Nb$_2$O$_5$ thin films obtained by chemical spray pyrolysis

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INTRODUCTION

Nb$_2$O$_5$ is a high band gap (3.3 eV) dielectric material (10 < ε < 100). It has a high index of refraction (2.2–2.6). In the form of thin films, it has been used as an electrochromic coating on glass due to the changing of transmission in the UV/visible/IR range from 85% to less than 20% by coating on glass due to the changing of transmission in the form of thin films, it has been used as an electrochromic material for various applications, such as in automotive windows, building glass, and displays. Electrochromic devices can change their color by applying an electric field, and have been studied extensively due to their potential use in energy-efficient windows.

The electrical properties of Nb$_2$O$_5$ change with temperature and can be altered by the introduction of dopant elements, such as Li, Na, or K. These dopants can change the conductivity of the material by several orders of magnitude, making it a promising material for applications in electrochromic devices. In this study, we present the first results of Nb$_2$O$_5$ thin films prepared by chemical spray pyrolysis using deposition substrate temperatures from 350°C to 500°C and thin-film post-annealing in air up to 900°C. Besides proofing the stoichiometry of Nb$_2$O$_5$, emphasis is made in this study on possible residuals from the precursor solution in the films by using XPS analysis combined with 4 keV Ar$^+$ ion bombardment. Furthermore, examinations of the films with respect to morphology (SEM), crystal structure (XRD) and optical transmittance are presented.

EXPERIMENTAL

Before deposition, the glass and fused silica substrates were cut to 2 cm by 2 cm pieces and subjected to conventional procedures of cleaning and degreasing. The spray solution of 50% bidistilled water, 49% ethanol and 1% acetic acid (by volume) contained 2 M NbCl$_5$ as precursor. Acetic acid has been added in order to stabilize the solution. The solution was injected into the air stream by means of a syringe pump. In the spray system, the high-pressure air stream through the nozzle is used to atomize the solution to very fine droplets which reach the heated substrate. Pyrolysis takes place there and an oxide film can grow. The spray conditions for Nb$_2$O$_5$ films are summarized in Table 1. The advantage of chemical spray pyrolysis is manifold: compact or porous films, depending on the spray conditions, can be obtained on large surfaces; doping can be easily performed by introduction of the doping element into the precursor solution; it is a cheap and environmentally friendly deposition technique since spraying is performed in ambient atmosphere using air as driving gas and, in most cases, aqueous precursor solutions.

In this work, we present the first results of Nb$_2$O$_5$ thin films prepared by chemical spray pyrolysis using deposition substrate temperatures from 350°C to 500°C and thin-film post-annealing in air up to 900°C. Besides proofing the stoichiometry of Nb$_2$O$_5$, emphasis is made in this study on possible residuals from the precursor solution in the films by using XPS analysis combined with 4 keV Ar$^+$ ion bombardment. Furthermore, examinations of the films with respect to morphology (SEM), crystal structure (XRD) and optical transmittance are presented.

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The chemical composition of the films was studied by XPS with a PHI 5700 instrument. A standard x-ray source
Table 1. Spraying conditions and average film thickness determined from transmission spectra for Nb₂O₅ films of different substrate temperatures and deposition times

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>Injection rate (ml/h)</th>
<th>Air pressure (bar)</th>
<th>Air flux (L/min)</th>
<th>Deposition time (min)</th>
<th>Spraying distance (cm)</th>
<th>Average film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>40</td>
<td>2</td>
<td>35</td>
<td>15/30</td>
<td>15/30</td>
<td>280/450</td>
</tr>
<tr>
<td>400</td>
<td>50</td>
<td>2</td>
<td>35</td>
<td>15/30</td>
<td>15/30</td>
<td>250/385</td>
</tr>
<tr>
<td>450</td>
<td>2</td>
<td>35</td>
<td>20</td>
<td></td>
<td></td>
<td>70/150</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>–/-</td>
</tr>
</tbody>
</table>

(15 kV, 300 W, Mg K α (1253.6 eV)) was used. The pressure in the chamber was about 10⁻⁷ Pa. For sputtering 4 keV Ar⁺ ions and Zalar sample rotation was used. The sputter rate is assumed to be approximately 3 nm/min as determined for Ta₂O₅ under identical sputter conditions. Binding energies (BE) of unspattered surfaces were referenced to the Nb 3d₅/₂ peak at 207.5 eV. Spectra were handled by PHI-Access V.6 and Multipak software, both from Physical Electronics (PHI, Eden Prairie, MN). The atomic concentrations were determined from C 1s, Cl 2p, O 1s and Nb 3d XPS peak areas using Shirley background subtraction and sensitivity factors provided by the spectrometer manufacturer (PHI).

RESULTS AND DISCUSSION

Figure 1(a) shows a cross-section SEM image of an Nb₂O₅ film deposited by 30 min spraying onto a glass substrate held at 350°C. As can be seen, at large scale, the film uniformly covers the substrate. At local scale, it shows a certain surface roughness, even holes, i.e. local film thickness variation. An average film thickness of roughly 500 nm can be estimated from the SEM picture of Fig. 1(a). Also we can see that the Nb₂O₅ film is of compact material. This made it possible to observe in the optical transmission spectra (not shown) interference maxima. However, those interference maxima are not well pronounced due to the varying film thickness, but permit us to estimate with the Swanepool method average film thicknesses which are given in Table 1. As can be seen, a value of 450 nm has been determined for the sample of 350°C substrate temperature and 30 min spraying, proximate to the one estimated from Fig. 1(a). Furthermore, from 4 keV Ar⁺ depth profiling in a Nb₂O₅ film of 400°C substrate temperature and 30 min spraying we could estimate a film thickness of 340 nm which is also near to the corresponding value given in Table 1. The main information from Table 1 is that the film thickness decreases drastically with increasing substrate temperature. At 500°C substrate temperature the film thickness is so small, i.e. the deposition velocity very low, that no interference effect in the transmission spectra could be observed. Figure 1(b) shows at lower magnification the top view of an Nb₂O₅ film sprayed, in that case, on fused silica held at 350°C. We can see that the holes of submicrometre size are equally distributed over the whole film surface. We found that with increasing substrate temperature the number of holes per surface unit diminishes. Practically none are found for a substrate temperature of 500°C when the film growth velocity is very low.

Figure 2 shows the XPS spectra of an Nb₂O₅ film of 350°C substrate temperature (top) and after annealing in air for 1 h at 700°C (bottom), of the original surfaces, and after 2 and 7 min of 4 keV Ar⁺ sputtering. O 1s, C 1s and Nb 3d photoelectron peaks are represented. Although the precursor was NbCl₅, no Cl has been detected by XPS. This is because NbCl₅ (10⁻² M) reacts readily with ethanol (50% of the solution) to Nb etoxide. The spectra of the unspattered sample surfaces were referenced in BE with the Nb 3d₅/₂ peak at 207.5 eV since only one doublet, i.e. one chemical state, is observed for Nb. The main contribution to the O 1s signal is then centred at 530.6 eV, both BE values characteristic for...
Figure 2. XPS spectra of an as-deposited Nb$_2$O$_5$ film of 350 °C substrate temperature (top) and after annealing in air for 1 h at 700 °C (bottom), of the original surfaces, and after 2 and 7 min of 4 keV Ar$^+$ sputtering.

The atomic concentrations (Table 2) of the unsputtered surfaces reveal an O/Nb ratio of about 2.5 in accordance with the stoichiometry of Nb$_2$O$_5$. All this shows that Nb is as Nb$^5+$, i.e. Nb$_2$O$_5$ has grown on the substrate during spraying. However, owing to the high amount of ethanol (49%) and acetic acid (1%) in the spray solution and their decomposition on the heated substrate, the O 1s and C 1s peaks also show contributions corresponding to carboxyl and hydroxyl groups. Figure 3 shows for the unsputtered surfaces of the as-deposited and annealed sample the fitting of the C 1s peak with aliphatic, hydroxyl and carboxyl bands centred at 286.0 eV, 289.0 eV and 292.0 eV respectively. Figure 3 shows clearly that film post-annealing in air at 700 °C reduces considerably the amount of the alcoholic component at the sample surface, i.e. the area of the fitting band at 286.6 eV decreases to less than half. On the other hand, the spectra of Fig. 2 after 2 and 7 min of 4 keV Ar$^+$ sputtering and the atomic concentrations given in Table 2 show that in the as-deposited sample the carbon concentration stays at about 7 at.% whereas in the 700 °C annealed sample the atomic concentration drops below 1 at.%. This shows clearly that the carbon contamination coming from the precursor solution is effectively eliminated in the film by post-annealing.

As a consequence the O/Nb ratio drops below 2.5. However, as can be seen from the O/Nb ratio in Table 2, the preferential sputtering of O seems to be somewhat lower in the 700 °C annealed sample. A reason could be that after annealing the Nb$_2$O$_5$ film has crystallized and thus presents somewhat higher chemical stability against 4 keV Ar$^+$ bombardment. All as-deposited Nb$_2$O$_5$ films were amorphous. XRD results have shown that post-annealing in air for temperatures >600 °C leads to a hexagonal Nb$_2$O$_5$ crystal structure (JCPDS 28-0317, Powder Diffraction Standard). A doublet at 28.9 in the XRD diagram (not shown) of the 700 °C annealed sample indicates that two phases of Nb$_2$O$_5$ are present in the film. The same effect has been observed for Nb$_2$O$_5$ films prepared by dip-coating and electro-deposition. Those phases are documented in the

Table 2. Atomic concentration (at.%) and ratio for an as-deposited Nb$_2$O$_5$ film (350 °C substrate temperature) and after annealing in air for 1 h at 700 °C, of the original surfaces, and after 2 and 7 min of 4 keV Ar$^+$ sputtering.

<table>
<thead>
<tr>
<th>Sample</th>
<th>4 keV Ar$^+$ (min)</th>
<th>C</th>
<th>O</th>
<th>Nb</th>
<th>O/Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>0</td>
<td>26.7</td>
<td>53.6</td>
<td>19.7</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.8</td>
<td>55.8</td>
<td>36.4</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>7.4</td>
<td>51.2</td>
<td>41.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Annealed</td>
<td>0</td>
<td>27.8</td>
<td>52.2</td>
<td>20.0</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.2</td>
<td>59.5</td>
<td>37.3</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.9</td>
<td>57.6</td>
<td>41.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

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Figure 3. Fitting to the C 1s peak of the as-deposited and 700 °C annealed Nb₂O₅ film.

literature²⁵ as so-called T or TT Nb₂O₅ phases corresponding to a pseudo-hexagonal crystal structure. In our samples, the grain size determined by the Scherrer method increased from 30 nm for 600 °C up to 100 nm for 900 °C post-annealing.

CONCLUSIONS

Nb₂O₅ has been obtained as a layered and compact material with a rough surface morphology on glass and fused silica by chemical spray pyrolysis. The carbon contamination in the films due to alcoholic and acetic components in the precursor solution could be identified and followed by XPS combined with 4 keV Ar⁺ sputtering. Post-annealing in air showed that the carbon contamination can be effectively eliminated and Nb₂O₅ stabilized in hexagonal crystal structure.

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