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Influence of Oxygen Partial Pressure on the Wetting Behaviour of Silicon Nitride by Molten Silicon

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Abstract

The influence of the oxygen partial pressure on the wetting behaviour in the system Si/Si_3N_4 has been studied at 1450°C using the sessile drop method. The results have shown that the contact angle is a strong function of the oxygen partial pressure. Complete wetting could be achieved at very low oxygen partial pressures of around 10^{-24} atm.

Der Einfluß des Sauerstoffpartialdrucks auf das Benetzungsverhalten im System Si/Si_3N_4 wurde mittels der Methode des liegenden Tropfens bei 1450°C untersucht. Die erzielten Ergebnisse zeigten eine starke Abhängigkeit des Benetzungswinkels vom Sauerstoffpartialdruck. Eine vollständige Benetzung wurde bei einem Sauerstoffpartialdruck von ca. 10^{-24} atm erzielt.

L'influence de pression partielle d'oxygène sur le comportement du mouillage dans le système Si/Si_3N_4 a été étudiée en utilisant la méthode de la goutte posée à 1450°C. Les résultats obtenus ont montré que l'angle de contact du système est une forte fonction de la pression partielle d'oxygène. Le mouillage parfait est obtenu pour de très faibles pressions partielles d'oxygène près de 10^{-24} atm.

1 Introduction

Silicon nitride (Si_3N_4) is considered to be a potential material for the production of solar cell grade silicon.[1,2] The wetting behaviour of Si_3N_4 is therefore of importance for the successful development of the technology. In addition, the wetting behaviour in the system Si/Si_3N_4 is a critical parameter for infiltrating molten silicon into a reaction-bonded Si_3N_4 in order to obtain a dense material.[3] Consequently, the wettability of this system has been investigated by many authors[1–13] by the sessile drop method. However, the contact angle values (Table 1) obtained in these studies are very scattered and depend strongly on the experimental conditions. Swartz[13] observed that the wetting of reaction-bonded silicon nitride (RBSN) and chemical vapour deposition (CVD) Si_3N_4 by Si at 1430°C was a strong function of the inert gas pressure and found near-zero contact angles at low total pressures.

According to the Young equation ($\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos\theta$), the contact angle θ of a liquid metal on a solid substrate depends simultaneously on the surface energies of the solid, σ_{SV}, and of the liquid, σ_{LV}, and on the interfacial energy, σ_{SL}, between the solid and the liquid. A variation of one of the three interfacial energies could in principle cause a change of θ. It is well known that the surface tension of liquid Si measured under different experimental atmospheres is quite different due to contamination of the Si surface by oxygen and varies between 720 and 880 mJ/m^2 near its melting point.[14] However, this total variation in σ_{LV} of only 160 mJ/m^2 cannot explain the strong variations in contact angle between 0 and 134° observed in the system Si/Si_3N_4 (Table 1). Therefore, the strong variation of θ is essentially due to that of σ_{SV} and/or σ_{SL}, both being directly linked to the nature of the Si_3N_4 substrate surface.

The oxidation of Si_3N_4 is a well known and much studied phenomenon. Even at low oxygen partial pressures, the contamination of a Si_3N_4 surface by oxygen is considered to be inevitable. Some studies[15,16] have revealed the presence of oxygen on the surface of CVD Si_3N_4 materials. Maguire and Augustus[15] suggested that the interaction between

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Table 1. Contact angle, θ, of molten silicon on various silicon nitride substrates

Substrate	*Temperature (°C)*	*Atmosphere*	*θ (degrees)*	*Ref.*
Polycrystal	1 500	Vacuum	<40	4
Sintered	1 430	He	82 ± 3	1
	T.m.p.	Vacuum	134	5
	1 430	Ar	48 ± 3	6
Hot-pressed	1 427	Vacuum	43	7
	1 482		10	
	1 430	He	50 ± 3	1
RBSN	(?)	Vacuum	<10	8
	1 430	He	34 ± 2	1
			51 ± 2	
	1 450	N_2	0	9
	1 500	Vacuum	25	10
	1 670	Ar	10	11
RBSN as-received	1 430	He	$68\sim91$	1
CVD	1 450	He	~50	2
	1 430	$H_2\pm H_2O$		12
		$P_{O_2}=1{\cdot}1\times10^{-19}$ atm	47	
		$P_{O_2}=8{\cdot}7\times10^{-21}$ atm	45	
		$P_{O_2}=6{\cdot}0\times10^{-21}$ atm	43	

oxygen and Si_3N_4 leads to the formation of a non-stoichiometric oxynitride SiO_xN_y layer on the Si_3N_4 surface. The thickness of this layer was analysed by these authors to be about 3 nm. The composition of the SiO_xN_y layer can vary over a large range depending on the oxygen concentration which in turn depends on the experimental conditions of the Si_3N_4 deposition.[16,17] In contact with Si, the oxygen in the SiO_xN_y layer can be eliminated by reaction between Si and SiO_xN_y, leading to the formation of a gaseous species, SiO:[15]

$$4SiO_xN_y + [3y + 4(x-1)]Si \leftrightarrows ySi_3N_4 + 4xSiO \quad (1)$$

The elimination of oxygen will increase with temperature and with decreasing total pressure and oxygen partial pressure.

It is interesting to note that the observations of Duffy *et al.*[2] indicate that the contact angle of molten Si on oxynitride layers in helium is initially high but decreases with time as the oxynitride layers are converted to β-Si_3N_4 according to reaction (1). The variation of θ with time has been observed also with sintered Si_3N_4 in argon[6] and CVD Si_3N_4 substrates in a H_2+H_2O mixture.[12] Barsoum and Ownby[12] observed a small decrease in θ with decreasing oxygen partial pressure P_{O_2} but only for a quite limited range of P_{O_2}.[12] In this work the sessile drop method has been used to study the influence of oxygen partial pressure on the wetting behaviour in the system Si/Si_3N_4 over a large range of P_{O_2}.

2 Experimental

The method used to obtain different oxygen partial pressures is identical to that employed by John and Hausner for the system Al/Al_2O_3.[18] A closed metal crucible is used which contains the Si sample on the Si_3N_4 substrate. Different oxygen partial pressures can be obtained with different metals as the crucible material (Me = Fe, Mo, Ta, Ti and Zr). In this case the oxygen partial pressure inside the crucible is determined by the corresponding metal/metal oxide equilibrium oxygen pressure which can be calculated using thermodynamic data.[19,20] The crucible is located inside a dense alumina tube, which is heated by $MoSi_2$ resistance elements. The tube is connected to a gas feed system and a vacuum device. The experiments are conducted in purified argon (purity of 99·998%) of total pressure of one atmosphere. The temperature is measured by a Pt/Pt + 10%Rh thermocouple located in the immediate vicinity of the sample. The furnace is heated to 1450°C with a linear heating rate of 4°C/min. The temperature at 1450°C is kept constant for 3 h and then the furnace is cooled down with a linear cooling rate of 4°C/min. The contact angle is determined after cooling.

The substrates used are commercial sintered silicon nitride (Ekasin S from ESK, Germany) which contains 3% Al_2O_3, 2% La_2O_3 and 1% Y_2O_3 as sintering aids. After mechanical polishing with diamond pastes of 1 μm, the average surface roughness of the substrates Ra is 0·06 μm. After

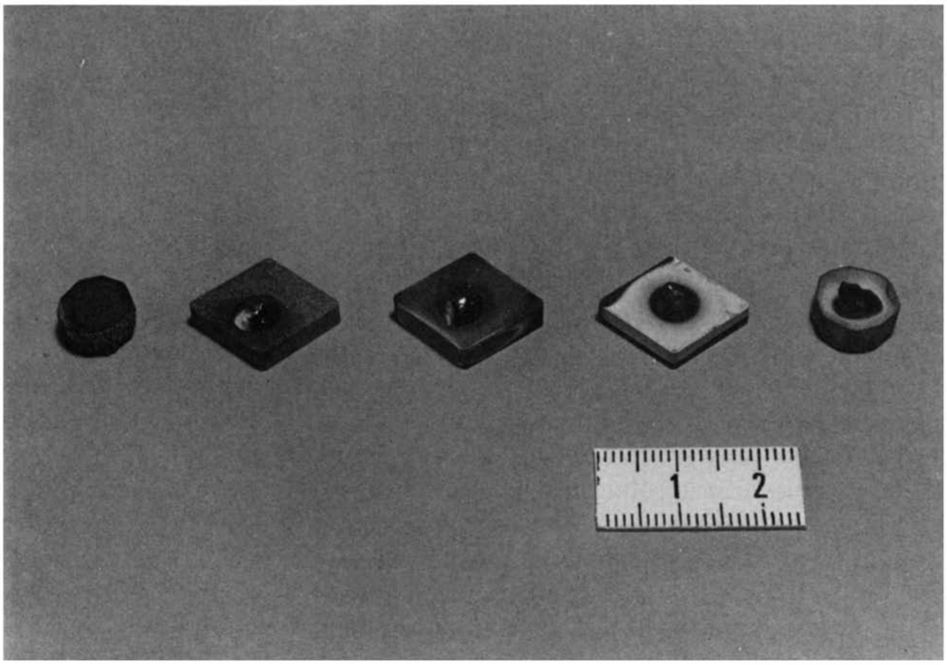

Fig. 1. Si drops on Si_3N_4 after wetting experiments at 1450°C under various oxygen partial pressures. From right to left: $P_{O_2} = 10^{-9}$ atm (Fe/FeO), $P_{O_2} = 10^{-9}$ atm (Mo/MoO_2), $P_{O_2} = 9{\cdot}0 \times 10^{-17}$ atm (Ta/Ta_2O_5), $P_{O_2} = 4{\cdot}4 \times 10^{-22}$ atm (Ti/Ti_2O_3) and $P_{O_2} = 3{\cdot}4 \times 10^{-24}$ atm (Zr/ZrO_2).

polishing, the substrates are ultrasonically cleaned in acetone and then dried in air.

High purity silicon (99·999%) is used in this study. Before each experiment the silicon sample of about 60 mg is etched in 40% hydrogen fluoride solution and then washed with water and acetone.

3 Results and Discussions

If iron is used as crucible material, the drop of Si appears as being not molten completely at 1450°C. Only the part which has been in contact with the substrate seems to have been in the liquid state. The contact angle, θ, is estimated to be approximately 180° in this case. In the case of molybdenum, a symmetric Si drop has formed and a contact angle of about 53° has been observed. In both cases the surfaces of the silicon and Si_3N_4 substrate are strongly oxidised. When a tantalum, titanium or zirconium crucible is used the molten Si has a metallic appearance; in the case of zirconium spreading has occurred (Fig. 1).

The measured contact angles at 1450°C and at a total pressure of 1 atm argon, together with those obtained by Barsoum and Ownby[12] at 1430°C and at a total pressure of 1 atm $H_2 + H_2O$ mixture are plotted in Fig. 2 as a function of the oxygen partial pressure. If Fe/liquid FeO in the case of the iron crucible and Mo/MoO_2 in the case of molybdenum crucible are taken as the possible equilibria of the reaction between the metal and the metal oxide, thermodynamic calculations indicate that the oxygen partial pressure of the Fe/FeO equilibrium and that of the Mo/MoO_2 equilibrium are very close to each other.[19,20] In view of the uncertainties of the experimental values of the free energy of formation of the oxides ($\pm 12{\cdot}5$ kJ/mol for FeO and ± 25 kJ/mol for MoO_2,[20] an oxygen partial pressure of about 10^{-9} atm is taken for both metal/metal oxide equilibria. From Fig. 2 it can be seen that the contact angle, θ, decreases sharply from 180° for the partially molten Si (Fe/FeO) to 53° (Mo/MoO_2).

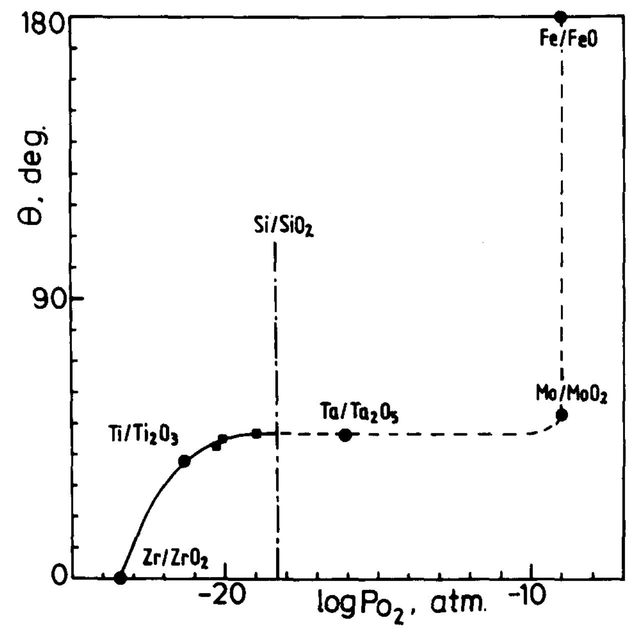

Fig. 2. Contact angle θ in the system Si/Si_3N_4 as a function of oxygen partial pressure P_{O_2} at 1450°C. The points noted by (■) are the results obtained by Barsoum and Ownby with CVD-Si_3N_4 substrates at 1430°C.[12]

This sudden variation of θ around $P_{O_2} \simeq 10^{-9}$ atm is attributed to the formation of a compact solid SiO_2 film.

Thermodynamic calculations indicate that the Si/SiO_2 equilibrium oxygen pressure at 1450°C is equal to $5{\cdot}0 \times 10^{-19}$ atm.[20] This means that the molten silicon would oxidise to SiO_2 at oxygen partial pressures above $5{\cdot}0 \times 10^{-19}$ atm. However, due to the reaction between Si and SiO_2 leading to the formation of the gaseous species SiO ($SiO_2 + Si \rightleftarrows 2SiO$) with an equilibrium pressure of $P_{SiO} \simeq 2{\cdot}0 \times 10^{-2}$ atm at 1450°C, a complete passive oxidation of liquid Si would be possible only at oxygen partial pressures far above $5{\cdot}0 \times 10^{-19}$ atm. In fact, studies of the solution of oxygen in liquid Si[21] have shown that complete surface oxidation does not occur until the oxygen partial pressure exceeds $\simeq 10^{-2}$ atm. Wagner[22] attributes this result to the separation of the Si surface from the ambient atmosphere by a gaseous boundary layer through which O_2 and SiO counter-diffuse. The boundary layer maintains a gradient in oxygen partial pressure from that of the ambient atmosphere to a value at the surface which can be less than that required for oxidation. As one result of Wagner's analysis, the liquid Si surface is not expected to oxidise (or solid SiO_2 formed on the Si surface is expected to deoxidise) at ambient oxygen levels below $\simeq 10^{-8}$ atm in a flowing atmosphere. This limit of P_{O_2} is very close to the value of P_{O_2} ($\simeq 10^{-9}$ atm) where the contact angle varies suddenly in the static argon atmosphere (Fig. 2). It is postulated that in the case of the iron crucible a thick SiO_2 film has formed at the Si surface, preventing the metal from free flowing. In the case of the molybdenum crucible the film has ruptured, resulting in a subsequent flow of the melt.

In the P_{O_2} range between 10^{-9} and $5{\cdot}0 \times 10^{-19}$ atm (Si/SiO_2), the contact angle, θ, remains practically constant ($\theta \simeq 48°$). This dependence of θ on P_{O_2} is probably due to the reactions $Si + O_2 \rightleftarrows SiO_2$ and $Si + SiO_2 \rightarrow 2SiO$ which would fix a local oxygen partial pressure ($\sim 5{\cdot}0 \times 10^{-19}$ atm) near the solid–liquid–vapour three-phase boundary. In the case where a metal crucible is used, by which a higher equilibrium oxygen partial pressure between the metal and the metal oxide than that of the Si/SiO_2 couple can be established, the Si itself can act as a possible oxygen getter and establish the corresponding oxygen partial pressure in the vicinity of the three-phase boundary. This would be an explanation for the plateau in Fig. 2 where all the values of θ are identical above 5×10^{-19} atm up to the point, where the flow of Si is prevented by a thick SiO_2 layer. A similar observation has been made in the case of the aluminium which has been investigated in a previous work.[18] The high oxygen affinity of aluminium and the relatively low temperature (700°C) used for the wetting experiments do not lead to the rupture of the aluminium oxide film formed on the aluminium surface and, consequently, the contact angle, θ, of the system Al/Al_2O_3 would be expected to increase with increasing oxygen partial pressure. The high oxygen partial pressures obtained by using copper and iron as the crucible materials induce an important thickening of the aluminium oxide film around the aluminium drop, and no complete melting of the aluminium on the sapphire substrates at 700°C could be observed in these cases.[18]

In the P_{O_2} range below $5{\cdot}0 \times 10^{-19}$ atm up to $3{\cdot}4 \times 10^{-24}$ atm (Zr/ZrO_2), the contact angle is found to decrease with decreasing P_{O_2}, due to the diminution of the oxygen content in the oxynitride SiO_xN_y layer which would exist on the surface of the Si_3N_4 substrate. Complete wetting ($\theta = 0$) occurs when a strong oxygen getter such as zirconium ($P_{O_2} = 3{\cdot}4 \times 10^{-24}$ atm) is present in the system. This result suggests that when metals are used as the crucible materials with a lower oxygen partial pressure than that of the Si/SiO_2 couple they can act as a getter for oxygen.

Sintered Si_3N_4 may contain secondary phases which are formed between the Si_3N_4 and the sintering additives. A possible influence on the wetting behaviour cannot be excluded. However, this effect is considered to be secondary in comparison with the influence of the oxygen partial pressure. This assumption is supported by the fact that the results reported here are in good agreement with the observations made by Barsoum and Ownby[12] who used CVD-Si_3N_4 which does not contain any sintering additive.

4 Conclusions

The influence of different oxygen partial pressures on the wetting behaviour in the system Si/Si_3N_4 has been investigated using the sessile drop method at 1450°C. The results demonstrate that the oxygen concentration in the system is responsible for the value of the contact angle and the interfacial reactions between Si and Si_3N_4. Under the experimental conditions an oxygen partial pressure of about 10^{-9} atm is the upper limit for the formation of a silicon drop which is completely molten. Below this limit the contact angle seems to remain constant to $5{\cdot}0 \times 10^{-19}$ atm and then decreases continuously with decreasing oxygen partial pressure. At very low oxygen partial pressures in the region of about 10^{-24} atm complete wetting can be achieved at 1450°C.

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