Rapid Synthesis of Epitaxial ZnO Films from Aqueous Solution Using Microwave Heating

Jacob J. Richardson and Frederick F. Lange

Supplementary Material

Thermodynamic Solubility Calculations

In order to predict the solubility of ZnO, the solution was modeled using thermodynamic equilibrium calculations. Equilibrium was assumed between crystalline ZnO and the aqueous solution. These calculations rely on standard thermodynamic data[1,2]. The thermodynamic data for all the species used in the calucations can be found in Table 1.

Using the chemical species in Table 1, the set of equalibrium expressions in Table 2 are used to descibe the behavior of the solution. Assuming the values of enthalpy, entropy, and heat capacity in Table 1 to be independent of temperature, a chemical potential of each species was calculated as a function of temperature according to Eq. 1.

Eq.1

$$\mu = \Delta H_f + C_p(T - 298.15) - T(\Delta S_f + C_p Log \frac{T}{298.15})$$

From these chemical potentials, the temperature dependent Gibbs free energy and an equilibrium constant were calculated for each equation in Table 2. The equilibrium constants were then set equal to the respective reaction quotients at equilibrium. The resulting set of equations was then solved simultaneously for all the activities as a function of temperature, pH, and total ammonia concentration. Applying dilute solution approximations, the calculated activity of each species was assumed to be equivalent to its respective equilibrium concentration in solution. The total solubility of ZnO was then calculated as the sum of the concentrations of all the zinc containing species. Supersaturation rate was calculated as the negative time derivative ZnO solubility as the temperature of the solution was changed. Wolfram Mathematica® 5 software was used to complete these calculations.

Table 1. Thermodynamic Data Used in the Calculations

Species	ΔH_f/J mol^{-1}	S/J K^{-1} mol^{-1}	C_p/J K^{-1} mol^{-1}	Source
H_2O*(l)*	-285830	69.95	75.375	1
ZnO*(c)*	-350460	43.639	41.05	1
OH^-*(aq)*	-229987	-10.878	-122.601	1
NH_3*(aq)*	-80291	111.294	-	1
NH_4^+*(aq)*	-132633	113.386	29.518	1
$Zn2^+$*(aq)*	-153971	-112.131	30.017	1
$Zn2^+$*(aq)*	-153385	-109.62	-25.94	2
$ZnOH^+$*(aq)*	-363970	62.76	41.84	2
$Zn(OH)_2$*(aq)*	-613410	61.55	33.47	2
$Zn(OH)_3^{2-}$*(aq)*	-881520	2.98	159.83	2
$Zn(OH)_4^{2-}$*(aq)*	-1124380	-27.51	89.54	2
ZnO_2^{2-}(aq)	-384300	-	-	1
ZnO_2H^-(aq)	-457144	-	-	1
$Zn(NH_3)^{2+}$(aq)	-185770	-	-	1
$Zn(NH_3)_2^{2+}$(aq)	-225099	-	-	1
$Zn(NH_3)_3^{2+}$(aq)	-264429	-	-	1
$Zn(NH_3)_4^{2+}$(aq)	-533500	301.248	-150.615	1

Table 2. Equilibrium Expressions Used in the Calculations

Reaction	ΔG(298 K)/Jmol^{-1}	Log K_{eq}(298 K)
H_2O *(l)* ↔ H^+ *(aq)* + OH^- *(aq)*	79942	-14.0
ZnO *(c)* + $2H^+$ *(aq)* ↔ Zn^{2+} *(aq)* + H_2O *(l)*	-63754	11.2
ZnO *(c)* + H^+ *(aq)* ↔ $ZnOH^+$ *(aq)*	-19211	3.4
ZnO *(c)* + H_2O *(l)* ↔ $Zn(OH)_2$ *(aq)*	38395	-6.7
ZnO *(c)* + $2H_2O$ *(l)* ↔ $Zn(OH)_3^-$ *(aq)* + H^+ *(aq)*	94434	-16.5
ZnO *(c)* + $3H_2O$ *(l)* ↔ $Zn(OH)_4^{2-}$ *(aq)* + $2H^+$ *(aq)*	167350	-29.3
ZnO *(c)* + H_2O *(l)* ↔ ZnO_2^{2-} *(aq)* + $2H^+$ *(aq)*	285856	-50.1
ZnO *(c)* + H_2O *(l)* ↔ ZnO_2H^- *(aq)* + H^+ *(aq)*	213013	-37.3
ZnO *(c)* + NH_3 *(aq)* + $2H^+$ *(aq)* ↔ $Zn(NH_3)^{2+}$ *(aq)* + H_2O *(l)*	-15511	2.7
ZnO *(c)* + $2NH_3$ *(aq)* + $2H^+$ *(aq)* ↔ $Zn(NH_3)_2^{2+}$ *(aq)* + H_2O *(l)*	58633	-10.3
ZnO *(c)* + $3NH_3$ *(aq)* + $2H^+$ *(aq)* ↔ $Zn(NH_3)_3^{2+}$ *(aq)* + H_2O *(l)*	132776	-23.3
ZnO *(c)* + $4NH_3$ *(aq)* + $2H^+$ *(aq)* ↔ $Zn(NH_3)_4^{2+}$ *(aq)* + H_2O *(l)*	-112638	19.7
NH_4^+ *(aq)* ↔ NH_3 *(aq)* + H^+ *(aq)*	52965	-9.3

References

1 E. L. Shock, D. C. Sassani, M. Willis, and D. a. Sverjensky, *Geochimica et cosmochimica acta*, 1997, 61, 907-50.

2 W. T. Thompson, C. W. Bale, and A. D. Pelton, *http://www.crct.polymtl.ca/FACT/*.