Understanding the Nucleation Kinetics Of Ga_2O and In_2O Suboxide MBE

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Abstract:

Ga_2O_3 is a transparent conducting oxide (TCO) with exciting electronic properties that are very promising for the next generation of high efficiency, high power electronics. In_2O_3 on the other hand is a well-established TCO used in industry as a transparent contact material. Their growth by conventional molecular beam epitaxy (MBE) is strongly limited by the formation and desorption of their volatile suboxides, Ga_2O and In_2O, respectively. For this reason a novel growth method, called suboxide MBE, has been developed to reduce the complexity of Ga_2O_3 and In_2O_3 growth kinetics while also increasing the growth rate and crystal quality. A growth model describing suboxide MBE has been developed. In this report, a new RHEED analysis method is presented to understand the nucleation kinetics during the suboxide MBE of Ga_2O_3 and In_2O_3. This method is based on a simple kinetic model which is fit to the experimentally obtained RHEED intensity data. Using this method, a time constant, τ, is extracted and found to correspond to the desorption rate constant, γ_{MeO2},of each suboxide. A direct correlation of the RHEED intensity method with the developed growth model for suboxide MBE is observed. Overall it is found that growth model parameters follow the expected trends for suboxide MBE. This new RHEED analysis method combined with the experimental growth rate allows us to determine the nucleation and growth behavior in the non-steady state during the suboxide MBE of Ga_2O_3 and In_2O_3.

Summary of Research:

Ga_2O_3 and In_2O_3 are transparent conducting oxides (TCO) possessing exciting properties and potential applications. These properties include very wide tunable band gaps (2.7-4eV and 4.7eV respectively), high n-type dopability, transparent optical behavior, and high conductivity[1]. These properties may lead to use in novel high efficiency, high power applications[1].

However, it has been observed that the 'conventional' MBE synthesis of (Ga, In)$_2O_3$ is strongly limited in the adsorption controlled regime[4]. For this reason, at Cornell University, a new growth method called suboxide MBE has been developed that improves the synthesis of Ga_2O_3 and In_2O_3 while reducing the complexity of their MBE growth kinetics. During conventional MBE, monoatomic Me (Ga, In) and O are supplied to the growth surface. The growth of Ga_2O_3 and In_2O_3 is limited by the formation of their respective suboxides Ga_2O and In_2O, respectively. In the new method, Me_2O is supplied instead of pure Me. This approach thus bypasses the growth rate-limiting step occurring during conventional MBE of these materials[2]. This results in Me_2O_3 growth being possible in the highly adsorption controlled regime and in turn leads to higher crystallinity in the synthesized TCO films.

To start the research, the Schlom group grew 19 Ga_2O_3 films, 11 In_2O_3 films, and 5 ITO films on (0001) sapphire under a variety of growth conditions including growth time (0.25 min-30 min), growth temperature (Ga:500-650C, In:600-900C), O_3 flux ($0.1*10^{-6}$ or $0.8*10^{-6}$nm min^{-1}) and suboxide flux (1-32 nm min^{-1}).

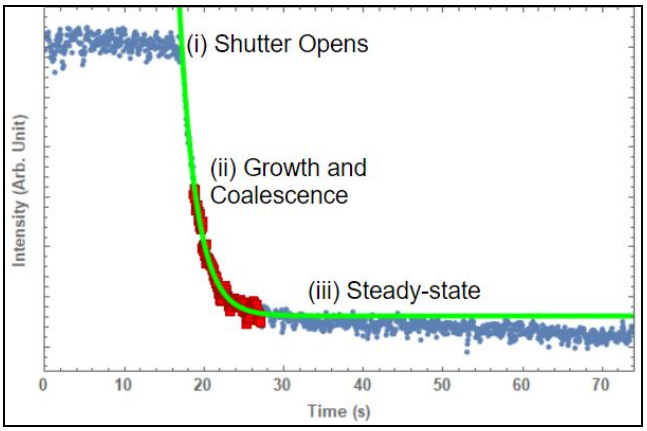

Figure 1: RHEED Intensity vs Time

Example of the RHEED intensity data analysis method. The blue points are the experimental data, the red points present the region being fit by Eq. (1), and the green line is the resultant fit. The different growth sequences are indicated in the figure by (i), (ii), (iii) and are explained in the text.

Figure 1 shows a selected data-set representing the new RHEED intensity analysis method. In sequence (i),

the suboxide and O fluxes are supplied and growth begins, resulting in an initial decrease of the RHEED intensity. In sequence (ii) growth and nucleation continue and the films begin to coalesce, resulting in an exponential decay in the signal intensity. Finally, in sequence (iii) the films fully coalesce and the signal reaches a steady-state minima. To gather the necessary kinematic data, each RHEED signal was fit along the exponential decay region to eq. 1.

Eq. 1 $$intensity = Ae^{-\frac{t}{\tau}} + b$$

In eq. 1 A is a pre exponential value, τ is the extracted time constant, t is the growth time, and b is a constant y-shift. The extracted time constant obtained by applying Eq. 1 to the experimental data (as shown in Fig. 1) depends on the suboxide flux, oxygen flux, or growth temperature. Analyzing the dependence of τ on the growth parameters allows the extraction of the nucleation kinetics during the suboxide MBE of $(Ga, In)_2O_3$ on Al_2O_3 (0001).

The goal of the research this summer was to develop an analysis method describing the growth kinetics during suboxide MBE in the non-steady state regime, and additionally, to strengthen the growth rate model developed by Vogt et al. This growth rate model reads as:

$$d_t n_{Ga_2O} = \phi_{Ga_2O} + \kappa_{Ga_2O} n_{Ga_2O} n_{O_3} + \gamma_{Ga_2O} n_{Ga_2O}$$

$$d_t n_{O_3} = \sigma\phi_{O_3} + \kappa_{Ga_2O} n_{Ga_2O} n_{O_3} + \gamma_{O_3} n_{O_3}$$

where $d_t n_{Ga2O}$ is the net change in suboxide surface concentration, κ_{Ga_2O} is the reaction rate constant and is the desorption rate constant[3]. A more detailed description of this model can be found in reference [3]. Vogt et al have solved this model for the steady state , i.e. for $d_t n_{Ga_2O} = 0$ [*Fig* 1. (*iii*)]. This research investigates the non-steady state regime, i.e $d_t n_{Ga_2O} \neq 0$ [Fig 1. (ii)], during suboxide MBE (see Fig. 1).

Results and Discussion

It was first found that the extracted τ has a linear relationship with growth temperature, T_g, for both materials (not shown here). These results suggest that τ corresponds to γ_{Ga2O} as it was expected that the fraction of particles desorping would increase as more thermal energy was available. Next, it was obtained that tau decreases with increasing suboxide flux (not shown here). Assuming that $\tau \propto \gamma_{Ga_2O}$, this result explains that an increase in adsorbate coverage increases the attractive lateral adsorbate-adsorbate interactions, leading to a lower desorption rate of the suboxide. To confirm this idea, we extracted the activation energy E_a for suboxide desorption at each given growth condition. For both materials a positive linear relationship is seen between the E_a and suboxide flux, supporting the theory of $\tau \propto \gamma_{Ga2O}$, with increased coverage increasing the binding energy. The final step to confirming $\tau \propto \gamma_{Ga2O}$ involved fitting the growth model using Wolfram Mathematica to match the timescale and growth rate, γ, of the experimental data, allowing us to extract estimates of κ_{Ga_2O} and γ_{Ga_2O}. These values were plo tted versus growth rate and had the correct trends of $\kappa_{Ga_2O} \propto \Gamma$ and $\gamma_{Ga2O} \propto \Gamma^{-1}$ for both materials, confirming the validity of the growth model (see fig. 2). Finally, it is observed that τ followed the same trend as γ_{Ga2O}, able to be modeled with the same equation, confirming that τ from the RHEED intensity fitting is proportional to γ_{Ga2O}.

To conclude, by fitting the exponential decay of the RHEED intensity signal the new method presented in this report allows the description of the suboxide MBE of Ga_2O_3 and In_2O_3 thin films in the non-steady state regime. In addition, this new RHEED intensity analysis method supports the growth rate model describing the suboxide MBE of thin films in the steady-state regime, as in Ref.[3].

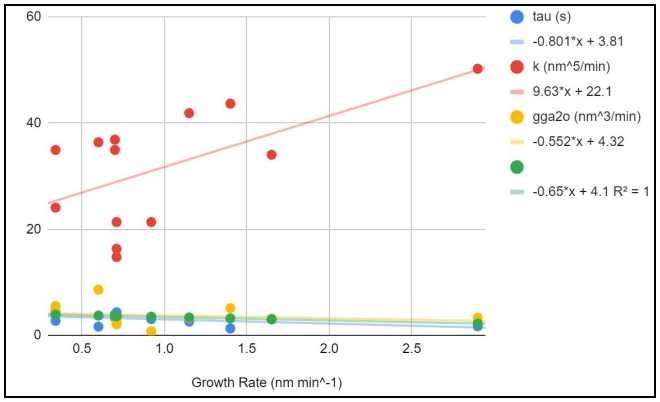

Figure 2: Reaction Constants vs Growth Rate

Results of fitting the model parameters where the red points represent values of κ_{Ga_2O}, yellow points are the desorption rate constant of Ga2o, and blue points are the extracted tau values by our model, Eq. (1). Units for the Y-axis values are given the respective parenthesis written in the figure legend.

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