Influence of thermal diffuse scattering and local stress on the precise measurement of Si$_{1-x}$Ge$_x$ composition by convergent beam electron diffraction* 

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Recently, we proposed an accurate compositional analytical technique for epitaxial Si$_{1-x}$Ge$_x$ thin films [S. Takeno, et al., Proceedings of 8APEM (8th Asia-Pacific Conference on Electron Microscopy), 497 (2004)]. The technique was based on two-beam CBED (Convergent Beam Electron Diffraction) with a novel correction method for the thermal diffuse scattering effect. Experimental results for the new technique showed excellent accuracy, equivalent to RBS (Rutherford Backscattering Spectrometry) analysis in low x cases. However, the validity of the analytical technique over a wide range of values of x has been unclear so far. In this paper, the applicable criteria of the correction method are discussed in detail from the viewpoints of temperature dependence of the Debye-Waller factor in the Si-Ge binary system, and the influence of the locally induced stress. [DOI: 10.1380/ejssnt.2006.359]

Keywords: Electron microscopy; Transmission high-energy electron diffraction; Silicon-germanium; Surface stress

I. INTRODUCTION

Precise estimation of local compositional fluctuation is one of the most desired and difficult analytical challenges in the research field of next-generation semiconductor devices. Recently, we proposed an accurate compositional analytical method for alloy crystal thin films by the two-beam CBED (Convergent Beam Electron Diffraction) technique with a novel correction method for the thermal diffuse scattering effect. We successfully demonstrated this method for Si$_{0.935}$Ge$_{0.065}$ epitaxial thin films in a small area of interest with high accuracy [1]. The method is based on the measurement of extinction distance $\xi_g$. The measurement method for $\xi_g$ by two-beam CBED was originally proposed by Kelly, et al. [2], and the local composition of the Si$_{1-x}$Ge$_x$ crystal can be numerically deduced from $\xi_g$ [3]. Our proposed analytical procedure is briefly described in Fig. 1 and consists of 5 stages. First of all, two-beam CBED patterns of the Si$_{1-x}$Ge$_x$ and Si crystals are observed. Second, the values of $\xi_g$ are experimentally determined by Kelly’s method. Third, the $P$ value is defined and obtained experimentally (The $P$ parameter is defined later). Fourth, correction of the thermal diffuse scattering effect on the measurement of $\xi_g$ for the Si$_{1-x}$Ge$_x$ crystal is performed. Finally, the accurate composition of the Si$_{1-x}$Ge$_x$ crystal is obtained by the theoretical calculation of $\xi_g$ vs. Ge composition $x$. We confirmed the main causes of error in measurement of $\xi_g$ by Kelly’s method [1]. They were excitation error deviation from the exact two-beam condition, deviation from the linear relationship in Kelly’s method, and the thermal diffuse scattering effect. For precise measurement of $\xi_g$, estimation and correction of thermal diffuse scattering effect are fundamentally important especially for large g reflection cases [4]. Recently, Delille, et al. [3, 5] also performed measurement of $\xi_g$ for Si and Si$_{1-x}$Ge$_x$ crystals by the two-beam CBED technique and pointed out that thermal diffuse scattering was a noticeable unwanted factor in the precise measurement of $\xi_g$ even if the profile fitting technique of the rocking curve was adopted. Based on this background, we defined and introduced the parameter $P(=\xi_g(Si)_{theo}/\xi_g(Si)_{exp})$ that is acquired from a standard crystal, i.e., Si substrate, as shown in Fig. 1, where $\xi_g(Si)_{theo}$ and $\xi_g(Si)_{exp}$ are theoretical and experimental extinction distances for pure Si crystal. The value of $\xi_g(Si)_{theo}$ is well known [6], and the parameter $P$ is considered to represent the effect of Debye-Waller factor. The experimental mean extinction distance of the Si$_{1-x}$Ge$_x$ crystal (denoted as $<\xi_g(SiGe)_{exp}>$) is corrected by application of $P$, i.e., correction for the thermal diffuse scattering effect is carried out by multiplying the value of $<\xi_g(SiGe)_{exp}>$ by $P$ [1]. However, in our previous report, only a low Ge concentration case, i.e., $x = 0.063$, was demonstrated by application of $P$. The theoretical validity of $P$ over a wide range of values of $x$ at various temperatures has been unclear so far. Therefore, precise estimation of Debye-Waller factor is significant. Additionally, the influence of local stress on the determination of the value of $P$ is uncertain, especially in locally strained cases such as epitaxial thin films. In this paper, we discuss in detail the influence of these unclear factors on the accuracy of our method, and show practical crite-

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The validity of $P$ for a wide range of values of $x$ at various temperatures was confirmed by a calculation technique of the Debye-Waller factor (described in the next section in detail), whereas the influence of local stress on the determination of the value of $P$ was revealed by the following experiment. Si$_{1-x}$Ge$_x$ thin film with nominal Ge composition of 10.9 percent atomic percent was used for this purpose. The film was epitaxially grown on Si(001) substrate, and the nominal composition was determined experimentally from pure Si standard crystal for this purpose. The film was epitaxially grown on Si(001) substrate, and the nominal composition was determined experimentally from pure Si standard crystal for this purpose.

II. EXPERIMENTAL

The validity of $P$ for a wide range of values of $x$ at various temperatures was confirmed by a calculation technique of the Debye-Waller factor (described in the next section in detail), whereas the influence of local stress on the determination of the value of $P$ was revealed by the following experiment. Si$_{1-x}$Ge$_x$ thin film with nominal Ge composition of 10.9 percent atomic percent was used for this purpose. The film was epitaxially grown on Si(001) substrate, and the nominal composition was determined experimentally from pure Si standard crystal for this purpose. The film was epitaxially grown on Si(001) substrate, and the nominal composition was determined experimentally from pure Si standard crystal for this purpose.

The local composition of the Si$_{1-x}$Ge$_x$ crystal can be numerically deduced from <\xi_{\text{Si-Ge}} \text{exp}>0 <\xi_{\text{Si-Ge}} \text{exp}>=<\xi_{\text{Si}} \text{exp}>=<\xi_{\text{Si}} \text{theo}>0 \text{ Ge composition} x_0

\begin{align*}
P &= \frac{\xi_{\text{Si-Ge}} \text{theo}}{\xi_{\text{Si-Ge}} \text{exp}} \left( \frac{\xi_{\text{Si}} \text{theo}}{\lambda F_g} \right) \\
\xi_{\text{Si-Ge}} \text{theo} & : \text{Theoretical extinction distance for Si-Ge} \\
\xi_{\text{Si-Ge}} \text{exp} & : \text{Experimental extinction distance for Si-Ge} \\
\xi_{\text{Si}} \text{theo} & : \text{Theoretical extinction distance for Si} \\
\xi_{\text{Si}} \text{exp} & : \text{Experimental extinction distance for Si} \\
V & : \text{Volume of unit cell} \\
\lambda & : \text{Wavelength} \\
\theta_B & : \text{Bragg angle} \\
F_g & : \text{Structure factor}
\end{align*}

where $a_i$, $d_g$, $\lambda$, $t$ are integer, interplanar distance of g, wavelength, and specimen thickness, respectively. $L_0$ and $L_i$ are distances between 000 and the exact g Bragg positions, and between i-th intensity minimum and the exact g Bragg positions, respectively. The measurement of distances $L_0$ and $L_i$ was performed using Gatan DigitalMicrograph within an error of one pixel, and the distance of $L_0$ was measured as about 1000 pixels. Therefore, the determination error of extinction distance and specimen thickness due to the measurement error of distances on CBED pattern was kept sufficiently small in our study.

III. RESULTS AND DISCUSSION

A. Influence of the thermal diffuse scattering at various temperatures on the $P$ value determination

In the newly proposed method, the value of $P$ has to be obtained using a standard material. The $P$ value is determined experimentally from pure Si standard crystal for
the compositional analysis of Si$_{1-x}$Ge$_x$. If Eq. (3) is confirmed for a certain value of $x$, the $P$ value is considered to be effective for the composition $x$.

$$\frac{\xi_g(Si)_{theo}}{\xi_g(Si)_{exp}} = \frac{\xi_g(SiGe)_{theo}}{\xi_g(SiGe)_{exp}}$$  \hspace{1cm} (3)

In other words, Eq. (4) must be satisfied for accurate analysis,

$$DW(0) \propto DW(x),$$ \hspace{1cm} (4)

since structure factor $F_g$ is modulated by the Debye-Waller factor and $\xi_g$ is in inverse proportion to $F_g$. ($DW(x)$ denotes the Debye-Waller factor for the composition $x$. $DW(0)$ means the Debye-Waller factor of the pure Si crystal.) We tried to evaluate the Debye-Waller factor for various Ge composition cases at various temperatures as follows. For substitutional disordered binary alloys like Si$_{1-x}$Ge$_x$, composition-dependent Debye-Waller factors for the alloys were successfully calculated by Shirley, et al. [9] and Frabboni, et al. [10]. Generally, $DW(x)$ is expressed as follows,

$$DW(x) = \exp\{C < u^2(x) >\},$$ \hspace{1cm} (5)

where $C$ is a constant related to the exact Bragg condition, e.g., $g = 004$ in this study, and $< u^2(x) >$ is the mean-square atomic displacement. The value of $< u^2(x) >$ is expressed at temperature $T$ as follows,

$$< u^2(x) > = \frac{3h^2}{4\pi^2k_BT} \cdot \frac{1}{M(x)} \cdot M(\theta(x)) \cdot \exp\left(\frac{\theta^2}{\theta(x)}\right)$$ \hspace{1cm} (6)

where $h$, $k_B$, $A$, $M(x)$ and $\theta(x)$ are Planck’s constant, Boltzmann’s constant, atomic mass unit, atomic weight of the composition $x$ and the Debye temperature for composition $x$, respectively [9, 11]. $M(x)$ and $\theta(x)$ are calculated by the following Eqs. (7) and (8),

$$M(x) = (1-x) \cdot M_{Si} + x \cdot M_{Ge},$$ \hspace{1cm} (7)

$$\theta^2(x) = \frac{(1-x) \cdot M_{Si} \theta_{Si}^2 + x \cdot M_{Ge} \theta_{Ge}^2}{M(x)},$$ \hspace{1cm} (8)

where $M_i$ and $\theta_i$ are the atomic weight and Debye temperature of the element $i$, respectively [10]. Calculated results for the atomic weight and the Debye temperature are shown in Fig. 2. The Debye temperature decreases as the Ge composition increases, whereas the atomic weight increases as the Ge composition increases. Figure 3 shows calculated results of the Debye-Waller factor $DW(x)/DW(0)$ vs. Ge composition $x$. At under 200 K, the error in the $P$ value is assumed to be less than 1% in the $0 < x < 0.8$ range since the difference between $DW(x)$ and $DW(0)$ is within 1%. Especially, in the temperature range from 150 to 200 K, excellent coincidence.
of $DW(x)$ and $DW(0)$ in the $x < 0.4$ range is confirmed. Even at room temperature, the error in the $P$ value is assumed to be less than 1% in the $0 < x < 0.45$ range. It may be concluded that the introduction of $P$ is an effective approach for a wide range of values of $x$ at various temperatures.

B. Influence of local stress on determination of the $P$ value

The influence of local stress on the determination of the $P$ value is an important subject to be discussed in the Si$_{1-x}$Ge$_x$/Si(001) case since a large complicated stress is considered to be introduced in the Si substrate as well as in the Si$_{1-x}$Ge$_x$ thin film [10]. Figure 4 is a typical cross-sectional bright field micrograph of a measured specimen, and both thickness and bend contours are observed. The thickness contours were frequently interrupted by the bend contours as indicated by a white arrow in Fig. 4. Such irregular contour pattern suggests the feature of specimen bending caused by the locally induced stress. For instance, we can recognize that the local stress is induced near the Si$_{1-x}$Ge$_x$/Si(001) interface region as shown by an encircled area in Fig. 4. Previously, Okuyama, et al. [12] directly revealed local stress, i.e., local lattice distortion in a bulk Si crystal near the SiO$_2$ precipitates by observation of HOLZ line broadening. The cause of the broadening is considered to be an abrupt lattice distortion. In order to ensure the locally induced stress, HOLZ pattern analysis was performed. Figures 5(a) and (b) show typical HOLZ patterns from Si substrate near the interface of Si$_{1-x}$Ge$_x$/Si(001), i.e., 50 nm away from the interface and sufficiently far from the interface, respectively. The incident beam direction was aligned [430]$_{Si}$ and nominal acceleration voltage was 200 kV for both Figs. 5(a) and (b). Pattern (a) consists of broadened HOLZ lines, whereas all HOLZ lines in (b) are sharp features. For instance, $-2 \, 2 \, 12$ and $-8 \, 10 \, -2$ HOLZ lines are clearly visible as a sharp configuration in Fig. 5(b), while it is hard to observe these lines in Fig. 5(a). This difference clearly indicates the existence of an abrupt stress near the interface of the Si$_{1-x}$Ge$_x$/Si(001) substrate, and the areas sufficiently apart from the interface may be assumed to be stress-free. Figures 6(a) and (b) show the two-beam CBED patterns for the stress induced and the stress-free areas, respectively. From the Kelly’s analysis, the ratio of the $P$ value $P_S/P_{SF}$ was found to be 0.99 ($P_S$ and $P_{SF}$ denote the $P$ value of the stress induced and the stress-free areas, respectively.). It may be concluded that the influence of the local stress is practically negligible for the rocking curve analysis of the two-beam CBED experiment even if the HOLZ lines are very sensitive to an abrupt change of stress. However, in the region very near to the Si$_{1-x}$Ge$_x$/Si(001) interface, the rocking curve was broadened (see Fig. 7). Overlapping of Si$_{1-x}$Ge$_x$ and Si crystals at the interface is a significant cause. This overlapping can be introduced by a slight tilting operation with regard to the alignment of the exact 004 two-beam condition. Inevitably, such a region is inappropriate for P value determination and should be avoided. The two-beam CBED patterns in Fig. 6 were observed at room temperature and may be considered to have a certain high background level for the rocking curves [13]. Such conditions are disadvantageous for the measurement of intensity minima of the rocking curves in Kelly’s method, and an energy-filtering technique can be strongly recommended [14]. However, the values of $P_S$ and $P_{SF}$ were almost the same even if a non-energy-filtering condition was adopted. The reason for this coincidence must be attributable to the thickness of the TEM specimens. Blake, et al. [4] and Allen [13] showed the effect of background on rocking curve analysis. They pointed out that the position of minima in rocking curves
is shifted away from the exact Bragg position because of the background. Generally, background level changes as the thickness of the TEM specimen changes. Therefore, arrangement of an appropriate specimen thickness is very important. The thickness of the specimens in the observed areas of Figs. 6(a) and (b) were very similar, i.e., both were about 90 nm, and the background profile of the rocking curves was assumed to have an almost the same configuration. This reproducibility is a favorable characteristic for $P$ value determination. In other words, it is significant to arrange TEM specimen thickness to be as close as possible for both Si$_{1-x}$Ge$_x$ and Si standard crystals even if a certain stress is induced in the Si standard. Tanaka, et al. [8] showed that the accuracy of Kelly’s method can be estimated by $R^4$ which is fourth power of correlation coefficient for the linear relationship in Kelly’s method [2]. In our proposed method, accuracy of a specimen thickness is confirmed by adopting a strict criterion, i.e., $R^4$ was kept larger than 0.985 [1]. Under this condition, error in specimen thickness measurement is considered to be less than 1%. For instance, following analytical result shows the importance of the arrangement of the specimen thickness. The $P$ value derived from Fig. 6(a) and the experimentally obtained value $<\xi_g (SiGe)_{exp}>$ were 0.90 and 130.1 nm, respectively. A typical two-beam CBED pattern for the Si$_{1-x}$Ge$_x$ crystal is shown in Fig. 8. The mean thickness of the Si$_{1-x}$Ge$_x$ crystal was calculated as 87 nm, which is almost the same as the Si standard. The corrected experimental mean value $<\xi_g (SiGe)_{exp}>$ was obtained as 117.1 nm, which can be converted to a Ge composition of 11.0 atomic percent. The nominal Ge composition obtained by RBS analysis was 10.9 atomic percent. These two values were almost the same. The result indicates that the influence of local stress is negligible, whereas the coincidence of the specimen thickness in both areas of Si$_{1-x}$Ge$_x$ and Si standard crystals is an important criterion for the accurate measurement of the extinction distance.

IV. CONCLUSIONS

The validity of the proposed $P$ value as a correction parameter for the error caused by thermal diffuse scattering for accurate $\xi_g$ measurement by two-beam CBED analysis, was discussed quantitatively. In the Si$_{1-x}$Ge$_x$ on Si(001) substrate case, the Debye-Waller factor of pure Si crystal is almost the same as that of Si$_{1-x}$Ge$_x$ crystal over a wide range of values of $x$, especially at low temperature. Additionally, the influence of local stress was found to be practically negligible in the rocking curve analysis of two-beam CBED patterns even if the HOLZ lines are anomalously broadened. These are very attractive characteristics for $P$ value determination. Moreover, careful arrangement of the TEM specimen thickness, making it as nearly the same as possible for both target and standard crystals, is definitely important for accurate measurement. At 100 kV, a specimen thickness of around 90 nm was favorable for the Si$_{1-x}$Ge$_x$/Si(001) case.
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