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Wet etching methods for perovskite substrates

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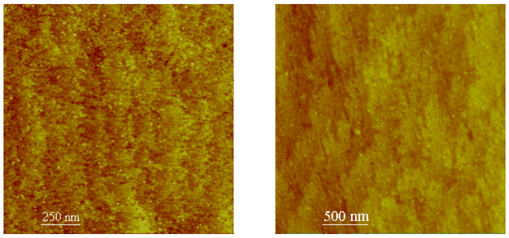
ABSTRACT

In oxide electronics substrates with atomically flat terraces are a request for growing high-quality epitaxial thin films. In this paper results on chemical etching of some substrates with perovskite, ABO_3, structure (e.g., $SrTiO_3$, LSAT - the $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$ solid solution, and $NdGaO_3$) are presented. In order to obtain high quality substrates, different etchants (NH_4F + HF, HCl + NH_4Cl, and HCl + HNO_3) with various pH values have been studied. From Atomic Force Microscopy (AFM), in air, we conclude that, irrespective of the etchant that has been used, a substrate surface with a BO_x terminated layer and atomically flat terraces without etch pits could be obtained. The pH-value and temperature of the etchant and the etching time, however, influence significantly the surface quality. Reflection high energy electron diffraction (RHEED) patterns confirmed the AFM results.

INTRODUCTION

Substrates with atomically flat surface are a request for growing high-quality epitaxial thin films of different oxide materials in a reproducible manner and with the intended properties. In choosing the proper substrate certain properties should be taking into account in relation with the film: a high surface quality, a low lattice mismatch (< 0.3 %), a similar thermal expansion coefficient (α), corresponding dielectric properties (ε, tan δ); also, interface stability, mechanical strength and, preferably, no phase transition and no twinning within the film deposition and working temperature range [1-3].
Furthermore, the terminating layer of a perovskite (001) ABO_3 crystal (i.e., for $SrTiO_3$ (001) this is TiO_2 or SrO) influences many characteristics of the surface. The morphology during a thermal treatment of the surface, epitaxial growth, microstructure (i.e., reconstructions, defects), the electronic structure and chemical properties are all determined by the composition of the surface, i.e., whether it is a BO_2, AO, or a mixed surface. A single terminated surface will turn out to be optimal with respect to mainly morphology and epitaxy. It is demonstrated that one can take advantage of the difference in properties of the elements in the different layers, e.g., solubility in acids, in order to achieve a nearly perfect and single terminated surface.
Of all perovskite materials, the $SrTiO_3$ (001) surface is studied in most detail, initially because of its photo-catalytic properties and, subsequently, as a substrate for thin films of other perovskite materials, like the high temperature superconductor.
Here, we present different wet etching procedures to obtain single terminated substrates with perovskite structure ($SrTiO_3$ (001), LSAT (001), and $NdGaO_3$ (100) and (001) – the perovskite structure with displaced oxygen ions was considered for $NdGaO_3$). AFM (contact and tapping mode) was the main technique used to characterize the surface morphology of the substrates after each step of the etching procedure. Further information was obtained from RHEED pattern.



a) b)

Figure 1. *AFM micrographs of a) $NdGaO_3$ (001) and b) $SrTiO_3$ (001) as - received substrates after a cleaning step by heating at 650^{o}C, for 30 min in O_2 flow.*

EXPERIMENTAL DETAILS

The as – received substrates

The crystal structure and the morphology of the commercially available (as received) substrates depend on the polishing method. The substrate surface exhibits fairly flat feature with random corrugations of up to 2 u.c. height and it is randomly terminated by either AO and BO_x planes; it consists of terraces, with disordered step ledges and islands on terraces with typical height differences of half and single unit-cell steps (Figures 1). Polishing and etching, however, usually lead to several kinds of defects on the surface and, therefore, to not-well-defined surfaces on an atomic scale (in the following these substrates will be called 'as-received'). Although unit-cell steps can be identified with AFM on as-received substrates after proper cleaning, the step ledges are very rough and further treatment is necessary to improve the surface quality.
Also, the surface presents impurities such as C and organic compounds with a negative influence on the substrate - film interface and, therefore, on the deposited film properties.

Annealing

Further treatments are needed in order to achieve a surface morphology with the desired quality. One possible way is the annealing, which can be achieved, generally, in air or oxygen. Annealing leads indeed to an atomically clean (the surface contaminants are easily removed) and stoichiometric surface (depending on the used atmosphere). The resulted surface (Figures 2) is a clear improvement in quality and crystallinity, but still consists of a mixture of A and B - site termination (as shown by the AFM and LFM micrographs in Figures 2 c and d). As mentioned above, these features are drawbacks for growing high - quality epitaxial thin films. Furthermore, thermal treatments at high temperatures may induce segregation at the surface, as well as oxygen deficiency and, therefore, nonstoichiometry at the surface.

Chemical etching

Much effort has been put in thermal treatments in different kinds of ambient, in attempts to obtain a single terminated surface. While the crystallinity is greatly improved, as can be judged from surface diffraction and scanning probe studies, these results still pointed to a mixed termination and it remains a question whether single termination can be achieved. Kawasaki *et al.* [4] suggested a chemical route to achieve single termination. Their combination of a chemical and thermal treatment leads to perfectly crystalline, TiO_2 terminated $SrTiO_3$ surfaces.

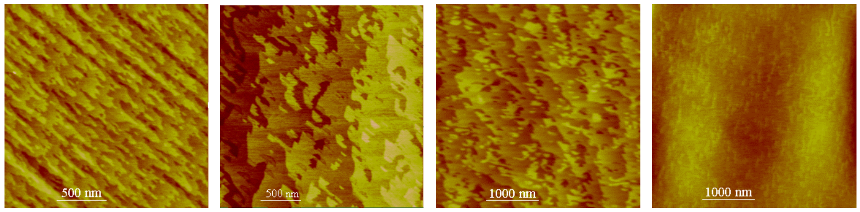


Figure 2. *AFM micrographs of a) LSAT (001) substrate, annealed at 1000^{o}C, 3h, in O_2; b) $NdGaO_3$ (001) substrate, annealed at 1000^{o}C, 1h, in air; d) $NdGaO_3$ (001) substrate, annealed at 950^{o}C, 1h, in O_2; c) LFM micrograph of $NdGaO_3$ (001) substrate, simultaneously recorded with (c).*

Based on their results we studied this treatment in detail and in contrast to their results we always observed etch pits [6], to our opinion due to a too low pH (~4,5) value of the solution, resulting in strong etching of the surface. Obviously, the formation of etch pits negatively affects the thin film growth.

In order to produce B - site single terminated perovskite substrates without etch pits, here chemical etching with different etchants has been used: the etchants HF - NH_4F (HF buffered solution, BHF), HCl + NH_4Cl, and HCl + HNO_3 (HCl : HNO_3 = 3 : 1 vol. ratio)

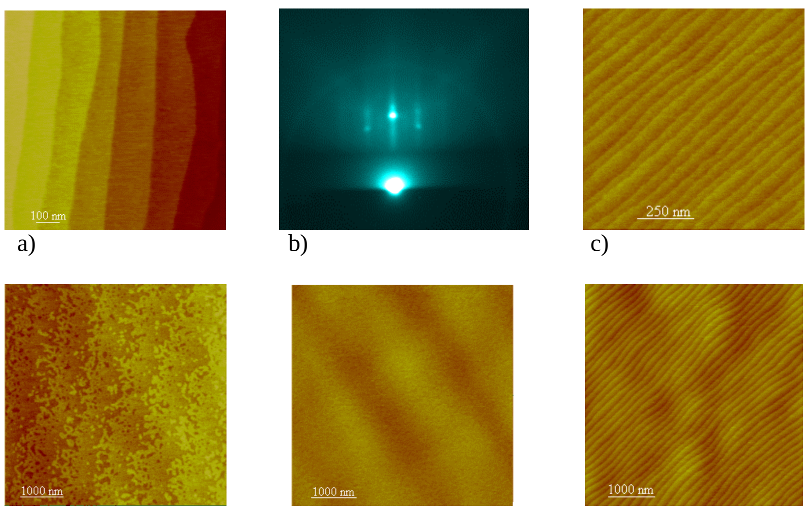
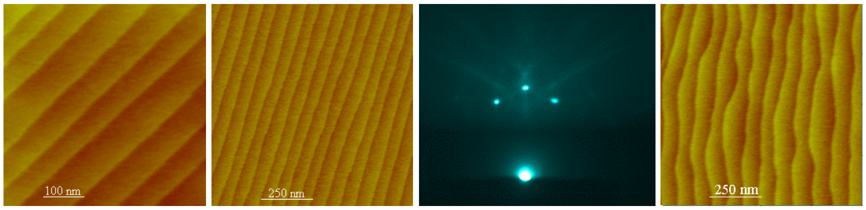


Figure 3. *AFM micrographs of etched substrates: a) $NdGaO_3$ (100) etched with BHF, annealed at 1000^{o}C, 2h, in air, b) RHEED pattern of the same substrate; c) $NdGaO_3$ (001) etched with HCl + NH_4Cl, annealed at 950^{o}C, 1h, in O_2; d) LSAT (001) etched with HCl + HNO_3, annealed at 1000^{o}C, 3h, in O_2; d) LFM micrograph simultaneously recorded with (c); d) $SrTiO_3$ (001) etched with BHF, annealed at 1000^{o}C, 1h, in O_2.*



a) b) c) d)

Figure 4. *AFM micrographs of etched substrates: a) $SrTiO_3$ (001) etched with HCl + HNO_3, annealed at 1000^oC, 1h, in O_2; b) $SrTiO_3$ (001) etched with HCl + NH_4OH at 70^oC, annealed at1000^oC, 1h, in O_2; c) RHEED pattern of substrate (c); d) $SrTiO_3$ (001) etched with BHF, annealed at 1000^oC, 1h, in O_2 .*

solutions with various pH values have been studied. The etching procedure is based on the methods developed for $SrTiO_3$ [5] and consists of an ultrasonic soak in demineralized water for up to 30 min, with B - hydroxide formation (B = Sr, La, Nd), followed by immersion in etchant for different periods of time (30 s to 10 min). The substrate is then rinsed with pure water, and finally dried in a nitrogen stream. The entire procedure takes place in an ultrasound bath, at temperatures between 20 and 70^oC (higher temperature for $SrTiO_3$ substrates). The etched samples are annealed at 950 – 1000^oC, for 1 - 3 h, in oxygen or air, in order to facilitate recrystallization.

The etching speed and conditions (type of etchant, temperature, pH) depend on the local atomic - scale configuration of the substrates surface (see Figures 3 and 4). The actual shape of the step edges depends not only on the pH of the etchant and on the etching time but also on the substrate miscut angle and direction. Due to different surface energy, chemical treatment of $SrTiO_3$ and $NdGaO_3$ substrates with high miscut angle can give better results if less reactive etchants (such as HCl + NH_4Cl and HCl + NHO_3 solutions) are used instead of BHF solution (see Figures 3c and 4 a, b, d). RHEED pattern of the proper etched and annealed samples shown sharp narrow spots corresponding to a surface with high crystallinity (see Figures 3b and 4c).

CONCLUSIONS

Irrespective of the etchant that has been used, a substrate surface with a BO_x terminated layer and atomically flat terraces without etch pits could be obtained after proper etching and annealing. The pH - value of the etchant and the etching time, however, influence significantly the surface quality. The shape of the step edges depends, also, on the substrate miscut angle and direction.

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