Thermodynamic Aspects of the Gas Atmosphere & Growth Mechanism in Carbothermal Vapour Phase Transport Synthesis of ZnO Nanostructures

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Abstract

The thermodynamic conditions of the Zn vapour in the growth atmosphere found in carbothermal reduction vapour phase transport growth of ZnO nanostructures are discussed. In typical growth conditions the Zn vapour is undersaturated and will only nucleate at energetically suitable accommodation sites such as Au-coated regions or ZnO buffer layers/seeds. We suggest that growth proceeds by Zn condensation at such sites and subsequent oxidation, consistent with experimental evidence that metal catalysts or pre-deposited ZnO nucleation points are required for ZnO nanostructure growth using carbothermal vapour phase transport.

1 - Introduction

ZnO is the subject of intensive research, with many applications envisaged in various areas, including p-type doping for LEDs and laser diodes, random lasing in nanocrystalline films, magnetic impurity doping and growth of multilayer structures for materials engineering [1]. Low dimensional ZnO nanostructures, such as nanorods, nanotubes, nanowires and nanobelts, have attracted attention because of their interesting properties in terms of fundamental physical concepts and for potential applications [1]. The small "footprint" area of these nanostructures means that they can grow on a wide variety of substrates with a much higher crystalline quality compared to thin films on mismatched substrates.

ZnO nanostructures have a wide range of morphologies which are sensitive to growth parameters such as temperature, substrate type, gas ambient and source species [1,2]. In order to reproducibly grow specific morphologies in a scaleable manner for applications it is necessary to develop a better theoretical understanding of ZnO nanostructure growth. In many cases of nanostructure growth the crystallite shape is not indicative of the equilibrium crystal habit alone and the growth process is affected both by the thermodynamic and kinetic aspects of the process. This view is strengthened by considering the growth of structures such as e.g. ZnO nanocastles, nanotetrapods and nanoflowers, where the morphology is clearly not governed solely by the ZnO crystal habit and must be due at least in part to kinetic aspects of growth [3]. At present there is a relative scarcity of theoretical work on ZnO nanostructure growth, certainly compared to the vast literature on the various observations of different synthesized morphologies.

A number of papers have been published by Barnard and co-workers [4] dealing with the effects of surface energies on nanostructure morphologies, i.e. the growth habit, and the effects of e.g. In contamination. Other workers have also considered aspects such as nanostructure nucleation and diffusion of surface species and the effects of gas atmospheres [5]. These works have opened a new avenue in ZnO nanostructure research. The intent of the present work is to quantify the Zn vapour gaseous atmosphere in conditions typically found in carbothermal reduction (CTR) vapour phase transport (VPT) growth and to comment on the implications for the associated growth mechanism. A detailed discussion of the CTR-VPT process may be found in references 6 and 7 [6,7].

2 - CTR-VPT growth of ZnO nanostructures - model

The growth of ZnO nanostructures via CTR-VPT is in principle reasonably simple but there are still a number of variable factors in the process. Figure 1 presents a qualitative summary of our present understanding of the CTR-VPT ZnO nanostructure growth process, listing the various aspects of importance in the process.

The first stage of CTR-VPT growth proceeds by the production of Zn vapour through the carbothermal reduction of ZnO powder [8]. The second stage of the process is Zn vapour transport from the source region to the substrate, via the inert gas flow. The third stage is the impingement of source species on the substrate, effectively the condensation of the source species and nanostructure nucleation. This stage is significantly affected by the nature (chemical and structural termination) of the substrate and its temperature. The final, fourth, stage of the process involves other interactions with the substrate including diffusion across the surface, re-evaporation and finally reaction of the Zn with oxygen at or on the substrate surface and crystal growth. The focus of this paper is to consider the first and, indirectly, the third stages of this process (generation of the constituent growth sources and condensation of the source species / nanostructure nucleation).

This general overview of the CTR-VPT process is supported by a wide range of experiments in our laboratory over a number of years, and also by comparison of our data with other data in the literature. Specifically it appears that the background flow of Ar used in our system (or more generally the inert background gas flow) removes the majority of the O_2 initially present in the growth chamber prior to growth (since the furnace tubes are usually stored in air when not in use), except for a small quantity of O_2 trapped close to the substrate surface which is removed more slowly via diffusion through a boundary layer (which we refer to as a "trapped" layer). We find that, without the use of an Ar background flow (or with insufficient flow time prior to attempted growth, typically 10 minutes in our system at 90 sccm Ar flow), the residual O_2 reacts very quickly with the carbon source material to create CO/CO_2 and no ZnO deposit is observed due to consumption of the C and thus no CTR reaction to generate Zn vapour. If a very long flushing period with Ar is used prior to attempted growth, again no ZnO nanostructure deposit is observed. These observations support the assumption of the existence of a small quantity of O_2 trapped close to the substrate surface, which acts as the oxygen source for growth and which is removed slowly via diffusion through a boundary layer. This means that the growth process naturally terminates after a certain period of time, thus limiting the nanostructure sizes. Other groups have reported the introduction of an external O_2 supply downstream of the source material and before the sample location, which can enable growth over extended durations [9]. We have not implemented this in our growth system because our sample substrates generally are located directly above the source material to ensure equal temperatures for both. This configuration works well in terms of deposit quantity and reproducibility and is also rather simple to model thermodynamically. We are currently undertaking computational fluid dynamics (CFD) modelling of our experimental system to quantify the hypotheses above and to compare the timescales from CFD to the observed experimental timescales for pre-growth flushing etc. Congruent sublimation of the ZnO powder to create Zn(g) and O_2(g) is not relevant as an oxygen source because this process only becomes significant at temperatures > 1200 ^{o}C which we have verified directly from unsuccessful attempts to grow ZnO using only ZnO source powder and also indirectly as noted above, when the C is removed by reaction with O_2, since no ZnO deposit is seen on the substrate due to the absence of the CTR reaction.

Thus in VPT growth using CTR of ZnO powders in our system, the main gaseous species in the growth chamber are Zn vapour (Zn(g)) and CO/CO_2. ZnO nanostructure growth appears to occur via reaction of Zn vapour at, or close to, the substrate surface with residual oxygen trapped there. Various other authors have ascribed ZnO growth to (a) Zn(g) condensation followed by oxidation [6] similar to us, (b) ZnO(g) condensation into crystalline ZnO [10], or (c) to a combination of such processes with the dominant one being dependent on experimental conditions [11]. The existence and stability of the ZnO(g) molecule has been a subject of study (and some controversy) for many years

[12] and may indeed contribute to growth in certain experimental scenarios, but we do not think that it is relevant in our experimental system.

3 - Results and Discussion:

CTR Reaction Thermodynamics

In order to examine the growth process in more detail, the nature of the CTR reaction, mentioned above, is studied in detail. The CTR reaction may be described by an Ellingham diagram, and using standard thermochemical data [13] the ΔG_r for the reaction $2ZnO(s)+2C(s)\rightarrow 2Zn(g)+2CO(g)$ is given by (with T measured in K):

$$\Delta G_r = 722 - 0.587T \text{ (kJ/mol}_{O2}\text{)} \tag{1a}$$

which is valid for temperatures > 700^0C. At lower temperatures, where CO_2 is the main product (the reaction is $2ZnO(s)+C(s)\rightarrow 2Zn(g)+CO_2(g)$);

$$\Delta G_r = 552 - 0.413T \text{ (kJ/mol}_{O2}\text{)} \tag{1b}$$

In both cases a molar equality or excess of carbon is assumed, which is normally the case in CTR-VPT growth. This allows us to calculate the equilibrium Zn(g) pressure. We neglect the effects on the chamber pressure of further reactions to form ZnO(g) or other species, based on the discussion in the preceding paragraph, and assume the equilibrium CO(g)/CO_2(g) pressure is entirely due to the species produced by the CTR reaction (i.e. neglecting any background contamination). The Zn(g) equilibrium pressure due to the CTR reaction is shown as curve (a) in figure 2, in the temperature range 300 – 2000 K. The Zn(g) vapour pressure in equilibrium with condensed Zn(s,l) as calculated from standard thermochemical data [13] in the same temperature range is shown as curve (b) in figure 2.

In order to relate these data to a specific experimental scenario, the total pressure of the system must be defined. As stated above, in our system the furnace tubes in which CTR-VPT growth occurs are open to the external atmosphere and thus the overall pressure is one atmosphere. The CTR reaction takes place in a background atmosphere of an inert gas. In order to model this situation we take the data shown in curve (a) of figure 2 for the Zn(g) equilibrium pressure and add it to the pressure of the CO(g)/CO_2(g) produced in the CTR reaction and the background atmospheric pressure in the tube due to Ar (1 atmosphere) and then renormalize the total pressure in the chamber back to one atmosphere. We then calculate the renormalized Zn(g) (and other gases') pressure by applying the same renormalisation factor to the data in curve (a) of figure 2. The renormalized Zn(g) pressure is shown in curve (c) of figure 2. We take this Zn(g) pressure as the actual Zn(g) pressure in the growth zone, from which Zn(g) supersaturation may subsequently be calculated. One major consequence of this procedure is that at temperatures where ΔG_r for reaction (1a) becomes negative (> ~ 1250 K) the Zn(g) and CO(g) pressures are "clamped" at a half atmosphere each (since the overall pressure is one atmosphere, as mentioned above) and dominate the composition of the growth zone. The procedure described above is certainly an approximation, but we believe it is a reasonably accurate way to model the rather complex processes in the growth system, and that it retains the essential chemistry and physics required to describe the process.

The key parameter describing the driving force for nucleation of species from the vapour phase is the supersaturation. The supersaturation is defined as [5]:

$$S = \frac{P - P_0}{P_0} \qquad (2)$$

where P is the actual pressure and P_0 is the vapour pressure in equilibrium with the condensed phase at the temperature of the substrate. Based on the data in figures 2(b) and 2(c), we have calculated the Zn(g) supersaturation in the growth zone in the temperature range 300 K to 2000 K and this is shown in figure 3.

It is clearly seen from figure 3 that at all temperatures the Zn(g) species is undersaturated, i.e. $S < 0$. In fact at very low and high temperatures the Zn(g) species has $S = -1$, the lower bound for this parameter. At temperatures around 1200 K the Zn(g) supersaturation peaks at ~ -0.7, slightly less than the temperature where ΔG_r for reaction (1a) becomes negative. At higher temperatures $S \rightarrow -1$ as $P_0 \rightarrow \infty$, while P remains clamped at 0.5 atmospheres as mentioned previously. We have assumed that the source material and substrate temperatures are equal. This situation is actually used in many CTR-VPT growth systems including ours, with the sample placed directly atop the source material location as stated above [6,7], and is a good approximation in many other systems where the sample is close to the source location in the growth zone [14].

The implications of these data for growth of ZnO nanostructures in a CTR-VPT system are discussed below. The main outcome of our analysis is that in typical CTR-VPT growth conditions as discussed above the Zn vapour is always undersaturated. The starting point to note in any discussion related to thermodynamic aspects of CTR-VPT growth is that these aspects by definition cannot fully deal with the kinetics of the growth process and associated chemical reactions, i.e. the second and fourth stages of this process shown schematically in figure 1. Clearly this means that the data above and the conclusions we draw from these data must be viewed as a general “infrastructure” from which to view the growth process. The kinetic aspects of the growth process, which are the subject of ongoing investigation, will clearly have important implications for determining the actual growth morphologies. Secondly, and related to the first point, the vapour pressures found above are upper limiting values, and kinetic aspects of the CTR reaction and vapour transport from source to substrate (even if the temperatures of source and substrate are identical) is likely to lead to smaller values of Zn(g) partial pressure at the substrate and lower supersaturations. Despite these caveats the thermodynamic results presented above do offer, via the upper bounds they supply, useful insights into the nature of ZnO nanostructure growth in CTR-VPT systems.

The overwhelming majority of experimental data from our and other groups’ results indicate that CTR-VPT growth (with equal source and sample temperatures) on the commonly used inert, smooth, bare Si/SiO_2, glass and Al_2O_3 substrates is always unsuccessful unless either (a) Au catalyst layers or (b) ZnO buffer thin films or seed particles are used. When such catalyst, buffer layers or seeds are used, ZnO nanostructure growth is seen only on the catalysed / buffered / seeded regions [15,16]. Clearly our results for the Zn(g) vapour, which is undersaturated at all temperatures, are fully consistent with these observations and such observations are easily explicable as being due to the combination of the vapour undersaturation (which precludes homogeneous gas phase nucleation and subsequent deposition on the substrate) with the absence of energetically suitable accommodation sites on uncatalysed / unbuffered /

unseeded substrates of the type commonly used (which precludes heterogeneous nucleation directly on the substrate).

Thus Zn atoms require energetically suitable accommodation sites where they may “stick” for sufficiently long to react with oxygen at the substrate surface and form a ZnO nanostructure nucleus, and such sites are provided by catalysed / buffered / seeded substrate regions; growth will only be seen on such regions. The reaction of oxygen with Zn atoms at the (suitably catalysed or buffered) surface proceeds to form ZnO nanostructures. The oxidation rate is temperature dependent with activation energy of 0.73 eV [17] and has received relatively little discussion in the ZnO nanostructure literature. However, given the wide diversity of ZnO nanostructure morphologies observed experimentally and the likelihood from the results and discussions above that Zn(g) condensation and oxidation is the main growth route we believe the temperature dependence of the oxidation rate will be important in determining the nature of the nanostructure growth morphology and perhaps determining details of growth in specific cases, e.g. between VS and VLS growth for the case of growth on substrate with catalytic metal particles or metal films [6].

We intend to focus our future work on studies of the kinetics of the growth process and specifically step IV of the schematic diagram in figure 1. We will study the interaction of condensing species with the substrate and nucleated ZnO nanostructures, including the diffusion of Zn atoms, their reaction with oxygen and their incorporation into the growing ZnO nanocrystals. We will also explore the relative timescales and energetics of these processes under different conditions and the consequent effects on the ZnO nanostructure morphology.

4 - Conclusions

We have reported data concerning the thermodynamic conditions of the Zn vapour in the growth atmosphere for CTR-VPT growth of ZnO nanostructures. We show that in our CTR-VPT conditions (which are typical of many systems reported in the literature) the Zn vapour is always undersaturated. The undersaturated Zn(g) species requires energetically suitable accommodation sites to “stick” for sufficiently long to react with oxygen at the substrate surface and form a ZnO nanostructure nucleus and such sites are provided by catalysed / buffered / seeded substrate regions, and thus growth will only be seen on such regions, consistent with experimental data. Based on various experimental data from our group and others we suggest that growth proceeds via oxidation at the surface of the Zn atoms at energetically suitable sites. We suggest that the complexity of ZnO nanostructure morphologies and the consequently diverse range of reported shapes may be related, at least in part, to the temperature dependence of the oxidation reaction and the related aspects of surface diffusion of Zn atoms, their reaction with oxygen, their incorporation into the growing ZnO nanocrystals and the varying timescales and energetics of these processes under different conditions.

We believe that the results presented above provide a general infrastructure in which to view ZnO nanostructure growth processes of the CTR-VPT type. Physical insights gained from the use of this thermodynamic infrastructure to understand the relatively narrow range of growth processes of the CTR-VPT type may ultimately be applicable to a broader range of ZnO nanostructure growth processes and may lead to more general understanding of the key aspects which determine the growth and morphology of this nanomaterial.

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6 - References

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7 - Figure captions

Figure 1:

Schematic, qualitative summary of the CTR-VPT ZnO nanostructure growth process, listing the various aspects of the process referred to in the text.

Figure 2:

Curves (a), (b) and (c) show: (a) Zn(g) equilibrium pressure due to the CTR reaction in the temperature range 300 – 2000 K; (b) Zn(g) vapour pressure in equilibrium with condensed Zn(s,l) as calculated from standard thermochemical data in the same temperature range; (c) Renormalized Zn(g) pressure in the same temperature range.

Figure 3:

Zn(g) supersaturation in the temperature range 300 K to 2000 K.

Fgure 1

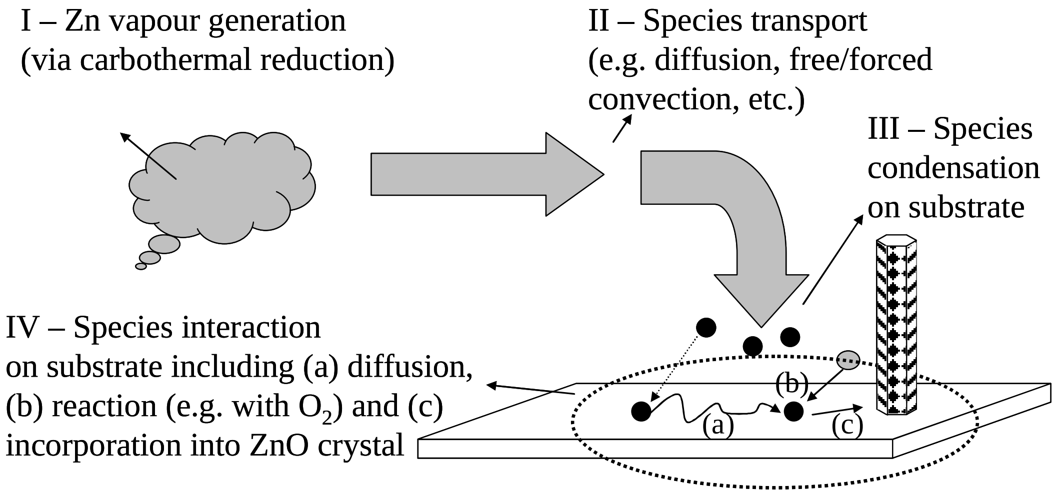
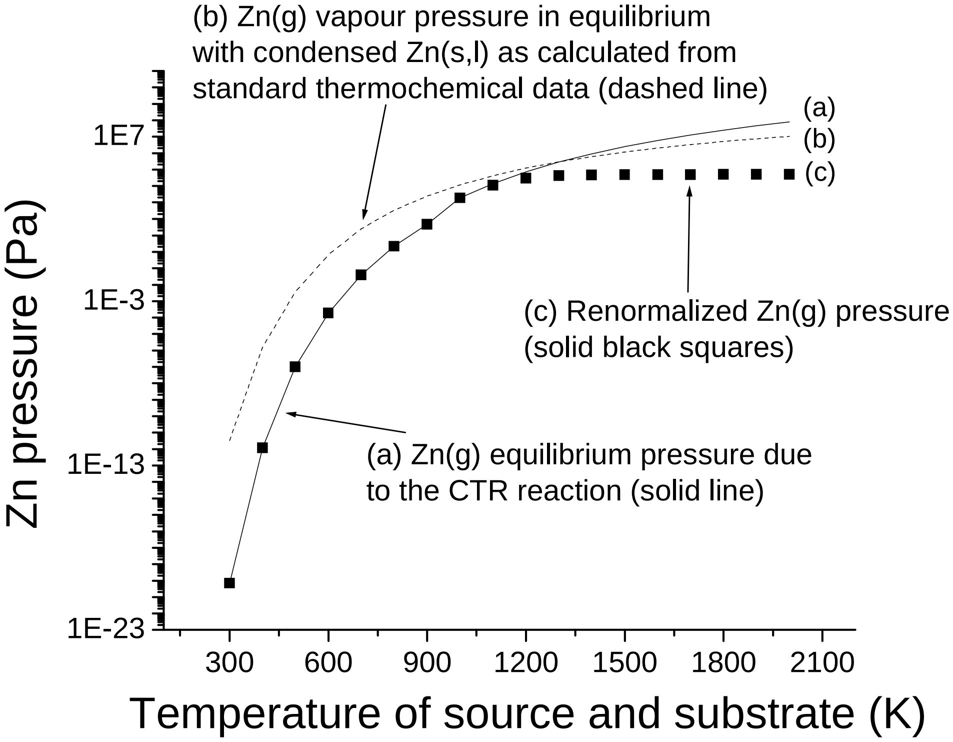
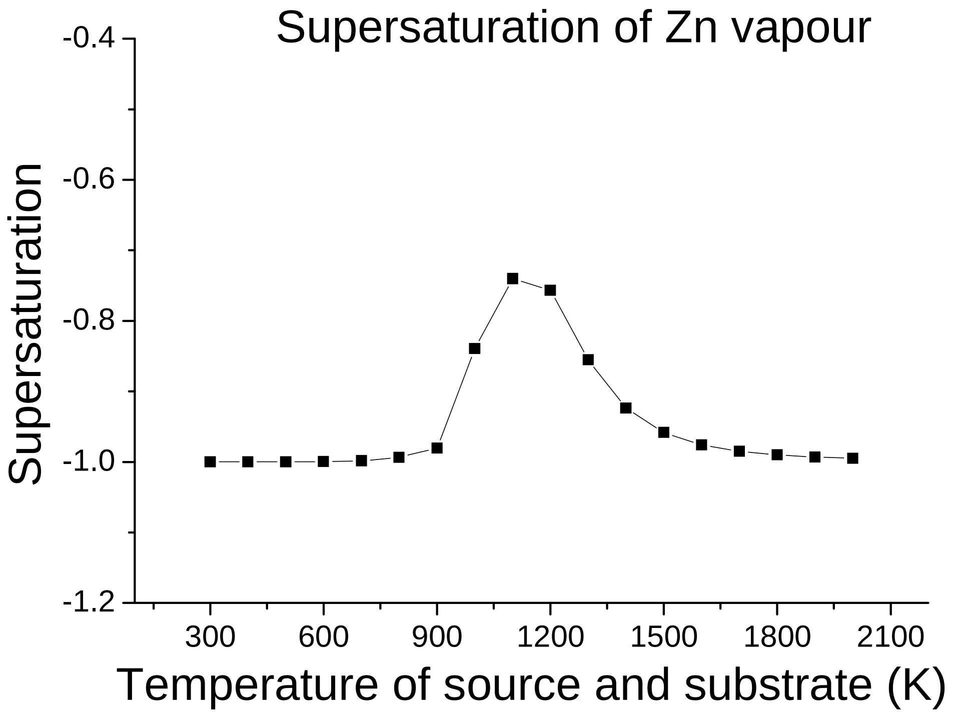

I – Zn vapour generation
(via carbothermal reduction)
II – Species transport
(e.g. diffusion, free/forced
convection, etc.)
III – Species
condensation
on substrate
IV – Species interaction
on substrate including (a) diffusion,
(b) reaction (e.g. with O_2) and (c)
incorporation into ZnO crystal
(a)
(b)
(c)

Figure 2


(b) Zn(g) vapour pressure in equilibrium
with condensed Zn(s,l) as calculated from
standard thermochemical data (dashed line)
(a)
(b)
(c)
(c) Renormalized Zn(g) pressure
(solid black squares)
(a) Zn(g) equilibrium pressure due
to the CTR reaction (solid line)
1E7
1E-3
1E-13
1E-23
Zn pressure (Pa)
300
600
900
1200
1500
1800
2100
Temperature of source and substrate (K)

<u>Figure 3</u>


Supersaturation of Zn vapour
Supersaturation
-0.4
-0.6
-0.8
-1.0
-1.2
300
600
900
1200
1500
1800
2100
Temperature of source and substrate (K)