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Atomic Structure Determination of $Ba_4Ti_5O_{10}$ and $Ba_4Ti_4O_{11}$ in Epitaxial Barium Titanate Nanodomains Using HRTEM and Electron Diffraction

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Perovskite $BaTiO_3$ thin films have a wide range of applications for advanced devices. Especially, epitaxial $BaTiO_3$ thin films are highly desirable for these advanced applications. So far, such epitaxial $BaTiO_3$ films have been successfully fabricated on different single-crystal substrates using various deposition techniques including RF magnetron sputtering, molecular beam epitaxy, metallorganic chemical vapor deposition and pulsed laser deposition. Among the deposition techniques, RF magnetron sputtering is becoming a very important deposition method due to its capability of depositing thin films over a large substrate area. The microstructure and physical properties of these films are strongly affected by the deposition conditions, such as chemical doping, deposition temperature, oxygen partial pressure, vacuum level, electric and mechanical stress fields and strain arising from the lattice and/or thermal expansion mismatch between the film and substrate.

Recently, we have fabricated barium titanate (BTO) thin films on MgO substrates using a home-made plasma assisted by RF magnetron sputtering system. A $BaTiO_3$ target of 99.999% purity was used for deposition. The MgO substrate surface was first cleaned using Ar plasma at room temperature for 10 minutes. The deposition temperature is 800 °C. A pressure of 1.333 Pa, an Ar gas flow rate of 10 cm^3/min and a RF power of 50 W were used for film deposition. The as-deposited films exhibit interesting ferroelectric properties entirely different from those of perovskite $BaTiO_3$ resulting from the presence of the two new superstructures formed during deposition. In this work, we report on the atomic structure determination of the two new structures using electron diffraction and HRTEM.

Systematic studies using X-ray photoelectron spectroscopy, X-ray diffraction and cross-section and plan-view TEM demonstrated that the BTO thin films consist of epitaxial nanodomains structures of two new superstructures $\boldsymbol{\Gamma_\gamma}$ and $\boldsymbol{H_\beta}$ (Figure 1). Due to the nanometer scale size of the domains and the complexity of the structure in the film, the single crystal x-ray diffraction technique was inadequate to conduct the crystallographic structure determination of the two new superstructures. We used nano-beam electron diffraction to reconstruct the three-dimensional diffraction space and hence the symmetry of the new superstructures. Both $\boldsymbol{\Gamma_\gamma}$ and $\boldsymbol{H_\beta}$ were found to be monoclinic structures with a space group of ***Cm*** (*b*-unique axis). The $\boldsymbol{\Gamma_\gamma}$ phase was identified as a monoclinic $Ba_4Ti_5O_{10}$ structure with a space group of ***Cm*** (No. 8, è-unique axis) and lattice parameters of a = 16.49 Å, b = 3.94 Å, c = 8.94 Å and β = 103°(Fig. 2(a)), while the $\boldsymbol{H_\beta}$ phase was identified as a monoclinic $Ba_4Ti_4O_{11}$ with a = 17.88 Å, b = 3.94 Å, c = 7.21 Å and $\beta = 98°$ (Fig. 2(b)). Atomic structural models for the two new superstructures were established by reconstructing the HRTEM images taken from the three major axes and refined by matching the simulated HRTEM images and calculated electron diffraction patterns with the experimental results. The two superstructures are epitaxially grown on MgO with their *b*-axis parallel to the growth direction followed by a primary orientation relationship:

[1] $(010)_{\Gamma\gamma} // (001)_{MgO}$, $[20\bar{1}]_{\Gamma\gamma} // [100]_{MgO}$ and $[104]_{\Gamma\gamma} // [010]_{MgO}$, for $\boldsymbol{\Gamma_\gamma}$

[2] $(010)_{H\beta} // (001)_{MgO}$, $[30\bar{4}]_{H\beta} // [100]_{MgO}$ and $[104]_{H\beta} // [010]_{MgO}$, for $\boldsymbol{H_\beta}$

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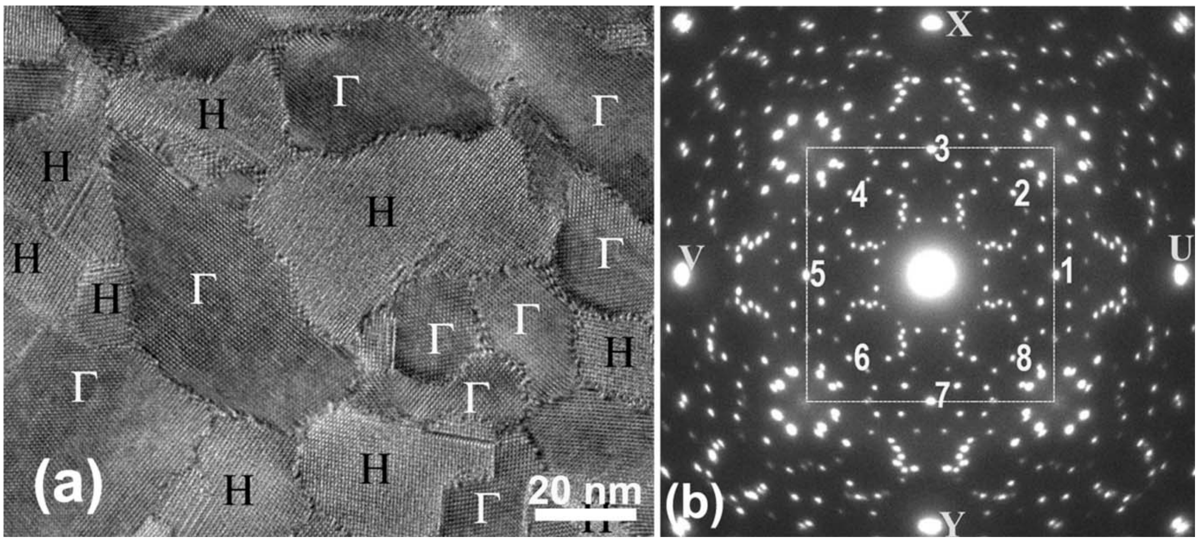

Figure 1. (a) Plan-view TEM image and (b) SAED pattern of the BTO thin films deposited using RF-magnetron sputtering showing the presence of multi-oriented nano-domain structures of two new superstructures (***Γ*** and ***H***).

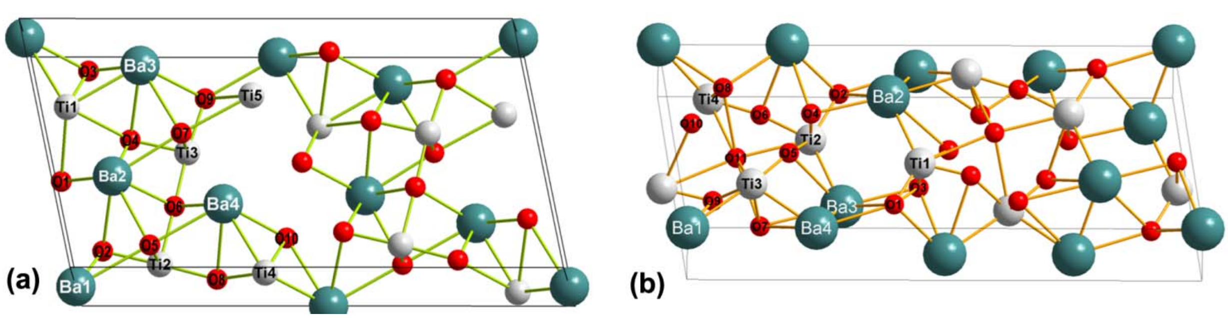

Figure 2. Illustration of the atomic structural model of (a) $\boldsymbol{\Gamma_z}$ ($Ba_4Ti_5O_{10}$) and $\boldsymbol{H_\beta}$ ($Ba_4Ti_4O_{10}$).

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