Thermodynamic and surface properties of liquid Ge–Si alloys

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ABSTRACT

In the present work, the surface tension of liquid Si and Ge has been measured by the pendant/sessile drop combined method over the temperature range of 1723–1908 K and 1233–1313 K, respectively. The new surface tension data, the molar volumes and the melting temperatures of silicon and germanium as well as the excess Gibbs energy data of the Ge–Si liquid phase are the inputs for Calphad type modelling to study the mixing behaviour in alloy melts. The energetics of mixing in liquid Ge–Si system has been analysed through the study of the concentration dependence of various thermodynamic (activity, enthalpy of mixing, Gibbs energy of mixing), surface (surface tension and surface composition) and transport (diffusivity) properties as well as the microscopic functions (concentration fluctuations in the long-wavelength limit and chemical short-range order parameter) in the framework of statistical mechanical theory in conjunction with the Quasi-Lattice Theory (QLT).

1. Introduction

The development of nanowires and the use of silicon, alone or in combination with other materials, such as germanium, gold or germanium/silicon heterostructures, can lead to the fabrication of much more performing electronic devices [1,2]. Semiconductors based on the SiGe materials are used in devices for telecommunications, for power electronics and cryogenic operations [3,4], while silicon-rich alloys of the Ge–Si and the Ge–Si–Sn systems are used for infrared detectors [5,6]. Despite the Ge–Si system is of great industrial and technological importance, the data on its thermodynamic [7–10] and, in particular, thermophysical properties [11,12] are still incomplete. The determination of the thermodynamic and the thermophysical properties of liquid Ge–Si alloys is hampered by the experimental difficulties related to high temperature measurements, strong reactivity of Si and Ge in contact with gaseous species present in the surrounding atmosphere and, in the case of classical experimental methods, reactions between alloy melts and container materials [13]. Therefore, it is only possible to estimate the missing property values in terms of theoretical framework. Indeed, there are many theoretical works related to different properties of liquid Ge–Si alloys; for example, a combined electronic-structure and statistical–mechanical approach has been used to study the thermodynamic properties of Ge–Si alloys [14], or Monte Carlo simulation method has been applied to describe the surface tension, the surface concentration and the surface entropy of liquid Si and Ge

[15]. An extended study of the surface properties that includes Ge–Si liquid alloys has been carried out by a standard Molecular Dynamics approach [16].

Silicon and germanium have a diamond cubic crystal structure and the same valence ($=4$) [17] that together with other empirical factors, such as size factor ($V_{Ge}/V_{Si}=1.22$) [18], electronegativity difference ($=0.11$) [19], electron concentration and solubility parameters support complete miscibility in the solid and the liquid state of the Ge–Si system, as indicates its simple lens type phase diagram [20]. The aforementioned information is not sufficient to completely describe the energetics and structure of liquid Ge–Si alloys. The nature of the interactions and the structural readjustment of the constituent atoms at the atomic scale can be deduced from theoretical modelling of observable indicators, such as the thermodynamic and the thermophysical quantities, by using the Quasi-Chemical Approximation (QCA) for regular solutions [21–24]. The microscopic functions, the concentration–concentration fluctuations in the long-wavelength limit [25] and the Warren–Cowley short-range order parameter elucidate the nature of ordering and the degree of order in the melt, respectively [26,27].

The surface tension literature data on liquid Ge and Si reported in Keene's review [28] together with the data published until 2006, collected by Mills and Su [29], including our present experimental results, exhibit a significant scatter. The surface tension of silicon and germanium measured at their melting points are in the ranges of 720–885 and 500–642 mN/m, respectively, while the temperature coefficient of silicon covers broader range of 0.016–0.74 and that of germanium takes values between 0.07 and 0.16 mN/m/K. In the present work the surface tension measurements of pure Si and

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Nomenclature

A, B	components of a binary alloy
a_i $(i=A,B)$	activity of component i
a	interaction energy parameter
b	interaction energy parameter
C_i $(i=A,B)$	composition of component i
$C, 1-C$	composition of components A and B
$C^s, 1-C^s$	surface composition of components A and B
$D_i(i=A,B)$	self-diffusion coefficient of component i
D_{id}	intrinsic diffusion coefficient for an ideal mixture
D_m	inter-diffusion coefficient of a binary alloy
E	configurational energy of the bulk
E_s	configurational energy of the surface phase
G_{ID}	ideal Gibbs energy of mixing
G_M	Gibbs energy of mixing
G_M^{xs}	excess Gibbs energy of mixing
H_M	enthalpy of mixing
k_B	Boltzmann's constant
N_A, N_B	number of atoms of components A and B
N_A^s, N_B^s	number of atoms of components A and B in the surface phase
N	total number of atoms
N^s	total number of atoms in the surface phase
N_0	Avogadro's number
P	pressure
P_{TOT}	total pressure
$q_i^{N_i}(T)$ $(i=A,B)$	atomic partition function of component i for the bulk
$q_{i_s}^{N_i^s}(T)$ $(i=A,B)$	atomic partition function of component i for the surface phase
p,q	surface coordination fractions
p_{O_2}	oxygen partial pressure
R	gas constant
S_M	entropy of mixing
$S_{cc}(0)$	concentration fluctuations
$S_{cc}(0, id)$	concentration fluctuations for the ideal mixing condition
T	absolute temperature
T_l	liquidus temperature
T_{exp}	temperature of a measurement
V_i $(i=A,B)$	atomic volume of the component i
Z	coordination number
α	surface area of a binary alloy
α_1	short-range order parameter
β	auxiliary variable for the bulk phase description
β^s	auxiliary variable for the surface phase description
γ	ratio of activity coefficients of A and B components
γ_i $(i=A,B)$	activity coefficient of component i
ε_{ij} $(i,j=A,B)$	energy of i–j bond for regular solution
μ_i (i=A, B)	chemical potential of component i
μ_i^s (i=A, B)	chemical potential of component i at the surface
ω	interaction energy of a binary alloy
σ	surface tension
σ_A	surface tension of pure component A
σ_B	surface tension of pure component B
Ξ^b	grand partition function for the bulk
Ξ^s	grand partition function for the surface phase

Ge have been performed by the pendant/sessile drop combined method over the temperature range 1723–1908 K and 1233–1313 K, respectively. The new surface tension experimental data of liquid Si and Ge are presented and compared with the literature data. Subsequently, these data were the input for theoretical modelling to study thermodynamics and thermophysical properties of liquid Ge–Si alloys.

2. Experimental

In this study, the pendant/sessile drop combined method has been applied to measure the surface tension of pure silicon and germanium. The new testing procedure combining in one test, carried out in the same device, two methods for surface tension measurements of liquid metals (the pendant drop and the sessile drop), was described in detail in [30]. This procedure allows a significant improvement in the accuracy of interfacial properties measurements at high temperature and can be considered as a quasi-containerless method. For this reason, in comparison with traditional sessile/large drop method, it is particularly suitable to measure highly reactive metals in the liquid state, such as Si and its alloys [13]. Such conditions can be achieved by applying a capillary (a very small contact area of the liquid metal drop with the container at the tip of a capillary only), together with fast manipulating with liquid metal (drop squeezing, movement and deposition) at high temperature under vacuum or protective atmosphere and accompanying with fast recording of the drop images by high-speed CCD camera. Additionally, in order to produce oxide-free droplets, necessary for accurate measurements of surface tension, the metal drop was in situ cleaned directly in the vacuum chamber by squeezing the metal through the alumina capillary of a special

design allowing mechanical removal of an oxide film at the sharp internal edges of the capillary.

Experimental complex, described in details in [31], equipped with several manipulators was used. It should be highlighted that the design of experimental complex, built from a few independent and directly interconnected vacuum chambers, allows to load and to remove the metal samples, the substrates and the capillaries without necessity to open the working (high temperature) vacuum chamber. A resistance furnace with a Ta heating element surrounded with Ta and Mo isolation screens was adopted. All elements of manipulators introduced inside Ta heater during the tests were also made from Ta. The presence of Ta, acting as an oxygen getter, assured an oxygen partial pressure p_{O_2} inside the test chamber that is imposed by thermodynamics of the $(4/5)Ta + O_2 \leftrightarrow (2/5)Ta_2O_5$ reaction. Accordingly, in the working temperature range 1233–1908 K, the oxygen partial pressure values of about 10^{-20} and 10^{-9} Pa, respectively, have been obtained.

High purity metals, Si (99.99999% single crystal) and Ge (99.9999% Marz grade) were used to prepare the samples. Before loading into the vacuum chamber of the furnace, the metal samples of desired volume (about 0.5 cm³) were mechanically cleaned by scratching, and then chemically rinsed with pure isopropanol in an ultrasonic bath. Subsequently, the selected sample was placed in the Al_2O_3 polycrystalline capillary (diameter=1.1 mm) and using a special manipulator, the capillary was introduced into the high temperature zone where a liquid metal was squeezed through the capillary to form a drop with appropriate dimensions allowing the profile acquisition correctly. The surface tension measurements were carried out under an atmosphere of flowing high purity Argon (99.99999%; $p_{TOT}=8.5 \times 10^4$ Pa). For each metal sample, the surface tension was measured as a function of temperature in a wide range above the liquidus point T_l, e.g. $T_l < T_{exp} < T_l+150$ K. The surface tension was measured as a function of temperature by steps of 50 K.