

## Electronic Supporting Information for "Tuning Electronic Properties in LaNiO<sub>3</sub> Thin Films by B-site Cu-substitution"

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## Ternary Combination Model for Estimating Cation Stoichiometry in Quaternary Complex Oxide by Atomic Layer Deposition

From a traditional point of view, using the method developed by Nilsen *et al.*<sup>1</sup>, the estimated relationship between the ratios of pulsed and deposited cation species in a quaternary process can be given as:

$$1 = D_A + D_B + D_C$$

with:

$$D_A = \frac{P_A U_A}{P_A U_A + P_B U_B + P_C U_C}, \quad D_B = \frac{P_B U_B}{P_A U_A + P_B U_B + P_C U_C}, \quad D_C = \frac{P_C U_C}{P_A U_A + P_B U_B + P_C U_C}$$

where  $D_M$  is the deposited content of cation  $M^{n+}$ ,  $P_M$  is the pulsed ratio of cation precursor  $ML_x$  and  $U_M$  is the growth per cycle (GPC) of binary oxide  $MO_y$ , respectively. This model has traditionally worked really well for ternary processes, especially when the employed cation precursors have exhibited similar chemistries, such as in  $LaFeO_3$  using  $La(thd)_3$  and  $Fe(thd)_3$ .<sup>1</sup>

However, we have found that when the binary theoretical model is extended to a quaternary system, the deviation has a tendency to render the model impractical in the sense that it fails to predict the resulting cation concentration. As a result of this, we here develop and introduce an alternate model for the relationship between the pulsed and deposited ratios, using a combination of two ternary compounds (for which one cation is the same in both compounds) to form a quaternary compound. This is often (but not always) a possible approach, since quaternary compounds are often *pseudo* ternary in the sense that two of the cations adopt similar coordination and positions in a unit cell. This is indeed the case for the system in this article,  $La(Cu,Ni)O_{3-\delta}$ . It is also the case in a range of other important functional materials, *e.g.* in  $Pb(Zr,Ti)O_3$ ,  $(K,Na)NbO_3$  and  $Ni(Fe,Co)_2O_4$ . In this *ternary combination model*, the GPCs and the absolute composition for two test processes A-B-O and A-C-O form the basis for the expected cation content in the films, which can be given as:

$$D_A = \frac{\alpha \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \beta \frac{P_{ACO} U_{ACO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}}}{\alpha \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \beta \frac{P_{ACO} U_{ACO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \frac{1}{\alpha} \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \frac{1}{\beta} \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}}}$$

$$D_B = \frac{(1 - \alpha) \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}}}{\alpha \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \beta \frac{P_{ACO} U_{ACO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \frac{1}{\alpha} \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \frac{1}{\beta} \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}}}$$

$$D_C = \frac{(1 - \beta) \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}}}{\alpha \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \beta \frac{P_{ACO} U_{ACO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \frac{1}{\alpha} \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}} + \frac{1}{\beta} \frac{P_{ABO} U_{ABO}}{P_{ABO} U_{ABO} + P_{ACO} U_{ACO}}}$$

where  $D_M$  is the deposited content of cation  $M^{n+}$ ,  $P_{MM^*O}$  is the pulsed ratio of the ternary compound recipe for  $MM^*O$  and  $U_{MM^*O}$  is the GPC (growth per cycle) of ternary oxide  $MM^*O_y$ , respectively. In the model as described above, cation A is the cation that is part of both ternary oxides in the combination (La).  $\alpha$  and  $\beta$  are factors determined by the ternary composition at the endpoints given a specific pulsing recipe and are given by the normalized cation concentration of cation A in the two ternary compounds that form the quaternary compound. *I.e.*, for the system in question here, a deposition of  $n \times [5 \times (\text{La}(\text{thd})_3 + \text{O}_3) + 2 \times (\text{Ni}(\text{acac})_2 + \text{O}_3)]$  is carried out, and the relative amounts of the cation species is analyzed. A second deposition of  $n \times [5 \times (\text{La}(\text{thd})_3 + \text{O}_3) + 2 \times (\text{Cu}(\text{acac})_2 + \text{O}_3)]$  is carried out, and the relative amounts of the cation species is analyzed. These two relative ratios are  $\alpha$  and  $\beta$ , respectively, which can then be fed into the model together with the measured GPCs ( $U_{MM^*O}$ ) of the two test depositions. These are the only four variables needed to use the model to estimate the composition range for the full ternary system.

This model does not only take into account that the concentration of cation A is dependent on the pulsed ratio between the two ternary recipes, but also the variable surface chemistry that cation A will experience during combination of the two ternary recipes.

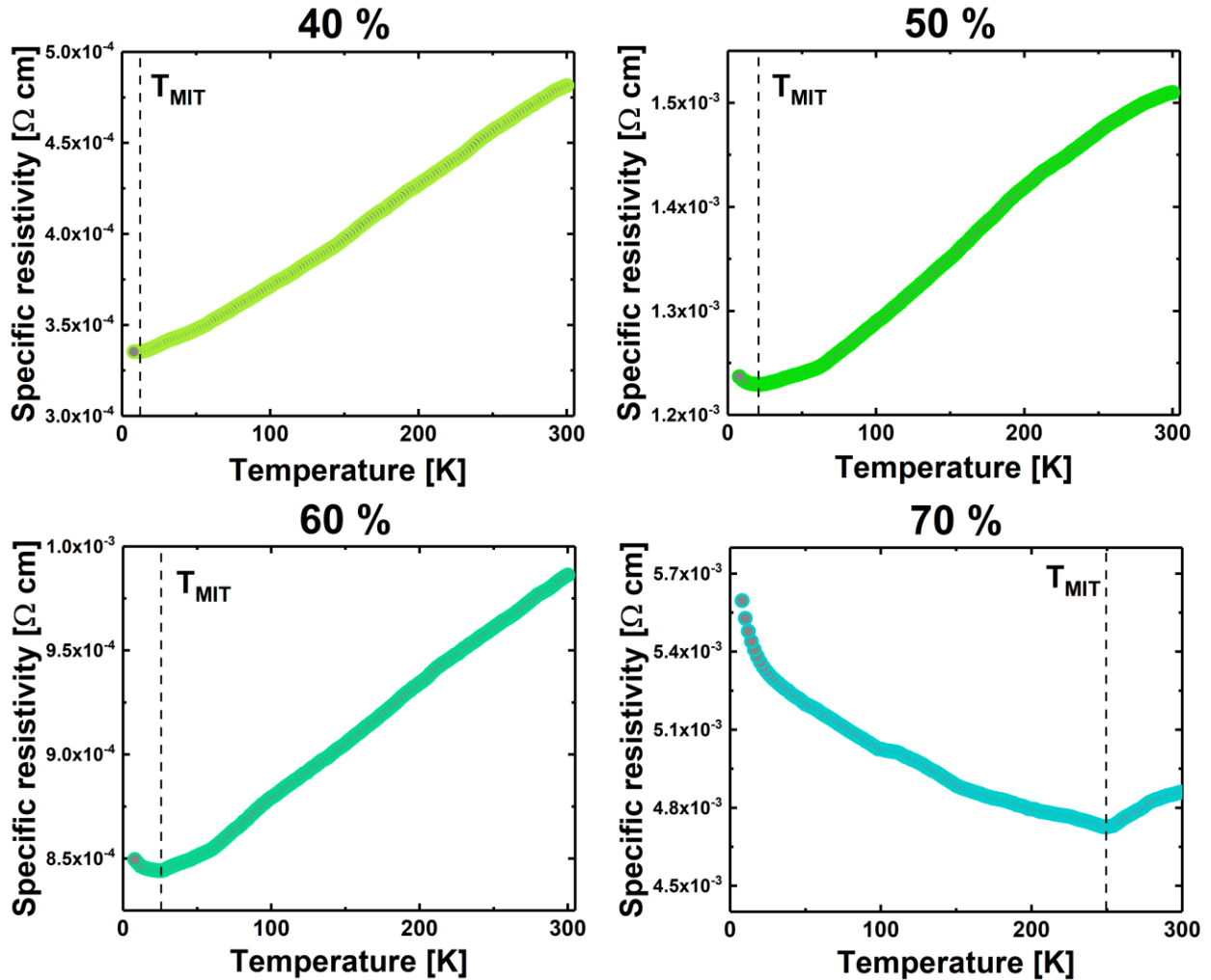
The pulsing recipe is very important. It is easy to imagine that two recipes with the same ratio can yield two widely different results. Take *e.g.*  $\text{LaNiO}_3$ , for which a stoichiometric compound is reported to result from a 0.71  $\text{La}/(\text{La}+\text{Ni})$  pulsed ratio. This stoichiometry is found for a recipe with 5 subsequent cycles of  $\text{La}(\text{thd})_3 + \text{O}_3$ , followed by 2 subsequent cycles of  $\text{Ni}(\text{acac})_2 + \text{O}_3$ . In this scenario, four of the  $\text{La}(\text{thd})_3$  pulses reacts with a  $\text{La-O}^*$ -primed surface, and one with a  $\text{Ni-O}^*$ -primed surface. One  $\text{Ni}(\text{acac})_2$  pulse reacts with a  $\text{Ni-O}^*$ -primed surface, while the other reacts with a  $\text{La-O}^*$ -primed surface. If the recipe was fully mixed, however, three  $\text{La}(\text{thd})_3$  pulses would react on a  $\text{La-O}^*$ -primed surface, with two reacting on a  $\text{Ni-O}^*$ -primed surface. The  $\text{Ni}(\text{acac})_2$  would always react on a  $\text{La-O}^*$ -

primed surface. These two scenarios are predicted to yield different results, and this has indeed been shown for the deposition of La-Ni-O. Thus, the model only works when the recipe is constant throughout ternary substitution.

<sup>1</sup> M. Lie, O. Nilsen, H. Fjellvåg, and A. Kjekshus, *Dalton T.* 2009, 481.

## Identification of MIT temperature based on linear plots of specific resistivity vs. temperature

The MIT temperatures were found by taking  $\delta\rho/\delta T = 0$ . This information is slightly difficult to see in the main manuscript, as the logarithmic plots tend to hide those points due to the small variation in resistivity as a function of temperature. The following plots are linear plots of specific resistivity vs. temperature, and may aid the reader in identifying the MIT temperatures as we have noted them in figure 8 of the main article.



Supporting Figure 1: Linear plots of specific resistivity as a function of temperatures for samples with 40, 50, 60 and 70 % pulsed incorporation of Cu.