

Copper diffusion in germanium: connecting point defect parameters with bulk properties

Chroneos, A. , Panayiotatos, Y. and Vovk, R.V.

Author post-print (accepted) deposited in CURVE May 2016

Original citation & hyperlink:

Chroneos, A. , Panayiotatos, Y. and Vovk, R.V. (2015) Copper diffusion in germanium: connecting point defect parameters with bulk properties. Journal of Materials Science: Materials in Electronics, volume 26 (5): 2693-2696.

<http://dx.doi.org/10.1007/s10854-015-2744-6>

Publisher statement: The final publication is available at Springer
via <http://dx.doi.org/10.1007/s10854-015-2744-6>

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the author's post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

CURVE is the Institutional Repository for Coventry University

<http://curve.coventry.ac.uk/open>

Copper diffusion in germanium: Connecting point defect parameters with bulk properties

A. Chroneos,^{1,2,a)} Y. Panayiotatos,³ and R. V. Vovk⁴

¹*Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom*

²*Faculty of Engineering and Computing, Coventry University, Priory Street, Coventry CV1 5FB, United Kingdom*

³*Department of Mechanical Engineering, TEI of Piraeus, P.O. Box 41046, Athens 12201, Greece*

⁴*Physics Department, V. Karazin Kharkiv National University, Svobody Sq.4, 61077 Kharkiv, Ukraine*

Abstract

Copper diffusion in germanium is fundamentally and technologically important as it has a very low activation energy and influences the precipitation and gettering of copper respectively. These constitute the understanding of copper's diffusion properties in germanium over a range of temperatures and pressures important. In the present study we use the $cB\Omega$ model in which the defect Gibbs energy is proportional to the isothermal bulk modulus (B) and the mean volume per atom (Ω). The elastic and expansivity data is used in the description of the $cB\Omega$ model to derive the copper interstitial diffusion coefficient in germanium in the temperature range 827 K to 1176 K. The calculated results are discussed in view of the available experimental data.

Keywords: Germanium; diffusion; Copper

^{a)}Electronic mail: alexander.chroneos@imperial.ac.uk

1. Introduction

Germanium (Ge) rivals silicon (Si) as it has superior carrier mobilities, low dopant activation temperatures and smaller band-gap [1-5]. In the early days of the semiconductor industry Ge was abandoned because of its poor quality native oxide [1]. Recently, the introduction of high- k gate dielectric materials has eliminated the requirement of a good quality native oxide in advanced nanoelectronic devices regenerating the interest on alternative materials such as Ge [6-8].

In Ge metals such as copper (Cu) have been used to increase the rate of crystallization and produce large grain crystals via the process of metal induced lateral crystallisation (MILC) [9]. Self-diffusion and most diffusion processes in Ge are governed by vacancies [10-16], whereas in Si self-interstitials also impact the defect processes [17,18]. Considering n -type dopant (P, As, and Sb) diffusion the most recent experimental and theoretical results are in agreement that it is vacancy-mediated [13,16]. From the p -type dopants indium diffuses with a vacancy-mechanism, whereas boron diffusion is interstitial but very slow [5,15]. Metal diffusion including Cu diffusion is an exception where interstitial-related mechanisms can be important [19-21]. In particular copper interstitials (Cu_i) can diffuse via direct interstitial or dissociative mechanisms and these are faster than vacancy-mediated mechanisms [19-21].

Interconnecting the defect Gibbs energy g^i (i = defect formation f, self diffusion activation act, or migration m) and bulk properties in solids has led to different models including the model by Zener [22] and the model by Varotsos and Alexopoulos [23-30]. In the model by Varotsos and Alexopoulos [23-29] (referred thereafter as the $\text{cB}\Omega$ model) it was proposed that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω . The $\text{cB}\Omega$ model was employed to

study the point defect processes in numerous materials [31-41], but it has not been systematically used to describe to investigate the diffusion processes in group IV semiconductors.

In the present study we describe using the $cB\Omega$ model the Cu interstitial diffusion coefficients in Ge using the isothermal bulk modulus and the mean volume per atom.

2. Methodology

For a monoatomic crystal with a single diffusion mechanism diffusion process can be described by the activation Gibbs energy (g^{act}), which is the sum of the Gibbs formation (g^{f}) and the Gibbs migration (g^{m}). The activation entropy s^{act} and the activation enthalpy h^{act} are defined via [31, 34]:

$$s^{\text{act}} = - \left. \frac{dg^{\text{act}}}{dT} \right|_P \quad (1)$$

$$h^{\text{act}} = g^{\text{act}} + Ts^{\text{act}} \quad (2)$$

The diffusion coefficient D is defined by:

$$D = f a_0^2 \nu e^{-\frac{g^{\text{act}}}{k_B T}} \quad (3)$$

Where f is the diffusion correlation factor depending on the diffusion mechanism and the structure, a_0 is the lattice constant, ν is the attempt frequency and k_B is Boltzmann's constant.

In the $cB\Omega$ model the defect Gibbs energy g^{i} is related to the bulk properties of the material via the relation [23-29]:

$$g^{\text{i}} = c^{\text{i}} B \Omega \quad (4)$$

Therefore, by Eqs. (3) and (4):

$$D = f a_0^2 \nu e^{-\frac{c^{\text{act}} B \Omega}{k_B T}} \quad (5)$$

This means that if there is an experimentally determined diffusivity D_i value at T_1 the c^{act} can be calculated assuming that the pre-exponential factor fa_0^2v can be determined. The calculation of the pre-exponential factor involves computing the diffusion correlation factor (which is dependent upon the diffusion mechanism and the crystal structure) and the attempt frequency. The attempt frequency is commonly approximated by the Debye frequency, which can lead to the introduction of errors. Thereafter, using c^{act} the diffusivity D_i at any temperature T_i can be calculated using Eq. 5 provided that the elastic data and expansivity are known for T_i . Importantly, c^{act} is to a first approximation a temperature and pressure independent constant [31, 34]. Finally, in the framework of the cBQ model anharmonic effects can be described by the temperature decrease in B and by the thermal expansivity.

3. Results and discussion

The control of self-, dopant and impurity diffusion is very important during device fabrication. The diffusion of Cu in Ge impacts the electronic properties and influences other diffusion related phenomena including the precipitation and gettering of Cu [21]. The control and understanding of these processes are of technological importance to control the contamination levels of electronic devices during processing [21].

In previous work it was determined that Cu interstitial diffusion in Ge can be described via the Arrhenius relation [21]:

$$D_{exp}^{Cu} = 3.2e^{-\frac{0.18}{k_B T}} \cdot 10^{-7} m^2 s^{-1} \quad (6)$$

In the present study, the expansivity data was taken from Kagaya *et al.* [42] and the isothermal bulk modulus data from Krishnan *et al.* [43]. These values [42-45] are

reported in Table 1 alongside the experimental Cu interstitial diffusion coefficients derived from Eq. 6. Typically, the method of the single experimental measurement can be employed to calculate the value of c^{act} in the cB Ω model but will depend upon the experimental error in the B, Ω parameters and the diffusivity value. Furthermore, there will be errors in the pre-exponential factor especially for materials where diffusion mechanisms are complicated. For these reasons here we employ the “mean value” method to calculate c^{act} [36, 39, 46, 47].

In the “mean value” method the linear behavior of $\ln D_{exp}^{Cu}$ with respect to $\frac{B\Omega}{k_B T}$ testifies the validity of the cB Ω model with the slope being c^{act} as it can be seen from Eq. 5. As it can be observed from Figure 1 there is a linear relation, which can be described by:

$$D_{cB\Omega}^{Cu} = 2.41 e^{-\frac{0.0158B\Omega}{k_B T}} \cdot 10^{-5} m^2 s^{-1} \quad (7)$$

Figure 2 is the Arrhenius plot for Cu interstitial diffusion coefficients in Ge determined by experiment [21] and calculated by the cB Ω model. Both this figure and Table 1 show that the cB Ω model is in excellent agreement with the experimental [21] Cu interstitial diffusion coefficients in Ge. Therefore, the cB Ω model describes Cu interstitial diffusion in Ge. Future studies will explore whether the cB Ω model can be employed to study other metals diffusing in Ge.

4. Conclusions

In the present study we employed the cB Ω model to describe metal diffusion in germanium. There is excellent agreement between the calculated and experimental diffusion coefficients of Cu interstitial diffusion in Ge in the temperature range considered. This extremely low activation energy diffusion process is a paradigm for related studies of metal diffusion in semiconductors and the present approach may be

extended to these systems. Additionally, the $cB\Omega$ model can provide information concerning the formation, migration and defect volumes in these systems over a range of temperatures and pressures.

References

1. C. Claeys, E. Simoen, Germanium-based technologies: from materials to devices, Elsevier, 2007
2. C. Janke, R. Jones, S. Öberg, P.R. Briddon, *J. Mater. Sci.: Mater. Electron.* **18**, 775 (2007)
3. G. Impellizzeri, S. Boninelli, F. Priolo, E. Napolitani, C. Spinella, A. Chroneos, H. Bracht, *J. Appl. Phys.* **109**, 113527 (2011)
4. A. Chroneos, *J. Mater. Sci.: Mater. Electron.* **24**, 1741 (2013)
5. A. Chroneos, H. Bracht, *Appl. Phys. Rev.* **1**, 011301 (2014)
6. M. Wu, Y.I. Alivov, H. Morkoc, *J. Mater. Sci.: Mater. Electron.* **19**, 915 (2008)
7. A. Ritenour, A. Khakifirooz, D.A. Antoniadis, R.Z. Lei, W. Tsai, A. Dimoulas, G. Mavrou, Y. Panayiotatos, *Appl. Phys. Lett.* **88**, 132107 (2006)
8. A. Chroneos, U. Schwingenschlögl, A. Dimoulas, *Ann. Phys. (Berlin)* **524**, 123 (2012)
9. S.R. Herd, P. Chaudhari, M.H. Brodsky, *J. Non-Cryst. Solids* **7**, 309 (1972)
10. M. Werner, H. Mehrer, H.D. Hochheimer, *Phys. Rev. B* **32**, 3930 (1985)
11. A. Chroneos, H. Bracht, R.W. Grimes, B.P. Uberuaga, *Appl. Phys. Lett.* **92**, 172103 (2008)
12. E. Hüger, U. Tietze, D. Lott, H. Bracht, D. Bougeard, E.E. Haller, H. Schmidt, *Appl. Phys. Lett.* **93**, 162104 (2008)
13. S. Brotzmann, H. Bracht, J. Lundsgaard Hansen, A. Nylandsted Larsen, E. Simoen, E.E. Haller, J.S. Christensen, P. Werner, *Phys. Rev. B* **77**, 235207 (2008)
14. A. Chroneos, R.W. Grimes, B.P. Uberuaga, H. Bracht, *Phys. Rev. B* **77**, 235208 (2008)
15. R. Kube, H. Bracht, A. Chroneos, M. Posselt, B. Schmidt, *J. Appl. Phys.* **106**, 063534 (2009)
16. H. Tahini, A. Chroneos, R.W. Grimes, U. Schwingenschlögl, H. Bracht, *Appl. Phys. Lett.* **99**, 072112 (2011)
17. A. Chroneos, C.A. Londos, E.N. Sgourou, *J. Appl. Phys.* **110**, 093507 (2011)
18. E. N. Sgourou, D. Timerkaeva, C.A. Londos, D. Aliprantis, A. Chroneos, D. Caliste, P. Pochet, *J. Appl. Phys.* **113**, 113506 (2013)
19. H.A. Tahini, A. Chroneos, S.C. Middleburgh, U. Schwingenschlögl, R.W. Grimes, *J. Mater. Chem. A* DOI: 10.1039/C4TA06210H
20. A. Giese, N.A. Stolwijk, H. Bracht, *Appl. Phys. Lett.* **77**, 642 (2000)
21. H. Bracht, *Mater. Sci. Semicond. Process.* **7**, 113 (2004)
22. C. Zener, *J. Appl. Phys.* **22**, 372 (1951)
23. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **15**, 411 (1977)
24. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **15**, 2348 (1977)
25. P. Varotsos, K. Alexopoulos, *J. Phys. (Paris) Lett.* **38**, L455 (1977)
26. P. Varotsos, W. Ludwig, K. Alexopoulos, *Phys. Rev. B* **18**, 2683 (1978)
27. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **22**, 3130 (1980)
28. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **24**, 904 (1981)
29. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **30**, 7305 (1984)
30. J. Philibert, *Defect Diffus. Forum* **249**, 61 (2006)

31. P. Varotsos, K. Alexopoulos, *Thermodynamics of Point Defects and their Relation with the Bulk Properties* (North-Holland, Amsterdam, 1986)
32. P. Varotsos, N. Sarlis, M. Lazaridou, *Phys. Rev. B* **59**, 24 (1999)
33. P. Varotsos, *Phys. Rev. B* **75**, 172107 (2007)
34. P. Varotsos, *J. Appl. Phys.* **101**, 123503 (2007)
35. H.B. Su, D.O. Welch, W. Wong-Ng, L.P. Cook, Z. Yang, *Appl. Phys. Lett.* **91**, 172510 (2007)
36. B.H. Zhang, X.P. Wu, *Appl. Phys. Lett.* **100**, 051901 (2012)
37. I. Sakelis, *J. Appl. Phys.* **112**, 013504 (2012)
38. B.H. Zhang, *AIP Adv.* **4**, 017128 (2014)
39. F. Vallianatos, V. Saltas, *Phys. Chem. Minerals* **41**, 181 (2014)
40. E.S. Skordas, *Solid State Ionics* **261**, 26 (2014)
41. P. Varotsos, K. Eftaxias, V. Hadjicontis, *Phys. Rev. B* **38**, 6328 (1988)
42. H.M. Kagaya, N. Shoji, T. Soma, *Phys. Stat. Solidi B* **139**, 417 (1987)
43. R. Krishnan, R. Srinivasan, S. Deverayanan, in *Thermal Expansion of Crystals*, Pergamon Press, Oxford (1979)
44. V. Hadjicontis, K. Eftaxias, *J. Phys. Chem. Solids* **52**, 437 (1991)
45. K. Eftaxias, V. Hadjicontis, *Phys. Stat. Solidi B* **160**, K9 (1990)
46. E. Dologlou, *J. Appl. Phys.* **110**, 036103 (2011)
47. A. Chroneos, R.V. Vovk, *J. Mater. Sci.: Mater. Electron.* DOI: 10.1007/s10854-014-2655-y

Table 1. Characteristic calculated and experimental [21] Cu diffusion coefficients in Ge alongside the elastic and expansivity data [42-45] used in the cBΩ model.

T (K)	B (10^{11}Nm^{-2})	Ω (10^{-29}m^3)	D_{exp}^{Cu} ($10^{-6}\text{m}^2\text{s}^{-1}$)	$D_{cB\Omega}^{Cu}$ ($10^{-6}\text{m}^2\text{s}^{-1}$)	$\frac{D_{cB\Omega}^{Cu} - D_{exp}^{Cu}}{D_{exp}^{Cu}}$ (%)
827	0.709	2.289	2.56	2.56	0
877	0.703	2.292	2.96	2.96	0
925	0.697	2.294	3.35	3.33	-1
975	0.690	2.298	3.76	3.75	0
1026	0.684	2.300	4.18	4.17	0
1074	0.678	2.303	4.58	4.57	0
1126	0.671	2.306	5.01	5.01	0
1176	0.665	2.309	5.42	5.41	0

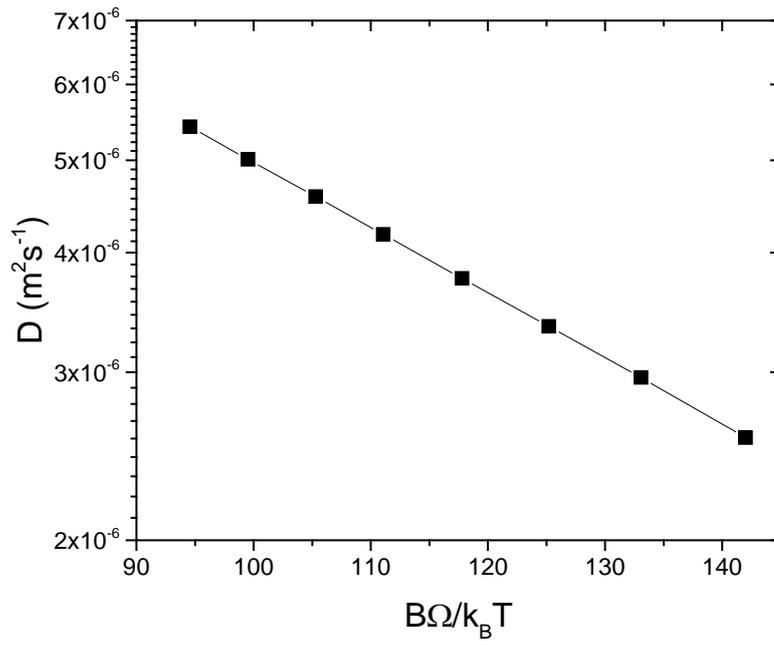


FIG. 1. The Cu diffusion coefficients in Ge with respect to $\frac{B\Omega}{k_B T}$.

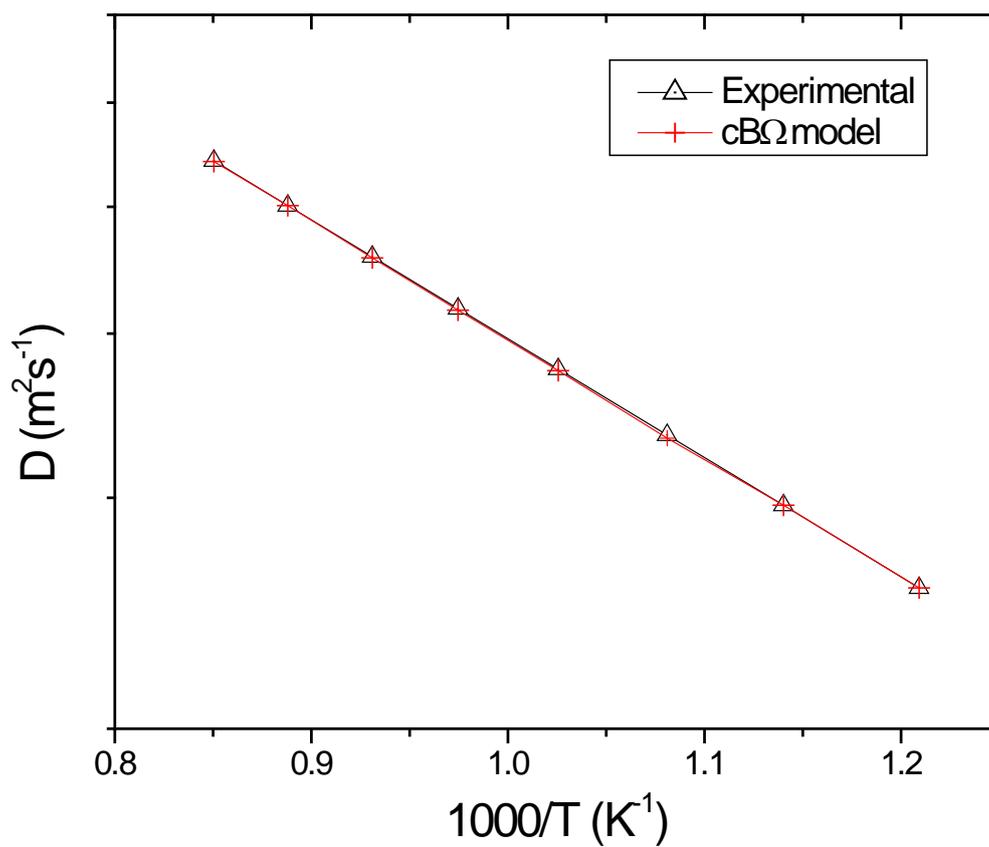


FIG. 2 The Arrhenius plot for Cu diffusion in Ge obtained by experiment [21] and calculated by the cBΩ model.