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The physicochemical properties of liquid Ga-Zn alloys

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ABSTRACT

In regard to the high transparency and superior electrical conductivity of thin-film transparent conductive oxides in applications such as transistors using a simple surface patterning and dip-casting process, the Ga-Zn system is very interesting. In this study, the density, surface tension and viscosity of liquid Ga-Zn alloys were measured using the discharge crucible method (DC). The obtained temperature dependency of physicochemical properties of Ga-Zn alloys were determined in the range of 323–823 K. The surface tension, viscosity and density of Ga-Zn alloys across a wide range of temperatures increased with increasing Zn content in the alloy. The obtained experimental results were compared with the Quasi Chemical Model for regular solutions (QCA) and Butler models for surface tension, and with several models for viscosity.

1. Introduction

Potential new applications of Ga alloys are of great interest, in particular in the fields of electronics, nuclear fuel and liquid cooling. Amorphous oxide semiconductors and thin-film Ga alloy transistors yield special properties that may be obtained with suitable additives [1–3]. Thin-film transparent conductive oxides with superior electrical conductivity, used extensively as transparent electrodes in flat panel displays and thin-film solar cells [3], are characterised by high transparency. The sol-gel method [4], which offers advantages such as large deposition area, simple equipment, low-cost fabrication, and highly homogeneous precursor sol, can be used to obtain the film. The move to liquid applications takes into account the microfluidic components [5] in microelectromechanical systems, and their great potential for, for example, switches, pumps, valves, sensors, and electrodes [6–9]. Ga-based alloys, characterised by low melting points, rather low electrical resistivity and thermal expansion [10–13], have potential applications in heating and cooling systems. Moreover, the liquid alloys which can be used for cooling systems in small modular reactors [14], which are very attractive due to their outstanding technical, economical and safety characteristics and fast-cooled reactor technology [15], are very promising for closing the nuclear fuel cycle. Furthermore, the Ga alloys could be used for the pyrochemical reprocessing of spent nuclear fuel, as working media [16,17]. The addition of Ga content to Sn-Zn alloys was also used for the design of lead-free electronic materials, especially in die-attaching [18–20], as the process increased the application of solders and allowed to smaller joint interfaces to be obtained.

However, information about the thermophysical properties of Ga alloys is required before they can be developed and applied. Experimental [21] and modelling [22,23] data is available in the literature for surface tension of the Ga-Zn system, as is modelling data [23] for viscosity. In this study, compatible data of the temperature dependency of the density, surface tension and viscosity of liquid Ga-Zn alloys were obtained, using the discharge crucible method (DC). The obtained experimental data for liquid Ga-Zn alloys was compared with literature and several models.

1.1. Experimental

The Ga-Zn alloys were prepared by melting accurately weighed amounts of high-purity metals (Ga, Zn, 99.999%) in a glove-box under a protective atmosphere of high purity argon, with water vapour, nitrogen and oxygen concentration lower than 0.1 ppm to avoid the oxidation of liquid alloys. Ga-Zn alloys with 3.6, 25, 50, 75 and 90 (wt %) additions of Zn (see Table 1 for chemical composition) were selected for the study. Using the same procedure as for Ga-Sn alloys [24], they were melted in a graphite crucible. Density, viscosity and surface tension measurements were then taken, using the DC method (described in detail elsewhere [25–28]). The method has been described several times [24–28], and based on the measured weight over a given period time, the density, surface tension and viscosity can be calculated. Using the numerical

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Table 1
Chemical compositions[a] of Ga-Zn alloys considered in this work.

Metals	Fraction purity	
Ga ingots[d]	0.99999	
Zn rods[c]	0.999999	
Chemical formulae	Ga-Zn alloys	
	w^a_{Ga}	w^b_{Zn}
$Ga_{96.36}Zn_{3.64}$	0.9636	0.0364
$Ga_{75}Zn_{25}$	0.7500	0.2500
$Ga_{50}Zn_{50}$	0.5000	0.5000
$Ga_{25}Zn_{75}$	0.2500	0.7500
$Ga_{10}Zn_{90}$	0.1000	0.9000

[a,b] Standard uncertainties u are u(w) = 0.0001 for Ga and Zn.
[c] Alfa Aesar GmbH & Co KG, CAS No 7440-66-6.
[d] Institute of Electronics Materials Technology.

solutions based on the relationship between the volumetric flow rate of liquid Q exiting the crucible through the orifice of fixed radius r_0, the head of the liquid is calculated using equation (1). Density, surface tension and viscosity were calculated for each alloy [24–29].

$$h = \frac{1}{2g}\left(\frac{Q}{\left(a_4\left(\frac{2\rho Q}{\pi r_0 \eta}\right)^3 + a_3\left(\frac{2\rho Q}{\pi r_0 \eta}\right)^2 + a_2\left(\frac{2\rho Q}{\pi r_0 \eta}\right) + a_1\right)\pi r_0^2}\right) + \frac{\sigma}{\rho g r_0} \quad (1)$$

where: ρ is the density of liquid (kg/m^3), g is gravitational acceleration (m/s^2), r_0 is the orifice radius in the bottom of crucible (m), σ is surface tension (mN/m), Q is free flow (m^3/s), η and σ are viscosity and surface tension, respectively, C_d is the discharge coefficient determined for a given crucible, based on the free flow of liquids with known density, *Re* is the Reynolds number, and a1, a2, a3 and a4 are the coefficients of the polynomial describing *Cd* versus *Re*. Based on dependences of changing mass over time, and using the numerical solutions obtained from equation (1), density, surface tension and viscosity were calculated for each alloy.

The temperature dependence of density and surface tension were described by linear equations, and the viscosity by an Arrhenius type equation. The data are listed in Tables 2–4, along with estimated standard deviation of the equation parameters, and values calculated at 723 K, respectively. The line for density and surface tension and the Arrhenius equation for viscosity were in good agreement with the experimental data, and the parameter R^2 = 0.996÷0.999. The experimental results of density, surface tension and viscosity are collected in Table S1-S3.

2. Modelling of physicochemical properties

2.1. Density

Taking into account the changing of molar volume, the ideal density ρ_{Ideal} for the Ga-Zn system was calculated using equation (2) [29]:

$$\rho_{Ideal} = \frac{1}{\frac{y_{Ga}}{\rho_{Ga}} + \frac{y_{Zn}}{\rho_{Zn}}} \quad (2)$$

where y_{Ga} and y_{Zn} are the concentrations of gallium and zinc (in wt %/100), and ρ_{Ga}, ρ_{Zn} are the densities of the pure components Ga and Zn as taken from Refs. [30] and [31], respectively.

As proposed by Brillo and Egry [32] the density may be expressed as:

$$\rho = \frac{C_{Ga}m_{Ga} + C_{Zn}m_{Zn}}{C_{Ga}\frac{m_{Ga}}{\rho_{Ga}} + C_{Zn}\frac{m_{Zn}}{\rho_{Zn}} + V_E} \quad (3)$$

where: C_{Ga}, C_{Sn} are the atomic concentrations of gallium and tin, m_{Ga} = 69.723 (g mol^{-1}) and m_{Zn} = 65.38 (g mol^{-1}) are the corresponding molar masses, and ρ_{Ga}, ρ_{Zn} are the densities of the pure components Ga and Zn as taken from Refs. [30] and [31], respectively. V_E is the excess volume, which is the difference between the real volume V and the ideal volume V_{Ideal} [32]. The authors [32,33] assume that the excess volume V_E depends on the concentrations according to

$$V_E = C_{Ga}C_{Zn}V_x \quad (4)$$

with V_X being a type of interaction parameter. In our case, the value of V_X obtained from such fit is approximately 0.12 (cm$^{3.}$ mol^{-1}).

2.2. Surface tension

The Butler and QCA models were used to model the surface tension of liquid Ga-Zn alloys. The QCA model was described in Ref. [22], and the final equation to calculate surface tension of alloys take the form:

$$\sigma = \sigma_i + \frac{k_B T(2-pZ)}{2\alpha}\ln\left(\frac{C^s}{C}\right) + \frac{Zk_BT}{2\alpha}\left[p\ln\left(\frac{(\beta^s - 1 + 2C^s)(1+\beta)}{(\beta - 1 + 2C)(1+\beta^s)}\right) - q\ln\left(\frac{\beta - 1 + 2C}{(1+\beta)C}\right)\right] \quad (5)$$

where β^s is the function (described in Ref. [22]) substituting the bulk concentration C by the surface concentration C^s, σ_i, (i = A, B)

Table 2
The coefficients[a] and their standard deviation[b] of linear temperature dependence of density (ρ = A + B·T) for Ga-Zn alloys, and density values, calculated at 723 K.[c]

Ga-Zn, w_{Zn}	A (g·cm^{-3})	u (A)	B (g·cm^{-3}T^{-1})	u (B)	ρ (723 K) (g·cm^{-3})	s (ρ)
Ga [30]	6.262		−0.000612		5.819	
0.0364	6.276	0.001	−0.000609	0.000003	5.836	0.001
0.2500	6.458	0.006	−0.000599	0.000009	6.024	0.001
0.5000	6.648	0.013	−0.000515	0.000019	6.276	0.002
0.7500	6.876	0.014	−0.000471	0.000019	6.536	0.002
0.9000	7.008	0.003	−0.000426	0.000003	6.700	0.001
Zn [31]	7.157		−0.000450		6.831	

[a] Estimated from linear regression error as implemented in the Grapher Software Package.
[b] Estimated from difference computed between experimental and calculated from linear density fit, $s(m) = \frac{1}{N}\sum_{i=1}^{N}|m^{exp} - m^{fit}|$, where N is the number of experimental points and standard deviation of density s(ρ).
[c] Standard uncertainties u are u(T) = 1 K, u(p) = 0.1 kPa at atmospheric pressure p = 0.1 MPa, w(X) = 0.0001 for Ga and Zn.