallite size broadening and strain broadening at FWHM is given by β .

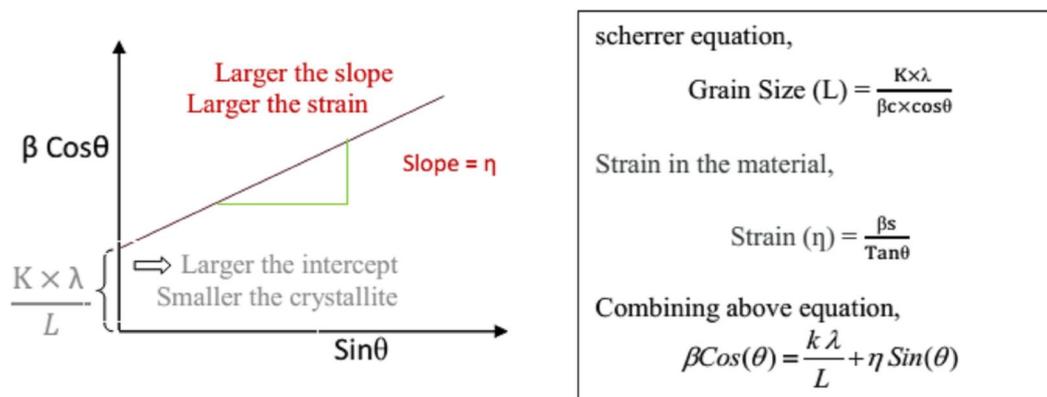


Figure 5: Schematic diagram to calculate crystallite size and strain

From above graph (figure 5) the values of L and η can be determined by plotting graph between $\beta \cos \theta$ vs. $\sin \theta$. Linear graph obtains the intercept at x axis helps in calculating the grain size and the slope gives value of strain in the film. Larger the intercept smaller the crystallite size and larger the slope larger the strain as shown in the above graph.

In the case of Ultra thin film (~2-100 nm), the epitaxial layer on the substrate will be very thin, causing to bring out the required characteristics of substrate rather than that of the epitaxial layer as shown in figure 6. In order

to mitigate this, the angle of incidence of x-ray is made very low, enhancing the diffraction signal from the film. Hence, allowing accurate determination of structure and quantification of lattice parameters of ultra thin films.

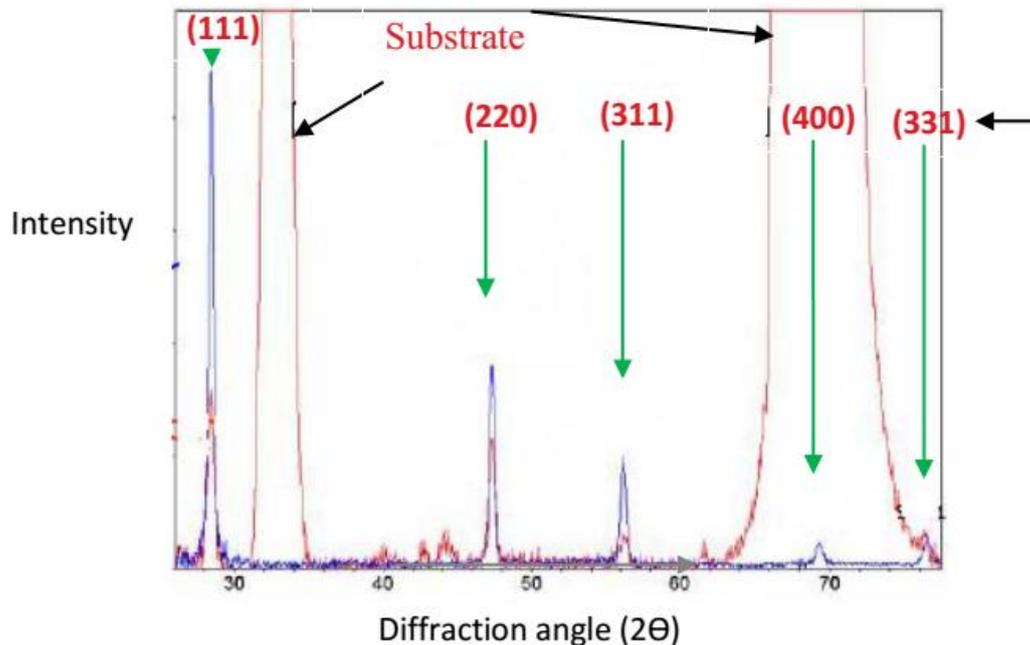


Figure 6: X-ray diffraction pattern of poly silicon film of 100nm on silicon substrate of orientation (100)

X-ray analysis also helps to know the texture orientation and their quantification by using pole figure analysis of texture materials. It may also be done by comparing relative peak height or area obtained from a 2θ scan with the expected relative intensity from a standard (same material) with no preferred orientation (Powder).

Other Applications:

This XRD method analyses atomic and sub atomic characteristics of cells, liquid crystalline biological sample, protein, nucleic acid, is also helps in the development of the design of complex artificial biological sample as well to modified their structure for desire result by combing different type of cells. For biological sample small angle x-ray diffraction is used. XRD reveals molecular size, elemental analysis, structure of biological sample. The interpretation of X-ray diffraction data of virus cell reveals the sequence of protein, nucleic acid, lipids etc. Also, in protein the relative sequence of amino acid torsion and bond length of cell in protein.

Drawback:

Due to the scattering of incoming x-ray from collimator, specimen support and air molecules rather than specimen material causes a distortion in the Intensity vs. diffraction angle (2θ) graph. The scattering which includes

incoherent (eg. Compton scattering) and coherent (Diffuse scattering) scattering contribute in distorting the results. This causes difficulty in analyzing the weak intensity signal in the XRD pattern.

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