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Final Draft
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Hoeglund, C.; Beckers, M.; Schell, N.; Borany, J.v.; Birch, J.; Hultmann, L.:

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In: Applied Physics Letters (2007) AIP

DOI: 10.1063/1.2731520

Topotaxial growth of Ti_2AlN by solid state reaction in AlN/Ti(0001) multilayer thin films

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(Received 9 March 2007; accepted 25 March 2007; published online 24 April 2007)

The formation of Ti_2AlN by solid state reaction between layers of wurtzite-AlN and α-Ti was characterized by *in situ* x-ray scattering. The sequential deposition of these layers by dual magnetron sputtering onto $Al_2O_3(0001)$ at 200 °C yielded smooth, heteroepitaxial (0001) oriented films, with abrupt AlN/Ti interfaces as shown by x-ray reflectivity and Rutherford backscattering spectroscopy. Annealing at 400 °C led to AlN decomposition and diffusion of released Al and N into the Ti layers, with formation of Ti_3AlN. Further annealing at 500 °C resulted in a phase transformation into $Ti_2AlN(0001)$ after only 5 min. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2731520]

The $M_{n+1}AX_n$ (n=1, 2, 3) phases are a family of multifunctional, ternary layered carbides and nitrides, where M is an early transition metal, A an A-group element, and X either C or N.[1] Early results on dc magnetron sputter deposited $M_{n+1}AX_n$ phase thin films were published for Ti_3SiC_2.[2] Recently, also results on nitrides in the form of epitaxial Ti_2AlN were reported, using reactive sputtering from either a compound 2Ti:Al target[3] or elemental Ti and Al targets.[4] It was shown that the microstructure is determined by the substrate temperature. Parallel basal-plane growth requires temperatures of at least 675 °C,[5] while lower temperatures induce growth with the c axis tilted 60° away from the substrate normal, accompanied by surface roughening.[4] Ti_2AlN layer formation was also observed by solid-state reaction in Ti/AlN diffusion couples intended for Ohmic contact design in wide band gap semiconductor applications.[6] However, studies this far are based on polycrystalline AlN material and require annealing times longer than 30 min[6] at 1300 °C with the concurrent formation of Ti_3AlN, Ti_3Al, and/or TiN.[6,7] Phase-pure Ti_2AlN was obtained at annealing temperatures beyond 800 °C.[6,8] Work on epitaxial films was only published for Ti/Al bilayers deposited onto AlGaN/GaN heterostructures, showing interfacial Ti_2AlN and Ti_3Al formation after annealing at 950 °C for 80 min.[9]

Here, we present results of *in situ* x-ray studies on epitaxial and phase-pure Ti_2AlN formed by solid-state reaction between epitaxial AlN and Ti at annealing temperatures as low as 500 °C in only 5 min.

The study was performed in a high vacuum sputter deposition chamber equipped with Be-windows,[10] mounted onto the goniometer of the ROBL beamline (BM20) at the European Synchrotron Radiation Facility, Grenoble. The setup enables *in situ* x-ray scattering measurements during film growth and postdeposition annealing at a base pressure of 1.9×10^{-4} Pa.

Reactive dual magnetron sputtering with two 1 in. diameter Al and Ti targets was used to grow epitaxial layers of wurtzite-AlN(0001) and α-Ti(0001) onto polished $Al_2O_3(0001)$ substrates, $10\times10\times1$ mm^3 in size. The nominal in-plane lattice mismatch between the substrate and AlN is +16%, and −5.4% between the individual AlN and Ti layers. The mismatches of AlN and Ti with respect to $Ti_2AlN(0001)$ are −4% and +1%, respectively, hence providing good conditions for epitaxial growth and $M_{n+1}AX_n$ phase formation. The substrates were degassed for 1 h at 675 °C, before ramping down to the deposition temperature of 200 °C. The temperature was controlled by a K-type thermocouple, cross-checked by pyrometry. The dc magnetron powers were set to 27 and 20 W for Al and Ti, respectively, and the substrate bias potential was set to −30 V. The partial pressures for AlN deposition were set to $p(N_2)/p(Ar)$ =0.05/0.33 Pa and to $p(Ar)$=0.48 Pa for Ti. These parameters were used to grow in total five sequential AlN and Ti layers, with thicknesses in the range of 10–26 nm. The as-deposited samples were then annealed to 400 °C for 60 min and 500 °C for another 90 min, with a ramping time of below 1 min.

All x-ray measurements were carried out using monochromatic synchrotron radiation of 1.051 Å. During each deposition step, time-resolved x-ray interference data were recorded to follow growth oscillations and roughness evolution. After each deposition and in-between each annealing step symmetric $\theta/2\theta$ x-ray diffraction (XRD) scans were taken to follow the epitaxial growth and to check for phase changes. Simulations of the x-ray reflectivity (XRR) data yielded data for the thickness and roughness of each layer.

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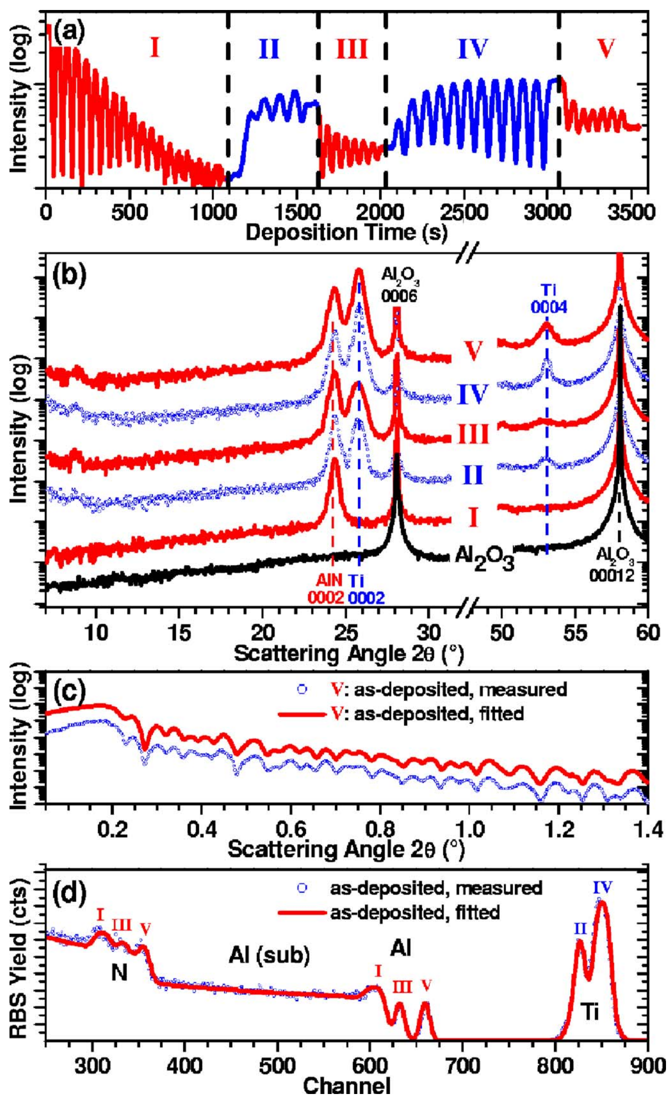

FIG. 1. (Color online) (a) *In situ* time-resolved x-ray interference. Regions I-V denote the alternating growth of AlN and Ti, with (I) 26 nm AlN, (II) 10 nm Ti, (III) 11 nm AlN, (IV) 20 nm Ti, and (V) 11 nm AlN. (b) *In situ* XRD data of sequential deposition steps of epitaxial AlN(0001) and Ti(0001) layers onto Al_2O_3(0001) at T_s=200 °C, recorded after growth of each individual layers I-V. (c) *In situ* XRR data along with the corresponding best fit simulation, offset for clarity reasons, and (d) *ex situ* RBS data of the as-deposited sample.

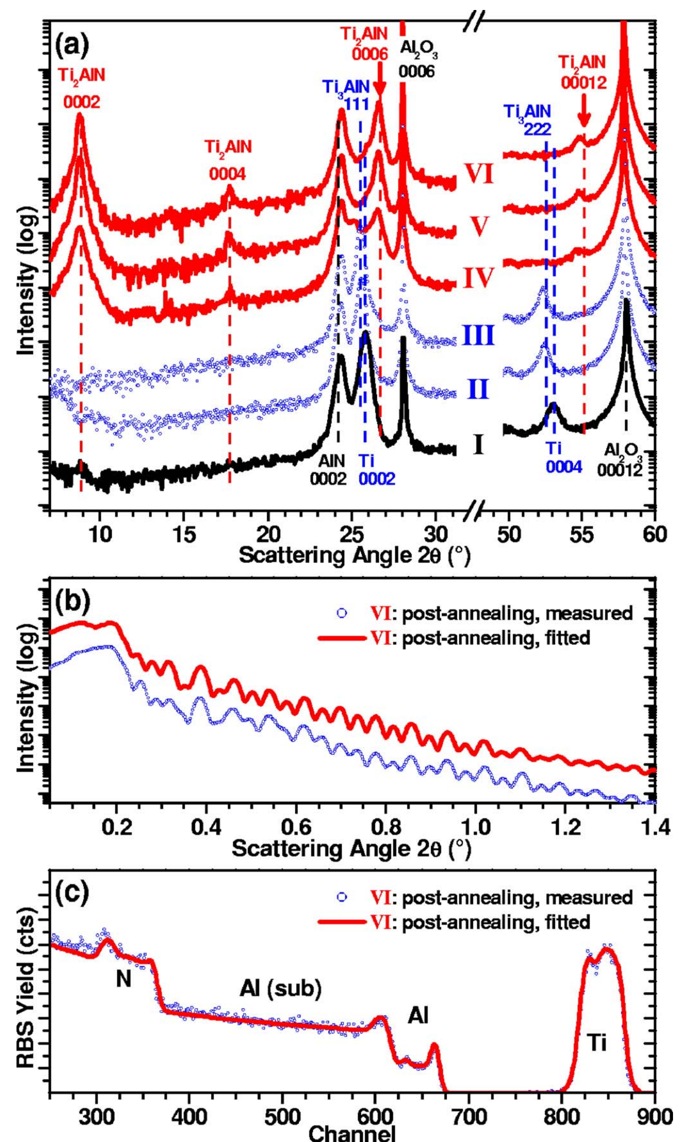

FIG. 2. (Color online) (a) *In situ* XRD data recorded for the as-deposited sample (I) and every 30 min during annealing to 400 °C for 1 h (II and III) and 500 °C for another one and a half hours (IV–VI). (b) *In situ* XRR data along with the corresponding best fit simulation, offset for clarity reasons, and (c) *ex situ* RBS data for the postannealed sample.

The film compositions and interdiffusion profiles after annealing and for a nonannealed reference sample were measured *ex situ* with Rutherford backscattering spectroscopy (RBS), using a 2 MeV He^+ beam at 70° incidence and 167° scattering angle.

Figure 1 displays data recorded during the deposition process. The oscillations in the time-resolved x-ray interference data of Fig. 1(a) correspond to the growth of each AlN and Ti layers. The decay in the oscillations during the AlN growth indicates roughening that can be attributed to the relatively low adatom mobility on the AlN(0001) surface at 200 °C. In contrast, the bonding on the Ti(0001) surface is weaker, hence the Ti has a higher adatom mobility which results in a rise of the oscillation amplitude caused by surface smoothening. The XRD data shown in Fig. 1(b) reveal basal-plane oriented heteroepitaxial growth throughout the Ti/AlN multilayer. Figure 1(c) shows the XRR data of the as-deposited sample before annealing. The fit to the scan yields thicknesses of 26 nm AlN, 10 nm Ti, 11 nm AlN, 20 nm Ti, and 11 nm AlN, which is in agreement with the thicknesses derived from the number of oscillations in the time resolved x-ray interference data in Fig. 1(a). The width of the individual Ti-to-AlN interfaces is less than 0.05 nm, which agrees with the smoothening observed in the time resolved x-ray interference, while the width of the AlN-to-Ti interfaces are ~0.5 nm. The RBS results for the as-deposited sample shown in Fig. 1(d) confirm that the layers are stoichiometric to within ±2 at. %. Also, the simulation of the separated element peaks in the scan proves that no intermixing of the AlN and Ti layers occurred during deposition.

Figure 2(a) shows XRD scans taken during annealing. Perovskite-Ti_3AlN was observed to form after 5 min of annealing at 400 °C. The reaction is completed as indicated by the constant intensity of the Ti_3AlN $\ell\ell\ell$ peaks during a holding time of 30 min. When the sample was heated to 500 °C, Ti_2AlN 000ℓ peaks emerged already after 5 min. After a holding time of 30 min, the Ti_3AlN peak vanished, while the Ti_2AlN 000ℓ peaks grew. After another 30 min at 500 °C

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the phase transformation was completed with a remaining AlN 0002 peak intensity. The Ti_2AlN formation is also manifested in the drastic change of the XRR curves, comparing Figs. 1(c) and 2(b). Fitting the XRR data yields thicknesses of 25 nm AlN, 13 nm Ti_2AlN, 4 nm AlN, 31 nm Ti_2AlN, and 3 nm AlN. This is supported by the RBS data of the annealed sample displayed in Fig. 2(c), which exhibits no separate AlN and Ti layers.

The above results with partly unreacted AlN layers suggest the following diffusion and phase transformation steps in the stack of diffusion couples.

(1) AlN decomposes at the interface to the highly reactive Ti at a temperature of 400 °C.
(2) Fast interstitial N diffuses into Ti,[11] which is known to have a large solid solubility range in the α phase, with possible ordering of the N on the (0001) planes.[12]
(3) The N diffusion is trailed by substitutional Al diffusion into the Ti:N, with formation of Ti_3AlN. Any TiN layers formed—as expected from the phase diagram—must be very thin in order not to block the further observed reactions due to the very limited solid solubility and low diffusion coefficient of Al in TiN.[11] By the same means, also Ti diffusion into the AlN is hindered.
(4) A temperature increase to 500 °C amplifies the AlN decomposition rate as well as the Al diffusivity in depth and laterally. Ti_2AlN then forms at the interface to Ti_3AlN by simultaneous Al and N ordering as well as expansion of the c axis.

In conclusion, epitaxial $Ti_2AlN(0001)$ layers can be synthesized by solid-state reaction of sputter deposited AlN/Ti(0001) multilayers during annealing at 500 °C for 5 min. The phase transformation is much accelerated compared to previously reported high temperature processes due to topotaxial reactions. The present results open up for low-temperature applications of $M_{n+1}AX_n$ phases, for example, as Ohmic contacts for semiconducting heterostructure films.

The authors acknowledge technical support from Jens Jensen and the Tandem Laboratory at Uppsala University for the RBS measurements. Financial support was given by the Swedish Foundation for Strategic Research (SSF), Strategic Research Center on Materials Science for Nanoscale Surface Engineering (MS^2E), and the Swedish Research Council (VR).

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