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A CONVERGENT BEAM, PARALLEL DETECTION X-RAY DIFFRACTION SYSTEM FOR CHARACTERIZING COMBINATORIAL EPITAXIAL THIN FILMS

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For the rapid structural characterization of combinatorial epitaxial thin films, we developed an X-ray diffraction system. A convergent X-ray beam from a curved crystal monochromator is focused on sample surface about 0.1 mm x 10 mm in size. Diffraction patterns of this area are simultaneously observed on the two-dimensional detector a within few degree. Thus, rocking curve profiles of combinatorial epitaxial thin films for one-column pixels can be measured rapidly with Bragg peak of substrate; the measurement time depends on the film thickness, but the most cases are within one minutes. The angular resolution of the present system is about 0.02° , which is sufficient enough to determine peak position of substrate and thin film. In characterizing combinatorial libraries, the spatial resolution is also important and it is about 0.1 mm x $(0.1/\sin\theta_B)$ mm for the present system, where θ_B , is Bragg angle of the diffraction. We can obtain such a high spatial resolution very easily without special and precise alignment of the sample position, because the two-dimensional topographic image can be observed on a detector. We applied the present method to characterization of combinatorial $[(\text{SrTiO}_3)_{10}/(\text{BaTiO}_3)_n]_{30}$ ($n=5, 10, 15$) superlattice on SrTiO_3 substrate grown by laser molecular beam epitaxy (laser MBE). There are three different periods of super-lattices, which were grown 1.7 mm length with 1 mm interval in each. The reflectivity and diffraction patterns from these three layers are measured very rapidly and easily. We could estimate the superlattice periods and quality of these layers from the obtained image data. From the observation, it is confirmed that the present method is very effective to measure X-ray diffraction from combinatorial epitaxial thin films and provides a lot of structural information of combinatorial libraries.

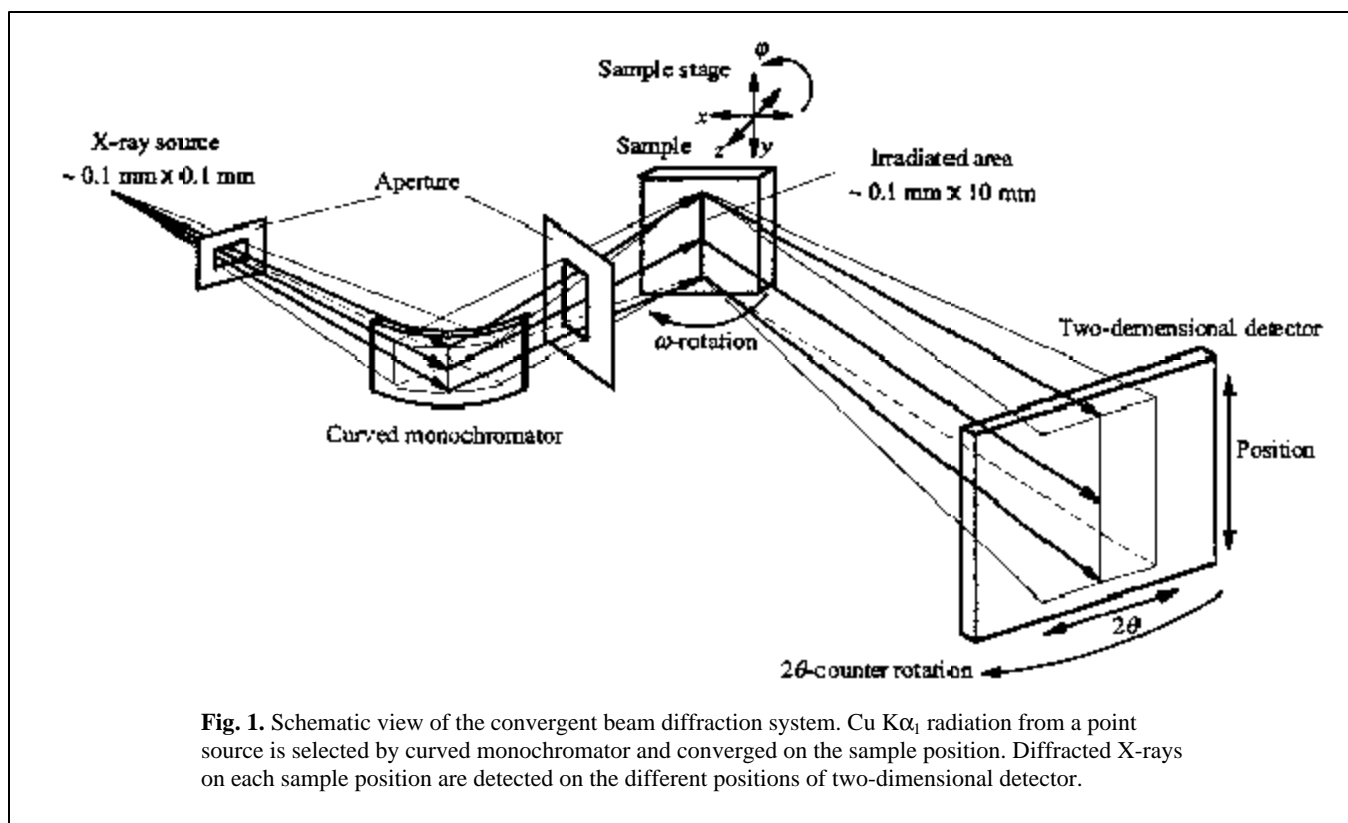
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1. Introduction

Multi-component epitaxial thin films have been studied extensively to produce new functional materials, such as superconductors and optical and magnetic devices. In order to optimize the material properties and obtain high-performance devices, we need to determine a large number of parameters, for example, the composition, structure of layers, superlattice periods and so on. Combinatorial synthesis [1-4] is considered to be extremely efficient to determine such conditions and discover new materials without laborious and time-consuming processes. Mastumoto et al. developed [5] an apparatus for combinatorial laser molecular beam epitaxy, which is very useful to synthesize highly doped films and artificial superlattices which could not be obtained under thermal equilibrium conditions. This technique provides us systematic studies for growing a large number of epitaxial thin films with different

compositions on a substrate under definite temperature and pressure conditions.

Whether a combinatorial library can yield a lot of thin films with different compositions on a substrate, without accurate and rapid characterization, it can not give much useful information. Although X-ray diffraction is an indispensable technique for characterizing epitaxial thin films, the irradiated area of a standard X-ray diffraction system is too large to illuminate each pixel individually. In addition, it is a very time consuming experiment to measure the X-ray diffraction pattern one by one for all of the combinatorial pixels with precise alignment of the sample position. In order to overcome these problems, E. D. Isaacs et al. developed an X-ray micro-beam system [6] using a synchrotron radiation (SR) source with a focusing mirror system.



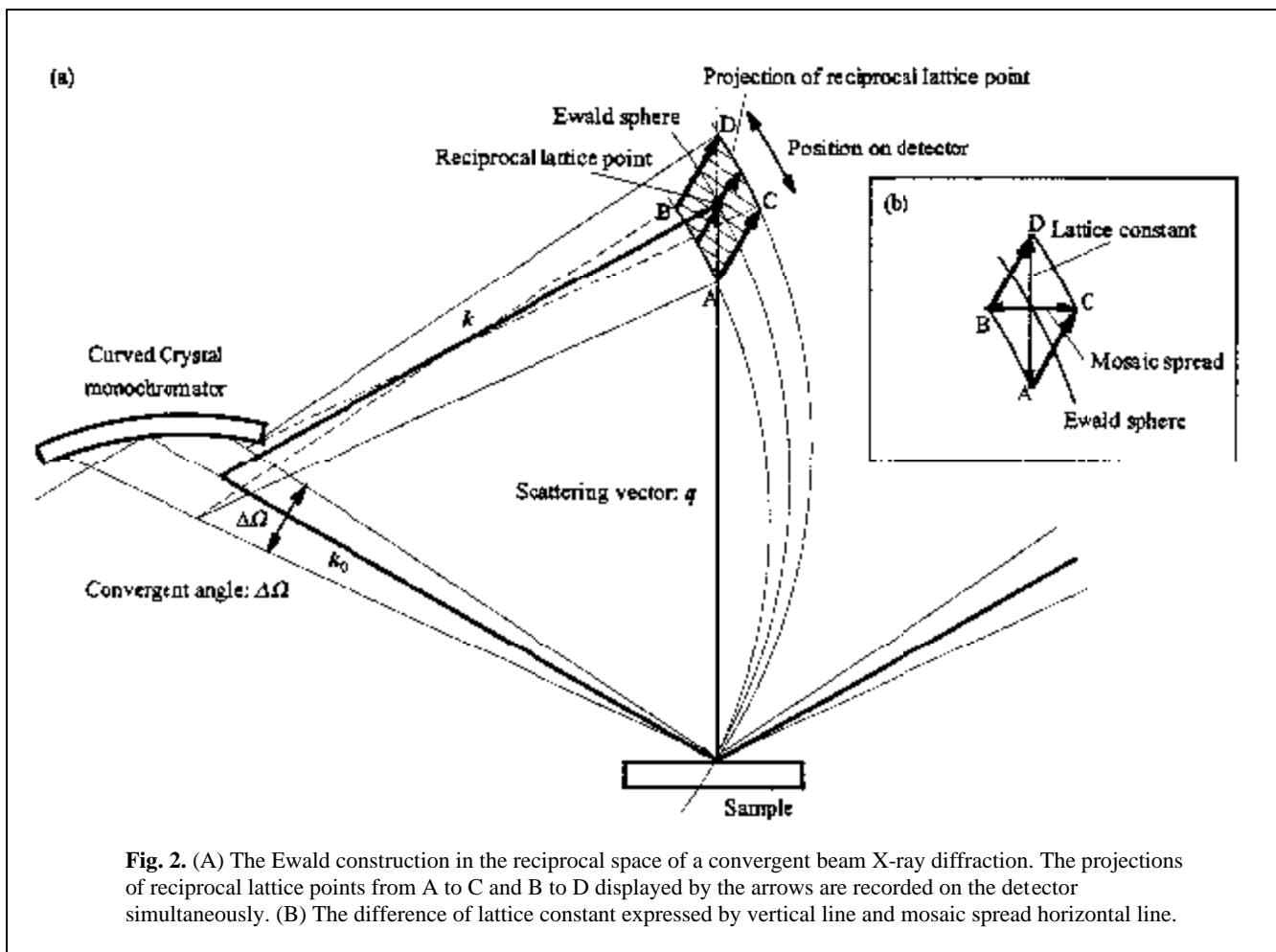
However, it is inconvenient to use SR facilities for characterizing combinatorial libraries, because SR can not be placed in each laboratory, where combinatorial synthesis is performed. For this reason, we developed an in-house X-ray diffraction system for the rapid characterization of combinatorial epitaxial thin films. We have utilized a convergent X-ray beam focused at the sample position produced by a curved crystal monochromator with a point focus X-ray source [7, 8]. The whole profile of a rocking curve within a few degree of the irradiated area can be measured simultaneously on a two-dimensional detector. By means of this system, diffraction patterns of one-column pixels could be measured within a few minutes with about 0.1 mm spatial resolution. This is extremely faster than the previous X-ray diffraction systems.

In this paper, the optical system and principle of convergent beam X-ray diffraction system will be first described and both angular and spatial resolution will be discussed. The method for estimating lattice constant of a thin layer in comparison with a substrate will be given for both normal and lateral direction. Finally, an example for characterizing combinatorial $[(\text{SrTiO}_3)_{10}/(\text{BaTiO}_3)_n]_{30}$ ($n=5, 10, 15$) superlattice on SrTiO_3 substrate grown by laser molecular beam epitaxy will be presented.

2. Convergent Beam X-ray Diffraction

An overview of our diffraction system is shown in Fig. 1. We used a 1.2 kW copper rotating anode fine focus X-ray generator, which has 0.1 mm x 0.1 mm appearance source size. X-ray beam is converged on a sample position by utilizing a curved crystal (e.g. Johan type quartz) monochromator, which selects only $\text{Cu } K\alpha_1$ radiation by eliminating $\text{Cu } K\alpha_2$, $\text{Cu } K\beta$ and white radiation. The focused $\text{Cu } K\alpha_1$ beam obtained was around 0.1 mm x 10 mm in size at the sample position with the convergence angle $\Delta\Omega$. 2° . As the sample and a two-dimensional detector are placed on ω and 2θ stage of two-circle goniometer, respectively, we can adjust the angle of incidence to the sample surface and move detector angle to observe any Bragg reflection from the sample.

The Ewald construction in reciprocal space of the convergent beam method is shown in Fig. 2 (a). The area that we can observe in reciprocal space is the region surrounded by two Ewald spheres, which is determined by the convergence angle as shown in Fig. 2. When a position sensitive X-ray detector is placed on the appropriate position, a projection of the limited area hatched in the Fig. 2 along the direction from A to C is recorded at once on the detector. When we measure single crystal substrate and epitaxial thin



films, diffraction peaks from both substrate and thin films can be observed simultaneously. However, if we measure polycrystalline material, the diffracted beam spread on to the two-dimensional detector and can not observe correct diffraction pattern. The diffracted X-rays at each sample position are recorded on the different vertical position of a two-dimensional detector as shown in Fig. 1. As a result, we can obtain whole profiles of rocking curves of substrate and also epitaxial films within two degrees for one-column pixels (vertical line on the sample surface shown in Fig. 1) simultaneously.

It should be noticed that lattice constant of the diffraction plane corresponds to the length of the scattering vector, which is indicated by vertical line in reciprocal space shown in Fig. 2(b). Mosaic spread of the crystal is expressed by horizontal line in the same figure. The present method could not distinguish these two differences because only the projection of the reciprocal space was observed. However, if we restrict convergent angle $\Delta\Omega$ narrower, the θ -scan

pattern along a curved line of Fig. 2(b) is observed simultaneously. Thus, reciprocal space map is also possible to be measured when the incident angle to the sample is changed step by step and recorded each 2θ -scan pattern.

As for two-dimensional detector both CCD and imaging plate* (IP) are suited for this purpose. Although the dynamic range of the image is greater in IP than CCD, the read out time of the later is much shorter than the former. The recent CCD detector for X-rays is much improved and has performances of high quantum efficiency and very low noise. Thus, the CCD could be of the best for this system. However all of the data shown in the present paper were those obtained by using IP because of its higher dynamic range.

The observation of the rocking curve of a Bragg reflection is usually not so easy especially for nearly

* Made by Fuji Film Co. LTD.

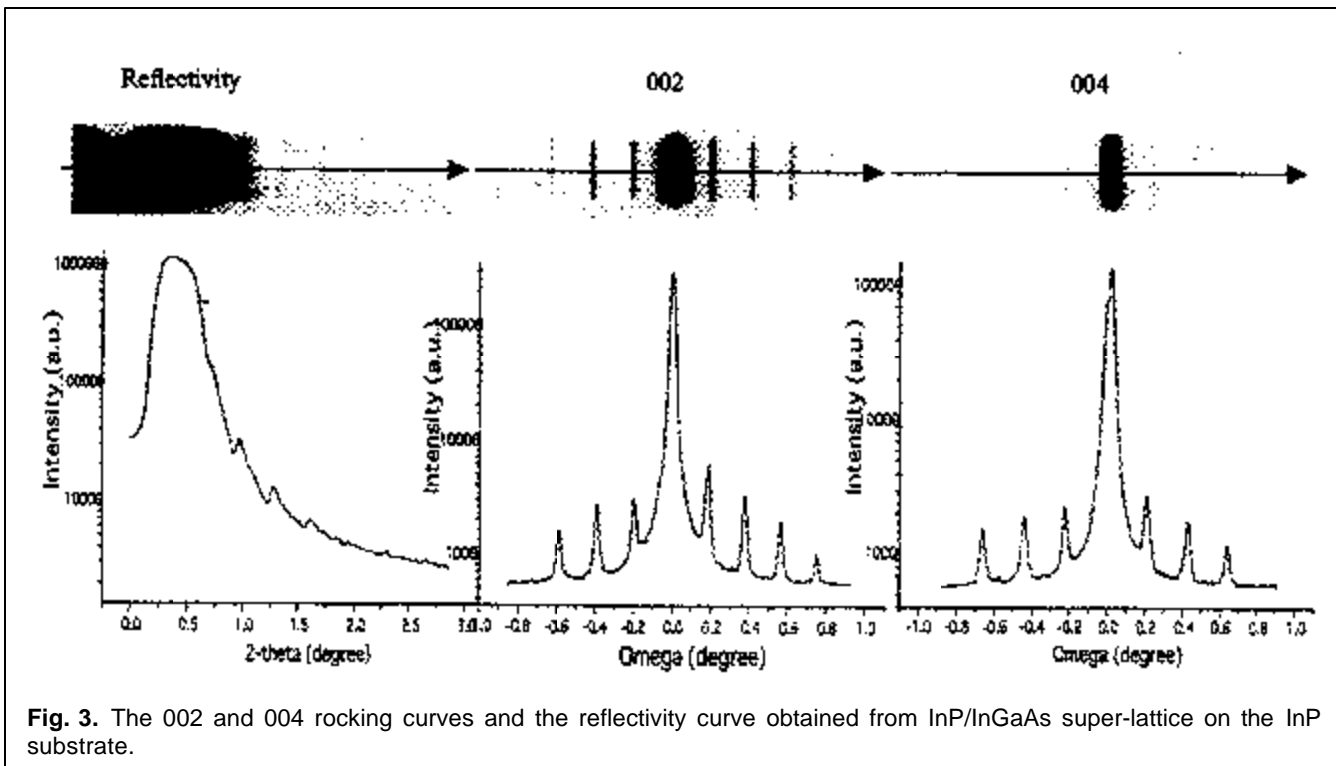


Fig. 3. The 002 and 004 rocking curves and the reflectivity curve obtained from InP/InGaAs super-lattice on the InP substrate.

perfect crystals, because the precise alignment of the sample is required in setting properly the ω -angles. Instead, it is considerably easy for the present method as high precession alignment is not required for the setting of ω - and the 2θ -angles.

The present method is also applicable to measure the reflectivity from thin films and super-lattices when the grazing incidence geometry is employed. X-ray reflectivity is known to be very useful for analyzing thin film. As examples of such observations we show the IP images of the profiles for the 002 and 004 rocking curves and the reflectivity curve for the sample (InP/InGaAs) super-lattice on InP substrate in Fig. 3. The exposure time to collect data was 30 seconds for the rocking curve and only 5 seconds for the reflectivity curve. We could obtain very easily and quickly these images. The figures shown below the photographs indicate the intensity profiles along line indicated by arrows in the IP images. If the two profiles observed around the 002 and the 004 points are compared the difference between them are noticed. For instance, the intensity of the third order satellite is stronger in high angle side of the 002, but opposite relation exists in the profile of the 004, suggesting the existence of the strain at the interface boundary between the InP and InGaAs layers due to compensate their lattice mismatch. The strain

distribution at the interface may be analyzed from the Fourier analysis of the satellite reflections.

In order to estimate the resolution of the present convergent beam method, the FWHM of rocking curve was observe for several Bragg reflections from a bear Si wafers: two rocking curves, the 111 and the 333 Bragg-reflections from (111)Si wafer and one rocking curve, the 004 from (001)Si wafer. The FWHM observed are in the order of $.02^\circ$ with some systematical increase with 2θ -angle. The width of a Bragg reflection is considered to be given by the convolution of several broadening.

Bragg reflection itself has a width, which is known as the intrinsic width of Bragg reflection and can be calculated if the crystal is perfect. We have such intrinsic broadening from the monochromator and the sample crystals in the present case. Angular broadening occurs also due to wave length dispersion in the case of non-parallel double crystal arrangement of the monochromator and sample crystal. There is a special line broadening which comes from the use of finite size of X-ray source and that of detector. The FWHM of the rocking curve can be, therefore, calculated taking into account those origins of line broadening. By assuming that each profile of the line broadening has a Gaussian shape, the FWHM can be calculated by the convolution of all broadening using the following equation,

Table 1 Resolution of the convergent beam X-ray diffraction.

Reflection index	ω_s	$\Delta\theta_\lambda$	$FWHM_{cal.}$	$FWHM_{obs.}$
hkl	(degree)	(degree)	(degree)	(degree)
111	0.0021	0.0004	0.021	0/-21
004	0.001	0.0098	0.023	0.025
333	0.0006	0.0186	0.028	0.033

$$FWHM_{cal.} = \sqrt{\omega_m^2 + \omega_s^2 + \Delta\theta_\lambda^2 + \Delta\theta_s^2}$$

ω_m : Intrinsic diffraction width of the monochromator.

ω_s : Intrinsic diffraction width of the sample crystal.

$\Delta\theta_\lambda = \frac{\Delta\lambda}{\lambda} (\tan\theta_m - \tan\theta_s)$: Angular broadening due to wavelength dispersion.

$\Delta\theta_s = \frac{f+p}{L_c}$: Broadening due to spatial resolution of the detector.

f: X-ray focus size

p: spatial resolution of the detector

L_c : Camera length

The FWHM of each reflection index was calculated by using the actual values of optical parameters, $f=0.1$ mm, $p=0.05$ mm and $L_c = 400$ mm and listed in Table 1. The calculations agree reasonably well with the observations. Thus, we may say that the resolution of this technique comes from mainly two origins: one due to special broadening which is independent of the angle and the other due to wave length dispersion come from non-parallel double crystal arrangement.

As for the analysis of individual pixels of combinatorial libraries, the spatial resolution on the sample is also important. The spatial resolution in vertical direction is determined by the X-ray source size f and it is around 0.1 mm. The spatial resolution in horizontal direction is limited by the beam width at the sample position w . Width of the irradiated area on the sample surface is $a = w/\sin\theta_B$, where θ_B is the Bragg angle of the reflection. When θ_B is 20°, for example, a is around 0.3 mm in the present optical

system. The spatial resolution of the present method is extremely higher than that of conventional X-ray diffraction systems; typical beam size of such a conventional system is in the range from 1 mm to 10 mm. Furthermore, when employing a knife-edge slit just in front of the sample surface and adjusting precisely it, we can get a more high spatial resolution.

3. Determination of Mismatch of Thin Films

In this section, we will discuss how to determine lattice mismatch between a substrate and an epitaxial grown thin film. Figure 4(a) shows the rocking curve of symmetrical 004 reflection observed from GeSi epitaxial thin film on (001)Si substrate. From this rocking curve profile, we can estimate the lattice mismatch along the [001] direction. The observed peak shift of GeSi thin film from Si substrate is $\Delta\omega = -0.244^\circ$. The mismatch is given as $\Delta d_{004}/d_{004} = -\Delta\omega$, $\cot\theta_B = 0.00618$.

In order to obtain lattice constant along in-plane direction of the epitaxial layer, we can also attain by measurement of two-asymmetric 115 reflections, They were taken by two-opposite direction of incident beams. The geometry of the measurement and observed data are shown in Fig. 4(b). It is noticed that the peak shifts of GeSi and Si substrate are different in two cases, ω_{0° and ω_{180° . This comes from the deformation of the unit cell of epitaxial layer due to the strain as illustrated in Fig. 4(b). The direction of the asymmetric lattice plane such as 115 is shifted by the unit cell deformation. We can estimate both lattice spacing d_{115} and shift of the orientation of (115) plane $\Delta\alpha$ from these two values of peak shift as follows,

$$\Delta\omega_{0^\circ} = \Delta\theta - \Delta\alpha = -0.442^\circ,$$

$$\Delta\omega_{180^\circ} = \Delta\theta + \Delta\alpha = -0.258^\circ,$$

$$\frac{\Delta d_{115}}{d_{115}} = -\Delta\theta \cdot \cot\theta_B = 0.0056$$

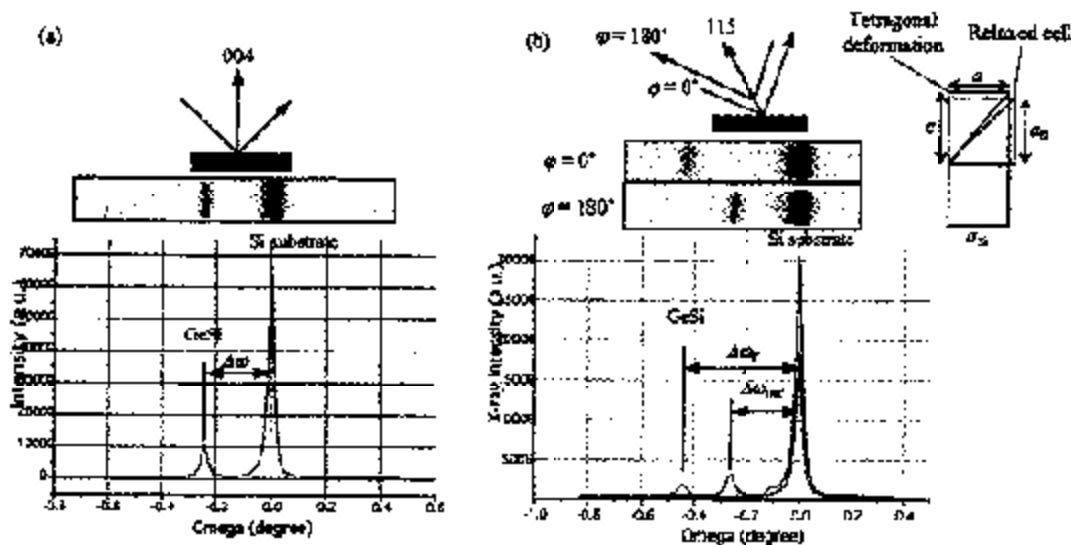


Fig. 4. Rocking curve of GeSi on Si substrate measured by convergent beam diffraction, (a) symmetric 004 reflection and (b) asymmetric 115 reflections with two-different incident beam directions. The unit cell deformation of the epitaxial layer is also illustrated.

$\Delta\theta$: shift of the Bragg angle of 115 from the substrate

$\Delta\alpha$: shift of the direction of (115) plane from the substrate = 0.092°

Assuming tetragonal deformation as illustrated in Fig. 4(b), the lattice constants a and c of in-plane and out-of-plane direction, respectively, can be estimated by the observed values of Δd_{115} and $\Delta\alpha$ as,

$$\frac{c}{a} = \frac{5}{\sqrt{1^2 + 1^2}} \tan(\alpha_{115} + \Delta\alpha) = 1.00613,$$

α_{115} : tilting angle of substrate (115) plane to the surface normal

$$c = d_{115} \sqrt{(1^2 + 1^2) \left(\frac{c}{a}\right)^2 + 5^2} = 5.4638 \text{ C}$$

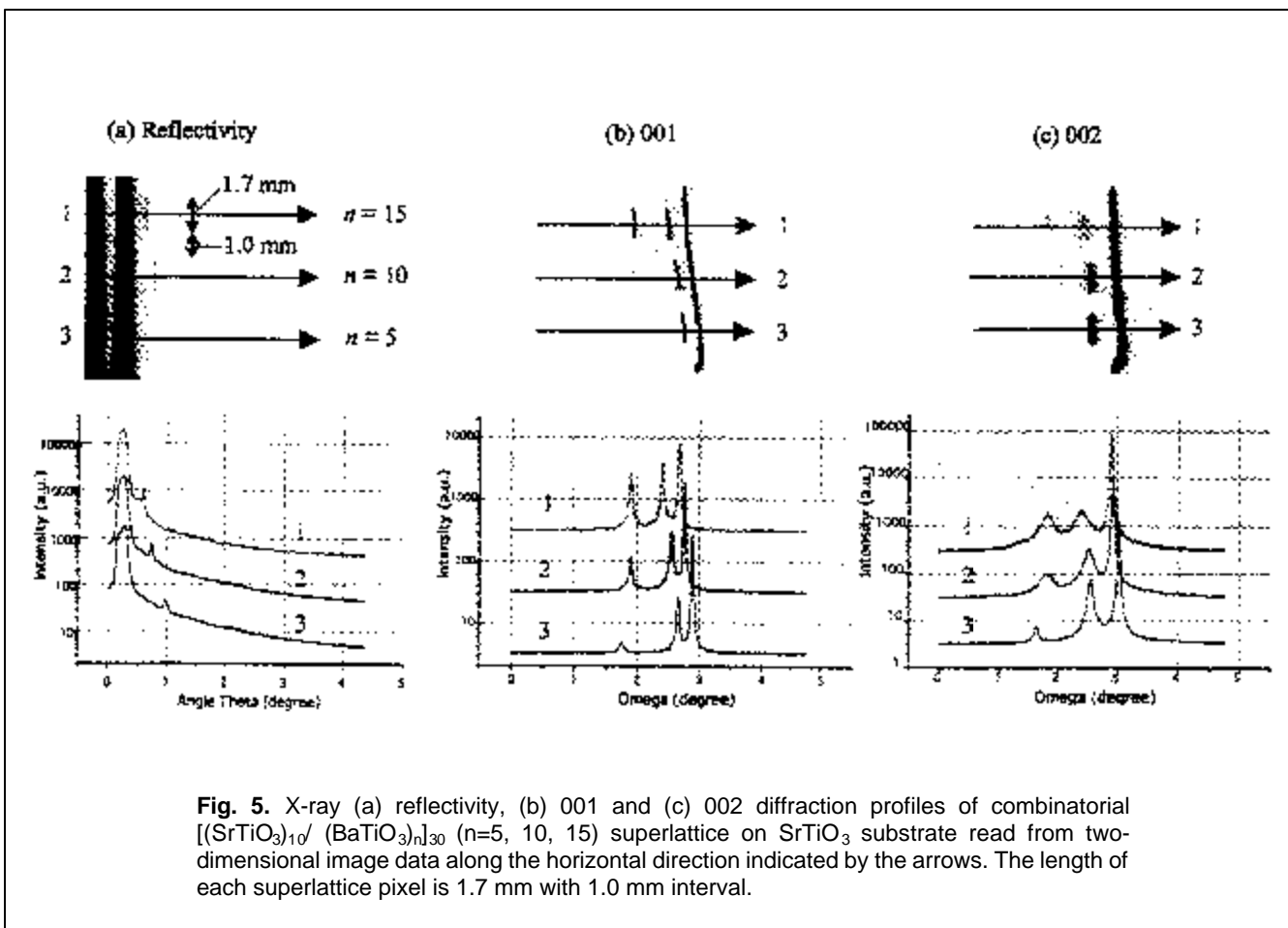
$$A = 5.4305 \text{ C}$$

The obtained in-plane lattice constant $a_{\text{GeSi}} = 5.4305 \text{ C}$ is very close to that of Si substrate $a_{\text{Si}} = 5.43088 \text{ C}$. Therefore, we can conclude that lattice constant of GeSi epitaxial layer is matched to that of substrate in the lateral directions and elongated to the out-of-plane direction. The later value is also given by symmetrical 004 reflection as mentioned above and the value is 5.4644 C, which is very close to the value obtained by asymmetric two-reflections 5.4638 C. Therefore, we could confirm the tetragonal deforma-

tion of GeSi epitaxial layer in this case. If these two values were not consistent, we should consider other type of deformation, for example monoclinic deformation. In any cases, the observation of the asymmetric reflections by the use of the present convergent method is very powerful and easy for analyzing epitaxial thin layers.

4. Application to the Combinatorial Materials

We examined measurement of combinatorial $[(\text{SrTiO}_3)_{10}/(\text{BaTiO}_3)_n]_{30}$ ($n=5, 10, 15$) superlattice on SrTiO_3 substrate made by laser molecular beam epitaxy [2]. The observed images of reflectivity, around 001 and 002 reflections of SrTiO_3 are shown in upper half of Fig. 5. We can clearly see three different periods of super-lattices, which were formed 1.7 mm length with 1 mm interval. Continuous lines of 001 and 002 reflections are Bragg peaks from substrate. The deformation of the substrate peak along the vertical direction is considered to be caused by a warp of the substrate. The present imaging technique gives us such a useful information that could not be given by other conventional X-ray diffraction technique. Spatial resolution in the vertical direction is about 0.1 mm. It is possible to estimate by the edge broadening of the diffraction pattern from the superlattice along the vertical direction. The value is consistent with that described in section 2. This high-spatial resolution of the



present method enables us to analyze 100 pixels in one-column of 10mm length, simultaneously. It means that the present technique provides extremely higher throughputs for combinatorial grown thin films than the ordinary X-ray diffraction techniques, including the use of the synchrotron radiation source is employed. Furthermore, it is not necessarily precise setting of the sample position, because the present method provides whole topographic image of the sample and easy to identify the position on the sample.

The X-ray reflectivity and diffraction profiles obtained by the imaging data are shown in lower half of Fig. 5. The position of superlattice peak in reflectivity curve is shifted due to different period of superlattice stacks corresponding to $n=5, 10, 15$. In addition, it is also noticed that the peak width is different between each superlattice period. These points could be discussed more precisely if we simulate reflectivity curves and compare with experimental data.

In the X-ray diffraction pattern shown in Fig. 5(b) and (c), we can see the satellite peaks at different

positions near the Bragg peak of substrate. It can be noticed that the width of satellite peak for $n=5$ superlattice is narrower than that for $n=10$ and 15. The ratio of satellite to substrate intensity is larger as increasing n for 001 reflection, whereas the ratio is smaller as increasing n for 002 reflection. We could obtain such a trend of combinatorial thin films very efficiently.

5. Remarks

We have developed a new method for analyzing the structure of epitaxial thin films grown by combinatorial synthesis systems with extremely high-throughput. The convergent X-ray beam is focused on the sample surface and the whole profile of a rocking curve of one-column pixels can be measured simultaneously on a two-dimensional detector. The angular resolution of the present system is about 0.02° and it is rather moderate but sufficient enough to determine peak position of substrate and thin film diffraction. The spatial resolution for resolve column pixels is about 0.1 mm, which is enough to analyze 100 pixels in the column of 10 mm length. It is very

sure from these special features of the present method that we can use widely for the analysis of the structure of epitaxial grown combinatorial thin film libraries.

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