Evolution and removal of ferroelectric domains on $KNbO_3$ film by an atomic force microscope with a conductive cantilever

Y. TOMITA, Y. MAEDA, K. KOBAYASHI
Department of Materials Science, Faculty of Engineering, Shizuoka University, 3-5-1, Johoku, Hamamatsu 432-8561, Japan
E-mail: tkkobay@ipc.shizuoka.ac.jp

Ferroelectric materials have attracted a great deal of attention from a viewpoint of ferroelectric random access memories (FRAM) [1–4]. The lateral size of a capacitor cell in a high-density FRAM was reduced to a few hundred nanometers. To understand the switching behavior in the high-density FRAM, nanostructures of ferroelectric domains were observed by an atomic force microscope (AFM). Besides observations of domain structures, an AFM with a conductive cantilever enables us to evolve and remove ferroelectric domains by applying an electric field between the conductive cantilever and a bottom electrode on which a ferroelectric thin film was deposited. In principle, the lateral size of ferroelectric domains can be reduced to the contact area of the conductive cantilever, e.g., a few nanometers. Thus, these ferroelectric domains are applicable to nonvolatile memories as large as 10 Tbit/cm^2. A ferroelectric film with the smooth surface and a large remanent polarization is required for the development of such high-density nonvolatile memories. Among ferroelectric materials, we are interested in $KNbO_3$ because of its large spontaneous polarization [5]. Despite the excellent ferroelectric property, there were few reports on the preparation of $KNbO_3$ thin films [5–8]. In the present work, we have prepared $KNbO_3$ thin films on $SrTiO_3$ (110) substrates by metal-organic chemical vapor deposition (MOCVD), and have searched for optimum conditions for the preparation of $KNbO_3$ films with the smooth surfaces. Under the optimum conditions, devices consisting of $SrRuO_3$/ $KNbO_3$ heterostructures are fabricated on $SrTiO_3$ (110) substrates, where $SrRuO_3$ film is used as a bottom electrode. The heteroepitaxial growth of $KNbO_3$ and $SrRuO_3$ films on $SrTiO_3$ substrates is expected because $SrRuO_3$ has perovskite structure and its lattice parameters are closed to those of $KNbO_3$ and $SrTiO_3$ [9, 10]. Ferroelectric domains are formed in the area of 200 nm × 400 nm by applying an external voltage between the $SrRuO_3$ films and the conductive cantilever of AFM. The ferroelectric domains are removed by applying a reverse bias voltage. We discuss a factor affecting the spatial resolution of the ferroelectric domains.

$KNbO_3$ films were prepared by an MOCVD technique. Potassium dipivaloylmethanate and niobium pentaetoxide were sublimed at 165 and 80 °C, respectively. Vapors of these precursors were introduced into a reaction chamber by Ar gas, and subsequently reacted with oxygen gas on a heated substrate. The reaction chamber was maintained at 200 Pa during the film growth. $KNbO_3$ films were deposited on $SrTiO_3$ (110) substrates heated at 700–900 °C. $SrRuO_3$ films as bottom electrodes were prepared by radio frequency (RF) magnetron sputtering. In the RF sputtering, $SrRuO_3$ powders were used as a target. $SrRuO_3$ films were deposited on $SrTiO_3$ (110) substrates heated at 750 °C at 30-WRF power. The sputtering was carried out at a pressure of 1 Pa in an atmosphere of 80% Ar and 20% O_2. The crystallinity and identification of these films were characterized by X-ray diffraction (XRD) measurements. Surfaces of these films were observed in an ambient-controlled chamber by an AFM (SPI 3800N SEIKO). A conductive cantilever was Au-coated Si_3N_4 with a force constant of 0.18 N/m and a resonance frequency of 25 kHz. AFM topographic images were taken at a repulsive force of 0.18×10^{-9} N. The evolution and removal of ferroelectric domains in the $KNbO_3$ film were carried out in an Ar atmosphere. The bias voltage of $+10$ to -10 V was applied between the bottom electrode of $SrRuO_3$ and the cantilever.

Fig. 1 shows XRD patterns of $KNbO_3$ thin films deposited on $SrTiO_3$ (110) substrates at 700, 800, and 900 °C. The peaks at 31.31 °C are assigned to the $KNbO_3$ (200) reflection. There are no other diffraction peaks of $KNbO_3$ in the range of 5–60 °C. The peak of $KNbO_3$(200) becomes sharp with an increase of a substrate temperature. In the inset of Fig. 1, the full width at half maximum (FWHM) of the XRD rocking curve of the $KNbO_3$ (200) peak is plotted as a function of a substrate temperature. FWHM value decreases with a substrate temperature. The crystallinity and the orientation of $KNbO_3$ films are improved with an increase of a substrate temperature. In particular, it is confirmed from XRD pole-figure measurements that the following epitaxial relationship is maintained for the $KNbO_3$ film deposited at 900 °C: $KNbO_3(100)\langle 001\rangle//SrTiO_3(110)\langle 001\rangle$.

$SrRuO_3$ films were grown on both $SrTiO_3$ and SiO_2 substrates at 750 °C by RF sputtering. Fig. 2a shows XRD patterns of the $SrRuO_3$ films 100 nm in thickness deposited on a $SrTiO_3$ substrate. The XRD in the range of 62–70 °C is shown in the insert. A shoulder at 67.0 °C denoted by an asterisk is assigned to $SrRuO_3$(242). The $SrRuO_3$ (121) and (242) peaks are seen near the $SrTiO_3$ (110) and $SrTiO_3$ (220) peaks. The preferential orientation, $SrRuO_3(121)//SrTiO_3(110)$, occurs in the

0022–2461 © *2004 Kluwer Academic Publishers*

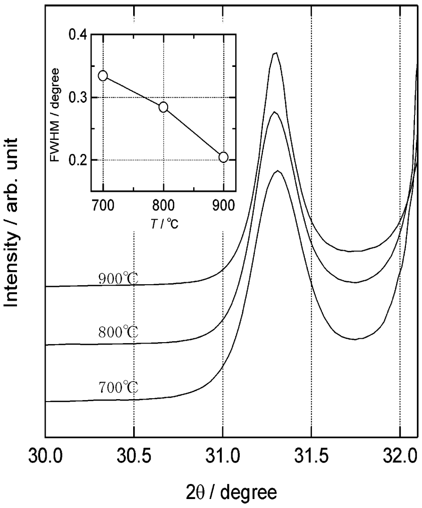

Figure 1 XRD patterns of $KNbO_3$ films deposited on $SrTiO_3$ (110) substrates at 700, 800, and 900 °C. Inset shows temperature dependence of FWHM for $KNbO_3$ (200) peaks in these films.

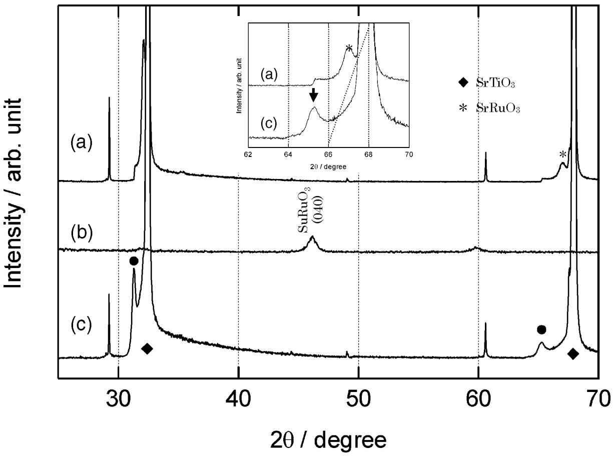

Figure 2 XRD patterns of: (a) $SrRuO_3$ film deposited on $SrTiO_3$ (110) substrate, (b) $SrRuO_3$ film deposited on SiO_2 glass substrate, (c) $KNbO_3$ film deposited on $SrRuO_3$ film. Diffraction peaks of $SrTiO_3$ substrate, $SrRuO_3$, and $KNbO_3$ are denoted by filled squares, asterisks, and filled circles.

$SrRuO_3$ film deposited on a $SrTiO_3$ substrate. The $SrRuO_3$ films exhibit a resistivity of 3×10^{-3} Ωcm, which is 15 times as high as that of orthorhombic single crystal. Such a high resistivity was reported in $SrRuO_3$ films deposited on $SrTiO_3$ (001) substrates, and was interpreted in terms of strains of crystal grains [9]. Fig. 2b shows XRD pattern of the $SrRuO_3$ film on a SiO_2 glass substrate. The diffraction peaks are weak and no preferential orientation is confirmed. The poor crystallinity of the film is attributable to lack of the epitaxial growth on a glass substrate.

A device consisting of $SrRuO_3$ and $KNbO_3$ films was fabricated as follows: A $SrRuO_3$ film 30 nm in thickness has been grown on $SrTiO_3$ (110) and SiO_2 glass substrates by RF sputtering, and subsequently a $KNbO_3$ film 300 nm in thickness was deposited on the $SrRuO_3$ film at 900 °C by MOCVD. XRD pattern of the device deposited on a $SrTiO_3$ (110) substrate is shown in Fig. 2c. No reflection peaks of the $SrRuO_3$ are seen in the XRD pattern. The top $KNbO_3$ film is preferentially oriented but its crystallinity is fairly poor in comparison with that of the $KNbO_3$ films deposited directly on a $SrTiO_3$ substrate.

Fig. 3 shows AFM topographic images of the surfaces of the $KNbO_3$ films deposited on $SrTiO_3(110)$ substrates at 700, 800, and 900 °C, together with an AFM topographic image of the $KNbO_3$ film deposited on the $SrRuO_3$ film. The right oblique in this figure indicates the $\langle 001 \rangle$ direction of the $SrTiO_3$ substrate plane. A large number of small crystal grains are seen on the surfaces of the films deposited at 700 and 800 °C. The surfaces of these films are very rough; surface roughness, Ra, is more than 250 nm. In the film deposited at 900 °C, crystal grains grow along the $\langle 001 \rangle$ direction and the surface roughness is reduced to 140 nm. The anisotropic growth of grains suggests epitaxial growth of the $KNbO_3$ film. The interpretation is consistent with the results of the X-ray pole figure measurements. As seen in Fig. 3d, the surface of the top $KNbO_3$ film on the $SrRuO_3$ film is very smooth, irrespective of its low crystallinity. This smooth surface is satisfactory for either evolution or removal of ferroelectric domains.

Fig. 4a shows an AFM topographic image in scanning area of 2 μm × 2 μm before the application of an electric field. In the AFM image, some grains of 100 nm are observed on the surface. In order to induce local polarization, the area of 200 nm × 400 nm enclosed by the dotted line in Fig. 4a was scanned at a voltage of 10 V. After a bias voltage of 10 V was turned off, an AFM topographic image was taken in scanning area of 2 μm × 2μm. The obtained AFM image is shown in Fig. 4b. It is a striking feature that a hump of 80 nm in height is formed in the area where an electric field has been applied. The hump remains unchanged for a few hours at room temperature. The AFM image reflects not only the topographic change of the $KNbO_3$ surface but also an electrostatic force between the cantilever and charges at the $KNbO_3$ surface. The piezoelectric effect gives rise to the elongation or contraction of $KNbO_3$ film along $\langle 200 \rangle$ direction. For instance, the deformation of 0.2 nm can be induced when an electric field of $1/3 \times 10^6$ V/cm is applied across the $KNbO_3$ film 300 nm in thickness. Thus, the piezoelectric effect on the AFM topographic image is negligible. Similar humps have been formed at the TiO_2 surface by applying -3.0 V in an O_2 atmosphere, and have been explained in terms of the adsorbed oxygen molecules, O_2^- [11]. The adsorption of oxygen molecules is not responsible for the origin of the hump because the positive voltage is applied to the device in an Ar atmosphere. Furthermore, no Au atoms are evaporated from a Au cantilever to the $KNbO_3$ surface at the positive bias voltage. Accordingly, the hump is due to an electrostatic force between the remanent polarization and the conductive cantilever. An applied electric field is parallel to the direction of the polarization, i.e., $\langle 200 \rangle$ direction, and its strength is attained to $1/3 \times 10^6$ V/cm at a bias voltage of 10 V. The electric field strength is enough to align spontaneous polarization toward c-axis [12]. Thus, the hump seems to depict a ferroelectric domain in the $KNbO_3$ film. The shape of the hump is slightly deformed from a rectangle of 200 nm × 400 nm. The symmetric expansion of the shape is due to

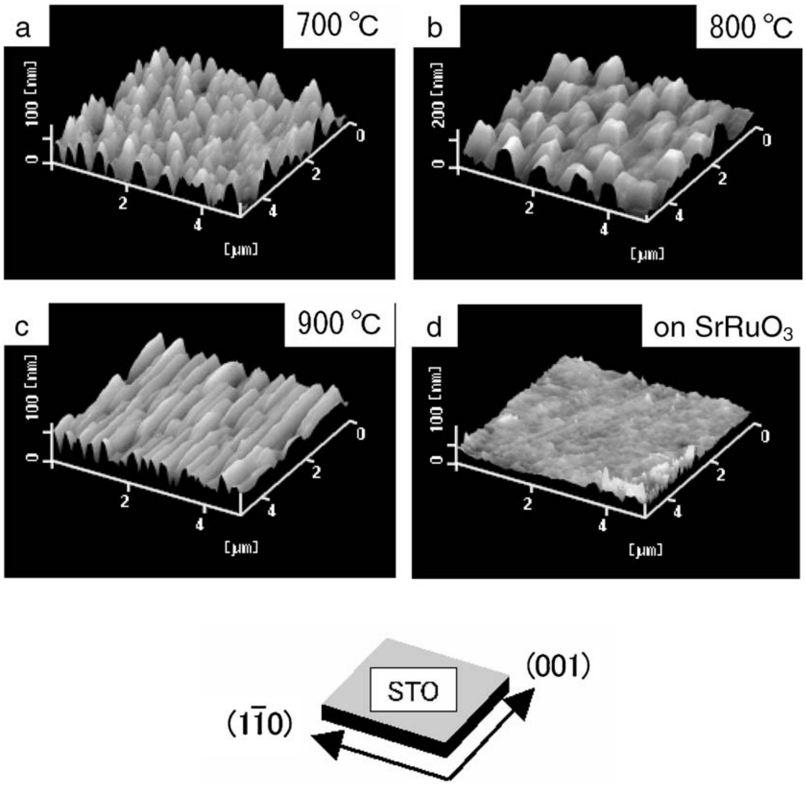

Figure 3 AFM images of $KNbO_3$ films deposited on: (a) $SrTiO_3$ (110) substrate heated at 700 °C, (b) $SrTiO_3$ (110) substrate heated at 800 °C, (c) $SrTiO_3$ (110) substrates heated at 900 °C, and (d) $SrRuO_3$ film heated at 900 °C.

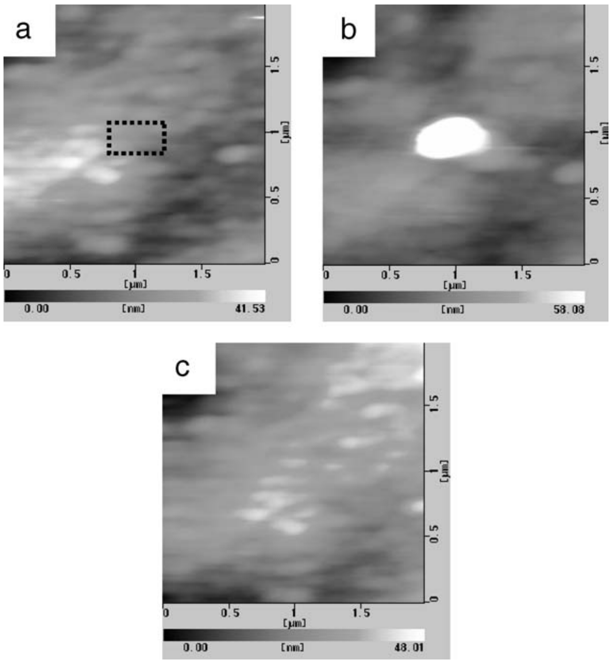

Figure 4 AFM images of $KNbO_3$ films: (a) before and (b) after applying 10 V, and (c) after applying −10 V. The area of 200 nm × 400 nm enclosed by the dotted line in Fig. 1a was scanned at 10 V.

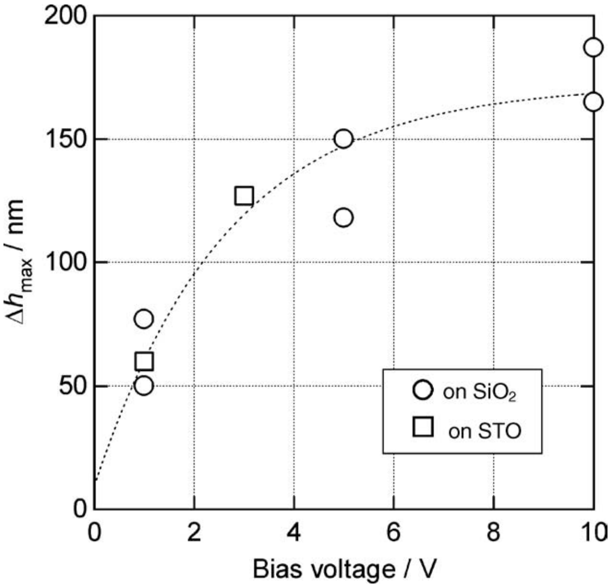

Figure 5 Height of humps as a function of an applied voltage. A dotted line is a guide line.

a lateral electrostatic force from the polarization and the asymmetric expansion is related to inhomogeneous distribution of the polarization near the grain boundary.

The area of 500 nm × 500 nm including the hump was scanned at −10 V, and subsequently an AFM topographic image of the area of 2 μm ×2 μm was taken at 0 V. Fig. 4c shows the AFM topographic image after the scanning at −10 V. It should be noted that the hump disappears in the AFM topographic image. The remanent polarization is diminished by the reverse voltage of −10 V; the coercive field is estimated to be $-1/3 \times 10^6$ V/cm. The formation of the reverse polarization, however, is not achieved by applying a bias voltage up to −10 V. Such an asymmetric switching can be attributed to the internal electric field produced in the vicinity of the film/electrode interface [13]. The internal field is added to a positive external field, but on the contrary weaken a negative external field. After a hump disappears, a hump is again formed on the $KNbO_3$ film by applying a voltage of +10 V. The evolution and removal of ferroelectric domains are reversible.

Fig. 5 plots the voltage dependence of the height of a hump, which is formed by applying an electric field to the area of 500 nm × 500 nm in the $KNbO_3$ films fabricated on either $SrTiO_3$ or SiO_2 substrates. The hump-height is proportional to the remnant polarization induced by an applied external field. The hump-height increases with an applied voltage and is nearly saturated near 10 V. The hump-height of 180 nm is attained at a bias voltage of 10 V, and is satisfactorily distinguished from the surface roughness of the $KNbO_3$ film. Although the hump-height at 10 V is satisfactory, the shape of the hump is deformed from the square of 500 nm × 500 nm. In contrast, the shape of hump formed at 1 V is almost a square of 500 nm × 500 nm. High resolution of ferroelectric domains is probably attained at a low bias voltage. As seen in Fig. 5, the hump-height formed at 1 V is as large as 50–80 nm. Accordingly, the preparation of a $KNbO_3$ film with the surface roughness of 5 nm or less is required for the development of high-density memories.

References

1. J. F. SCOTT and C. PAZDE ARAUJO, *Science* **246** (1989) 1400.
2. R. MOAZAMI, C. HU and W. H. SHEPHERD, *IEEE Trans. Electron Devices* **39** (1992) 2044.
3. C. A. PAZ DE ARAUJO, J. D. CUCHLARO, L. D. MCMILLAN, M. C. SCOTT and J. F. SCOTT, *Nature* **374** (1995) 627.
4. T. MIHARA, H. WATANBE and C. A. PAZ ARAUJO, *Jpn. J Appl. Phys.* **33** (1994) 5281.
5. B. M. NICHOLS, B. W. WESSELS, J. A. BELOT and T. J. MARKS, *Mat. Res. Soc. Symp. Proc.* **541** (1999) 741.
6. Y. XU, C. CHENG, Y. LOU and J. D. MACKENZIE, *Ferroelectrics* **195** (1997) 283.
7. V. GOPALAN, H. KIE, W.-Y. HSU and R. RAJ, *ibid.* **152** (1994) 55.
8. A. ONOE, A. YOSHIDA and K. CHIKUMA, *Appl. Phys. Lett.* **69** (1996) 167.
9. K. TAKAHASHI, T. OIKAWA, K. SAITO, S. KANEKO, H. FUJISAWA, M. SHIMIZU and H. FUNAKUBO, *Jpn. J. Appl. Phys.* **41** (2002) 5376.
10. C. W. JONES, P. D. BATTLE, P. LIGHTFOOT and W. T. A. HARRISON, *Acta Cryst.* **C45** (1989) 365.
11. K. KOBAYASHI, Y. TOMITA and S. YOSHIDA, *Nano. Lett.* **2** (2002) 925.
12. B. A. TUTTLE, B. C. BUNKER, D. L. LAMPPA, R. G. TISSOT and J. L. YIO, *Ceram. Trans.* **11** (1990) 329.
13. A. GRUVERMAN, A. KHOLKIN, A. KINGON and H. TOKUMOTO, *Appl. Phys. Lett.* **78** (2001) 2751.

Received 23 February
and accepted 18 March 2004