Investigation of composition and origin of the intermediate layers at the Ga2O3/AlN and Ga2O3/Al2O3 interfaces

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Background incl. aims
Intermediate layers have been observed at the interfaces between Ga_2O_3 and Al_2O_3 [1] as well as Ga_2O_3 and AlN [2]. These layers exhibit the crystal structure of the substrate but with altered composition. For the first heterostructures, stabilization of the intermediated layer due to strain was proposed under the assumption of pure α-Ga_2O_3. Recently, it was shown that the composition is about 25% Ga [3] only. To better understand their physical origin, the composition of samples grown under different conditions were investigated using TEM and complemented by DFT computations.

Methods
For composition determination different methods were employed: energy dispersive x-ray spectroscopy (EDX) evaluated using ThermoFisher's Velox software, composition determination from quantitative HAADF-STEM [4] and strain state analysis from measurement of atomic distances [5]. Measurements were carried out in a probe-corrected ThermoFisher Spectra 300 and an imaging-corrected FEI Titan 80-300 on specimens prepared using a FEI Nova 200 FIB by the lift-out technique. DFT studies were performed using VASP [6]. Specimens were grown by molecular beam epitaxy (MBE), MOCATAXY [2] and suboxide MBE [2].

Results
Fig. 1 a) and b) show a HRSTEM image and a Ga concentration profile measured on a Ga_2O_3/ Al_2O_3 interface formed by MBE in conditions, where actually no growth can be observed. The afore mentioned α-$(AlGa)_2O_3$ intermediate layer with a Ga concentration of about 25% can be seen as the layer with higher intensity. The composition of this sample formed at 300 °C for 3 minutes was rather similar to samples obtained at 700 °C for 180 minutes and at 700 ° C for 3 minutes. This result shows that the composition significantly differs from the one (100% Ga) proposed in Schewski et al. [1]. To elucidate whether the layer stabilizes due to strain for the low concentration, DFT computations were carried out. For that, strained and unstrained α- and β-Ga_2O_3 unit cells were generated and Al atoms according to different concentrations were substituted. All possible atomic configurations in 1x1x1 cells were considered. Their mean values and respective standard deviations are displayed in Fig. 2 a) as function of Ga concentration. In general, the strained β-phase has significantly higher energy compared to all other cases due to the very large strain. In the limits (100% Ga and 0% Ga) unstrained β-Ga_2O_3 and α-Al_2O_3 are found to be energetically lowest as expected. This means that critical concentrations exist at which the energies of the 3 cases cross: Strained α-$(AlGa)_2O_3$ was found lower in energy up to Ga concentrations of 33% compared to β-$(AlGa)_2O_3$. β-$(AlGa)_2O_3$ becomes lower in energy than unstrained α-$(AlGa)_2O_3$ above about 62 % Ga. This shows that the occurrence of the layer can be explained just by its low concentration. In order to elucidate its origin further, Al_2O_3 surface slabs were generated in which two Al atoms were substituted by Ga atoms, respectively. Fig. 2 b) shows the energy difference between a cell, in which both Ga atoms were in the 2 topmost layers compared to cells where one Ga atom is in the topmost layer and the second atom is placed deeper in the slab as a function of distance of the second atom to the top atom.

Two cells could be identified for which the second atom being deeper in the crystal was energetically lower than both atoms close to the surface. These special positions were found within the topmost 3 atomic double layers and thus, it could be possible that Ga atoms chemisorbing can diffuse into the topmost 3 double layers of the substrate resulting in an effective concentration of 33% Ga. Fig. 1 c) and d) show HRSTEM images of MOCATAXY (with In as catalyst) and suboxide MBE grown Ga_2O_3/AlN samples. A bright layer with wurtzite type crystal structure can be observed similar to the Ga_2O_3/Al_2O_3 interfaces. In e) respective relative lattice distance profiles are shown for both samples. Simulated lattice distances as a function of Ga concentration are depicted in f). For the suboxide MBE the comparison results in a nearly pure GaN composition of the layer, whereas for the MOCATAXY sample the measured lattice distance is larger than all simulated ones indicating that In atoms have been incorporated into the layer. Note, that we neglected O incorporation in these considerations. Further studies in this direction are under way.

Conclusion

Our measurements and computations for the Ga_2O_3/Al_2O_3 interface show that the intermediate layer's composition is significantly smaller than assumed in previous publications and its occurrence can be explained by the low Ga concentration. For the Ga_2O_3/AlN interface a nearly pure GaN layer was found, possibly containing In in the case of In-mediated MOCATAXY.

Keywords
Composition determination, DFT, Ga_2O_3

Graphic:

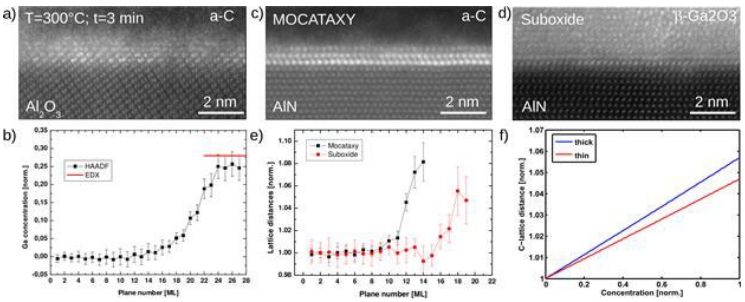

Fig. 1: a) HRSTEM image of the Ga_2O_3/Al_2O_3 interface. b) Ga concentration measured from HAADF and EDX showing a composition of about 25% and 28%, respectively. The composition is comparable with other samples grown at higher temperatures and for longer growth times. c) and d) HRSTEM images of the Ga_2O_3/AlN interface for a MOCATAXY- (In as surfactant) and suboxide grown sample. In both samples the crystal lattice of the substrate is preserved at the interface but a higher contrast indicates a finite Ga concentration e) Measured normalized c-lattice distances for the MOCATAXY and the suboxide sample. f) Computed c-lattice distance as function of Ga concentration. By comparison a nearly pure GaN composition can be determined for the suboxide sample. For the MOCATAXY sample the measured lattice distance is larger than the maximum theoretical one indicating an incorporation of In.

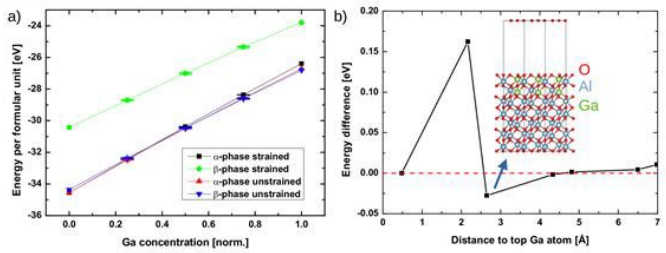

Fig. 2: a) Energy per formular unit of unstrained α- and β-phase cells as well as respective cells strained biaxial to the Al_2O_3 substrate. For the strained cells lattice plane distances in growth direction were relaxed using DFT. Errorbars indicate standard deviations over all possible atom configurations in the 1x1x1 cells. b) Energy difference of Al_2O_3 surface slabs with different substitutions of 2 Al atoms by Ga as a function of distance of the second Ga atom to the top Ga atom. The energy difference is computed w.r.t. the reference structure, which has 2 Ga atoms in the two top metal layers. For the shown series the position of the top atom is kept fixed and the second atom is placed deeper in the slab. Two cells are found to exhibit lower energy as the reference cell.

Keywords:

Composition determination, DFT, Ga_2O_3

Reference:

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