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Fabrication and structural characterization of TiO nanoparticle soft-landed on substrate by the magnetron sputtering-gas aggregation method

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Abstract. We have succeeded to fabricate the thin film mainly or entirely consisting of nano-crystallites TiO on a substrate at room temperature by using the magnetron sputtering combined with the gas aggregation method which has the capability to deposit grown small particles and/or clusters of the desired compound material on the substrate in soft-landed mode. The important experimental parameters to control the growth of TiO particles are identified as partial pressure of additional oxygen gas, growth-reaction distance L_{td}, and LN_2 cooling of growth chamber. The smallest averaged diameter of TiO nano-particles is 5.62 nm and size distribution being from 2 to 8 nm under 50 mm of L_{td}. The compositional uniformity is confirmed by EDS and EELS. The chemical state of the film observed by Ti 2P XPS peak confirms the primarily growth of TiO and indicates the formation of minor content of amorphous $Ti_{1-x}O_x$ and/or $Ti_{1-x}C_x$ particularly at the surface of the film.

PACS. 81.15.Cd Deposition by sputtering – 81.10.-h Methods of crystal growth; physics of crystal growth – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 61.66.-f Structure of specific crystalline solids

1 Introduction

Among transition metal oxides, conductive titanium monoxide (TiO) with NaCl type crystal structure, which has low electrical resistivity combined with a high anti-diffusion efficiency to prevent the interface degradation [1] and a lattice parameter close to MgO used as a substrate for epitaxial growth of lead zirconia titanate (PZT) [2], has recently considered as favorable thin films materials for the application in low resistance contact metallization in microelectronics layered structures [3]. Particularly, TiO as an intermediate layer has promising role to enhance the growth of the appropriate PLZ phase and to reduce the mutual diffusion of the different layer materials for the performance improvement of the layered ferroelectric device [4].

The following three works have been only known as the TiO thin film fabrication: (1) double step by reactive evaporation at 300 °C followed by annealing at 550 °C [5], (2) one step by reactive ion beam sputtering at 600 °C [6], and (3) one step by oxygen-ion-assisted physical vapor deposition at <100 °C [3]. The applied high temperature in the first two methods is disadvantage for the fabrication of the layered ferroelectric device. In third method, there are difficulties to control precisely the ratio of metal vapor flux and oxygen vapor flux as well as the densities of those fluxes to assure homogeneous growth of TiO_x ($x = 1$) compound with very narrow range of x according to the equilibrium-phase diagram of titanium/oxygen system.

The aim of the present study is to examine the possibilities of the magnetron sputtering combined with the gas aggregation method [7,8], which has the capability to deposit the small particles and/or clusters of the desired compound materials as developed originally by Harberland et al. [9], for the fabrication of the thin film consisting mainly or entirely of nanoparticles of TiO phase on a substrate at room temperature. Their crystal structure and morphology, compositional uniformity, and chemical state of the film, have been identified by transmission electron microscopy (TEM), selected area electron diffraction (SAED), energy dispersive spectroscopy (EDS), electron energy loss spectroscopy (EELS) and X-ray photo-electron spectroscopy (XPS) respectively.

2 Experimental

The nano particles of TiO were grown by the magnetron sputtering combined with the gas aggregation method by

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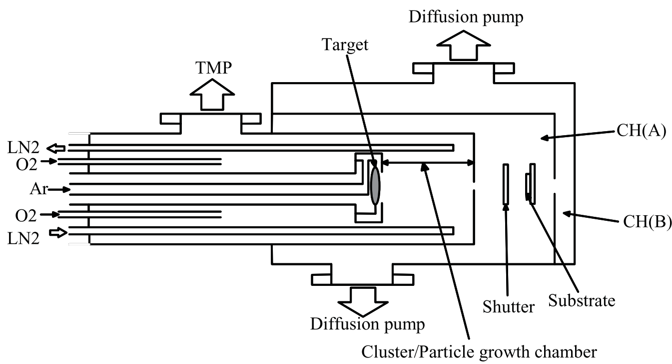


Fig. 1. Schematics of the magnetron sputtering-gas aggregation source and the experimental set-up for the film deposition. The distance between the Ti target and the aperture is denoted as L_{td}. The distance between the aperture and the substrate is fixed to 30 mm. The shutter is provided in the front of the substrate holder. The deposition chamber (CH-A) is separated from the outer chamber (CH-B) by the diaphragm with 2 mm ϕ hole.

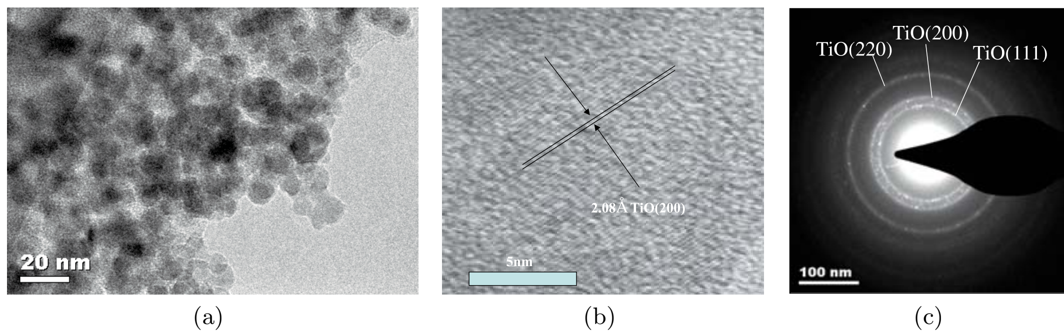


Fig. 2. Low-magnified TEM images of the deposited thin film under L_{td} = 50 mm (a), HRTEM image of the same sample (b), and SAED ring pattern (c).

following our previous reports [8,9]. The source consisted of a DC magnetron sputtering gun with Ti target, a cylindrical reaction-chamber for TiO formation under the oxidation reaction of the sputtered Ti atoms/clusters, and a liquid nitrogen reservoir to cool down the generated compound particles at high temperature for the control of the particle size distribution has shown schematically in Figure 1. The base pressure in the source was 3×10^{-4} Pa. The surface of Ti target (50 mm ϕ) was cleaned by pre-sputtering with Ar gas in prior to the deposition.

Firstly Ti atoms and clusters was sputtered off the Ti target by DC magnetron sputtering under 2×10^2 Pa in Ar gas pressure with constant electric power of 300 W. The hot sputtered atoms and/or clusters was cooled down, aggregated and reacted by the collision of the surrounding mixture gas of Ar with 2.6×10^2 Pa and oxygen with 2.6 Pa in partial pressure. The pressure value of oxygen was set at the maximum to keep the continuous and stable sputtering ignition. Consequently, the nano-sized TiO_x compound particles were grown in the reaction-chamber.

Then, the flux of the particles was spouted to the adjacent vacuum vessel kept at 3×10^{-4} Pa through the aperture with 2 mm in diameter at the end of the source and directly being deposited on a substrate at room temperature apart from the aperture by 30 mm in soft-land mode. The substrates used were either copper mesh with micro grid carbon film (hereafter called "micro grid") or glass. To control the particle size of TiO, the growth reaction distance between the sputtering target and the aperture (L_{td}) was set at 50 mm as an optimal condition and the wall of the reaction-chamber and aperture were cooled down to LN_2. The crystal structure, morphology, compositional uniformity, and chemical state, of the deposited particulates thin film were characterized by TEM, SAED, EDS, and EELS (JEOL 2010 FEF at 200KV, and JEOL JEM 4000EX at 400KV for high resolution TEM (HRTEM) image) and XPS (Physical Electronics, ESCA-5700ci.) respectively. In EELS, Ω-type energy filter was installed to the JEOL 2010 FET. The samples used for those characterizations by TEM and the related analysis were soft-landed TiO particles and/or clusters directly on a micro grid and the sample for XPS was those on a glass.

To confirm the optimal experimental parameters for the deposition of the film mainly or entirely consisting of nano-particles of TiO crystal, the three experiments under the following different conditions were additionally carried out: (1) zero oxygen partial pressure, (2) different L_{td} at 150, 100, 50 and 20 mm, and (3) no coolant of LN_2. The results of those experiments are summarized in Section 3.4.

3 Results and discussion

3.1 Crystal structure

Figures 2a, 2b and 2c show the low magnification TEM image, HRTEM image, and SAED ring pattern of the sample deposited under L_{td} = 50 mm respectively. The film are identified as polycrystalline TiO from Figure 2c, where (111), (200) and (220) lattice plane of TiO with NaCl crystal structure are indexed. From Figure 2a, the deposited film is composed by many nano-crystallites TiO with the particle diameter of 5.62 nm averaged over 225 particles. There are no particles with a distinct faceted shape. The particle diameter is distributed from 2 to 8 nm as shown in the histogram of Figure 3. A HRTEM lattice image of Figure 2b is indexed as TiO (220). The high

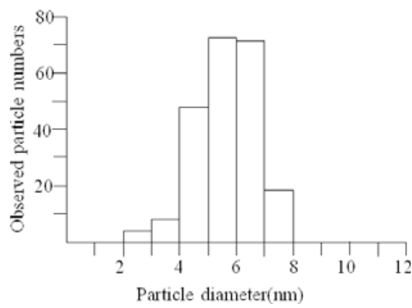
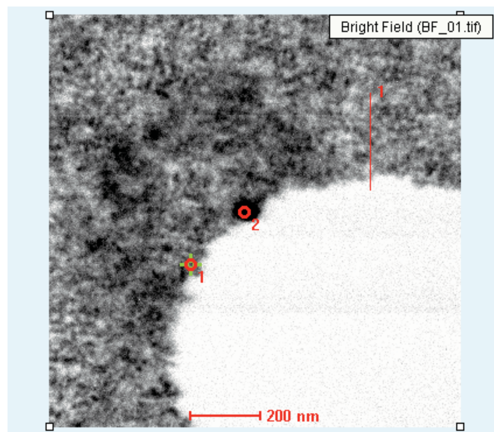


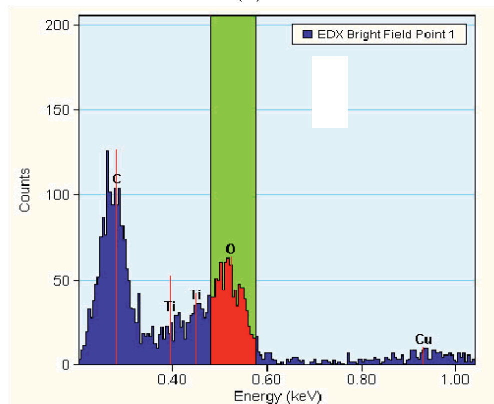
Fig. 3. The distribution of the diameter of the TiO particles deposited under L_{td} = 50 mm.

Table 1. Comparison between the lattice spacing appeared in JCPDS card and that obtained from SAED ring pattern and the lattice image in HRTEM.

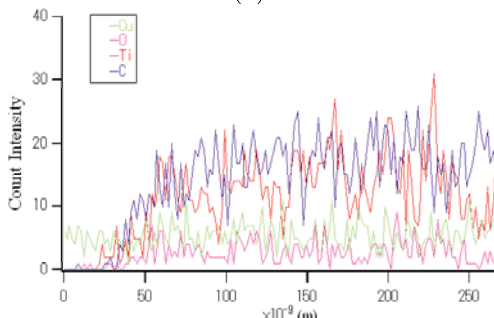
	A: JCPDS (Å)	B: Calculated (Å)	$(A - B)/A$ (%)
TiO111	2.407	2.473	–2.7
TiO200	2.085	2.098	–0.6
TiO220	1.475	1.489	–0.9
TiO311	1.259	1.250	–0.7
TiO420	1.205	0.938	–0.4



(a)



(b)



(c)

Fig. 4. (a) Low-magnified bright field s-TEM image of the deposited film giving the position of EDS profile, (b) a typical spot EDS spectrum taken from position 1 indexed in (a), (c). Line profile along the line from the edge of micro grid to the inner part indicated in (a).

density and fine crystal quality of the fabricated nano particles by the present method are confirmed.

The lattice spacing values of TiO films obtained from SAED and HRTEM lattice image agree satisfactorily with those of bulk values [10] as shown in Table 1. Consequently, the fabricated TiO particles and/or clusters are grown without strain under the present experimental conditions. This result strongly supports the feasibility of our examined method for the fabrication of TiO thin film with high crystal quality.

3.2 Compositional uniformity

The chemical composition of the obtained film was analyzed by EDS installed in the used JEOL 2010 FET TEM Two kinds of EDS profiles were carried out: two spots and line profiles shown as the bright field image of scanning TEM (s-TEM) mode in Figure 4a. The representative spot and line profile of EDS results are shown in Figures 4b, and 4c respectively. The elements C, Ti, O, and Cu are detected either in spot or line profiles. We can safely say that Cu element come entirely from mesh of the micro grid, while C comes mostly from micro grid substrate and small portion of it is contamination from vacuum pump. In the line profile, intensity profiles of Ti and O are quite proportional and this confirms the compositional uniformity of the deposited TiO thin film.

Figure 5 shows EELS of the deposited thin film. Ti-L2 and Ti-L3 peaks due to the core excitation from Ti $2p_{1/2}$ to $3d$ and from $2p_{2/3}$ to $3d$ as well as O-K peaks can be clearly observed, although C-K peak is not appeared. This strongly suggests the present film is composed of Ti-O compound and coincides with SAED observation.

3.3 Chemical state

We measured Ti $2p$ core level of the deposited film by XPS as shown in Figure 6 to investigate the chemical state. For the comparison, XPS of the TiO_2 thin film composed of anatase type poly-crystals previously reported by Miao et al. [11] is also cited. The observed Ti $2p$ peak values of TiO are smaller than those of TiO_2 by 1eV. The previously reported Ti $2p_{3/2}$ peak is 454.7 eV for the bulk TiO sample prepared by high-temperature annealing at 1300–1500 °C of materials which were initially prepared by direct combination of high purity elements in Vycor glass or fused-silica tubes at temperature <700 °C [12].

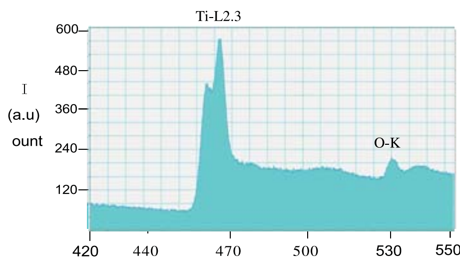


Fig. 5. EELS of the deposited film.

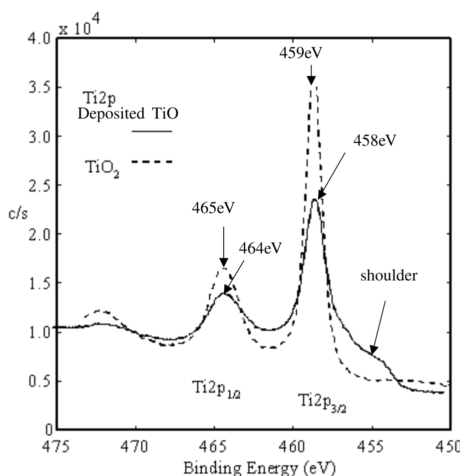


Fig. 6. Comparison between XPS spectra of Ti $2p$ from the deposited TiO thin film and that from the polycrystalline anatase TiO_2 film.

However, this reported value seems to be too low to refer, when we take account the recent theoretically calculated adiabatic electron affinities of TiO and TiO_2 and TiO_3 as 1.25, 1.60, and 3.34 eV respectively [13]. Those affinity values support our presently observed shift in the binding energy.

The shoulder observed at 455 eV suggests the possible existing of amorphous $T_{1-x}O_x$ and/or $Ti_{1-x}C_x$ particularly at the surface of the film. This topic is again discussed in Section 3.4.

3.4 The influence of the experimental parameters on TiO growth

In the case of zero oxygen partial pressure, the growth of TiO crystallites is extremely reduced, whereas particles of crystal TiC and amorphous $Ti_{1-x}O_x$ and $T_{1-x}C_x$ with averaged diameter of nanometers size are characterized by TEM, SAED, EDS, EELS and XPS in the deposited films. This reveals that the addition of oxygen gas even at low partial pressure is essential to enhance the oxidation reaction of sputtered Ti element to TiO.

The average sizes of the particles increase up to 9.97 nm at L_{td} = 100 mm and 10.28 nm at 150 mm respectively, and the size distribution is becoming wider than that observed for L_{td} = 50 mm. Under L_{td} < 50 mm, amorphous $Ti_{1-x}O_x$ is apparently fabricated, although TiO crystallites with smaller averaged diameter than 5.62 nm are observed. This implies that the critical value of L_{td} to deposit the film mainly or entirely consisting of nano-crystallites TiO is 50 mm.

The averaged particle size increases up to 9.87 nm and the size distribution expands from 4 to 14 nm without LN_2 coolant. This confirms the importance of the cooling process during the growth of small particulates.

Consequently, the adopted experimental parameters; oxygen partial pressure: 2.6 Pa, L_{td}: 50 mm, and cooling of growth chamber with LN_2 coolant, are confirmed to be optimal for the fabrication of the nano crystallites TiO.

4 Conclusions

Using the magnetron sputtering-gas aggregation method, we have succeeded to fabricate the thin film consisting mainly or entirely of nano-crystallites TiO on the substrate at room temperature in the soft land mode under the optimal experimental parameters of partial pressure of additional oxygen gas, growth reaction distance L_{td}, and LN_2 cooling of growth chamber. The smallest averaged diameter of TiO nano-particles is 5.62 nm and the diameter distribution being from 2 to 8 nm under $L_{td} = 50$ mm. The compositional uniformity is confirmed by EDS and EELS. The chemical state of the film from XPS of Ti $2p$ peak confirms the primarily growth of TiO in the film and indicates the formation of minor content of amorphous $Ti_{1-x}O_x$ and/or $Ti_{1-x}C_x$ particularly at the surface of the film.

This is the world first achievement to deposit TiO crystallites on substrate at room temperature and the method being prospect for the preparation of the layer material for the ferroelectric device.

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