OPTIMIZAREA MORFOLOGIEI SUPRAFEȚEI SUBSTRATURILOR DE $NdGaO_3$ (110) PRIN TRATAMENTE TERMICE ŞI CHIMICE

IMPROVED SURFACE MORPHOLOGY OF (110) $NdGaO_3$ SUBSTRATES BY THERMAL AND CHEMICAL TREATMENTS

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The results of the influence of thermal and chemical treatments on the surface morphology of (110) $NdGaO_3$ ***substrates are described in this paper. The treated surfaces were analysed by Atomic Force Microscopy (AFM), in air, and by in-situ high pressure Reflection High Energy Electron Diffraction (RHEED). The thermal treatment of substrates resulted in a*** NdO_{1+x} ***single terminated surface, while a surface with*** GaO_{2-x} ***terminating layer and atomically flat terraces without etch pits could be obtained by chemical etching in a*** $HF + NH_4F + H_2O$ ***solution, followed by an annealing step at high temperatures (900-1000°C) in air or in oxygen flow, for surface recrystalization.***

În acest articol sunt prezentate rezultatele influenței pe care tratamentele termice şi chimice le au asupra morfologiei suprafeței substraturilor de $NdGaO_3$ ***cu orientare (110). Suprafețele astfel tratate au fost analizate prin intermediul microscopului de forță atomică (MFA), în aer, şi difracției prin reflexie de electroni cu energie înaltă (DREEI), in-situ. Un tratament termic optim al substraturilor de*** $NdGaO_3$ ***(110) a rezultat într-o suprafață cu o terminație de*** NdO_{1+x}, ***în timp ce prin tratamentul chimic cu o soluție*** $HF + NH_4F + H_2O$ ***s-a obținut o suprafață terminată în*** GaO_{2-x} ***şi cu terase cu rugozitate la nivel atomic. Tratamentul chimic a fost urmat de un tratament termic la temperaturi de 900-1000°C, în aer sau în oxygen, în scopul recristalizării suprafeței substratului.***

Keywords: *$NdGaO_3$, surface morphology, AFM, RHEED, annealing, chemical treatment*

1. Introduction

In choosing the proper substrate, certain properties of it have to be considered in relation to the deposited film, such as: an atomically smooth surface, a low lattice mismatch (< 0.3 %), a similar thermal expansion coefficient (α), and corresponding dielectric properties (ε, tan δ) [1]. The substrate surface morphology, the chemistry of terminating layer, as well as the substrate miscut angle will influence the film's growth mode. When growing films of compounds with layered structure, such as high temperature superconductors (HTSc) [2,3], the composition of the substrate terminating layer can determine the surface morphology of the film [4,5], as well as the stacking sequence, as was shown for, e.g., $YBa_2Cu_3O_{7-\delta}$ grown by pulsed laser ablation on $SrTiO_3$ [6]. Therefore, substrates with a single terminated surface is required for reproducible thin film growth with respect to morphology and epitaxy [2-8].

One of the substrates most used as template for epitaxial growth of thin films with layered structure is (110) $NdGaO_3$. It has a perovskit type (ABO_3) crystal structure with displaced oxygen ions (a pseudocubic cell that is slightly distorted in comparison with the primitive perovskite structure) [9]; therefore, the crystal structure of the (110) $NdGaO_3$ is rather orthorhombic than cubic. Among the lanthanide gallates, it is the only oxide with no structural phase transitions below ~ 900 °C, being used to grown twin free thin films of HTSc [10], infinite layer phases [11], or other compounds (e.g., GaN, Sr_2RuO_4) [12,13]. Also, low rf loss of $NdGaO_3$ makes this substrate more suitable for microwave applications than, e.g., $SrTiO_3$.

Regarding the surface treatments, Ohnishi *et al.* [14] have shown that an A-site (i.e., $NdO_{1+\delta}$) single terminated (001) $NdGaO_3$ surface can be obtained after 2h annealing in air at high temperature (1000 °C), as demonstrated by coaxial impact-collision ion scattering spectroscopy (CAICISS) measurements. However, there are no reports of studies on the effect of chemical etching on the surface morphology of $NdGaO_3$ substrates. Different solutions (e.g., HCl, HNO_3) have been used in order to remove the surface contaminants, but no details on the influence of this process on the surface properties were given [15].

The morphology of the as-received (commercial) substrates is determined by the polishing method, their surface being characterized by a mixed termination (i.e., AO and BO_2 for a perovskite oxide). In this paper, chemical and thermal treatment methods, used to improve the surface morphology and, also, to control the chemistry of the terminating layer, are presented for the (110) $NdGaO_3$ single crystal substrates.

2. Experimental methods

2.1 Thermal procedures

Single crystal wafers with dimensions of

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$10\times10\times1\ mm^3$ were used for annealing and chemical etching experiments after an initial cleaning step (20 min in acetone and then other 20 min in ethanol, in an ultrasonic bath) done in order to remove any organic contaminants from the surface. The annealing experiments of the as-received or chemically etched substrates have been performed in a tube-oven, using flowing oxygen (at a rate of 50 to 400 sccm) or in air. The substrates were placed on an Al_2O_3 boat inside the quartz tube of the oven. For re-growth or recrystallization of the step ledges the annealing was done at high temperatures (900-1000 ºC). The temperature was ramped to the desired value with a rate of 10 °C/min. The annealing temperature and time was selected based on the substrates vicinal angle (the lower this angle value, the higher the temperature and longer the time).

2.2 Chemical etching procedure

$NdGaO_3$ has a layered structure consisting of alternating stacks of NdO_{1+x} and GaO_{2-x} atomic layers, with NdO_{1+x} a basic oxide and GaO_{2-x} an acidic oxide [16]. Chemical etching considers the layered structure of the substrate material and the difference in chemical reactivity of the constituent oxides. The etching procedure is based on the method developed for $SrTiO_3$ [17-19]. By this method, one of the surface oxides (i.e., the one with base character, e.g., NdO_{2-x} in case of $NdGaO_3$) is selectively removed by means of a chemical reaction. In finding the right etching conditions (i.e., the etching time and the pH of the etchant), one has to consider several parameters, such as: the characteristic surface properties of the substrate (e.g., the type of constituent oxides, the vicinal angle); the correlation between etching speed and the orientation of the miscut angle vs. in-plane crystallographic axes, the etching being more aggressive with increasing this angle [19], and, off course, the reactivity (pH) of the etching solution.

The commercial available BHF solution (12.5 vol% HF + 87.5 vol% NH_4F; pH=4.5) used for $SrTiO_3$ etching [17-19] was too strong for the purpose of this work. Therefore, an etchant with a lower reactivity was prepared for removing $NdO_{1+\delta}$ from (110) $NdGaO_3$ surface. The etching solution consisted of commercial BHF + NH_4OH (37 vol%) + deionized water (Q_2, [20]), the resulted solution having a pH = 5.0-5.5. The deionised water (pH = 6-7, R = 10-15 MΩ) used for the etching experiments was produced with a Millipore Elix equipment. By this procedure, the reactivity of this modified-BHF (m-BHF) solution was suitable for reproducible preparing atomically smooth (110) $NdGaO_3$ substrates surface without etch pits.

The general etching procedure consisted of several steps [17-19]. The substrates were first soaked in Q_2 water for up to 0.5 h (depending on the substrate miscut angle, the lower this angle value, the longer the soaking time used). Taking into account the differences in chemical properties of the $NdGaO_3$ substrate constituent oxides, the aim of this step is the selective transformation of the surface NdO_{1+x} in a hydroxide complex, $[Nd(OH)_3\cdot xH_2O]$, that is then removed from the surface by immersion of the substrate in the m-BHF etchant for 30 to 120 s. The etching time is selected so that the lower the substrate vicinal angle value, the longer the etching time. The entire procedure takes place in an ultrasonic bath, at room temperature. The substrates are then rinsed for few seconds with deionized water and ethanol, and then dried with nitrogen flow. The etched samples are finally annealed at 950-1000 ºC for 0.5-4 h in air or oxygen flow (50-200 sccm) to facilitate surface recrystallisation. The m-BHF solution selectively removes the surface NdO_{1+x} to form an atomically smooth surface terminated by the GaO_{2-x} plane. The atomic smoothness of the substrate surface was confirmed by AFM and RHEED data.

2.3. Morphological characterization

The surface morphology after the chemical or thermal treatments was analysed by means of *ex-situ* AFM (Digital Instruments NanoScope E), in contact mode, and *in-situ* high-pressure RHEED (Staib Instruments RHEED system operable at pressures up to 0.50 mbar, with a KSA 400 Imaging and Analysis software for real time data acquisition). The RHEED patterns presented in this paper were recorded at 5×10^{-2} mbar O_2 and a substrate temperature of 550 °C.

3. Experimental results

3.1 Thermal treatment

In Figure 1 an AFM topographic image and the corresponding RHEED pattern of the surface of an as-received (110) $NdGaO_3$ substrate after cleaning in acetone and ethanol is shown. While the surface of such as-received substrates can be considered atomically flat, step ledges of the terraces are rough and sometimes hardly visible. The formation of streaks on the RHEED pattern for this surface indicates roughening due to the presence of surface defects. Next, the evolution of surface morphology was studied after *ex-situ* annealing in air or in O_2 flow. A topographic AFM image of the surface morphology for a (110) $NdGaO_3$ wafer annealed for 0.5 h at 1000 °C in air is shown in Figure 2. An atomically flat surface with terraces of one unit cell height was obtained after this thermal treatment. The surface quality is further confirmed by the RHEED analysis (Fig. 2), showing a 2D pattern and Kikuchi lines characteristics of a highly ordered surface. The result of annealing in an O_2 flow (100 sccm) for 0.5h at 1000 °C is shown in Figure 3. As for the thermal treatment in air, the AFM and the RHEED data showed the formation of an atomically flat

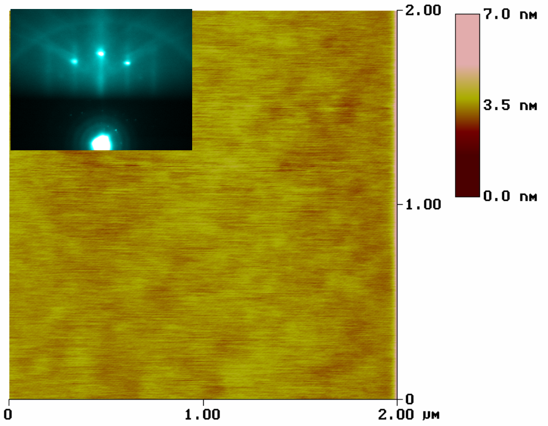


Fig 1 - As-received (110) NdGaO$_3$ substrate: AFM image and the corresponding RHEED pattern / *Morfologia suprafeței unui substrat de NdGaO$_3$ (110), netratat chimic sau termic: imagini de la MFA şi DREEI.*

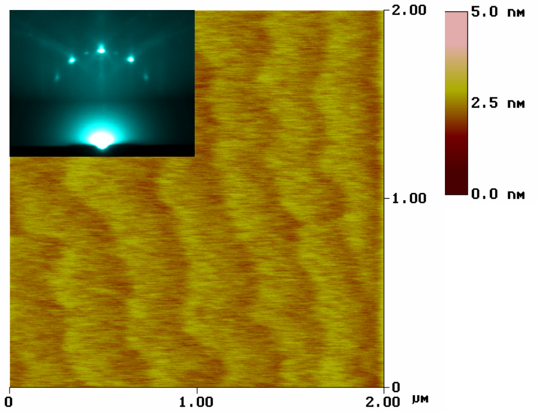


Fig. 2 - (110) NdGaO$_3$ substrate annealed 0.5 h at 1000 °C, in air: AFM image and the corresponding RHEED pattern. A terraced structure with steps of one unit cell can be seen / *Morfologia suprafeței unui substrat de NdGaO$_3$ (110) tratat termic în aer la 1000 °C, timp de 0,5 ore: imagini de la MFA şi DREEI. Imaginea de la MFA indică o suprafață formată din terase, cu înălțimea terasei egală cu cea a unei celule atomice (0,386 nm).*

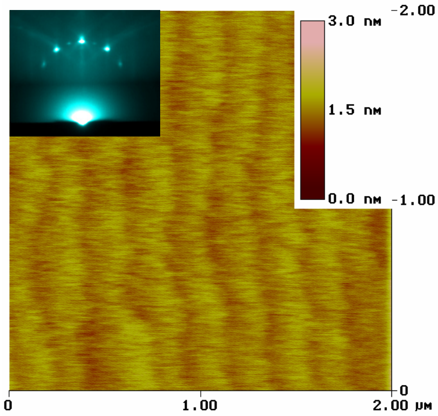


Fig. 3 - (110) NdGaO$_3$ substrate annealed 0.5 h at 1000 °C, in O$_2$ flow (100 sccm): AFM image and the corresponding RHEED pattern showing the formation of a surface with a terraced structure with steps of one unit cell / *Morfologia suprafeței unui substrat de NdGaO$_3$ (110) tratat termic în O$_2$ (100 sccm) la 1000 °C, timp de 0,5 ore: imagini de la MFA şi DREEI. Imaginea de la MFA indică o suprafață formată din terase, cu înălțimea terasei egală cu cea a unei celule atomice.*

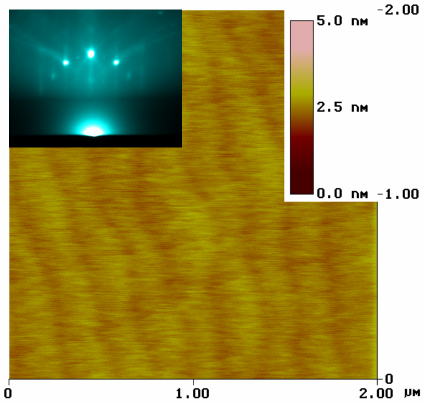
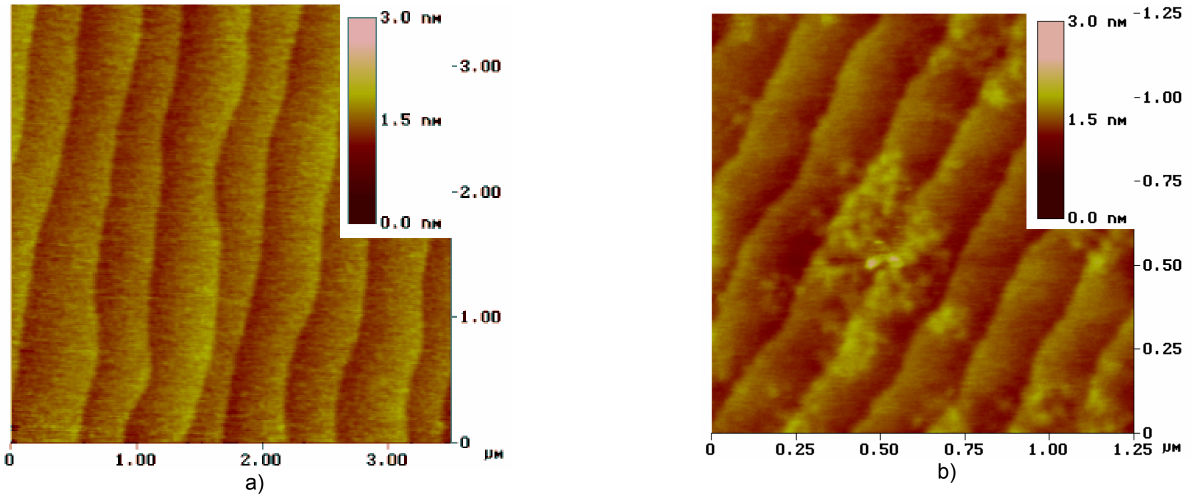


Fig. 4 - (110) NdGaO$_3$ substrate chemically etched for 1 min in m-BHF solution and subsequently annealed for 2 h at 1000 °C in an O$_2$ flow (100 sccm): AFM image and the corresponding RHEED pattern / *Morfologia suprafeței unui substrat de NdGaO$_3$ (110) tratat chimic timp de 1 minut într-o soluție de m-BHF şi apoi termic în O$_2$ (100 sccm) la 1000 °C, timp de 2 ore: imagini de la MFA şi DREEI.*



a)

b)

Fig. 5 - Evolution of the surface morphology after exposure to air for 1 month: topographic AFM images of (110) NdGaO$_3$ substrate a) chemically etched for 1 min in m-BHF solution and then annealed for 30 min at 1000 °C in O$_2$ flow (100 sccm), and b) annealed for 30 min at 1000 °C in O$_2$ flow (100 sccm) / *Evoluția morfologiei suprafeței pentru substraturi de NdGaO$_3$ (110) expuse la umiditatea din aer timp de o lună: imagini de la MFA pentru a) un substrat tratat chimic timp de 1 minut în soluție de m-BHF şi apoi termic în O$_2$ (100 sccm) la 1000 °C, timp de 0,5 ore şi b) un substrat tratat termic în O$_2$ (100 sccm) la 1000 °C, timp de 0,5 ore (fără tratament chimic).*

surface with one-step height terrace structure, surface quality confirmed by the 2D RHEED pattern. The annealed (110) $NdGaO_3$ surfaces are expected to have an NdO_{1-x} termination, as was shown by Ohnishi et al. [14] for the (001) $NdGaO_3$ substrates.

3.2 Chemical etching

Chemical etching was applied with the aim of reproducibly obtaining single terminated (110) $NdGaO_3$ substrates, with $GaO_{2-\delta}$ as surface termination. The result of such surface treatment is shown in Figure 4. Following the procedure described above, the substrate was first soaked in deionised water for 20 min, then etched in the m-BHF solution for 2 minutes, manually rinsed with Q_2 water for 20 seconds, then dried in ethanol and with a nitrogen stream. To facilitate surface recrystalization the sample was annealed in an O_2 flow (100 sccm) at 1000 ºC. A surface morphology characterised by a terraced structure with one-unit cell steps has resulted after this procedure, as shown in Figure 4. The RHEED pattern of the etched and subsequently annealed wafer shows sharp narrow 2D spots and Kikuchi lines characteristic of a surface with high crystallinity.

3.3 Determination of the termination layer

Since $NdO_{1+\delta}$ and $GaO_{2-\delta}$ surfaces have specific chemically properties [16], the composition of the topmost layer for the etched and subsequent annealed or just annealed (110) $NdGaO_3$ substrates are expected to be different. For elucidating the composition of the terminating atomic layer, two (110) $NdGaO_3$ samples, one chemically etched and annealed and the other one just thermally treated, were stored in air for 1 month. As showed by the AFM observations (Fig. 5), the etched surface (Fig. 5a) was not affected by the contact with moisture from the air. In contrast, the surface of the annealed substrate degraded in time (Fig. 5b), due to hygroscopic properties and reactivity with CO_2 from air of $NdO_{1+\delta}$ [16]. From the difference of stability in air of the $NdO_{1+\delta}$ and $GaO_{2-\delta}$ surfaces (i.e., $GaO_{2-\delta}$ is stable, while $NdO_{1+\delta}$ is not) [16], it can be concluded that the annealed (110) $NdGaO_3$ is terminated in $NdO_{1+\delta}$, while the chemically etched surface has a predominantly $GaO_{2-\delta}$ termination.

4. Discussion and conclusions

When growing films of compounds with layered structures, the exact stacking sequence is governed by the substrate-film interface; therefore, the substrate termination layer is expected to have a large influence on the final structural and morphological properties of the film. Ex-situ thermal and chemical etching methods were developed to prepare single terminated (110) $NdGaO_3$ single crystal substrates, with control of the composition of the top layer. For the thermal procedure, the annealing temperature was selected so that sufficient atomic mobility will enable the formation of a well-defined surface, with terraced structure; their formation is dependent on annealing temperature and time. The steps form as a result of lowering of the total free energy of the system [20]. For the (110) $NdGaO_3$ substrates used for this study, characterized by a miscut angle of ~ 0.1-0.3°, annealing in air or in oxygen flow for 0.5 h at 950 °C resulted in a single terminated surface. The topmost layer after thermal treatment is considered to be $NdO_{1+\delta}$ [14, 19]. By considering the layered structure, selective removal of surface $NdO_{1+\delta}$ was achieved through chemical etching with a modified commercial BHF solution, followed by annealing, resulting in a $GaO_{2-\delta}$-terminated $NdGaO_3$ surface, free of etch pits. The resulted surface morphology was studied *ex-situ* by AFM and *in-situ* by high-pressure RHEED. They showed that by these procedures atomically flat, well crystallized surfaces, with terraces one unit cell height can be obtained. The superstructure periodicity is absent for the surfaces chemically and/or thermally treated (in air or in O_2 flow).

In conclusion, chemical and thermal treatments on (110) $NdGaO_3$ substrates were used in order to obtain surfaces with different chemistry for the topmost layer, i.e., annealing results in a predominantly $NdO_{1+\delta}$ surface, while chemical etching gives a predominantly $GaO_{2-\delta}$ surface, respectively.

Aknowledgements: This work was supported by the Romanian Ministry of Education and Research, project number 1476/2006 (Human Resources project), and by CNCSIS–UEFISCSU, project number PNII – IDEI ID_743/2007. V. L. acknowledges the group of Physikalisches Institut, Experimentalphysik II, Universität Tübingen (Germany) for providing him access to characterization facilities, including for RHEED studies.

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