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Nucleation and Stoichiometry Dependence of rutile-TiO_2(001)/GaN(0001) Thin Films Grown by Plasma-Assisted Molecular Beam Epitaxy

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ABSTRACT

In this work we explore both the initial nucleation and the stoichiometry of rutile-TiO_2(001) grown on wurtzite GaN(0001) by radio-frequency O_2-plasma molecular beam epitaxy. Two studies are performed; in the first, the dependence of the growth on stoichiometry (*Ti-rich* and *O-rich)* is observed using reflection high energy electron diffraction and high resolution transmission electron microscopy. In the second study we examine the effect of different initial nucleation surfaces (i.e. *Ga-terminated* and *excess Ga-terminated*) and compare the interfaces and bulk crystallinity of the TiO_2(001) films grown on top of these surfaces. High-resolution transmission electron microscopy and x-ray diffraction measurements show a better interface for TiO_2(001)/*Ga-terminated* - GaN(0001) as compared to the TiO_2(001)/*excess Ga-terminated* - GaN(0001).

INTRODUCTION

Considerable interest has been shown of late in transition-metal oxides. One case is the titanium dioxide system, which can have applications as a high-k dielectric gate insulator for Si-based devices[1]. In this work we explore the growth of rutile-TiO_2(001) on wurtzite GaN(0001) by oxygen plasma-assisted molecular beam epitaxy. We study the dependence of the growth on both the stoichiometry of the TiO_2(001) film. From reflection high-energy electron diffraction (RHEED) we find 2-dimensional growth for the Ti-rich growth conditions and 3-dimensional for O-rich. We also examine the influence of the GaN termination on the growth, using GaN films that are terminated with a Ga-bilayer or that have additional Ga on the surface (*Ga-terminated* and *excess Ga-terminated,* respectively). For the latter case we find in x-ray diffraction (XRD) measurements the presence of additional peaks at $2\theta = 52.95836° \pm 0.00693$, which implies the existence of additional phases besides the rutile TiO_2(001). In addition, high-resolution transmission electron microscopy (HRTEM) performed on these samples show a higher degree of disorder for the films grown on top of *excess Ga-terminated*, as compared to the samples grown on top of the *Ga-terminated* surface.

EXPERIMENT

The growth experiments are performed in a hybrid oxide-nitride MBE system utilizing gallium effusion cell as a Ga source, and mini-Ti ball titanium sublimation pump as a titanium source. The O_2 and N_2 gases were delivered through a custom designed hybrid rf-plasma source; the O_2 and N_2 flow rates were in the range of 1.80 – 3.17, and 1.83 sccm, respectively. Throughout the entire growth, the rf-plasma power for both gases (O_2 and N_2) was maintained constant at 400 W. The substrates were commercially available wurtzite Ga-polar GaN(0001) grown by hydride vapor phase epitaxy (HVPE). After the substrates are ultrasonically cleaned with acetone and isopropanol, they are loaded into the MBE chamber and deoxidized by heating and nitridation at a temperature of 900 °C for 30 minutes, while keeping the N_2 flow rate to 1.83 sccm and rf-plasma power of 400 W. For both studies, the growth begins with a 45 nm thick

GaN buffer layer which is grown under a *Ga-rich* regime at a substrate temperature of T_S = 650 °C. For the first stoichiometric study, the surface prior to the deposition of TiO_2 is prepared as a *Ga-terminated* surface – annealing the films at a T_S = 750 °C for 10 minutes, followed by a Ga deposition for 90 seconds (which produced a RHEED pattern with pseudo-1x1 streaks, known to corresponds to ~ 2 Ga monolayers on the surface[3]). For the second study, we prepared two sets of samples with distinct initial nucleation surfaces: i) *Ga-terminated* (the procedure was described above), ii) *excess Ga-terminated*. The *excess Ga-terminated* surface was obtained by simultaneously closing the Ga shutter and shutting off the N_2 radio-frequency plasma. This process generally results in extra Ga atoms on the surface over and above the terminate 2 monolayers (since our growth of the GaN film is performed in the Ga-rich regime for which >2 monolayers of Ga are present on the surface, and this excess Ga persists even when the GaN growth is stopped). For both studies, the rutile-TiO_2(001) thin films were grown at T_s ~ 600 ^oC, and with a thickness of ~ 40 - 50 nm. The growth is monitored *in-situ* by RHEED using a 20 keV electron-beam, and the films are studied *ex-situ* by XRD with Cu Kα X-rays, HRTEM and selected area electron diffraction (SAED).

RESULTS & DISCUSSION

Figure 1(a) and (b) show RHEED patterns of the *Titanium-rich* and *Oxygen-rich* regimes of growth of the TiO_2(001), taken along ‹11$\underline{2}$0› the orientation of the GaN(0001) substrate. The respective growth regime is obtained in a given growth run simply by varying the ratio of the Ti flux (current to Ti-ball) to oxygen pressure (for fixed plasma power). We find a streaky RHEED pattern in the *Titanium-rich* regime, indicative of smooth (2-dimensional) growth, whereas the pattern is spotty for the *Oxygen-rich* regime, indicative of rough (3-dimensional) growth.

For growth runs that performed in the Ti-rich regime, starting with a streaky RHEED pattern, we generally find that the pattern coverts to a spotty one after some time. The amount of time that the streaky pattern is maintained depends on the Ti flux, with longer times for a higher flux (i.e. for fixed oxygen pressure). We interpret this phenomenon as reflecting a drop in the actual Ti flux with time, since just after the Ti shutter is opened the Ti-ball will have a higher temperature compared to that achieved in steady-state some minutes later. Figure 1(c) shows a HRTEM image of one such TiO_2(001) film grown on top of GaN(0001), where we see the *Titanium-rich*, and *Oxygen-rich* regimes of growth separated by a *Transition* regime. For this sample, once the Ti shutter was opened the RHEED pattern appeared as in Fig. 1(a) and it stayed for ~ 10 minutes (2 nm-thickness worth of TiO_2(001) growth layer), after which a transition period of ~ 9 minutes followed [marked *Transition* in Fig. 1(c)]. During this transition period, another pair of streaks, as positions indicated by the white arrows in Fig. 1(b), started to appear. After another 5 – 10 minutes of TiO_2(001) growth the RHEED pattern transformed into a very spotty RHEED pattern as in Fig. 1(b). (We should also mention that the O_2 rf-plasma MBE source does not have a shutter, therefore the oxygen plasma was turned on 3-4 minutes before the sample was exposed to both O_2 and Ti fluxes; this simultaneous exposure was achieved by blocking the sample from the direct line-of-sight of the O_2 plasma using a 180° rotation of the sample manipulator.) As can be seen in Fig. 1(c), the Ti atoms outnumbered O atoms for about 12 minutes of growth, after which the O takes over and creates the *Oxygen-rich* regime of growth. To our knowledge, this is the first *Oxygen-rich* MBE regime growth for rutile-TiO_2(001) reported in the literature.

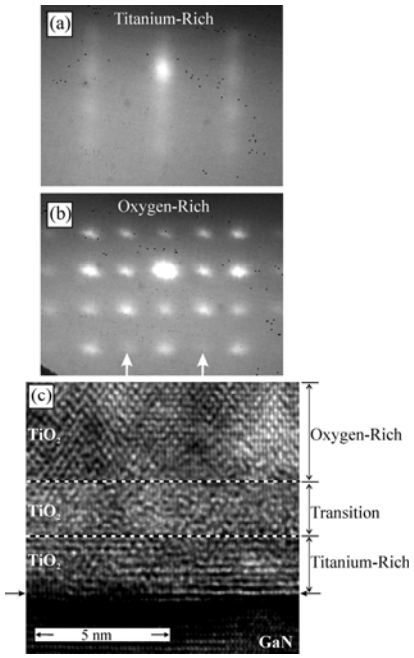

Figure 1. (a) Typical RHEED pattern of *Titanium-rich* regime, (b) typical RHEED pattern of *Oxygen-rich* regime (the white arrows indicate the appearance of extra diffraction spots as the growth becomes *Oxygen-rich*), and (c). HRTEM of TiO_2(001)/GaN(0001) showing three different regimes of growth: *Titanium-rich*, *transitional*, and *Oxygen rich*,

Data for our nucleation study of the dependence of the TiO_2(001) growth on the starting GaN(0001) surface structure is shown in Figs. 2 – 5. Figure 2 shows the RHEED patterns recorded during the growth of *Ga-terminated* and *excess Ga-terminated* films, recorded along the ‹11$\underline{2}$0› GaN(0001) crystal orientation. Figures 2(a) and (d) show the RHEED patterns of HVPE-grown GaN(0001) substrate after introduction into the MBE system followed by 30 minutes of heating at T_S = 900 °C and a nitridation step [N_2 flow rate set at 1.83 sccm, and rf-plasma power set at 400 W]. Figures 2(b) and (e) show the RHEED patterns after 30 min of GaN growth (~ 50 nm thickness) and preparation of the nucleation surface on that buffer layer as described in the Experiment section. Both of the *Ga-terminated* and *excess Ga-terminated* surfaces show very similar RHEED patterns as seen in Figs. 2(b) and (e). Qualitatively, the fact that the RHEED patterns look dim and streaky is indicative of a very smooth surface (as directly revealed in scanning tunneling microscopy studies of films prepared in the same MBE system under very similar conditions[4]). Figures 2(c) and (f) show the RHEED patterns after ~ 50 nm TiO_2(001) thin films growth on the *Ga-terminated* and *excess Ga-terminated* surfaces, respectively. Both types of films exhibit *Oxygen-rich* growth conditions. Since the TiO_2(001) layers are grown under the same conditions, the RHEED patterns for both *Ga-terminated* and *excess Ga-terminated* surfaces look undistinguishable as seen in Figs. 2(c) and (f).

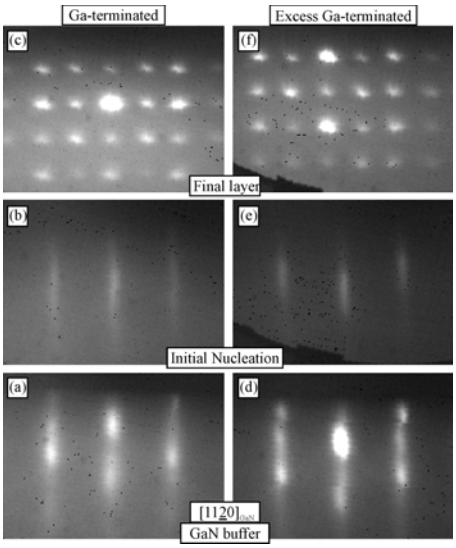

Figure 2. RHEED patterns during substrate preparation and TiO_2(001) growth on *Ga-terminated* (left hand side) and *excess Ga-terminated* (right hand side) GaN. Panels (a) and (d) shows the patterns after cleaning of the HVPE-grown substrate, (b) and (e) show the patterns after growth of the GaN and preparation of the surface, and (c) and (f) show the patterns after the final growth of the TiO_2(001) layer. All images were acquired along the [11$\underline{2}$0] direction of the GaN substrate.

Although the RHEED results for the two nucleation conditions are practically indistinguishable, we find greater difference between the TiO_2(001) films in XRD. Shown in Figure 3 are typical XRD spectra over the range $0° < 2\theta < 100°$ for both types of films. The pure rutile phase of TiO_2(001) films is indicated in both films by the presence of 200 and 400 reflections which have $2\theta = 39.34052° \pm 0.00224$ and $84.62234° \pm 0.00432$ (*Ga-terminated*), and $2\theta = 39.41434° \pm 0.00381$ and $84.72686° \pm 0.00716$ (*excess Ga-terminated*) respectively. All other Al_2O_3 [0006 & 000$\underline{1}\underline{2}$] and GaN [0002 & 0004] expected reflections are also seen in the spectra. The measured FWHM of the 200 TiO_2(001) peaks in 2θ (*Ga*-terminated) is $0.26522° \pm 0.00884$, and $0.21368° \pm 0.01399$ (excess Ga-terminated), which are slightly better than the previously reported value of 0.31° by Hansen (*et al.*)[2]. Assuming an average value of $\lambda = 0.1542$ nm for the incident x-ray wavelength, we determined a lattice constant for *Ga-terminated* films of $a = 0.4581 \pm 0.00002$ nm, and $a = 0.45728 \pm 0.00005$ for *excess Ga-terminated* films. Comparing the bulk lattice constant for rutile, $a_{rutile} = 0.459365$ nm[2], we conclude that we have a slight out-of-plane compression for both *Ga-terminated* and *excess Ga-terminated* films. In addition for *excess Ga-terminated* films (red, upper spectrum in Fig. 3) the XRD results show all the peaks present in *Ga-terminated* films plus an extra peak present at $2\theta = 52.95836° \pm 0.00693$ (black arrow in Figure 3). This extra peak indicates the existence of another crystalline phase present at the TiO_2/GaN interface.

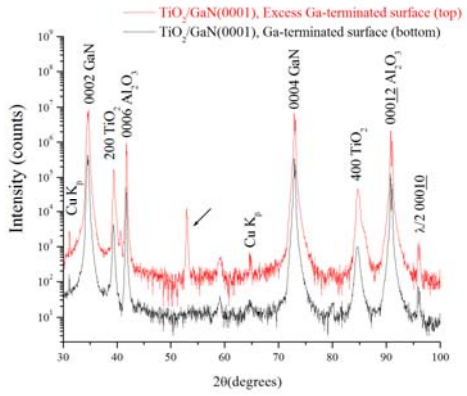

Figure 3. XRD spectra for TiO_2(001) films grown on top of GaN(0001) substrates prepared with *Ga-terminated* (black, bottom) and *excess Ga-terminated* (red, top) initial nucleation surfaces. Both films *Ga-terminated*, and *excess Ga-terminated* have two sapphire peaks [0006 & 00$\underline{12}$], two GaN peaks [0002 & 0004], and two TiO_2(001) peaks [002 & 004]. The excess *Ga-terminated* films show the presence of an extra peak [$2\theta = 52.95836° \pm 0.00693$] (black arrow), which implies the existence of an additional interface phase.

We have studied the GaN/TiO_2 interface by HRTEM, with the results shown in Figs. 4(a), and (b). The interface between TiO_2(001) and GaN is shown by the black arrows in images. We find that the interface between TiO_2 and GaN in the *Ga-terminated* [Fig. 4(a)] film is of somewhat higher quality than that for the *excess Ga-terminated* [Fig. 4(b)] film. This observation is based not only on these two HRTEM images shown here, but also on many others obtained at different regions of the same films (not shown).

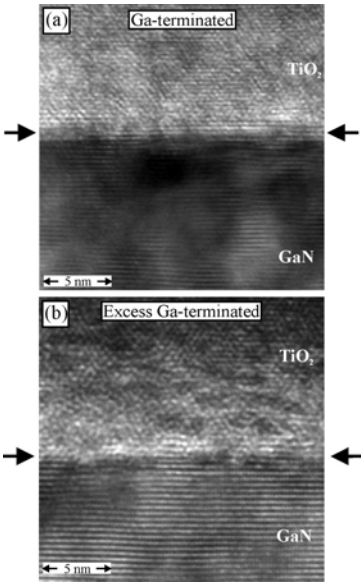

Figure 4. (a) HRTEM of TiO_2(001)/GaN(0001) for: (a) *Ga-terminated* initial nucleation surface, and (b) *excess Ga-terminated* initial nucleation surface. The black arrows in (a) and (b) show the interface between TiO_2(001) and GaN(0001).

Figure 5 shows SAED patterns for GaN buffer layer [Fig. 5(a)], TiO_2(001) grown on top of *Ga-terminated* initial nucleation surface [Fig. 5(b)], and TiO_2(001) grown on top of *excess Ga-terminated* initial nucleation surface [Fig. 5(c)]. The higher intensity diffraction spots

obtained from the *excess Ga-terminated* [Fig. 5(c)] film indicates a better bulk crystallinity as compared to the *Ga-terminated* film [Fig. 5(b)].

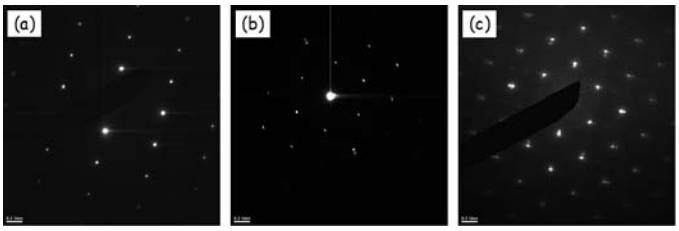

Figure 5. SAED for: (a) GaN buffer layer, (b) TiO_2(001) grown on top of GaN(0001) *Ga-terminated* initial nucleation surface, and (c) TiO_2(001) grown on top of GaN(0001) *excess Ga-terminated* initial nucleation surface.

The results presented in Figures 3, 4, and 5 suggest that although the interface TiO_2(001)/*excess Ga-terminated*-GaN(0001) does not look as good as the TiO_2(001)/*Ga-terminated*-GaN(0001) one, still the bulk crystallinity is better than the TiO_2(001)/*Ga-terminated*-GaN(0001) one. This, actually, agrees very well with our presumption that the extra peak observed in the XRD of *excess Ga-terminated* film is coming from the interface. We believe that the extra Ga atoms present on the interface, for excess *Ga-terminated* films, confer a better chance for the TiO_2 film to have a better crystal lattice relaxation as compared to the *Ga-terminated* films.

CONCLUSIONS

In conclusion, we have grown rutile-TiO_2(001) on GaN(0001) by plasma-assisted MBE, and we have studied the dependence of the growth on both the Titanium to Oxygen stoichiometry during the TiO_2(001) growth as well as on the Ga stoichiometry of the starting GaN surface. We find that the TiO_2(001) film grows with a much smoother morphology when grown under Ti-rich conditions. Additionally, we find that the presence of excess Ga on the GaN surface when the TiO_2(001) growth is initiated leads to improved cystallinity of the TiO_2(001), although we also observe in this case the presence of a small amount of interface phase other than rutile TiO_2(001).

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