High-speed deposition of oriented orthorhombic NaTaO₃ films using laser chemical vapor deposition

Ali M. Huerta-Flores a,1, Jianchao Chen b,1, Akihiko Ito b,c,#, Leticia M. Torres-Martínez d, Edgar Moctezuma a, Takashi Goto b

a Facultad de Ciencias Químicas, Universidad Autónoma de San Luis Potosí, San Luis Potosí 78290, Mexico
b Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
c Graduate School of Environment and Information Sciences, Yokohama National University, Yokohama 240-8501, Japan
d Universidad Autónoma de Nuevo León, Facultad de Ingeniería Civil, Departamento de Ecomateriales y Energía, Nuevo León 66455, Mexico

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ABSTRACT

We demonstrated the high-speed laser chemical vapor deposition of orthorhombic NaTaO₃ (o-NaTaO₃) films. The orientation of the o-NaTaO₃ films was changed from (101) to (112) to (001) plane as the increase of deposition temperature from 823 to 913 K. o-NaTaO₃ films had faceted surfaces and columnar cross sections. The deposition rates of o-NaTaO₃ films were 48–120 μm h⁻¹, which are 192–6000 times higher than those offered by wet-chemical routes.

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1. Introduction

NaTaO₃ is a perovskite-related photocatalytic material for water-splitting under ultraviolet light [1,2]. NaTaO₃ powders have been synthesized by solid state reaction, sol-gel, hydrothermal and solvothermal methods to study the effect of crystallinity and morphology on photocatalytic activity [1,3]. Although the role of polymorphs is still controversial, the fabrication of NaTaO₃ thin films is difficult, and the small deposition rates were also drawback. On the other hand, although physical vapor deposition (PVD) and chemical vapor deposition (CVD) have been used for conformal deposition of films at a high deposition rate, Na composition in these films is difficult to control for the vapor deposition because Na is a volatile element. Thus far, neither the PVD nor CVD have barely been synthesized using the wet chemical route. However, controlling the phases and morphologies of NaTaO₃ thin films is difficult, and the small deposition rates were also drawback. On the other hand, although physical vapor deposition (PVD) and chemical vapor deposition (CVD) have been used for conformal deposition of films at a high deposition rate, Na composition in these films is difficult to control for the vapor deposition because Na is a volatile element. Thus far, neither the PVD nor CVD have been reported for preparing NaTaO₃ films. Laser CVD has advantages as a method for preparing oxide films as it allows control of phases [12], orientations [13,14], and morphologies [15] with a significant deposition rate. It has shown excellent controllability of multicomponent oxides containing volatile elements, Ba, Li, and Na, in β-alumina films [16–18]. In this letter, we demonstrate the high-speed deposition of orthorhombic NaTaO₃ films having different orientations using laser CVD.

2. Experimental procedures

A schematic of the laser CVD apparatus has been reported elsewhere [14]. Na dipivaloylmethanate (Na(dpm); Toshima Manufacturing, Japan) and Ta pentaisopropoxide (Ta(O-i-C₃H₇)₅; Kojundo Chemical Laboratory, Japan) were evaporated at 403 K and 533 K, respectively. The flow rates of Ar and O₂ gases were 1.7 × 10⁻⁶ and 2.5 × 10⁻⁶ m³ s⁻¹, respectively. The total pressure in the chamber was kept at 0.4 kPa. Polycrystalline AlN substrate
was preheated to 823 K. The deposition temperature \( (T_{\text{dep}}) \) was changed from 823 to 1003 K by increasing the laser power from 43 to 192 W.

The phase compositions were studied using X-ray diffraction (XRD, Rigaku Ultima IV). The microstructures were observed using a scanning electron microscope (SEM, Hitachi S-3100H). The deposition rate was calculated from the film thickness and deposition time (0.6 ks).

3. Results and discussion

Fig. 1 depicts a schematic of the crystal structures of orthorhombic and cubic NaTaO\(_3\) drawn using the VESTA software [19]. At room temperature, NaTaO\(_3\) has an orthorhombic structure with rhombic orientation (space group: \( Pbnm \); ICSD No. 88375; o-NaTaO\(_3\)) with Na displacement and TaO\(_6\) tilting (Fig. 1(a)). The phase of NaTaO\(_3\) changes as temperature increases, adopting an orthorhombic structure with pseudocubic orientation (\( Cmcm \); No. 88376) at 720 K (Fig. 1(b)), followed by a tetragonal structure (\( P4/mbm \); No. 88377) at 835 K, and a cubic structure (\( Pm\bar{3}m \); No. 88378) at 809 K (Fig. 1(c)) [8]. Although a monoclinic cell (\( P2/m \); ICSD No. 28606) was once used to study the phase transition of NaTaO\(_3\) for the sake of convenience [20] instead of orthorhombic cells [21,22], latter structural analysis using neutron and synchrotron sources by Athee et al. [23], and Kennedy and Night et al. [8,24,25] support orthorhombic structures as low-temperature phases.

The films prepared at \( T_{\text{dep}} = 823 \) K were indexed as o-NaTaO\(_3\) (Fig. 2(a)). Peak splitting due to the low symmetry of o-NaTaO\(_3\) was observed at around \( 2\theta = 40^\circ \) (inset in Fig. 2(a)), 58° and 73°. As \( T_{\text{dep}} \) increases to 853 K, the peak splitting becomes a broad spectrum but the shoulders on 112 peak at \( 2\theta = 32.5^\circ \) suggested the orthorhombic symmetry. The orientation of the o-NaTaO\(_3\) films changed from the (101) to (112) orientation (Fig. 2(b)). The films prepared at \( T_{\text{dep}} = 883–973 \) K were indexed as o-NaTaO\(_3\) with (001) orientation (Fig. 2(c)). The films prepared at \( T_{\text{dep}} = 1003 \) K was a mixture of o-NaTaO\(_3\) and Na\(_2\)Ta\(_4\)O\(_{11}\).

NaTiO\(_3\) films had a columnar structure, independent of \( T_{\text{dep}} \) (Figs. 3(a), 3(b)). The deposition rates of (101)-, (112)- and (001)-oriented o-NaTaO\(_3\) films were 120, 105 and 93 \( \mu \)m h\(^{-1} \), respectively. The deposition rate decreased from 120 to 48 \( \mu \)m h\(^{-1} \) as the increase of \( T_{\text{dep}} \) from 823 to 1003 K. Pyramidal and roof-like facets were formed on the top of columns, which would be associated with (112)- and (110)-oriented o-NaTaO\(_3\) grains in (112)-oriented o-NaTaO\(_3\) film at \( T_{\text{dep}} = 853 \) K (Fig. 3(c)). Two faces would correspond to the o-NaTaO\(_3\) (100) and (010) planes, whereas the other face in pyramidal facet would correspond to the (001) plane (Fig. 3(e)). The (001)-oriented o-NaTiO\(_3\) films at \( T_{\text{dep}} = 913 \) K had a square terrace structure (Fig. 3(d)), which corresponded to the (001) plane of o-NaTiO\(_3\) (Fig. 3(f)).

Table 1 lists the preparation of NaTaO\(_3\) films in literature. NaTaO\(_3\) films were prepared via surface reactions between Na solutions and Ta substrate. NaOH reacted with Ta\(_2\)O\(_5\) layer formed on the surface of Ta foil [26–28] and NaNO\(_3\) reacted with Ta foil or TaO\(_x\) layer, which had been deposited on (100) SrTiO\(_3\) substrate by pre-sputtering [29,30]. These NaTaO\(_3\) films were composed of nanocube or granular grains. Porous NaTaO\(_3\) films were deposited...
In either process, the deposition rates for the preparation of NaTaO₃ films were ranged between 0.02 and 0.25 μm h⁻¹ due to a prolonged post annealing time. Laser CVD can prepare o-NaTaO₃ films having a columnar structure with the control of orientation at significant deposition rates (48–120 μm h⁻¹), which are 192–6000 times higher than those offered by wet-chemical routes.

4. Conclusions

The oriented o-NaTaO₃ films were prepared using laser CVD. The orientation of the o-NaTaO₃ films was changed from (101) to (112) to (001) plane as the increase of deposition temperature from 823 to 913 K. NaTaO₃ films comprised columnar grains with pyramidal and roof-like, and square terrace structures. The maximum deposition rate of the o-NaTaO₃ films were 120 μm h⁻¹.

Table 1
Comparison of the NaTaO₃ films prepared by different methods: surface reactions between Na precursor and Ta substrate, and depositions from Na and Ta precursors.

<table>
<thead>
<tr>
<th>Method</th>
<th>Substrate</th>
<th>Phase</th>
<th>Tdep (K)</th>
<th>Rdep (μm h⁻¹)</th>
<th>Orientation</th>
<th>Morphology</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface reactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrothermal Ta</td>
<td>o</td>
<td>393–453 K</td>
<td>–</td>
<td>–</td>
<td>Random</td>
<td>Nanocube to granular</td>
<td>[26]</td>
</tr>
<tr>
<td>Hydrothermal Ta</td>
<td>o</td>
<td>363–423 K</td>
<td>–</td>
<td>–</td>
<td>Random</td>
<td>Nanocube</td>
<td>[27]</td>
</tr>
<tr>
<td>Hydrothermal Ta</td>
<td>c</td>
<td>473 K</td>
<td>0.08–0.25</td>
<td>–</td>
<td>Random</td>
<td>Nanocube to granular</td>
<td>[28]</td>
</tr>
<tr>
<td>Flux</td>
<td>Ta</td>
<td>773 K</td>
<td>0.2³</td>
<td>–</td>
<td>Random</td>
<td>Nanocube</td>
<td>[29]</td>
</tr>
<tr>
<td>Flux</td>
<td>TaOₓ/ (100) SrTiO₃</td>
<td>873 K</td>
<td>–</td>
<td>–</td>
<td>(100)⁵</td>
<td>Nanocube</td>
<td>[30]</td>
</tr>
<tr>
<td>Film depositions</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Sol–gel</td>
<td>Quartz or Si</td>
<td>m</td>
<td>923–973 K</td>
<td>0.02²</td>
<td>(111)⁶</td>
<td>Honeycomb-structured porous</td>
<td>[31]</td>
</tr>
<tr>
<td>Laser CVD</td>
<td>AlN</td>
<td>o</td>
<td>823 K</td>
<td>120</td>
<td>(101)¹</td>
<td>Columnar with pyramidal and roof-like tops</td>
<td>Present study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>o</td>
<td>853 K</td>
<td>105</td>
<td>(112)²</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>o</td>
<td>913 K</td>
<td>80</td>
<td>(001)³</td>
<td>Columnar with terrace tops</td>
<td></td>
</tr>
</tbody>
</table>

* Temperatures for post annealing.
* Thickness divided by total process time including dipping, calcination and post annealing.
* Epitaxial growth.
* Templated growth.

Fig. 3. Cross-sectional (a, b) and surface (c, d) SEM images of (a, c) the (112)-oriented o-NaTaO₃ film at Tdep = 853 K, and (b, d) the (001)-oriented o-NaTiO₃ film at Tdep = 913 K. Images (e, f) display top-view schematic of the pyramidal facet and square terrace structure for the (112)- and (001)-oriented o-NaTiO₃ grains, which correspond to dashed circles in images (c, d), respectively.
Acknowledgements

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