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Fundamentals of Self-Diffusion in Amorphous Si-(B-)C-N

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1. Introduction

Using solid state thermolysis of pre-ceramic polymers, it is possible to produce amorphous Si-(B-)C-N ceramics which are a new form of a glassy-like state with an enormous stability range up to 1700 °C (see e. g. [1,2]). Si-(B-)C-N ceramics are promising candidates for the design of ultra-high temperature stable structure materials. The thermal stability and the crystallization depend sensitively on diffusion controlled atomic re-arrangement processes [3], which necessitates the investigation of self-diffusion. The determination of the B, C, N, and Si self-diffusivities is carried out with ion implanted stable isotopes and Secondary Ion Mass Spectrometry (SIMS). Details on synthesis and on the experimental set-up can be found in Refs. [4,5]. Two types of ceramics are investigated, $Si_3BC_{4.3}N_2$ (pre-annealed at 1720 °C) and $Si_{2.6}C_{4.1}N_{3.3}$ (pre-annealed at 1460 and 1350 °C).

2. Results and Discussion

As shown in the Arrhenius plot of Fig. 1 the determined self-diffusivities of Si, B, C, and N in Si-B-C-N are very low and are in the same order of magnitude. This means that diffusion controlled atomic arrangement processes governing crystallization are not dominated by one type of element but are influenced by all elements rather equally. A thermally activated behaviour is observed in analogy to crystalline materials, which can be described by an Arrhenius line. Very high activation enthalpies, ΔH^D, between 5.7 and 7.3 eV and pre-exponential factors, D_0, between 10^{-3} and 5 m^2/s are obtained [4,5]. For Si-C-N ceramics, the Si diffusivities for samples pre-annealed at 1460 and 1350 °C can be fitted with a unique straight line, indicating that diffusion is independent of the pre-annealing temperature in the temperature range investigated. The diffusivities are about one order of magnitude higher than those of Si-B-C-N, however, nearly the same activation enthalpy is obtained [5]. Measurements with neutron scattering [6] exhibited that amorphous Si-(B-)C-N is phase separated in the nm range. Comparison of the diffusivities in Si-C-N and in amorphous Si_3N_4 [7] indicate that the N and Si diffusion in Si-(B-)C-N takes place via phase-separated amorphous $Si_{3+0.25x}C_xN_{4-x}$ domains, and B diffusion via BNC_x domains.

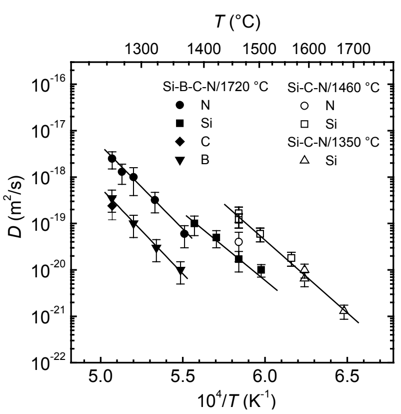

Fig. 1 Self-diffusivities as a function of reciprocal temperature in Si-(B-)C-N.

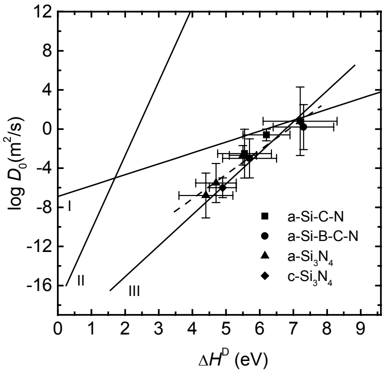

Fig. 2: Plot of ΔH^D vs. log(D_0) for the self-diffusion in amorphous Si-(B-)C-N in comparison to other materials. For details see text.

An overview on the self-diffusivities in amorphous Si-(B-)C-N ceramics in relation to literature data is given in Fig. 2, where ΔH^D is plotted versus log D_0. The data for crystalline metals (0.5 - 3 eV) [8] form straight line I, illustrating the existence of a compensation law in this kind of materials. Also located on that line are the data of crystalline semiconductors like Si (4.8 eV), Ge (3.1 eV) [9] and SiC (7.3 – 9.5 eV) [10] within an estimated error of $\Delta(\log D_0) = \pm 1$. The data of Si-(B-)C-N form also a linear relation between D_0 and ΔH^D away from line I (dashed line) together with the data of amorphous and crystalline Si_3N_4 [7], indicating a similar diffusion mechanism in materials with structures based on SiN_4 tetrahedra. Also given in Fig. 2 is the straight line III, which is formed by Si diffusivities in crystalline silicates [11] and which is very close to the data of Si-(B-)C-N. Here the basic structure element is a SiO_4 tetrahedron, which is quite similar to a SiN_4 tetrahedron. Completely different are the data of metallic glasses (line II), where a collective diffusion mechanism is operating [8].

3. Conclusion

In this paper the fundamentals of self-diffusion in amorphous, polymer-derived Si-(B-)C-N ceramics are outlined, as obtained with ion implanted stable isotopes and SIMS. The results are compared to other categories of materials.

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References

[1] E. Kroke et al., Mat. Sci. Eng. R26 (2000) 97.
[2] J. Bill, F. Aldinger, Adv. Mat. 7 (1995) 775.
[3] H. Schmidt, G. Borchardt, A. Müller, J. Bill, J. Non-Cryst. Solids 341 (2004) 133.
[4] H. Schmidt et al., J. Appl. Phys. 88 (2000) 1827.
[5] H. Schmidt et al., J. Non-Cryst. Solids 298 (2002) 232.
[6] J. Haug et al., Chem. Mater. 16 (2004) 72 and 83.
[7] H. Schmidt et al., Appl. Phys. Lett. 85 (2004), 582.
[8] F. Faupel et al., Rev. Mod. Phys. 75 (2003) 238.
[9] W. Frank in: Crucial Issues in Semiconductor Materials and Processing Technologies, S. Coffa, F. Priolo, E. Rimini, J. M. Poate (eds.), Kluwer, Dordrecht, 1992, 383.
[10] Hj. Matzke in: R. Freer (ed.), The Physics and Chemistry of Carbides and Borides, Kluwer, Dordrecht, 1989, p. 365 and references cited therein.
[11] F. Béjina, O. Jaoul, Earth Plan. Sci. Lett. (1997) 229.