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Structural Analysis of Artificial Superlattice by X-ray Diffraction Method

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ABSTRACT Crystal structure of superlattices is unique to both diffraction angles and shapes of satellite peaks. There are two models for calculating the x-ray diffraction (XRD) intensities of superlattice: in the one a periodic step function is used; in the other the composition modulation is described by Fourier series. The XRD profiles simulated with the former model did not take account the atomic inter-diffusion at the interface of superlattices. Therefore, the latter model was employed in order to evaluate the effect of the inter-diffusion, which was calculated by Fick's second law. Artificial superlattices with different structures were prepared by molecular beam epitaxy (MBE) method.

1. INTRODUCTION

The studies of superlattices have reported as a result of new physical phenomena observed in the superlattices. It is universally accepted that artificial superlattices can be produced where the constituents have not only the same crystal structures but also the different ones because deposition techniques have been developed. For the presence of periodicity of the materials, it is often possible to optimize the desired properties. To understand the physical properties is limited by the characterization of the samples. The shape, intensity and location of reflections from the advantage lattice and the satellite peaks allow the characterization of the structure for superlattices [1]. X-ray diffraction (XRD) is a suitable technique for studying the structure of superlattices. By comparing the measured intensity profiles with the calculated ones for the modeled superlattice, it is possible to evaluate the structure.

In this study, we have reported the structural analysis of artificial superlattices with the structure of $[(BaTiO_3)_n/(SrTiO_3)_m]_l$ (n,m,l:integer) by XRD method. In order to characterize the detailed structures of the superlattices, both step model and phonon model [2] have been employed; there has been few reports using the latter one to simulate the XRD profiles. Superlattices have been prepared by molecular beam epitaxy (MBE) method.

2. EXPERIMENTAL PROCEDURE

2.1 Fabrication of artificial superlattices

Artificial superlattices of $[(BaTiO_3)_n/(SrTiO_3)_m]_l$ were fabricated by MBE method. The substrates were mirror-polished $SrTiO_3$ (100) single crystals, which were heated at 700 ℃ for 1h in oxygen pressure of 10^{-6} Torr before depositing. The schematic diagram of the designed structure for superlattice is shown in Fig. 1. The MBE apparatus was equipped with three pyrolytic boron nitride

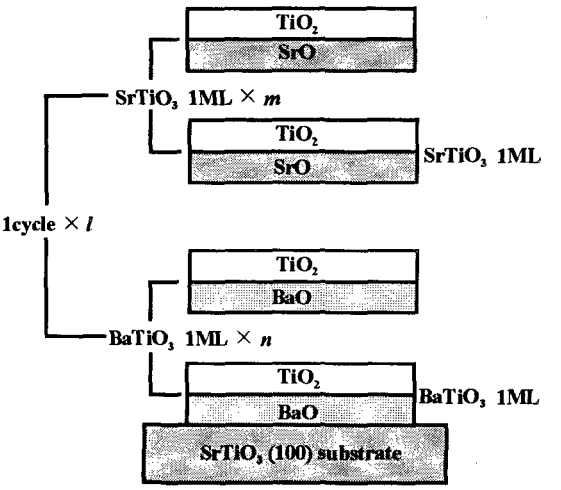

Fig. 1 Structures of $[(BaTiO_3)_n/(SrTiO_3)_m]_l$ artificial superlattice

Table 1. Deposition conditions of $BaTiO_3/SrTiO_3$ artificial superlattice

◆Substrate temperature	590℃		
◆Background pressure			
(before the deposition)	1.9×10^{-8} Torr	(during the deposition)	$8.5\times10^{-6}\sim1.5\times10^{-5}$ Torr
◆K-cell parameters			
	deposition rate		K-cell temperature
Ba	1 M.L./min		527~535℃
Sr	1 M.L./min		400~430℃
◆EB-gun parameters			
Ti	0.5~1 M.L./min	emission current	20~30 mA
◆ECR plasma gun parameters			
O_2 flow rate	0.2 sccm	I_A current	80mA
Pf power	200W	Pr power	60W

crucibles heated by tungsten wire (K-cells), two electron-beam-heated sources (EB-guns), and an electron cyclotron resonance plasma source as an oxidation assist for source metals. Both Ba and Sr were evaporated from K-cells, while Ti from EB-gun. For fabrication of superlattices, BaO, SrO and TiO_2 were alternatively deposited layer-by-layer on the substrate. The depositing conditions are listed in Table 1. The chemical analysis of the specimens by inductively coupled plasma-atomic emission spectrometry (ICP-AES) showed that the mole ratio of Ba/Sr to Ti was stoichiometric.

2.2 Characterization of artificial superlattices

The structures of the prepared samples were verified by comparing simulated and observed XRD profiles. In order to evaluate the effect of inter-diffusion at the interface of the superlattices, each of the specimens was annealed at 500℃, 600℃, 700℃, 800℃ for 1h after depositing, respectively.

3. SIMULATION OF XRD PROFILES FOR SUPERLATTICES

3.1 Expression of superlattices

Two models allows easy numerical computation of the XRD intensities of superlattices. The one uses a periodic step function; and the other a Fourier series to describe the variation of chemical composition and lattice spacing perpendicular to the substrate.

The first model, the simplest one to express an artificial superlattice, is a so-called "step model" [2].

A variety of superlattice models have been based on a step model [3-5], although the step model does not refine the fluctuation caused by inter-diffusion at the interfaces of superlattice. In this study, the step model was employed to evaluate if the produced superlattices have the structures with a complete alternation of chemical composition or not. In the step model, the diffracted amplitude is given by

$$A(\mathbf{h}) = \sum_{h_1,h_2,h_3} \exp[2\pi i(h_1n_1+h_2n_2+h_3n_3)] \times \left[\begin{array}{l} F_A\sum_{n=0}^{N_A-1}\exp[2\pi i h_3(n+\frac{1}{2})d_A/d_0] \\ +F_B\exp[2\pi i h_3 N_A d_A/d_0] \\ \times\sum_{n=0}^{N_B-1}\exp[2\pi i h_3(n+\frac{1}{2})d_B/d_0] \end{array}\right] \quad (1)$$

where F_A and F_B are the structure factors for layer A and B. $\mathbf{h}$ is defined in the reciprocal lattice of the average crystal with the lattice spacing d_0 .

In order to take the influence of inter-diffusion at the interfaces into account, the other model was used, which is called "phonon model" [2]. In the phonon model, the lattice spacing of the nth plane is given by

$$d_n = d_0(1+\Delta_1\cos 2\pi n/N+\Delta_2\cos 4\pi n/N+\cdots) \quad (2)$$

where Δ_1 and Δ_2 are the amplitudes of the lattice variation. The structure factor of the nth plane is described by

$$F_n = F_0(1 + \varphi_1 \cos 2\pi n / N + \varphi_2 \cos 4\pi n / N + \cdots) \quad (3)$$

where F_0 is the average value of the structure factor, and φ_1 and φ_2 are the amplitudes of the structure factor variation caused by the variation of composition. The amplitude of x-ray diffraction is presented by

$$A(\mathbf{h}) = \sum_{n_1 n_2 n} F_0 \exp[2\pi i(h_1 n_1 + h_2 n_2 + h_3 n_3)] \exp[i h_3 N \Delta_1 \sin\frac{2\pi n}{N}] \exp[i h_3 N \frac{\Delta_2}{2} \sin\frac{4\pi n}{N}] \cdots. \quad (4)$$

In this study, number of the terms for Fourier series was extended to six.

3.2 Fitting calculated and observed XRD profiles

Compared the calculated XRD profiles from these models to the experimental results, the convolution of instrumental function for diffractometer, Lorentz-polarization factor, and absorption of x-ray were incorporated in the calculation. The convolution is an integral operation defined by [6]

$$y(t) = \int_{-\infty}^{\infty} h(\tau) \cdot x(t - \tau) d\tau \quad (5)$$

where $y(t)$ is the calculated result, $h(t)$ is the instrumental function, and $x(t)$ is the result of the convolution integral operation. The XRD profiles of $SrTiO_3$ single crystal were substituted for the instrumental function. In this study, "simulated" XRD profiles suggested the calculated ones that were able to compare to the observed ones.

4. RESULTS AND DISCUSSION

Figure 2 and 3 show the simulated profiles of XRD using a step model and the experimental results for $[(BaTiO_3)_5/(SrTiO_3)_5]_8$ and $[(BaTiO_3)_{10}/(SrTiO_3)_{10}]_4$ superlattices, indicating that the measured XRD profiles were almost consistent with the simulated ones. From these results, we concluded that we prepared the artificial superlattices with the designed structures by our MBE system.

The variation of ratio of 1st satellite peak to 0th satellite peak as a function of heating temperature is shown in Fig. 4, which indicated that the ratio

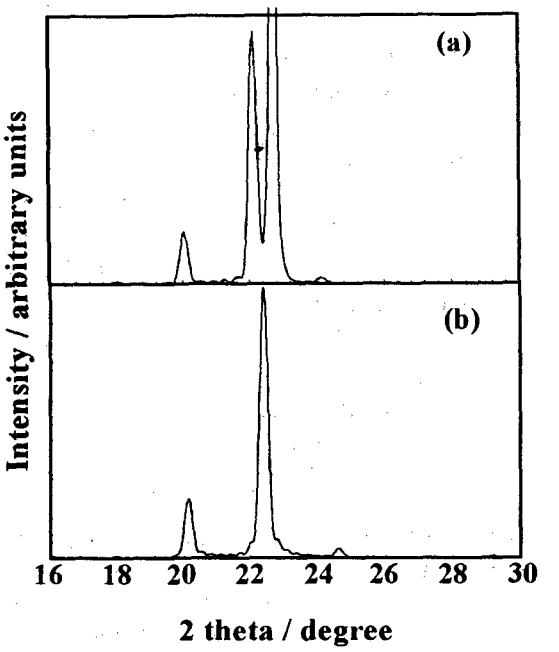

Fig. 2 XRD profiles for $[(BaTiO_3)_5/(SrTiO_3)_5]_8$: (a) observed and (b) simulated by a step model

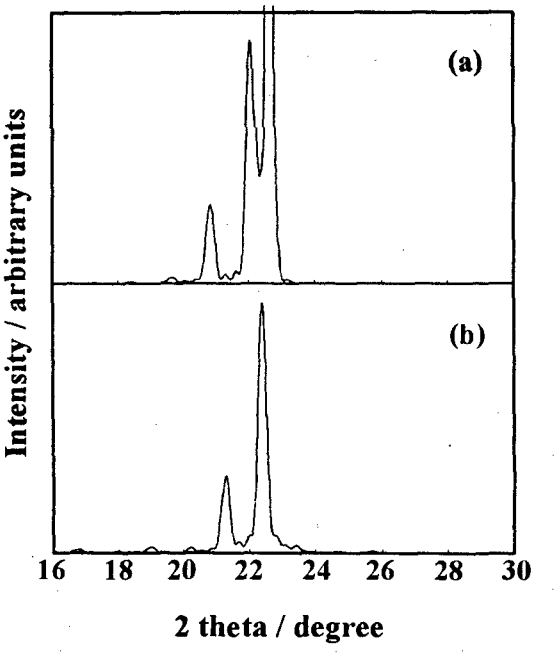

Fig. 3 XRD profiles for $[(BaTiO_3)_{10}/(SrTiO_3)_{10}]_4$: (a) observed and (b) simulated by a step model

decreased with increasing heating temperature. We supposed that the decrease of intensity ratio was caused by the inter-diffusion between Ba and Sr in the superlattices, and we tried to estimate the degree of inter-diffusion from XRD profile-simulation by a phonon model. The profiles of inter-diffusion calculated from Fick's second law were expressed by Fourier series with six terms, and we obtained the XRD profiles of diffused superlattices. The simulated results using the phonon model indicated that the decrease of intensity ratio was influenced by the variation of composition in the superlattices. From the results, it was found that the XRD profiles of diffused superlattices were obtained from the ratio of 1st satellite peak to 0th satellite peak. We obtained the concentration changing of Ba and Sr in the superlattices from the measured XRD profiles. Figure 5 illustrates the simulated variation of concentration in the $[(BaTiO_3)_5/(SrTiO_3)_5]_8$ superlattice. In the case of preparing good-quality-superlattices, it is important to prevent inter-diffusion originated in heating the substrate. Figure 5 indicates that it can be found most suitable condition of deposition using the simulations by the phonon model. The reflections from superlattices were influenced in that from the substrate, and the profiles of diffusion were not strictly correct. However, it is possible to express the relative changing of Ba and Sr concentration.

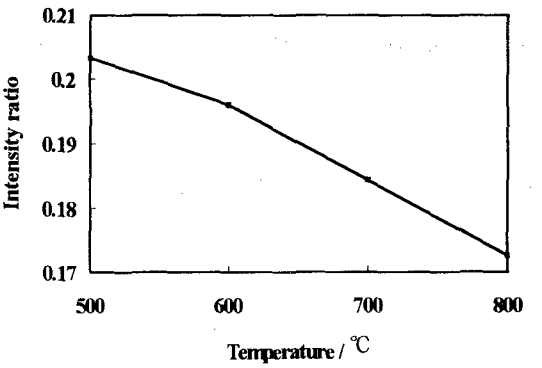

Fig. 4 Annealing temperature dependence on variation of intensity ratio

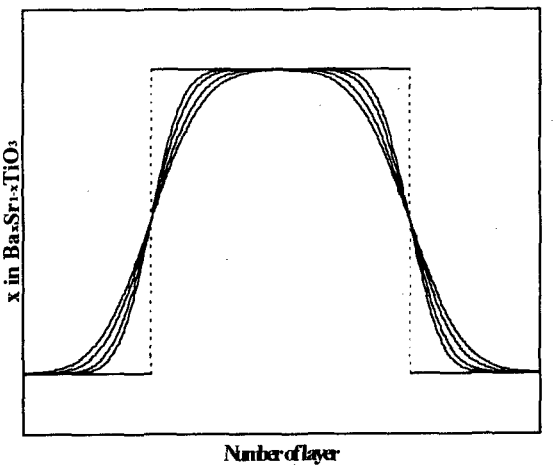

Fig. 5 Variation of Ba and Sr concentration on the $[(BaTiO_3)_5/(SrTiO_3)_5]_8$ superlattice

5. CONCLUSION

The simulated XRD profiles using a step model were well-consistent with the experimental results, indicating that the designed structures were fabricated in the superlattices. Using the simulation results by a phonon model, it is possible to evaluate the effect of inter-diffusion between Ba and Sr in the superlattices. The experimental results included the strong reflection from the substrate, and we obtained the relative changing of Ba and Sr concentration in the superlattices.

REFERENCES

1. L. Esaki, L. L. Chang and R. Tsu, Proceedings of the 12th International Conference on Low Temperature Physics,1971 (Edited by E. Kanda, Tokyo:Keigaku), 551
2. A. Segmüller and A. E. Blakeslee, J. Appl. Cryst. 6 (1973), 19
3. I. K. Schuller, Phys. Rev. Lett. 44 (24) (1980), 1597
4. E. E. Fullerton and I. K. Schuller, Phys. Rev. B 45 (16) (1992), 9292
5. M. Sohma and K. Kawaguchi, J. Appl. Phys. 75 (4) (1994), 1952
6. H. P. Klug and L. E. Alexander, X-ray Diffraction Procedures, John Willey & Sons, 1974