Quantitative analysis of X-Ray diffraction spectra for determine structural properties and deformation energy of Al, Cu and Si

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Abstract. X-Ray Diffraction (XRD) method was used to analysis structural properties of Al, Si and Cu as cubic crystal system. Existence of Al, Si and Cu was investigated with the joint committee on powder diffraction standards (JCPDS) by 96-901-3104 for Si, 96-431-3215 for Al and 96-901-1605 for Cu respectively. In this paper we determine the concentration of our sample from the 3 or 4 peak area and the intensity of each peak. The content of Al, Si and Cu are 78.97%, 80.69% and 82.51% respectively. Relative texture coefficient (RTC) value investigated from diffraction by using h k l plane. Energy density, stress and strain were calculated using uniform density model (UDM), uniform stress deformation model (USDM), uniform deformation energy density model (UDEDM) and size-strain plot method. For the crystallite size we applied the Scherrer equation, Williamson-Hall (W-H) analysis and Size-Strain plot (SSP) method. High correlations the crystallite size found from the results by Scherrer, W-H, and SSP.

1. Introduction

X-ray diffraction (XRD) is conventional practice for study analysis materials. From diffraction data the crystalline size, strain, stress and density energy of material determinated. Materials nanoparticle is the most commonly calculated sample using Williamson Hall method. Based on the needs and functions of the material is very high, then done a fairly complete calculation to determine the right size. Semiconductor materials such as ZnO and Fe3O4 are one of the most commonly used materials[1,2]. Reference [3,4,5] using the same materials and methods, but the relative texture calculations and percentages have not been presented. In this study, in addition calculate the size, we will also calculate the texture and a percentage of the material content [4]. We propose to obtain the many expressions for each sample as a cubic system by several calculation methods. The Relative Texture Coefficient (RTC) for Si, Al and Cu has been determined using the peak intensities of the diffracted from [hkl] planes. Texture is an important variable for knowing about influence physics and chemistry for the samples [4]. The diffraction widening provides information on crystalline size and lattice strain [3], particle size is not same crystalline size. Crystal imperfections will cause the distribution of lattice strain. The d-spaces of the Bragg equation are affected by these two variables (size - strain) in different ways. Both causing widening of peaks and increased intensities and shifting.
the position of the x-axis (2 degrees) accordingly [6]. Scherrer equation is often used to calculate the crystal size of the XRD data for each hkl plane. Calculating the strain used by the equation $\beta = 4\tan(\theta)$ as its effect on widening peak [7]. In different ways, Williamson-Hall (W-H) method is good for estimate crystalline size and strain. The result of its method was crystallite size ($D$), lattice strain ($\varepsilon$), lattice stress ($\sigma$) and lattice strain energy density ($u$). W-H plotting had four plotting were uniform deformation method (UDM), uniform stress deformation model (USDM), uniform deformation density model (UDEDHM) and size-strain plot method (SSP). In this paper, we present the compare result measure of crystallite size with Scherrer method and (W-H) method.

2. Experimental

Silicon (Si), Aluminium (Al) and Copper (Cu) as a cubic system used in this study. Si is second greatest abundant element on the earth after oxygen, and often used to make optic’s sensor [8] but in nature pure Si rarely found. Besides that, Si used for making semiconductor materials, which will have an important role in the optical equipment industry [9]. Aluminium is soft and malleable metal with silvery-white lightweight. Al is often used in electrical transmission lines because it is a good electrical conductor [10]. According to reference [9] the advantage of using powder (Al), can improve combustion performance. Cu is metal with good electrical conductivity, low costs and very high thermal, besides that it most widely used materials in the world [11,12,13]. Crystal phases of the each sample powders Si (Shimadzu), Al (CAT 1056) and Cu (CAT 2703) were determined by X-ray diffraction (Shimadzu 7000) using wavelength ($\lambda$) 1.54 Å for CuKα radiation (40kV and 30mA), scan range from 20° to 80°, sampling pitch and scan speed was 0.02° and 2 deg/min respectively.

3. Data Analysis

3.1 Compound

Si, Al, and Cu content according to Join Committee Diffraction Standard (JCPDS): 96-901-3104 [14], 96-431-3215 [15], and 96-901-1605 [16] respectively. We calculate lattice parameters, use the Material Analysis Using Diffraction (MAUD) with standard data crystallography information file (CIF) 4507226 [17] for Si, 1502689 [18] for Al and 4105681 [19] for Cu. In this paper, we determine the concentration of the samples by the peak area and the difference in intensity of each diffraction peak. By using calculation:

$$P_I (%) = \frac{I_0}{\sum I_a} \times 100\% \quad (1)$$

$$P_P = \frac{A_0}{\sum A_a} \times 100\% \quad (2)$$

$P_I$ and $P_P$ were percentage of content with diffraction intensities and pixel area value, respectively. $I_0$ is the intensity that matches the sample compound, $I_a$ is all peak in diffraction data. $A_0$ is an area of the pixel at the peak corresponding to the sample compound, $A_a$ is all areas at the each diffraction peak.

3.2. Relative Texture Coefficient (RTC)

Relative texture coefficient (RTC) value investigated from diffraction of the hkl plane. In this study, we investigated variation reflection line [111], [202], [131], [040], [313] for Si, [111], [200], [202], [311] for Al then [111], [200], [202] for Cu. RTC can be calculated by using the following equation [15].

$$RTC_{(hkl)} = \frac{R_{(hkl)}}{\sum R_{(hkl)}} \times 100\%; \quad R_{(hkl)} = I_s(hkl)/I_p(hkl) \quad (3)$$

$I_s(hkl)$ is diffraction intensities measured in the sample, $I_p(hkl)$ is diffraction intensities from standard sample. Investigation characterizes the crystalline variation RTC values shown in figure 2 for each sample.
3.3. Young Modulus

Young Modulus $(E_{(hkl)})$ determined by using equation below \(^{[20]}\), as we know

$$E_{(hkl)} = \frac{\sigma}{\varepsilon}$$  \(4\)

Where $\sigma$ and $\varepsilon$ is the stress and strain of the crystal, respectively. According to ref \(^{[20]}\) substituting variable $[hkl]$ on the $1/E_{(hkl)}$ for cubic crystal system can be expressions:

$$\frac{1}{E_{(hkl)}} = s_{11} - 2s_0 \frac{(hk)^2+(hl)^2+(kl)^2}{(h^2+k^2+l^2)^2}$$  \(5\)

Compliances ($s_{11}$ and $s_0$) in units $10^{-12}$m$^2$/N for (Al = 15.7 and 3.55), (Cu=15 and 14.67) and (Si 7.68 and 3.54) respectively. $E_{(hkl)}$ calculation based on Hooke’s law can be used for calculating stress, strain and energy deformation of the crystal.

3.4 Size and Strain

As we are shown in figure 1, all samples were not pure. Full width at half maximum (FWHM) of all diffraction peaks allow us to estimate the crystalline size and lattice strain. According several reference \(^{[14,15,16]}\) hkl plane for each sample can be determined. Crystalline size (D) and lattice strain ($\varepsilon$) can be calculated by;

$$D = k\lambda/(\beta \cos \theta)$$  \(6\)

$$\varepsilon = \beta/4*tan\theta$$  \(7\)

$K$ is shape factor for crystal in direct space, $\lambda$ is wavelength incident radiation from x-ray diffractometer and $\beta$ peak width parameters must corrected to resolve the instrument effect. According to reference \(^{[7]}\), the FWHM parameters can expressions: $\beta^2 = (\beta^2)_{s} - (\beta^2)_{exp}$ ; $\beta_s$ is the width from standard sample and $\beta_{exp}$ is width from measured. The contribution the both (D and $\varepsilon$) to the line broadening of the diffraction data can be described by \(^{[7]}\):

$$\beta = \beta_{D} + \beta_{\varepsilon}$$  \(8\)

Assumption peak width ($\beta$) is the sum peak width from Size and Strain. That’s mean, combination those aspects are convoluted in the FWHM of the diffraction peak. It explains in the several Williamson-Hall methods.

3.5 Williamson-Hall Methods

3.5.1 Uniform Deformation Model (UDM)

Crystal imperfection gives a broadening effect on the diffraction peak. Size and strain have difference contribution for a line broadening. Equations (6 & 7) explain the difference of both, when the peak widening occurs, then the value of $\varepsilon$ will decrease while the widening of the peak is small then $\varepsilon$ increases. But the above explanation has the opposite effect for D. Substitutions of equations (6,7) and (8) will yield the (9) equation as the relation between the widening of the peak in size and strain.

$$\beta = \frac{k\lambda}{D\cos \theta} + 4\varepsilon \tan \theta ; \text{multiply by } \cos\theta$$

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta$$  \(9\)

The above equation is UDM Williamson-Hall plots, we can extract the size and strain from the $y$-intercept and slope. Plotting analysis makes plot analysis make x-axis as $4\sin(\theta)$ and y-axis as $\beta\cos(\theta)$. UDM assumes the strain is uniform for the all directions.

3.5.2 Uniform Stress Deformation Model (USDM)

Hook’s Law describes the limits of stress and strains that material can experience. The proportionality between strain and stress illustrated as linear profile. Equation (4.a) is qualified to estimate small strain of the crystal. in USDM x-axis and y-axis are $(4\sin(\theta)/E_{(hkl)})$ and $(\beta\cos(\theta))$ respectively. Substitution
of equations (4.a) and (8) will yield the equation (9) as the peak widening relation to the stress. Equation (9) can be written as follows:

$$\beta = \left(\frac{k\lambda}{D}\right) + \left(\frac{4\sigma \sin \theta}{E(hkl)}\right)$$  \hspace{1cm} (9)

This method extracted D from the y-intercept and Stress ($\sigma$) from the slope. For $1/E_{(hkl)}$ is obtained from the equation (4).

3.5.3 Uniform Density Energy Deformation Model (UDEDM)

Uniform density energy deformation model (UDEDM) is a way to determine energy density of a crystal \[^3\]. Based on the equation (4.a) we know that relationship, both of energy density with strain and young’s modulus. Where, $u = \left(\frac{\varepsilon^2 E_{(hkl)}}{2}\right)$ then, the equation (9) can be written in the form of :

$$\beta = \left(\frac{k\lambda}{D}\right) + \left(4 \sin \theta \left(\frac{2u}{E_{hkl}}\right)^{\frac{1}{2}}\right)$$  \hspace{1cm} (10)

Plot of $\beta \cos \theta$ as x-axis and $(4\sin \theta / (E_{hkl}/2))$ as y-axis, the slope from it can be extracted to measure the energy density of crystal and the y-intercept for crystallite size. UDEDM assume the crystals are a homogeneous isotropic, but in many cases, its not real \[^{17}\].

3.6 Size Strain Plot (SSP)

The widening the diffraction peak line, size-strain parameters can be obtained taking into account the mean. According to the reference \[^{6,5}\] SSP method has a low precision, but it needs to be done to check back our W-H calculation. Because using the SSP method in isotropic line broadening, average size-strain parameters can be obtained easily. Equation (11) is approximation to estimate crystallite size and strain values with SSP method \[^{3,5,6}\].

$$(d\beta \cos \theta)^2 = \frac{K}{\lambda} (d^2 \beta \cos \theta) + \left(\frac{\varepsilon}{2}\right)^2$$  \hspace{1cm} (11)

In figure (6), $d^2 \beta \cos \theta$ as x-axis and $(d\beta \cos \theta)^2$ as y-axis for all peak each samples from 2\(0 = 20^\circ\) to 80\(^0\). Fit to data D extracted from the slope and $\varepsilon$ extracted from the y-intercept.

4. Result and Discussion

4.1 Compound and Texture

Figure 1 shows the diffraction patterns of Si, Al and Cu samples. The diffraction pattern of each material shows the dominance of Si, Al and Cu in each sub image. We can determine the phase of samples by following to reference \[^{14,15,16}\]. Percentage of purity levels were measured using intensity and peak diffraction peak areas. The calculation results from equations (1 and 2) we obtain Cu 82.5%, Al 80.6% and Si 78.9%. In table 1 the lattice calculation using MAUD application shows an error <10\(^{-4}\), it is quite representative of the actual lattice size value. The size of the cell volume in the cubic crystal can be calculated using the equation $V = a^3$. The largest cell volume is owned by Si and the smallest crystal cell volume is owned by Cu. The size of the cell volume affects the density of the material, in other words a material with a small cell size is a heavy material. The percentage of the texture of the sample can be seen in figure 3. The highest texture coefficient is owned by Cu 56% in the hkl field [111], the second highest is Al 39% in the hkl [111] and the last is owned by Al 34% in the hkl [200]. That means the good surface of the Cu and Si samples will be seen the hkl plane [111], whereas Al is the hkl plane [200].
Figure 1. X-ray diffraction pattern of Si, Al, and Cu as cubic system crystal

Table 1. Structural parameters of Si, Al, and Cu by XRD pattern analysis

| Element | hkl  | \(d_{\text{hkl}}\) (Å) | Lattice Parameter (Å) | Volume (nm\(^3\)) | Error          |
|---------|------|-------------------------|-----------------------|---------------------|----------------|
| Si      | 111  | 3.13                    | \(a=b=c\)=5.42        |                     | 15.92          |
|         | 202  | 1.92                    |                       |                     | Error = 1.98E-04 |
|         | 131  | 1.64                    |                       |                     |                |
|         | 040  | 1.36                    |                       |                     |                |
|         | 313  | 1.25                    |                       |                     |                |
| Al      | 111  | 2.33                    | \(a=b=c\)=4.04        |                     | 6.59           |
|         | 200  | 2.02                    |                       |                     | Error = 1.70E-04 |
|         | 202  | 1.43                    |                       |                     |                |
|         | 311  | 1.22                    |                       |                     |                |
| Cu      | 111  | 2.07                    | \(a=b=c\)=3.59        |                     | 4.62           |
|         | 200  | 1.80                    |                       |                     | Error = 3.46E-04 |
|         | 202  | 1.27                    |                       |                     |                |
4.2 Crystal Geometry

In this paper, the geometry of crystals has been calculated using several methods. Scherrer, W-H and SSP are some of the intended methods. Scherrer method shows the crystal size of each peak. Size variations are obtained from Scherrer calculations. It comes from different FWHM values at each peak. Scherrer method is qualified as an initial calculation for crystal size. The result of Scherrer method obtained the size of crystals for Si is (17 to 28) nm almost the same as the reference \([20,22]\), Al is (31 to 35) nm smaller than the reference \([24,25]\) and Cu is (19 to 25) nm smaller than the reference \([23]\). Size variations can be due to differences in sample preparation of each reference. The result of the W-H plot can be seen in figure 4 to 6. Figure 4 is a uniform density model (UDM), it informs the size and strain of the crystal. Strains obtained from the UDM method were (1.9 for Si, 0.4 for Al and 1.6 for Cu) with units of \(10^{-3}\). Figure 5 is a uniform stress density model (USDM), it informs size extracted from y-intercept and stress extracted from the slope. Stress obtained from the USDM method were (230 for Si, 270 for Al and 110 for Cu) with units of Mpa. Figure 6 is a uniform deformation energy density model (UDEM), it informs size extracted from y-intercept and energy extracted from the slope. Energy density obtained from the UDEDM method were (184 for Si, 5.6 for Al and 90 for Cu) with units of KJm\(^3\). Size strain plot (SSP) method, it informs size extracted from y-intercept and stress extracted from the slope. Table 2 shows all geometric parameters of the samples.

![Figure 2](image_url). Composition of Al, Si and Cu determined by intensity variation and peak area method.
Figure 3. Relative texture coefficient for each miller indices

Figure 4. Particle Size and Strain for Uniform density Model (UDM)
Figure 5. Uniform stress density model (USDM). Size extracted from y-intercept and stress extracted from the slope.

Figure 6. Uniform deformation energy density model (UDEDM). Size extracted from y-intercept and energy extracted from the slope.
Figure 7. Size-strain plot method (SSP). Size extracted from y-intercept and stress extracted from the slope.
Table 2. Geometric parameters of Si, Al and Cu

| Sample | Scherrer Method | Williamson-Hall Method | Size-Strain Plot Method |
|--------|-----------------|------------------------|------------------------|
|        | $D$ (nm) | $\varepsilon$ (nm) | $\sigma$ (Mpa) | $U$ (Mpa) | $\sigma$ (Mpa) | $U$ (Mpa) |
| Si     | [111] 17 [202] 19 [040] 28 [313] 22 | 15 | 1.9 | 16 | 1.5 | 230 | 15.4 | 1.6 | 230.9 | 184 | 25 | 1.54 | 223 | 173 |
| Al     | [111] 31 [200] 31 [202] 35 [311] 34 | 30 | 0.4 | 30.8 | 0.4 | 27 | 29 | 0.41 | 27.2 | 5.6 | 31 | 0.37 | 25 | 4.78 |
| Cu     | [111] 19 [200] 20 [202] 25 | 16 | 1.6 | 16.0  | 1.3 | 110 | 17.4 | 1.86 | 123.4 | 90 | 13 | 1.38 | 117 | 81.2 |

5. Conclusion
In this paper several method used to quantitative analysis of x-ray diffraction spectra for determine structural properties and deformation energy of Al, Cu And Si. Scherrer calculation, Williamson Hall model and Size-Strain Plot Method are good and very helpful to estimate X-RD properties.

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