

# Method for Determining Crystal Grain Size by X-Ray Diffraction

Kai He, Nuofu Chen,\* Congjie Wang, Lishuai Wei, and Jikun Chen\*

The crystal grain size can be quantitatively calculated by Scherrer equation according to the diffraction peak broadening in the XRD curves. Actually, the results calculated by the Scherrer equation are the thickness that perpendicular to the crystal planes. However, in the actual XRD measurements, the broadening of the diffraction peaks is not only because of the Micro-level changes of crystal such as grain size and lattice distortion, but also due to the instrumental broadening. Thus, the Scherrer equation is less reliable if the full width at half maximum caused by the physical broadening is smaller than that caused by the instrumental broadening. In this paper, it is concluded that the applicable range of the Scherrer equation will increase with the increasing diffraction angle. As an example of Scherrer equation's application, the calculation result for the maximum applicable scope of Si(100) films is 137 nm.

## 1. Introduction

In 1895, Roentgen discovered a highly penetrating ray, but people were not clear about the essence of this ray at that time, therefore they used an unknown symbol "X" to name it, known as X-ray. By 1912, Laue discovered the crystal X-ray diffraction effect, which can easily determine the structure of the crystal material at the atomic level without damaging the samples. A large number of important informations of polycrystal can be indicated by X-ray diffraction experiments such as phase composition, lattice parameters, crystallite size, lattice distortion and so on. Hence the X-ray diffraction of polycrystal is widely used nowadays.

The wavelength scope of X-ray applied in crystal diffraction experiments is generally 50–250 pm, which is approximately the same as that of crystal lattice.<sup>[1]</sup> Generally the X-ray used for crystal diffraction is produced by X-ray tube, one part of the X-ray is the "white" ray which comprises continuous wavelength,

generated by the kinetic energy loss when the anode material collides with the electrons. The other part of X-ray is the characteristic X-ray with specific wavelength generated by electron energy level transition of the anode material. The  $K_{\alpha}$  ray, comprising  $K_{\alpha 1}$  ray and  $K_{\alpha 2}$  ray, is produced when the electrons transit from the L layer to the K layer. Meantime, the transition of electrons from the M layer to the K layer generates  $K_{\beta}$  ray, which should be removed by filter or crystal monochromator, namely, monochrome process.

Ideally the diffraction peaks obtained by X-ray diffraction should be narrow and symmetrical. However the peaks have certain widths and shapes in practice.

This is because the Bragg law is only applicable to the perfect crystal, that is, the crystal structure with infinite repetition of the lattice, but crystals in actual measurements do not match this property. In 1918, the relationship between the crystal grain size and the full width at half maximum (FWHM) of diffraction peak was deduced by Scherrer for the first time, known as the Scherrer equation.<sup>[2]</sup> By using the Scherrer equation, we can quantitatively calculate the relationship between the FWHM of diffraction peak and the crystal grain size.

However, in the actual XRD measurements, the broadening of diffraction peak is not only because of the Micro-level changes of crystal such as grain size and lattice distortion, which are called physical broadening, but also due to the non-ideal focus of the light source, leading to the deviation of the diffraction from the strict focusing geometry, namely, instrumental broadening. The value of instrumental broadening has close connection with the X-ray tube voltage and the slit width (including divergence slit, receiving slit and receiving slit sol). Generally, the range of FWHM caused by instrument itself is between  $0.06^{\circ}$  and  $0.09^{\circ}$ . However, the FWHM of monocrystal sample is far less than  $0.06^{\circ}$ . Thus, the Scherrer equation will be less reliable if the FWHM caused by the physical broadening is smaller than that caused by the instrumental broadening. Cullity<sup>[3]</sup> et al. proposed that the application scope of the Scherrer equation should not exceed 200 nm due to the limitation of the diffractometer resolution; and Muniz<sup>[4]</sup> calculated the range of the application can be up to 1  $\mu\text{m}$  when the diffraction angle is larger than  $60^{\circ}$ , which is based on the dynamical theory of X-ray diffraction.

In this paper, we based on the mathematical derivation of the Scherrer equation and showed that the Scherrer equation can only measure the thickness that perpendicular to the crystal

K. He, Prof. N. Chen, C. Wang, L. Wei  
School of Renewable Energy Sources  
North China Electric Power University  
Beijing 102206, China  
E-mail: nfchen@ncepu.edu.cn

Dr. J. Chen  
School of Materials Science and Engineering  
University of Science and Technology  
Beijing, 100083, China  
E-mail: jikunchen@ustb.edu.cn

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plane, that is, the height of the crystal grain, but not the crystal grain size parallel to the direction of the crystal plane. We also concluded that the applicable range of the Scherrer equation is increased with increasing diffraction angle. Meantime, we took Si(100) as an example and calculated the actual maximum applicable scope of Scherrer equation for Si(100) is 137 nm, which concerning both the physical broadening and instrumental broadening. The simulation of the film thickness of Ge(220), C(002) and Al(220) is 121 nm, 114 nm and 133 nm respectively.

## 2. The Scherrer Equation and Application Scope

### 2.1. Interference Phenomenon

The interference phenomenon refers to the phenomenon that two coherent light waves are strengthened or weakened in a specific place due to the spatial coherent superposition. As a kind of electromagnetic wave with remarkably short wavelength, X-ray has the same phenomenon. The occurrence condition of interference depends on the phase difference or the optical path difference of the two light waves. According to the wave superposition principle, when the vibration frequency of two waves is identical, the vibration direction parallel to each other and the phases are same or constant, there will be interference phenomenon. The vibration of two sources can be expressed by the following equations;

$$E_{01} = A_{01} \cos(\omega t + \varphi_{01}) \quad (1)$$

$$E_{02} = A_{02} \cos(\omega t + \varphi_{02}) \quad (2)$$

In which  $\varphi_{01}$  and  $\varphi_{02}$  represent the initial phase of two sources respectively. The following equations express the vibration when the two waves arrive at the point P simultaneously:

$$E_{01} = A_{01} \cos \left[ \omega \left( t - \frac{r_1}{v_1} \right) + \varphi_{01} \right] \quad (3)$$

$$E_{02} = A_{02} \cos \left[ \omega \left( t - \frac{r_2}{v_2} \right) + \varphi_{02} \right] \quad (4)$$

In which  $r_1$  and  $r_2$  are the propagation distance of two waves respectively,  $v_1$  and  $v_2$  represent propagation velocity of each wave. when the two waves interact at point P, the squared amplitude can be expressed as:

$$A^2 = A_{01}^2 + A_{02}^2 + 2A_{01}A_{02} \cos \Delta\varphi \quad (5)$$

The Intensity distribution:

$$I = I_{01} + I_{02} + 2\sqrt{I_{01}I_{02}} \cos \Delta\varphi \quad (6)$$

The phase difference at random time:

$$\begin{aligned} \Delta\varphi &= \omega \left( \frac{r_1}{v_1} - \frac{r_2}{v_2} \right) + (\varphi_{01} - \varphi_{02}) \\ &= \frac{2\pi}{\lambda} (n_2 r_2 - n_1 r_1) + (\varphi_{01} - \varphi_{02}) \end{aligned} \quad (7)$$

In which  $\lambda$  is the wavelength of source,  $n_2$  and  $n_1$  represent refractive index,  $n_2 r_2 - n_1 r_1$  is optical path difference. For the

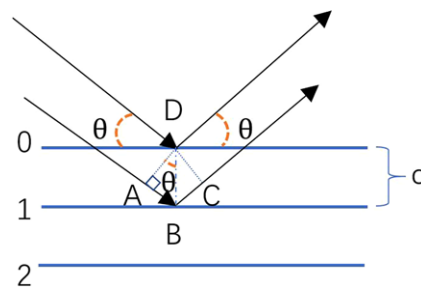


Figure 1. The diffraction conditions of Bragg equation.

reason that the optical path difference can be considered as same as the geometric length difference in the same medium, We consider  $n_1$  and  $n_2$  as 1. Because  $\varphi_{01} - \varphi_{02}$  maintain constant due to the sources are coherent lights, the phase difference depends only on the geometric optical path difference:

$$\Delta\varphi = \frac{2\pi}{\lambda} (r_2 - r_1) \quad (8)$$

When the optical path difference is an even multiple of  $\frac{\lambda}{2}$ ,  $\cos \Delta\varphi$  equals to 1, the squared amplitude and light intensity reach the maximum, leading to constructive interference; when the optical path difference is odd times of  $\frac{\lambda}{2}$ , the result is inversed, the destructive interference is generated.

### 2.2. The Scherrer Equation

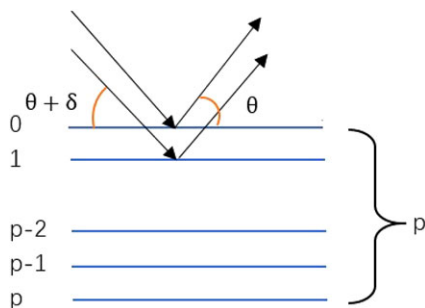
When the crystal composed by parallel atom planes is irradiated by the X-ray, most X-ray diffraction of atom planes will vanish due to the phenomenon of destructive interference, and the other part of X-ray diffraction will enhance mutually. Therefore, the X-ray diffraction of the crystal can be regarded as the reflection of some atom planes to the X-ray, which is the basis for deriving the Bragg equation. For the same crystal lattice, there is no optical path difference for the incident and reflected X-ray, so the interference cannot be produced. Hence the only thing we need to consider about is the interference of different crystal lattice. In this paper, we discuss the interference between adjacent atom planes, assuming that the distance between adjacent planes is  $d$ . As we can see in the **Figure 1**.

When we make the perpendiculars to the incident and reflected line through the point D respectively, the optical path difference  $AB + BC$  equals to  $2d \sin \theta$ . Due to the condition of constructive interference, the interference of neighboring atom planes can be enhanced when the optical path difference is an even multiple of  $\frac{\lambda}{2}$ .

That is:

$$2d \sin \theta = 2n \times \frac{\lambda}{2} = n\lambda \quad (9)$$

This is the essential condition of generating X-ray diffraction in crystal, which is also called Bragg equation. Using the Bragg equation to derive the Scherrer equation may help us understand the application scope of the Scherrer equation intuitively. As shown in **Figure 2**, the grain height  $D$  that perpendiculars to



**Figure 2.** X-ray scattering in crystal plane lattice.

a certain crystal plane equals to  $pd$  when there are  $p$  layers of crystal lattices whose interplanar spacing is  $d$ .

Considering the interference between adjacent atom planes firstly, the optical path difference can be expressed as follows when the X-ray and planes meet the requirement of the condition of Bragg reflection:

$$2d \sin \theta = n\lambda \quad (10)$$

And when the incident angle changes, the optical path difference can be expressed as:

$$2d \sin(\theta - \delta) = n\lambda - \Delta l \quad (11)$$

or

$$2d \sin(\theta + \delta) = n\lambda + \Delta l \quad (12)$$

When the optical path difference equals to the odd times of  $\frac{\lambda}{2}$  ( $\Delta l = \frac{\lambda}{2}$ ), meeting the requirement of destructive interference, the light wave disappears completely. For the crystal grain which comprises  $p$  layers lattice planes, the destructive interference happens between the initial layer and the layer of  $\frac{p}{2}$ , the layer of 1 and  $\frac{p}{2} + 1$  the layer of  $\frac{p}{2} - 1$  and  $p$  when the incident angle  $\theta$  changes a certain angle of  $\delta$ . Hence, the angle  $\theta - \delta$  and  $\theta + \delta$  can be considered as the angles where the diffraction peak arise and vanish respectively. The Mathematical relations are expressed as follows<sup>[1]</sup>:

$$\Delta l_{\frac{p}{2}} = \frac{\lambda}{2} \quad (13)$$

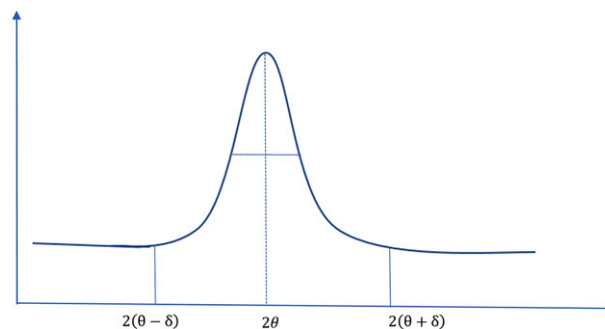
$$\left(\frac{p}{2}\right) 2d \sin \theta = \left(\frac{p}{2}\right) n\lambda \quad (14)$$

$$\left(\frac{p}{2}\right) 2d \sin(\theta + \delta) = \left(\frac{p}{2}\right) n\lambda + \frac{\lambda}{2} \quad (15)$$

$$\sin(\theta + \delta) = \sin \theta \cos \delta + \cos \theta \sin \delta \quad (16)$$

When  $\delta$  is small,  $\cos \delta \approx 1$ ,  $\sin \delta \approx \delta$ ,

$$\begin{aligned} \left(\frac{p}{2}\right) 2d \sin(\theta + \delta) &= \left(\frac{p}{2}\right) 2d (\sin \theta \cos \delta + \cos \theta \sin \delta) \\ &= \left(\frac{p}{2}\right) 2d \sin \theta + \left(\frac{p}{2}\right) 2d \delta \cos \theta \\ &= \left(\frac{p}{2}\right) n\lambda + pd\delta \cos \theta \end{aligned} \quad (17)$$



**Figure 3.** The presence of X-ray diffraction peaks at the Bragg angle.

That is:

$$\left(\frac{p}{2}\right) n\lambda + pd\delta \cos \theta = \left(\frac{p}{2}\right) n\lambda + \frac{\lambda}{2} \quad (18)$$

Because  $D = pd$ , the above equation can be expressed as:

$$D\delta \cos \theta = \frac{\lambda}{2} \quad (19)$$

For the reason that the arise of the diffraction peak is at the angle of  $\theta - \delta$ , as shown **Figure 3**.

$$m \approx 2\delta$$

Hence,

$$m = \frac{\lambda}{D} \cos \theta \quad (20)$$

In which  $m$  is the FWHM.

The accurate Scherrer equation can be obtained when the relationship between the diffraction peak width and the grain size is further considered from the viewpoint of wave superposition:

$$m = \frac{K\lambda}{D \cos \theta} \quad (21)$$

In which,  $D$  is the crystal grain size,  $\lambda$  is the wavelength of X-ray,  $\theta$  is the diffraction angle.  $K$  is the Scherrer constant, ranging from  $\approx 0.62$ – $2.08$ . The value of  $K$  is related to the reflection form and crystal form,<sup>[5]</sup> which is well discussed by J.Langford.<sup>[6]</sup> We usually take  $K$  as  $0.89$ . It is worth noting that the expression of  $K$  is in the form of radian when we take  $K$  as  $0.89$ . So the value of the FWHM should also be expressed in the form of radian in order to ensure the consistency of the unit during the whole calculation process.

### 2.3. The Application Scope of the Scherrer Equation

Consequently, based on the discussion above, it can be concluded that the results calculated by the Scherrer equation are crystal grain height that perpendicular to the crystal planes, instead of the grain size of a certain grain in the horizontal direction. For the monocrystal thin film samples whose grain size are much larger than the thickness of the film, the results calculated by

the Scherrer equation are only the thickness of the film, which are far less than the actual grain size. For instance, Peng Wang<sup>[7]</sup> et al. prepared the monocrystal germanium film with a thickness of 60 nm by the method of Al-induced. Through the EBSD test, Ge film grain size reached 100  $\mu\text{m}$ , which is much larger than the thickness of Ge film, in that situation, if the sample is tested by XRD and calculated by the Scherrer equation, the result is no more than 60 nm, which is far less from the actual grain size. Therefore, the Scherrer equation does not apply to the grain size of the thin film material with thin thickness or the material whose grain size is much larger than the film thickness.

At the same time, the Scherrer equation is only valid for a certain size range of the grain size. For the reason that the derivation of the Scherrer equation is based on the hypothesis that the scatter of incident radiation to each atom is independent, so people did not take into account the crystal atoms type, reflection structure factor, or linear absorption coefficient. Therefore, the application scope of the Scherrer equation had not been taken into consideration at that time.

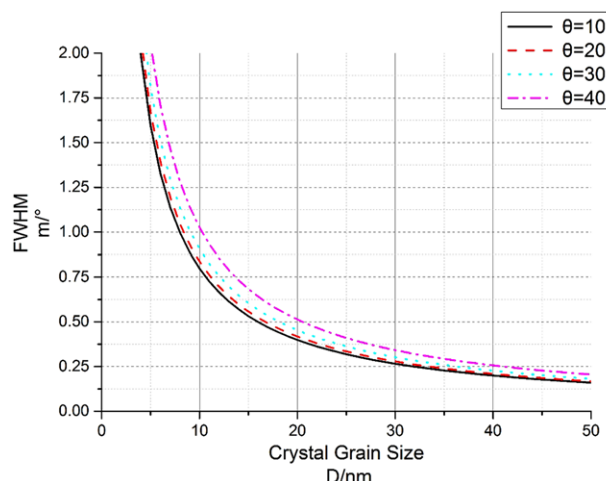
For the past few years, it has been found that the X-ray diffraction kinematics theory which is the basis of the derivation of the Scherrer equation is more appropriate for small-scale crystal grain, so the Scherrer equation is only applicable to the small crystal grain size. The same conclusion can be drawn from further calculation of the Scherrer equation. We take  $K$  as 0.89,  $\lambda$  is the X-ray diffraction wavelength of 0.154056, and convert the FWHM unit to angle. The Scherrer equation can be written as:

$$m = \frac{0.89 \times 0.154056 \times 180}{\pi D \cos \theta} = \frac{7.85581}{D \cos \theta} \quad (22)$$

As we can see, the crystal grain size is inversely proportional to the FWHM( $^\circ$ ) when the diffraction angle takes a certain value. A series of function relationships between the FWHM and crystal grain size can be obtained when the diffraction angle changes. Here we take the diffraction angles of 10, 20, 30 and 40 $^\circ$  respectively, the function curves between the FWHM and crystal grain size are shown as follows

In the **Figure 4**, the variation of the crystal grain size has a great influence on the FWHM when the grain size is less than 10 nm, however when the crystal grain size increases, the variation of the FWHM become unapparent with the increasing grain size. Therefore the results calculated by the Scherrer equation become more imprecise due to the weaker broadening effect when the crystal grain size increases. because the inverse proportional function coefficient increases as the X-ray diffraction angle increases, the FWHM corresponding to the same crystal grain size is also increased. For that reason, the application scope of the Scherrer equation for crystal plane with larger diffraction angle is wider than that of crystal plane with smaller diffraction angle. This is consistent with the conclusion based on the dynamical theory, when the diffraction angle is larger than 60 $^\circ$ , the range of the application can be up to 1  $\mu\text{m}$ .<sup>[4]</sup>

However, the above discussion is based on the ideal conditions of X-ray diffraction. In the actual XRD measurements, the diffraction peak broadening is related to both the physical broadening and instrumental broadening. Therefore, the application scope of



**Figure 4.** The relationship between crystal grain size and diffraction peak.

the Scherrer equation in practice is far less than that in the ideal condition. The relationship of actual FWHM, FWHM caused by instrument and FWHM caused by crystal grain size is connected with the shape of diffraction peak. When the diffraction peak conforms to Lorentz distribution, the actual FWHM of X-ray diffraction peak can be expressed as follows:

$$m = m_1 + m_2 \quad (23)$$

When the diffraction peak conforms to Gaussian distribution, the actual FWHM of X-ray diffraction peak can be expressed as follows:

$$m^2 = m_1^2 + m_2^2 \quad (24)$$

In which  $m_1$  is the FWHM caused by instrument,  $m_2$  is the FWHM caused by crystal grain size.

The Scherrer equation can be written as follows when the FWHM unit in the Scherrer equation is converted into angle:

$$D = \frac{180 K \lambda}{\pi m_2 \cos \theta} \quad (25)$$

That is:

$$m_2 = \frac{180 K \lambda}{\pi D \cos \theta} \quad (26)$$

Therefore, the actual FWHM of diffraction peak in Lorentz distribution can be expressed as:

$$m = m_1 + \frac{180 K \lambda}{\pi D \cos \theta} \quad (27)$$

the FWHM of diffraction peak in Gaussian distribution can be expressed as

$$m^2 = m_1^2 + \left( \frac{180 K \lambda}{\pi D \cos \theta} \right)^2 \quad (28)$$

The grain size  $D$  can be seen as infinite when a monocrystal sample is measured by XRD, so the FWHM caused by crystal grain size tends to 0:

$$m_2 = \frac{180K\lambda}{\pi D \cos \theta} \approx 0 \quad (29)$$

Therefore, the FWHM is only caused by instrument in this situation.

We make use of the Si(100) standard sample to measure the FWHM caused by XRD equipment. The equipment was manufactured by BRUKER company (target material: Cu, the power of X ray generator: 2.2kw, the accuracy of measurement). In software of MDI Jade5.0, it can be found that the FWHM of (400) diffraction plane ( $2\theta = 69.13^\circ$ ) is  $0.07^\circ$ . Thus it can be determined that the FWHM caused by instrument is  $0.07^\circ$ . Then, the actual FWHM of diffraction peak in Lorentz distribution or Gaussian distribution can be expressed respectively as:

$$m = 0.07 + \frac{180K\lambda}{\pi D \cos \theta} \quad (30)$$

or

$$m^2 = 0.07^2 + \left( \frac{180K\lambda}{\pi D \cos \theta} \right)^2 \quad (31)$$

The crystal grain size obtained by the Scherrer equation will be unreliable if the FWHM caused by the crystal grain size is smaller than it caused by the instrument. Therefore, the crystal grain size, which causes the same value of FWHM as instrument does, is considered to be the maximum value of the available range of Scherrer equation.

In order to determine the maximum applicable range of the Scherrer equation for Si (100), We take  $K$  as 0.89,  $\lambda$  as 0.154056 which is the X-ray diffraction wavelength and  $\theta$  as (400) diffraction peak angle of  $35^\circ$ , and that is:

$$0.07^2 = \left( \frac{180K\lambda}{\pi D \cos \theta} \right)^2$$

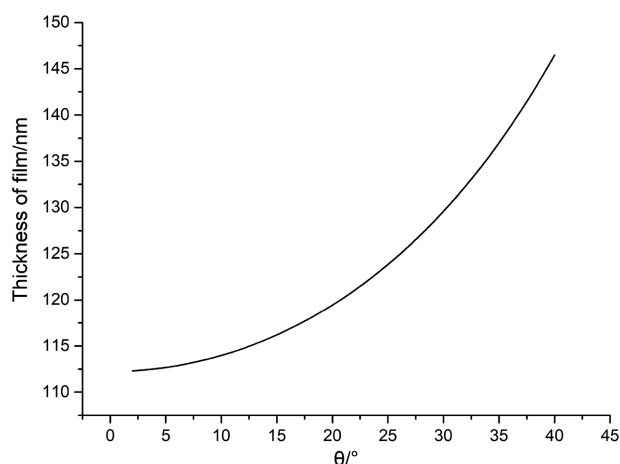
Thus:

$$\begin{aligned} 0.07 &= \frac{180K\lambda}{\pi D \cos \theta} \\ &= \frac{180 \times 0.89 \times 0.154056}{\pi D \cos 35} \end{aligned}$$

$$D \approx 137 \text{ nm} \quad (32)$$

We can see, no matter what shape of diffraction peak it is, the calculating result is same. Therefore, the applicable range of maximum crystal grain size for Si(100) is 137 nm.

For the monocrystal film of different material, which has different crystal direction and diffraction angle, We also calculate the relationship between the diffraction angle and thickness of



**Figure 5.** The relationship between thickness of film and diffraction peak.

film, because the Scherrer equation can be expressed as follows:

$$\begin{aligned} m &= \frac{0.89 \times 0.154056 \times 180}{\pi D \cos \theta} \\ &= \frac{7.85581}{D \cos \theta} \end{aligned}$$

Here, We take  $m$  as 0.07, which is the FWHM caused by instrument, then the relationship between  $D$  and  $\theta$  can be expressed as:

$$D = \frac{112.24}{\cos \theta}$$

The figure of relationship between thickness of film and the diffraction peak can be showed as **Figure 5**.

### 3. Conclusions

In the actual X-ray diffraction experiments, the X-ray diffraction broadening effect results from both instrument and crystal itself. The FWHM can be connected with the crystal grain size(which is actually the grain height) by the Scherrer equation. There are two questions worth paying attention to when we use the Scherrer equation: (1) The result obtained from the Scherrer equation is actually the grain height perpendicular to the crystal plane, Therefore, when the sample is a monocrystal thin film material, that is, the crystal grain size is much larger than its sample thickness, the Scherrer equation is no longer applicable. In that case, the sample can be investigated by electron backscattered diffraction (EBSD), the measurable grain size range is micron level, and the resolution of EBSD is  $0.1 \mu\text{m}$ , it can also analyze the crystal structure and orientation of microdomains, which is widely used in the investigation of crystal.<sup>[8]</sup> (2) the applicable range of the Scherrer equation increases with the increasing diffraction angle, and because the diffraction peak is mainly due to both the instrument and the crystal grain size, the Scherrer equation is also inapplicable when the affect of instrument is more notable than that of crystal itself. According to the calculation, the applicable range of maximum crystal grain size for Si(100) is 137 nm.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

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