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Palladium diffusion in germanium

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Abstract

Palladium diffusion in germanium is fundamentally and technologically important as it has an extremelly low activation energy and this can impact metal induced lateral crystallisation to produce large grain crystals. Recent theoretical studies calculated that the activation energy of migration of palladium in germanium is 0.03 eV. This constitute the experimental determination of the palladium diffusion properties very difficult. In the present study we calculate palladium diffusivity in germanium by employing theoretical results and comparing to the diffusion of copper in germanium. Finally, by employing a thermodynamic model we derive a relation describing palladium diffusivity to bulk materials properties.

Keywords: Germanium; diffusion; palladium

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1. Introduction

In the past years has germanium (Ge) has been considered as a rival to silicon (Si) for nanoelectornic devices as it has low dopant activation temperatures, superior carrier mobilities, and smaller band-gap [1-5]. Although Ge was important in the early days of the semiconductor industry it was abandoned because of its poor quality native oxide (GeO_2) [1]. The introduction of high-*k* gate dielectric materials has led to the reconsideration of Ge as it eliminated the need for a good quality native oxide in advanced nanoelectronic devices [6-8].

In the past years there has been a concerted effort by the community to investigate diffusion processes in Ge [9]. There is consensus that self-diffusion and most diffusion processes in Ge are mediated by vacancies [10-16], contrary to Si where self-interstitials also influence defect processes [17,18]. From the *p*-type dopants indium is transported with a vacancy-mechanism and boron diffusion is interstitial and very slow [5,15]. The diffusion of *n*-type dopants (P, As, and Sb) is very important for *n*-type Ge-MOSFET with the most recent experimental and density functional theory (DFT) results being in agreement that it is vacancy-mediated [13,16].

Metal atom diffusion is an exception as interstitial-related mechanisms can be prevelant [19-21]. It has been experimentally determined that copper interstitials (Cu_i) in Ge diffuse via direct interstitial or dissociative mechanisms and these are faster as compared to vacancy-mediated mechanisms [19-21]. The diffusion of Pd in Ge has not been investigated experimentally although it is important for the production of large grain crystals through the process of metal induced lateral crystallisation (MILC) [22]. In a recent hybrid density functional theory study, Tahini *et al.* [19] calculated that the direct interstitial mechanism is energetically favourable

for Pd diffusion in Ge and that the activation energy of migration for this process is only 0.03 eV. This very low activation energy verifies the extremely fast transport of Pd in Ge and justifies in part the absence of experimental studies. Given that in the study of Tahini *et al.* [19] the Pd diffusion mechanism was identified to have similar features with Cu (for which there exist reliable experimental results [21]) we will propose in the present study a way to calculate the Pd diffusivities. Finally, the Pd diffusion properties will be connected to the bulk properties via a thermodynamic model.

2. Relation between Pd and Cu diffusivities

The diffusion coefficient *D* of a dopant in a solid can be defined by:

$$D = f a_0^2 \nu e^{-\frac{g^{act}}{k_B T}} \quad (1)$$

Where f is the diffusion correlation factor (depends upon the diffusion mechanism and the structure), a_0 is the lattice constant, ν is the attempt frequency and k_B is Boltzmann's constant.

The calculation of the pre-exponential factor involves the diffusion correlation factor (which is dependent upon the diffusion mechanism and the crystal structure) and the attempt frequency. The attempt frequency for Pd in Ge is given by:

$$\nu = \nu_D \sqrt{\frac{m_{Pd}}{m_{Ge}}} \quad (2)$$

where ν_D is the Debye frequency, m_{Pd} and m_{Ge} are the masses for Pd and Ge respectively.

In a recent hybrid DFT study, Tahini *et al.* [19] calculated that Pd and Cu diffusion in Ge is via the direct interstitial mechanism with similar features. Consequently, the diffusion correlation factor f that depends upon the diffusion

mechanism and the structure is the same for both the Pd and Cu direct interstitial diffusion. Considering Eqs. (1) and (2) the Pd diffusivity (D^{Pd}) and Cu diffusivity (D^{Cu}) are linked by:

$$D^{Pd} = D^{Cu}\sqrt{\frac{m_{Pd}}{m_{Cu}}}e^{\frac{g_{Cu}^{act}-g_{pd}^{act}}{k_BT}} \tag{3}$$

In previous work it was determined by Bracht [21] that Cu interstitial diffusion in Ge is described by the Arrhenius relation:

$$D^{Cu} = 3.2e^{-\frac{0.18\,eV}{k_BT}} \cdot 10^{-7}m^2s^{-1} \tag{4}$$

Therefore, by considering Eqs. (3) and (4) and the activation energy of migration derived by Tahini *et al.* [19] the Pd diffusivity is given by:

$$D^{Pd} = 4.14\,e^{-\frac{0.03\,eV}{k_BT}} \cdot 10^{-7}m^2s^{-1} \tag{5}$$

Figure 1 is the Arrhenius plot for Pd and Cu interstitial diffusion coefficients in Ge. It can be concluded from this figure that Pd diffusivities in Ge are lower than Cu. Pd diffusivities with respect to temperature are very small reflecting the extremely low activation energy of migration.

3. Connecting point defect parameters with bulk properties

In the present study we will employ the model by Varotsos and Alexopoulos (refered thereafter as the cBΩ model) [23-29] to interconnect the defect Gibbs energy g^i (i = defect formation f, self diffusion activation act, or migration m) with the bulk properties. In the cBΩ model it was proposed that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω, with c being the constant of proportionality The cBΩ model has been used for the study of the point defect processes in numerous materials [30-35]. Here we describe using the cBΩ model the

Pd intersitial diffusion coefficients in Ge using the isothermal bulk modulus and the mean volume per atom.

In the cBΩ model the defect Gibbs energy g^i is related to the bulk properties of the material via the relation [23-29]:

$$g^i = c^i B\Omega \quad (6)$$

Therefore, by Eqs. (1) and (6):

$$D = f a_0^2 \nu e^{-\frac{c^{act} B\Omega}{k_B T}} \quad (7)$$

Here the mean value method [33-35] is used to limit the dependence of c^{act} upon experimental uncertainties in the determination of the diffusivities, the expansivity and isothermal bulk modulus. In the mean value method a linear behavior of lnD^{Pd} with respect to $\frac{B\Omega}{k_B T}$ indicates that the cBΩ model is valid with the slope being c^{act} (refer to Eq. 7). There is indeed a linear relation between lnD^{Pd} with respect to $\frac{B\Omega}{k_B T}$ that can be described by:

$$D_{cB\Omega}^{Pd} = 3.94 e^{-\frac{0.0026 B\Omega}{k_B T}} \cdot 10^{-7} m^2 s^{-1} \quad (8)$$

Table 1 reports characteristic calculated Pd diffusion coefficients in Ge alongside the elastic and expansivity data [36-39] used in the cBΩ model. This table shows that the cBΩ model is in excellent agreement with the calculated diffusion coefficients of Pd in Ge. Differences between the calculated diffusivities and those calculated within the cBΩ model are less than 1%.

4. Conclusions

In the present study we employed previous experimental and theoretical results to calculate the diffusivity of Pd in Ge for a range of temperatures. The extremely low activation energy of migration of Pd in Ge is a paradigm and the

present approach can be extended to systems were the experimental determination of dopant diffusivities is difficult. At any rate the present calculations are a first approximation and experiments will be required to determine the diffusivities of Pd in Ge. Finally, we calculated a relation within the cBΩ model to calculated the Pd diffusivity. This can be extended in future work to investigate other defect properties related to Pd in Ge.

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. S. Brotzmann, H. Bracht, J. Appl. Phys. **103**, 033508 (2008)
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. A. Chroneos, J. Mater. Sci.: Mater. Electron. 24, 1741 (2013)
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. S.R. Herd, P. Chaudhari, M.H. Brodsky, J. Non-Cryst. Solids **7**, 309 (1972)
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. P. Varotsos, J. Appl. Phys. **101**, 123503 (2007)
31. B.H. Zhang, X.P. Wu, Appl. Phys. Lett. **100**, 051901 (2012)
32. I. Sakelis, J. Appl. Phys. **112**, 013504 (2012)
33. B.H. Zhang, AIP Adv. **4**, 017128 (2014)
34. F. Vallianatos, V. Saltas, Phys. Chem. Minerals **41**, 181 (2014)
35. A. Chroneos, R.V. Vovk, J. Mater. Sci.: Mater. Electron. DOI: 10.1007/s10854-014-2655-y
36. H.M. Kagaya, N. Shoji, T. Soma, Phys. Stat. Solidi B **139**, 417 (1987)
37. R. Krishnan, R. Srinivasan, S. Deverayanan, in Thermal Expansion of Crystals, Pergamon Press, Oxford (1979)
38. V. Hadjicontis, K. Eftaxias, J. Phys. Chem. Solids **52**, 437 (1991)
39. K. Eftaxias, V. Hadjicontis, Phys. Stat. Solidi B **160**, K9 (1990)

Table 1. Characteristic calculated Pd diffusion coefficients in Ge alongside the elastic and expansivity data [36-39] used in the cBΩ model.

T /K	B $/10^{11}Nm^{-2}$	Ω $/10^{-29}m^{3}$	D^{Pd} $/10^{-7}m^{2}s^{-1}$	$D_{cB\Omega}^{Pd}$ $/10^{-7}m^{2}s^{-1}$
827	0.709	2.289	2.72	2.72
877	0.703	2.292	2.78	2.79
925	0.697	2.294	2.84	2.85
975	0.690	2.298	2.90	2.90
1026	0.684	2.300	2.95	2.95
1074	0.678	2.303	2.99	3.00
1126	0.671	2.306	3.04	3.04
1176	0.665	2.309	3.08	3.08

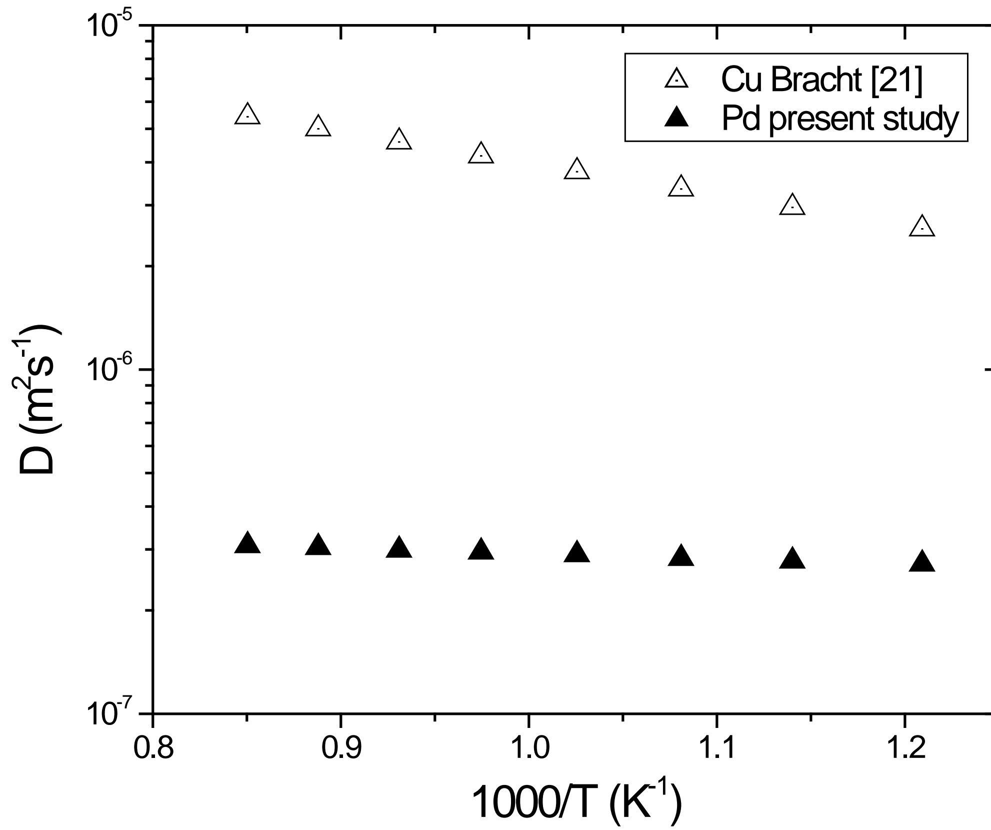

Figure 1 The Arrhenius plot for the calculated Pd diffusion as compared to the experimental Cu diffusion in Ge determined by Bracht [21].