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Analysis of $L2_1$-ordering in full-Heusler Co$_2$FeSi alloy thin films formed by rapid thermal annealing

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The authors developed a new analysis approach for evaluation of atomic ordering in full-Heusler alloys, which is extension of the commonly used Webster model. Our model can give accurate physical formalism for the degree of atomic ordering in the $L2_1$ structure, including correction with respect to the fully disordered $A2$ structure, i.e., the model can directly evaluate the degree of $L2_1$ ordering under a lower ordering structure than the complete $B2$-ordering structure. The proposed model was applied to full-Heusler Co$_2$FeSi alloy thin films formed by rapid thermal annealing. The film formed at $T_{RTA}=800$ °C showed a high degree of $L2_1$ ordering of 83% under a high degree of $B2$ ordering of 97%. © 2009 American Institute of Physics. [DOI: 10.1063/1.3075989]

Recently, full-Heusler alloys, such as Co$_2$FeSi (Ref. 1) and Co$_2$MnSi,2,3 attract considerable attention since they have an unique half-metallic band structure4 with high Currie temperature. In particular, Si-containing full-Heusler alloys are a promising material for spin injector/detector of Si-based spin devices such as spin metal-oxide-semiconductor field-effect transistors,5–7 since they can be formed by siliconization reaction activated by rapid thermal annealing (RTA) that is commonly used formation process for metal source/drain technology in advanced CMOS devices. Recently, we reported that full-Heusler Co$_2$FeSi alloy thin films were successfully formed by RTA using silicon-on-insulator (SOI) substrates.$^8$

A fully ordered atomic arrangement in full-Heusler alloys is the $L2_1$ structure, however, the partially disordered $B2$ and fully disordered $A2$ structures also exist. Half-metallicity in full-Heusler alloys is sensitive to their atomic arrangement and degrades with deterioration of atomic ordering.$^9$ Therefore, characterization of atomic ordering in the $L2_1$ structure is an important concern for half-metallic full-Heusler alloys.$^{10}$ Nevertheless, the standard approach to evaluate the degree of atomic ordering in full-Heusler alloys still leaves some issues. In this paper, we developed a novel analysis approach to evaluate atomic ordering in full-Heusler alloys, extending the commonly used Webster scheme. The proposed model was applied to full-Heusler Co$_2$FeSi alloy thin films formed by RTA.

The $L2_1$ structure of full-Heusler $X_2YZ$ alloys (such as Co$_2$FeSi) is composed of eight stacked body-centered cubic (bcc) lattices shown in Fig. 1(a). The outside sublattice that consists of the eight cubic lattices is occupied by $X$ atoms, and the inside cubic sublattice that consists of the body-centered sites of each bcc lattice is regularly occupied by $Y$ and $Z$ atoms, as shown in Fig. 1(b). In full-Heusler alloys, two kinds of disordering exist. When the $YZ$ sublattice is randomly occupied by $Y$ and $Z$ atoms, i.e., disordering in the $YZ$ sublattice occurs, the ordering structure is reduced to the $B2$ type. (Hereafter, this disorder process is denoted by $Y-Z$ disordering.) Furthermore, when disordering between the $X$ and $YZ$ sublattices occurs, the ordering structure is lowered to the $A2$ type. (Hereafter, this disorder process is referred to as $X-YZ$ disordering.)

In general, these ordered/disordered structures can be identified by x-ray diffraction (XRD) analysis using the following features on relations between atomic orderings and superlattice diffraction lines: $Y-Z$ disordering extinguishes odd superlattice diffraction lines [that are defined by the index relation of $h$, $k$, and $l$=odd numbers, e.g., (111)]. Furthermore, even superlattice diffraction lines $[|h+k+l|/2=2n+1$, e.g., (200)] vanish under $X-YZ$ disordering. On the other hand, fundamental diffraction lines $[(h+k+l)/2=2n$, e.g., (220)] are independent of the ordering structures.

The traditional analysis approach$^{11,12}$ proposed by Webster has been extensively used to evaluate the degree of atomic ordering in full-Heusler alloys. In the Webster framework, ordering features in full-Heusler alloys are divided into two factors, i.e., the degree of $B2$ ordering, and the degree of $L2_1$ ordering. The degree of $B2$ ordering, $S_{B2}$, represents that of $X-YZ$ disordering (the definition will be discussed later). Although the degree of $L2_1$ ordering, $S_{L21}^{W}$, can

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be defined by the same manner as that of B2 ordering (also discussed later), the disordering parameter $\alpha_W$ that is defined by a fraction of $X$ atoms on the $Z$ sites is generally used to evaluate $L_2_1$ ordering. Both $S_{wB2}$ and $\alpha_W$ represent an index of the degree of $Y-Z$ disordering, however, the definition and physical meaning are different. $S_{wB2}$, $\gamma_{L2_1}$, and $\alpha_W$ can be easily determined from XRD intensity ratios between superlattice and fundamental lines.\textsuperscript{11}12 (The corrected formula to deduce $\alpha_W$ was presented in Ref. 12.) The Webster model can give accurate formalism for the degree of B2 ordering.\textsuperscript{11} On the other hand, $\alpha_W$ is given under the hypothesis of the complete B2 structure of $S_{B2}=100\%$. Namely, $\alpha_W$ in the Webster model has no influence of $X-Y$Z disordering. In other words, when $S_{B2}$ is less than 100\%, the physical meaning of $\alpha_W$ is ambiguous. It should be noted that although $\alpha_W$ represents the fraction of $X$ atoms on the $Z$ sites, the number of $Y$ atoms on the $Z$ sites also depends on the degree of B2 ordering.

Extending the Webster model, we developed physical formalism for the degree of $L_2_1$ ordering including correction from the degree of B2 ordering. Table I shows a definition of the number of atoms at each site (in unit of a Co$_2$Fe$_x$Si$_1$ molecule). In the table, $2x(0.5 \leq x \leq 1)$ and $y(x/2 \leq y \leq x)$ are the number $n_{Co}$ of Co atoms on the $X$ sites, and the number $n_{Fe}$ of Fe atoms on the $Y$ sites, respectively. The number of Si atoms on the $Z$ sites is also $y$, where we assumed that $X-Y$ and $X-Z$ disorderings occur equiprobably, which is the same as the assumption of the Webster model\textsuperscript{11}12. The other values can be easily deduced under the assumption of the stoichiometric composition. The proposed model can express two $X-Y$ and $Y-Z$ disorderings simultaneously. The degree of B2 ordering, $S_{B2}$, is defined as follows:

$$S_{B2} = \frac{n_{Co} \times x - n_{random}}{n_{Co} \times x} = 2x - 1,$$

where $n_{Co}$ of $X (=1)$ is the number of Co atoms on the $X$ sites for the most random distribution of Co atoms in the A2 structure, and $n_{Co}$ of $X (=2)$ is the number of Co atoms on the $X$ sites in the fully ordered $X$ sublattice of the perfect B2 structure. In practice, $S_{B2}$ can be obtained from XRD measurements using the following relation between even superlattice and fundamental lines:

$$\frac{I_{200}}{I_{220}} = (2x - 1)^2 \frac{I_{200}}{I_{220}} = S_{B2} \frac{I_{200}}{I_{220}},$$

where $I_{200}/I_{220}$ is an experimentally obtained intensity ratio between (200) and (220) diffraction lines, and $I_{200}/I_{220}$ is the (calculated) ideal diffraction intensity ratio for the perfect B2 structure (that is whole the $X$ sites are occupied only by Co atoms). The expression of $S_{B2}$ in our model corresponds to that in the Webster model ($S_{B2}=S_W$). The degree of $L_2_1$ ordering, $S_{L2_1}$, can also be defined by the following relation:

$$S_{L2_1} = \frac{n_{Fe} \times y - n_{random}}{n_{Fe} \times y} = \frac{2y - x}{2 - x},$$

where $n_{Fe}$ of $Y (x/2)$ is the number of Fe atoms on the $Y$ sites for the most random distribution of Fe atoms in the $YZ$ sublattice, and $n_{Fe}$ of $Y$ is that for the fully ordered $YZ$ sublattice. The codomain of $S_{L2_1}$ depends on $S_{B2}$ and it is limited to a range of $0 \leq S_{L2_1} \leq \frac{1 - S_{B2}}{2}$. Note that $S_{L2_1}$ can take a finite value even under $S_{B2}=0$ since $L_2_1$-ordering portion without $Y-Z$ disordering can remain when the $X$ sublattice are fully disordered (a half amount of whole the Fe and Si atoms is required for the fully disordered $X$ sublattice). $S_{L2_1}$ can be obtained from the following relation,

$$\frac{I_{111}}{I_{220}} = (2y - x)^2 \frac{I_{111}}{I_{220}} = S_{L2_1} \left(\frac{3 - S_{B2}}{2}\right) \frac{I_{111}}{I_{220}}.$$

This relation can be easily deduced by the ordinary procedure\textsuperscript{11} from crystal structure factors ($F_{111}=4f_x+a_2$ and $F_{220}=4(2f_x+y_f+d_f)$) and average atomic scattering factors at each site [$f_x=2xf_{Co}+(1-x)f_{Fe}+(1-x)f_{Si}$, $f_y=(1-x)f_{Co}+(y-x)f_{Fe}+(x-y)f_{Si}$, and $f_z=(1-x)f_{Co}+(x-y)f_{Fe}+(y-x)f_{Si}$]. It should be noted that $S_{L2_1}$ cannot be determined only by the odd superlattice line, and that $S_{L2_1}$ also depends on the degree of B2 ordering. In the Webster framework, $S_{L2_1}$ is given by $S_{wL2_1}=1-2\alpha_W$ using the general definition shown in the second part of Eq. (3) and it is given by the relation of $I_{111}/I_{220}=S_{wL2_1}$ in our model. When $S_{B2}=100\%$ ($x=1$), our $S_{L2_1}$ formula ($=2y-1$) is identical with Webster’s $S_{wL2_1}=(1 - 2\alpha_W)$ (since $x=1$). Webster’s disordering parameter is expressed by $\alpha_W=1-y$. Moreover, $S_{L2_1}$ can evaluate the degree of $L_2_1$ ordering under a particular $S_{B2}$ value of $S_{B2} < 100\%$.

Figure 2 shows $S_{L2_1}$ as a function of $S_{B2}$ with various diffraction intensity ratios $I_{111}/I_{220}$. The solid curves

| TABLE I. Definition of the number of atoms at each site in full-Heulser Co$_2$Fe$_x$Si$_1$ alloy (in unit of a Co$_2$Fe$_x$Si$_1$ molecule). |
|----------------|----------------|----------------|
| $X$ sites | $Y$ sites | $Z$ sites |
| Number of Co atoms | $2x$ | $1-x$ | $1-x$ |
| Number of Fe atoms | $1-x$ | $y$ | $x-y$ |
| Number of Si atoms | $1-x$ | $x-y$ | $y$ |
show $S_{L_2}$ in our model, and the solid circles show $S_{W}^{SL}$ in the Webster framework that can be only plotted on $S_{B2}=100\%$, $S_{L_2}$, and $S_{W}$ increase with increasing $I_{111}^{\text{full-order}}$. Although $S_{L_2}$ are identical with $S_{W}$ when $S_{B2}=100\%$, $S_{L_2}$ decreases with decreasing $S_{B2}$. It should be emphasized that $S_{L_2}$ can be evaluated for overall $S_{W}^{SL}$, whereas $S_{W}^{SL}$ is only defined at $S_{B2}=100\%$ ($x=1$).

The developed model was applied to RTA-formed Co$_2$FeSi thin films. Recently, we reported that full-Heusler Co$_2$FeSi alloy thin films were successfully formed by RTA-induced silicidation reaction utilizing SOI substrates. Detailed experimental procedure was described in Ref. 8. After Co and Fe films were deposited on a SOI substrate in an ultrahigh vacuum, the silicidation was performed by RTA in N$_2$ atmosphere. RTA temperature $T_A$ was varied in a range between 600–800 °C. The thicknesses of Co and Fe layers were determined so that the stoichiometric composition was achieved. The depth profiles of constituent elements were determined using these intensity ratios. Figure 3 shows XRD patterns measured with in-plane configuration for the samples formed at $T_A$ ranging from 600 to 800 °C. Above $T_A=650$ °C, the three (−111), (002), and (2−20) diffraction peaks were clearly observed, indicating the formation of the $L_2$ ordered structure. The degree of atomic orderings in the films was estimated using these intensity ratios. Figure 4 shows $S_{B2}$, $S_{L_2}$, and $S_{W}^{SL}$ as a function of $T_A$. In order to deduce these indices, the intensity ratios $I_{111}^{\text{full-order}}/I_{111}^{\text{full-order}}$ and $I_{002}^{\text{full-order}}/I_{2−20}^{\text{full-order}}$ shown in Eqs. (2) and (4), respectively, were calculated using International diffraction tables for crystallography volume C and D with the correction of multiplicity. The sample formed at $T_A=800$ °C showed a high degree of atomic ordering of $S_{L_2}=83\%$ under $S_{B2}=97\%$. It is dearly shown that $S_{L_2}$ was overestimated in comparison with $S_{L_2}$, and that the deviation from $S_{L_2}$ increased with decreasing $S_{B2}$ as described in Fig. 4.

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