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Laser Molecular Beam Epitaxy of Multilayer Heterostructure $SrNb_{0.05}$ $Ti_{0.95}O_3/La_{0.9}Sr_{0.1}MnO_3$ in 10000 Unit-Cell Layers *

HUANG Yan-Hong(黄延红)[1], HE Meng(何萌)[1], TIAN Huan-Fang(田焕芳)[1], ZHAO Kun(赵昆)[1,2], LÜ Hui-Bin(吕惠宾)[1**], JIN Kui-Juan(金奎娟)[1], LI Jian-Qi(李建奇)[1], YANG Guo-Zhen(杨国桢)[1]

[1]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080*

[2]*Department of Mathematics and Physics, China University of Petroleum, Beijing 102249*

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Ten thousands of unit-cell multilayer heterosturctures, $[SrNb_{0.05}Ti_{0.95}O_3/La_{0.9}Sr_{0.1}MnO_3]_3$ (SNTO/LSMO), have been epitaxial grown on $SrTiO_3$ (001) substrates by laser molecular beam epitaxy. The monitor of in-situ reflection high-energy electron diffraction demonstrates that the heterosturctures are layer-by-layer epitaxial growth. Atomic force microscope observation indicates that the surface of the heterosturcture is atomically smooth. The measurements of cross-sectional low magnification and high-resolution transmission electron microscopy as well as the corresponding selected area electron diffraction reveal that the interfaces are of perfect orientation, and the epitaxial crystalline structure shows the orientation relation of SNTO(001)//LSMO(001), and SNTO[100]//LSMO[100].

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Epitaxial growth of artificial crystalline perovskite oxide materials becomes one of the most exciting areas in condensed matter physics and material science because of their remarkable properties and the applications. In recently years, the heterostructures and multilayer structures of perovskite oxide have attracted a great deal of attention because the artificial materials with unique properties can be constructed by using the different perovskite building blocks, and some new physical properties and the enhancement of properties were found due to the interface effects.[1−6] However, it is not easy to obtain the high-quality heterostructure with the increase of the films thickness due to the lattice parameter misfits of different materials and interfacial stress as well as the dislocations. Lee *et al.*[2] reported the three-component superlattice grown up to 2500 unit-cell (about 1 μm) in thickness on a $SrTiO_3$ (STO) substrate. We also reported the layer-by-layer epitaxial growth of perovskite oxide films and superlattices as well as grown up to 7000 unit-cell (about 2.8 μm) $BaTiO_3$ film on an STO substrate.[7] In this Letter, we report the epitaxial growth of multilayer $SrNb_{0.05}Ti_{0.95}O_3/La_{0.9}Sr_{0.1}MnO_3$ heterosturctures in 10000 unit-cell (about 4 μm). To our best knowledge, it is the first time to epitaxially grow oxide multilayer heterostructure in 10000 unit-cell layers with atomic precision. It is expected to apply the method to a number of other functional oxides integrated.

The heterojunctions consist of three layers $SrNb_{0.05}Ti_{0.95}O_3$ (SNTO) and three layers $La_{0.9}Sr_{0.1}MnO_3$ (LSMO) alternately grown on STO substrates, $[SrNb_{0.05}Ti_{0.95}O_3/La_{0.9}Sr_{0.1}MnO_3]_3$ (SNTO/LSMO). As mentioned in our previous work, in order to obtain the high-quality films, a computer-controlled laser molecular-beam epitaxy (laser MBE) system equipped with in-situ reflection high-energy electron diffraction (RHEED) was used to fabricate the heterojunctions.[7] The first LSMO layer was grown on STO substrates at the substrate temperature of 630°C and under a oxygen pressure of 3×10^{-3} Pa. The second layer was SNTO grown at the same temperature as the first layer and under an oxygen pressure of 4×10^{-4} Pa. The third and the fifth layers were the same condition as the first layer, and the fourth and the sixth layers were under the same condition as the second layer. During the epitaxial growth, the substrate temperature was maintained at 630°C and the energy density of the pulse laser (308 nm, duration 20 ns, repetition rate 2 Hz) was about 1 J/cm^2. The growth process of the heterostructure was monitored by the *in-situ* and real-time RHEED. The growth rates were one unit-cell per 26 pulses and 30 pulses for LSMO and SNTO, respectively. The structure of the heterostructures was characterized by the RHEED, x-ray diffraction (XRD), transmission electron microscopy (TEM), and atomic force microscopy (AFM).

Figure 1 shows the RHEED intensity oscillations at the beginning of the LSMO growth. The insets, a, b, and c, in Fig. 1 display the RHEED patterns of an STO substrate, LSMO and SNTO films, respec-

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**To whom correspondence should be addressed. Email: hblu@aphy.iphy.ac.cn

tively. The sharp and bright RHEED patterns and the undamping RHEED intensity oscillations could be observed during the films growth, indicating that the heterostructure was layer-by-layer epitaxial growth.

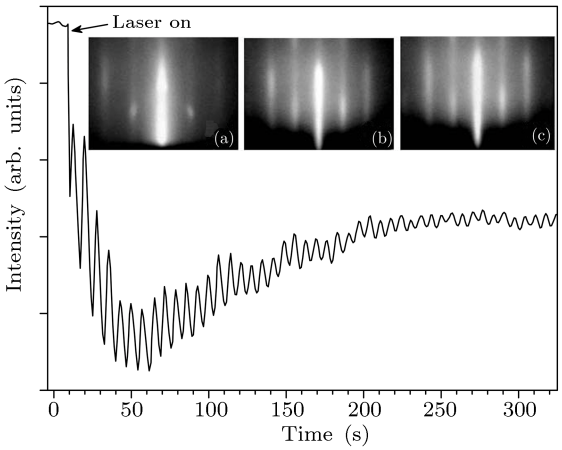

Fig. 1. RHEED intensity oscillation monitored on the specular beam spot during the growth of the LSMO on STO substrate. The insets are RHEED patterns: (a) STO substrate, (b) LSMO film, (c) SNTO film.

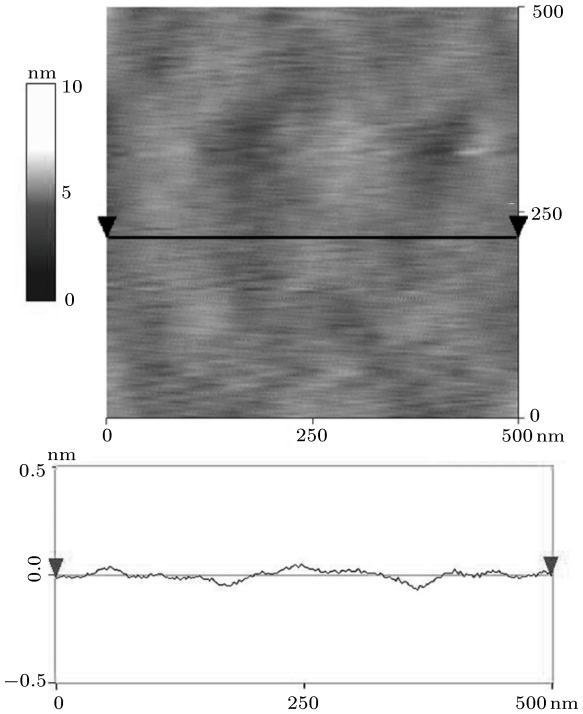

Fig. 2. Two-dimensional AFM image of SNTO/LSMO heterostructure surface. The bottom is the height profile along the black line in the 2D image.

Figure 2 is a two-dimensional (2D) AFM image of the heterostructure surface after growth, and the bottom is the height profile along the black line in the 2D image. The root-mean-square surface roughness is 0.222 nm in an area of 500 nm×500 nm, indicating the heterostructure surface keeps atomically smooth after growing 10000 unit-cell layers of SNTO/LSMO.

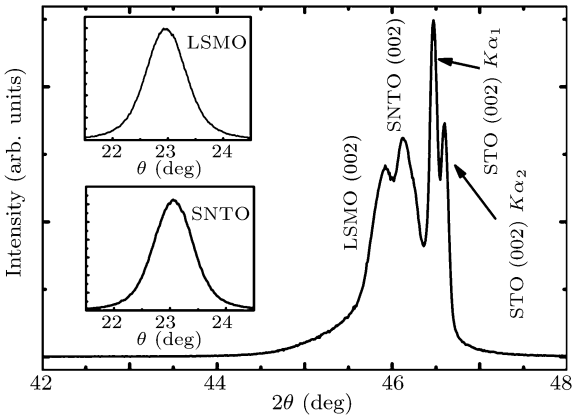

Fig. 3. XRD θ–2θ scan curve of SNTO/LSMO heterostructure grown on the STO substrate. The insets show the ω rocking curves for the (002) peaks of LSMO and SNTO.

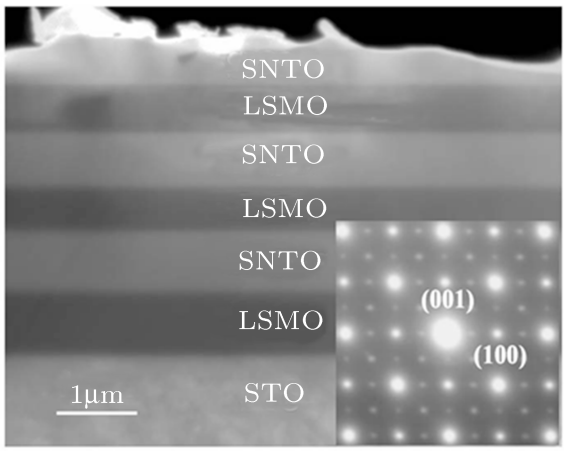

Fig. 4. Low magnification cross-sectional TEM image of SNTO/LSMO heterostructure grown on STO substrate. The inset is the corresponding SAED pattern.

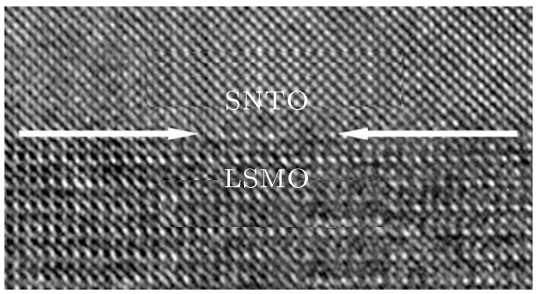

Fig. 5. A typical cross-sectional HRTEM image of the interface between LSMO and SNTO layers in the heterostructure.

Figure 3 shows the XRD $\theta-2\theta$ scan pattern of the multilayer heterostructure. Except for LSMO (00l), SNTO (00l) and STO (00l) peaks, no other peaks can be observed from the impurity phases or randomly oriented grains. The XRD ω rocking curves display

the full-width at half-maximum of 0.86° for the LSMO (002) peak and 0.83° for the SNTO (002) peak, respectively. This means that the thin films of heterostructure are single phase with *c*-axis orientation.

The structure of the multilayer heterostructure was further confirmed using the low magnification cross-sectional TEM and the cross-sectional high-resolution TEM (HRTEM). Figure 4 displays a low magnification cross-sectional TEM image of an SNTO/LSMO multilayers. Every interface is very clear and smooth. The film thickness, obtained from the TEM image, is in agreement with that calculated from the number of RHEED oscillation. The inset in Fig. 4 shows the selected area electron diffraction (SAED) pattern from the region containing SNTO layer, the LSMO layer and STO substrate. Figure 5 displays a typical cross-sectional HRTEM image of the interface between LSMO and SNTO layers in the heterostructure. The interface is very sharp and no interfacial reaction layer and deviation of crystalline orientation have been observed. The HRTEM and SAED images confirm that the multilayer heterostructure is perfectly 2D layer-by-layer growth and the epitaxial crystalline structure shows the orientations of

SNTO (001)//LSMO (001)//STO (001)

SNTO [100]//LSMO [100]//STO_3[100].

In summary, the heterostructures of multilayer LSMO and SNTO with 10000 unit-cell layers have been fabricated on STO (001) substrates by laser MBE, and the progress has been made in controlling the growth of films at an atomic level. The measurements of RHEED, XRD, AFM, TEM and SAED demonstrate that the heterostructures are nearly perfect layer-by-layer epitaxial growth, and the surface and interfaces are atomically smooth. Up to now, we can layer-by-layer epitaxial growth the perovskite oxide films and heterostructures as well as superlattices from a few unit-cell layers to 10000 unit-cell layers. It is expected that the fabrication of artificial perovskite materials would open up the possibilities in new materials explore and device developments.

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