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Interfacial reaction of MgO/TiO_x superlattice thin films

F. Imai, K. Kunimori and T. Uchijima
Institute of Materials Science, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305 (Japan)

H. Nozoye*
National Chemical Laboratory for Industry, 1-1 Higashi, Tsukuba, Ibaraki 305 (Japan)

Abstract

The interfacial solid state reaction was investigated over the temperature range from 525 to 600 °C by annealing MgO/TiO_x supperlattice thin films. X-ray diffraction satellite peak intensities around MgO(200) decreased exponentially after an initial drop. Also, the modulation wavelength of the film increased exponentially with annealing time. Formation of Mg_2TiO_4 occurs at the interface between the MgO layer and the TiO_x layer and/or at the grain boundary of the superlattice. The apparent activation energy of the interfacial solid state reaction was determined.

1. Introduction

Because of the recent discovery of ceramic superconductors, investigation of artificially structured ceramic thin films has become increasingly attractive because they may have advantageous properties not observed in natural materials. To create and to use these artificially structured ceramic thin films, in particular ceramic superlattices, it is important to accumulate fundamental data on chemical, mechanical and thermal stability. The study of the solid state reactions of ceramic superlattices will provide not only valuable information about their thermal stability but also new methods of synthesizing metastable ceramics structures.

The solid state reaction of $MgO–TiO_2$ has attracted much attention for the growth of spinel materials because of their optical properties and as a dielectric material. The reaction between magnesium oxide and titanium oxide was first studied by Hautefeuille [1]. Since then many experiments have been conducted on the solid state reaction of $MgO–TiO_2$. Jander and Bunde [2] and Tanaka [3] found that a solid state reaction occurred between the interface of MgO powder and TiO_2 powder forming $MgTiO_3$ or Mg_2TiO_4. Yamaguchi and Tokuda [4] and Nicol and Roy [5] prepared spinel crystals by contacting an MgO single crystal with a TiO_2 single crystal. Hesse and Bethge [6, 7] synthesized an Mg_2TiO_4 film on an MgO(100) single crystal by depositing TiO_2 (anatase). Hultman and coworkers [8, 9] investigated the interfacial solid state reaction at the TiN–MgO interface.

Recently we synthesized MgO/TiO_x superlattice thin films on MgO(100) single crystals [10, 11]. Although there have been many reports on interdiffusivities on metal–metal multilayered thin films, to our knowledge no interdiffusion measurement has been carried out for ceramic multilayered films. In this study we will discuss interdiffusivity and the solid state reaction at the interface of the MgO/TiO_x superlattice from the decay rate of Bragg satellite intensities and changes in periodicity.

2. Experimental details

The syntheses of superlattices were performed in a stainless steel ultrahigh vacuum evaporation chamber. Since the experimental details were described in ref. 10 and ref. 11, here we describe an outline of the synthesis of superlattices. Superlattices were synthesized on cleaved MgO(100) single-crystal substrates by alternating deposition of a titanium oxide layer and a magnesium oxide layer. The titanium oxide layer was synthesized by a novel reactive deposition method [12]; oxygen gas pulses were introduced after deposition of one atomic layer of titanium metal from an electron beam evaporation source. According to the surface reaction of titanium and oxygen, one unit layer of TiO_x was synthesized on the substrate by this method. The titanium oxide (TiO_x) which was thus synthesized was of reduced anatase form and x was close to 2 [10]. The thickness of one unit layer of TiO_x was 3.26 Å. After synthesis of preset units of TiO_x on the substrate, MgO was deposited on a TiO_x layer by a separate electron beam evaporation source. The growth of superlattices was monitored with reflection high energy electron

*Author to whom all correspondence should be addressed.

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TABLE 1. Composition of the as-grown MgO/TiO_x superlattices

Specimen	Periodicity (Å)	Thickness of MgO (Å)	Mg:Ti mole ratio
A	59.66	20.54	0.868
B	58.89	19.77	0.836
C	58.48	19.36	0.818
D	57.81	18.69	0.790

diffraction. The periodicity and surface morphology were observed with X-ray diffraction (XRD) and atomic force microscopy (AFM) in air. Both TiO_x and MgO grew epitaxially on an MgO/TiO_x superlattice [10, 11]: however, the interfacial morphologies of $MgO-TiO_x$ and TiO_x-MgO were different; for example, $MgO-TiO_x$ means the interface in which an MgO layer exists on a TiO_x layer. The $MgO-TiO_x$ interface was rough compared with the TiO_x-MgO interface. In this experiment, the number of TiO_x units and the total number of superlattice layers were fixed at 12 and 30, respectively. Reproducible evaporation of an insulated target with an electron beam evaporation source was difficult because of charging up of the target during irradiation of electron beam. So the thickness of MgO was determined by subtracting the thickness of TiO_x layers from the wavelength of the periodicity determined with XRD. All the specimens used in this study are listed in Table 1. In the small angle scattering region of XRD, sixth to seventh satellite Bragg peaks were observed for all the specimens. Furthermore, around MgO(200) and MgO(400) reflections, Bragg peaks of the superlattice were observed. The specimens were annealed in an electric furnace at 525, 550, 575 and 600 °C respectively, and their thermal reactions were monitored intermittently with XRD and AFM at room temperature.

3. Results and discussion

3.1. Solid state reaction at the interface

Representative results of the change in the XRD pattern for a superlattice with annealing time are shown in Fig. 1. Each peak intensity was normalized with respect to the MgO(200) diffraction. It is obvious that the peak intensity decreased with annealing time. Moreover, each peak position was shifted to a lower diffraction angle, which means that the periodicity of the superlattice was expanded.

The decrease in intensity of the satellite peaks with annealing time is shown in Fig. 2. The initial decay of each intensity was rather steep, but each peak intensity decreased exponentially after the initial drop. The initial drop might be attributed to structural relaxation

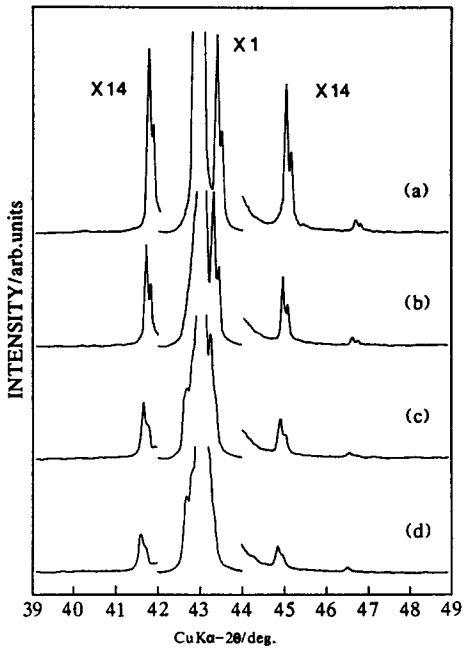

Fig. 1. Changes in XRD diffraction pattern from MgO/TiO_x superlattices with annealing time at 575 °C: (a) as-deposited; (b) 60 min; (c) 120 min; (d) 180 min.

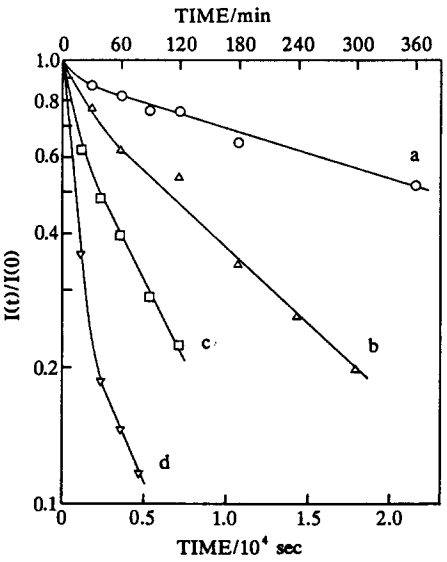

Fig. 2. Decay of (111) satellite intensities with annealing time. The annealing temperatures were 525 °C (curve a), 550 °C (curve b), 575 °C (curve c) and 600 °C (curve d).

especially at the rough $MgO-TiO_x$ interface and also to the strain relief of the reduced anatase form[13, 14]. By assuming that the exponential decay at a later stage in Fig. 2 represents the intrinsic interfacial process, that is the interdiffusion of MgO and TiO_x, the interdiffusivity coefficients D were calculated to be $1.22 \times 10^{-23}\,m^2\,s^{-1}$, $2.95 \times 10^{-23}\,m^2\,s^{-1}$, $5.31 \times 10^{-23}\,m^2\,s^{-1}$

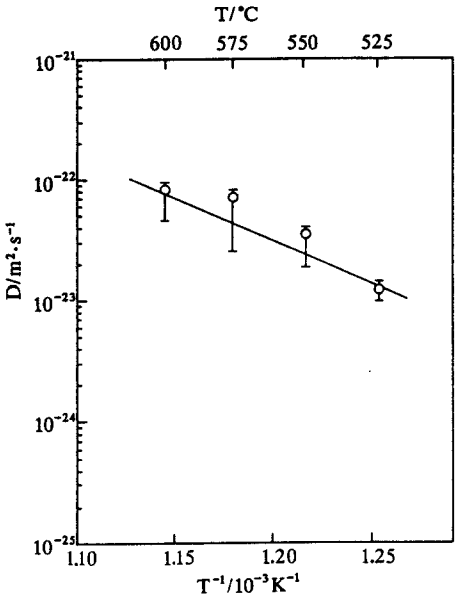

Fig. 3. Arrhenius plot of the interdiffusion coefficient D for MgO/TiO_x superlattices.

and 7.24×10^{-23} m^2 s^{-1} for 525 °C, 550 °C, 575 °C and 600 °C respectively [15, 16]. The temperature dependence of the interdiffusivity coefficient in the range from 525 to 600 °C is shown in Fig. 3 and is expressed as

$$D = 8.66 \times 10^{-15} \exp(-134.5 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}$$

Simultaneously with the decrease in the peak intensities, a continuous shift of the peaks to lower diffraction angles was also observed as described above. The peak shifts are due to the increase in the modulation wavelength resulting from the interdiffusion of MgO and TiO_x which leads to the formation of the magnesium titanate phase. In reality three different types of crystal have been reported so far to be formed by the interfacial reaction between TiO_2 and MgO; Mg_2TiO_4 (inverse spinel) [6, 7], $MgTi_2O_4$ (normal spinel) [17] and $MgTiO_3$ [2, 3]. The lattice mismatch between MgO and spinels is less than 2.8%. Moreover although MgO and spinels have the same crystal form (*i.e.* cubic form), $MgTiO_3$ has a different form (*i.e.* rhombohedral form). Therefore $MgTiO_3$ is probably not formed at the interface. However, the exact phase of the magnesium titanate could be determined from the direction of the peak shift. The increase in the modulation wavelength means that the volume of the magnesium titanate produced is larger than the sum of volumes of TiO_x and MgO reacted. As shown in Table 2, the formation of Mg_2TiO_4 causes expansion of the thickness. On the contrary, formation of $MgTi_2O_4$ and $MgTiO_3$ causes contraction. Therefore from the direction of the peak shift we can definitely determine that Mg_2TiO_4 was formed by the interfacial reaction. This conclusion is

TABLE 2. Relative volume change caused by the interfacial reaction between MgO and TiO_x (assuming that 10 Å of magnesium titanate was formed by the reaction)

Crystal	Density (g cm^{-1})	Consumption (Å)		Relative change in volume (%)
		TiO_x	MgO	
Mg_2TiO_4	3.52	4.501	4.944	+5.55
$MgTi_2O_4$	4.05	11.536	3.168	−47.04
$MgTiO_3$	3.91	6.676	3.667	−3.43

supported by the fact that Mg_2TiO_4 is exclusively formed by the solid state reaction between MgO and TiO_2 [6, 7].

From two satellite peaks observed around the MgO(200) diffraction, the nth number of the Bragg satellite peaks can be assigned from the following equation:

$$n = \sin\theta_n/(\sin\theta_{n+1} - \sin\theta_n)$$

Using this n value we can determine the modulation wavelength d of the superlattices from the Bragg equation:

$$d = n\lambda/2 \sin\theta_n$$

where λ is the wavelength of Cu Kα. Accordingly, changes in modulation wavelength of superlattices can be calculated from the peak shift and this reflects the degree of the solid state reaction. The activation energy can be calculated from Arrhenius plots of the rate of the change of the modulation wavelength. The value thus determined ($E_a = 169.5$ kJ mol^{-1}) was close to the value ($E_a = 134.5$ kJ mol^{-1}) calculated from Arrhenius plots of interdiffusivity. The slight difference in the activation energies may reflect the difference in the diffusion process; that is homogeneous and inhomogeneous processes which produce Mg_2TiO_4.

3.2. Solid state reaction at the grain boundary

In XRD of specimens B, C and D, the growth of a new peak was observed at lower diffraction angles of the MgO(200) peak. For specimen B, the new peak began to grow at $2\theta = 42.57°$ ($d = 2.122$ Å) after annealing for 240 min (Fig. 1). For specimen C, the peak began to grow at $2\theta = 42.61°$ ($d = 2.120$ Å) after annealing for 120 min. For specimen D, the new peak began to grow at $2\theta = 42.61°$ ($d = 2.125$ Å) after annealing for 40 min, and two peaks were observed at $2\theta = 42.56°$ ($d = 2.128$ Å) and $2\theta = 42.70°$ ($d = 2.121$ Å) after annealing for 102 min. The intensities of these two peaks increased linearly until an annealing time of 120 min. At this time, the satellite peaks corresponding to the artificial periodicity almost disappeared. After that, the growth rate of the peaks decreased. The lattice constants of these two peaks were close to those of the (400) diffraction of inverse spinel ($d = 2.116$ Å) and normal spinel

($d = 2.110$ Å). Since rather sharp XRD peaks for spinels were observed from the early stage of the reaction, the XRD peaks are caused by the inhomogeneous growth of Mg_2TiO_4 at the grain boundary and/or interface of the superlattice. Further support for this inhomogeneous reaction was obtained from the AFM observation of the surface of the film after annealing for 80 min at 600 °C; the formation of many islands (radius *ca.* 200 Å, height *ca.* 100 Å) was confirmed. These islands might be due to Mg_2TiO_4 grains formed on the surface.

4. Conclusion

We have found that a homogeneous solid state interdiffusion leading to formation of Mg_2TiO_4 (inverse spinel) occurs in MgO/TiO_x ceramic superlattice thin films. From the analysis of the decrease in the XRD intensity and the shift in the XRD peak we obtained the apparent activation energy of the reaction. Simultaneously with this homogeneous reaction the inhomogeneous reaction at grain boundaries and/or interfaces was also observed.

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