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THERMAL ANALYSIS OF THE DIRECT NITRIDATION OF SILICON TO Si_3N_4

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The direct nitridation of different silicon powders was investigated by thermogravimetry. The chemical composition of the final product, produced unter the optimum nitridation conditions, varied in the region between $Si_3N_{3.41}$ and $Si_3N_{3.93}$, depending on the basic material. The reasons for the incomplete nitridation ratio are discussed.

The nitridation was kinetically analyzed, and the activation energies of the nitridation reaction were determined. The mechanisms of the prereaction and the main reaction generally correspond to phase boundary reactions with different reaction orders.

Si_3N_4 exhibits excellent chemical and mechanical properties up to high temperatures. It also has a high strength at high temperatures, a good oxidation resistance, a good corrosion resistance to many melts, and a good temperature-shock resistance. It can be used up to temperatures of about 1300°. Cheap native raw materials of various qualities are available. Si_3N_4 is specially applied as a material for engine and turbine construction, for combustion furnaces and for metallurgical equipment. Such Si_3N_4 is produced either by the nitridation of Si powder after forming of the object (RBSN), or by the sintering of ultrafine Si_3N_4 powder under hot pressing (HPSN) or hot isostatic pressing (HIPSN).

The ultrafine Si_3N_4 powder can be produced by the direct nitridation of Si powder, by the carboreducing nitridation of SiO_2, and by the gas or liquid-phase reaction between silicon chloride and ammonia. The preferred route is the direct nitridation of Si powder in a N_2/H_2 gas mixture, followed by fine grinding.

The process of the phase transition Si/Si_3N_4 depends on the temperature programme and the $N_2:H_2$ ratio in the nitriding gas mixture, according to the equilibrium diagram (Figs 1 and 2). Hence the conditions for direct nitridation are as follows:

— a nitrogen-rich, dry nitriding gas, to prevent the thermal decomposition of Si_3N_4 during nitridation;

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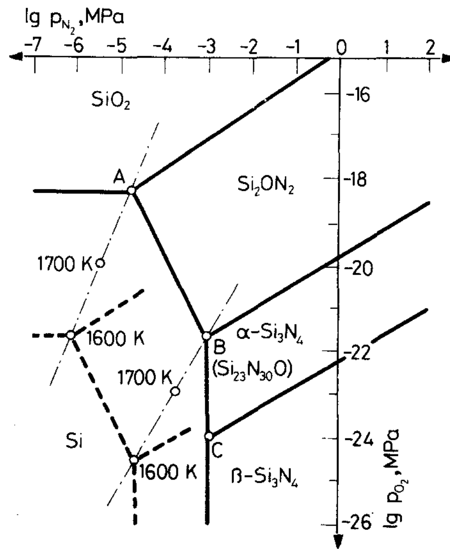

Fig. 1 Equilibrium diagram for the system Si—O—N at 1800 K

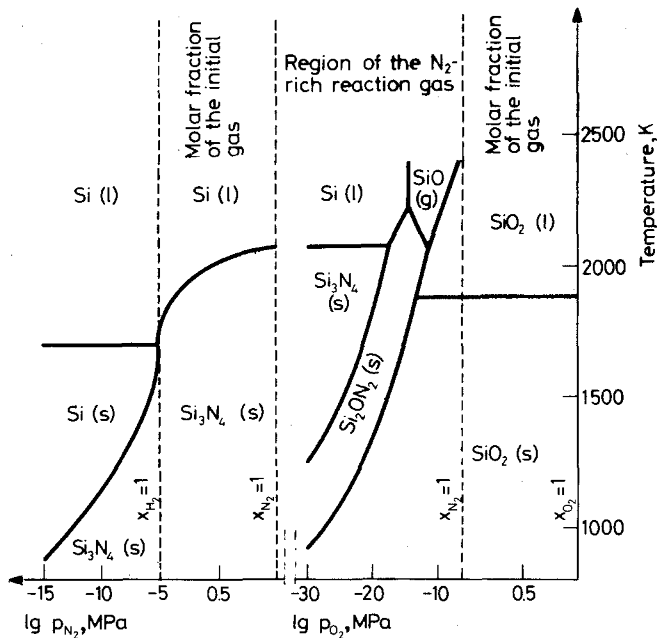

Fig. 2 Equilibrium diagram for the system Si—O—N—H

— a very low O_2 partial pressure, to prevent the preferred reaction of Si or Si_{34} to SiO_2 as the thermodynamically most stable phase;

— high reaction temperature, but below the region of decomposition of Si_3N_4 and below the melting point of Si, to increase the region of existence of the Si_3N_4 phase and to decrease the negative influence of the oxygen impurities in the nitriding gas [1].

Experimental

The general conditions of direct nitridation must also be fulfilled in the thermoanalytical investigation. The course of the nitridation and the nitridation degree were determined by thermogravimetry with a Mettler TA-1 thermoanalyzer. A high-temperature furnace with an additional molybdenum protective tube (to remove the oxygen traces in the TA-1), a W-WRe crucible holder, and special Si_3N_4 crucibles were used for these measurements. The 0.08 cm^3 crucibles were produced by the RBSN method. They do not oxidize silicon as the usual Al_2O_3 crucibles do, they are compatible with the reactive sample materials and with the reducing gas atmospheres, and they are stable up to above 1400° (see Fig. 3). The

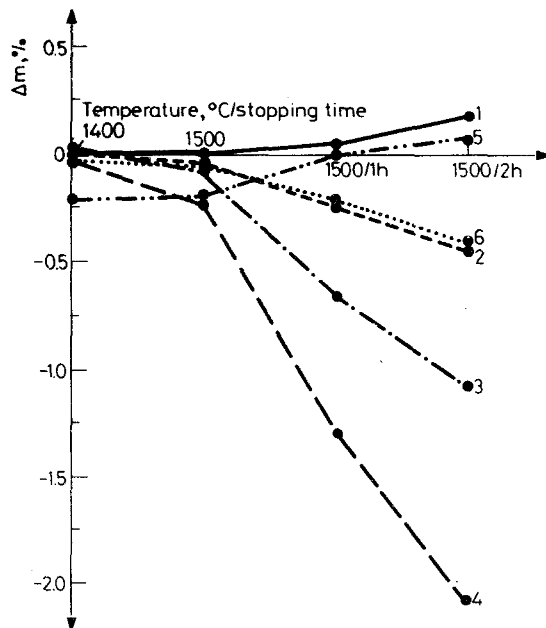

Fig. 3 Mass variation of Si_3N_4-crucibles in N_2/H_2

standard rate of heating was 10 deg min^{-1} up to 1250°, then 1 deg min^{-1} up to 1450°. The nitriding gas atmosphere used was 10 l h^{-1} purest nitrogen containing 400 ppm hydrogen, but as free as possible of oxygen and moisture. Traces of oxygen and water were removed with a solid electrolytic cell. The hydrogen was admixed into the nitrogen stream through a tempered rubber tube. The H_2/H_2O contents were determined with a solid electrolytic cell [2].

The sample material used in these measurements, its preparation and selected analytical data are listed in Table 1. The sample mass was 50 mg.

Table 1 Silicon basic material for the direct nitridation

Substance	Preparation	Analysis	
		O	Fe
		mass-%	
Semiconductor A	sieved <40 μm	0.3	0.04
Semiconductor B	sieved <40 μm	0.8	0.03
Flying dust f (fine)	with HF cleaned	1.5	0.003
Flying dust g (coarse)	ground and with HF cleaned	0.7	0.075
Technical Si 1	5 min ground	0.9	0.87
Technical Si 2	20 min ground	1.8	0.87

The thermogravimetric data were recorded with an MPS 4944 microcomputer, while the data processing, including the kinetic analysis, was performed with a KRS 4201 minicomputer [3]. The nitridation degree was calculated fom the thermogravimetrically determined mass increase on the assumption that this is caused only by the N_2-absorption of the silicon (the impurities in the Si and the loss in mass due to decomposition of already formed Si_3N_4 were neglected.

Results and discussion

The process of direct nitridation of the various Si materials is illustrated in Fig. 4. The nitridation generally begins slowly, with a prereaction between 1200 and 1300°. Above 1300° it proceeds quickly. Only the fine portion of the flying dust is nitrided in one stage, but not till higher temperature. The most important thermoanalytical results on the direct nitridation of the various Si materials are listed in Table 2. The chemical composition of the final product produced under the above nitridation conditions is between $Si_3N_{3.41}$ and $Si_3N_{3.93}$, depending on the basic material and especially on its oxygen content. This means that the nitridation degree is between 85 and 98%.

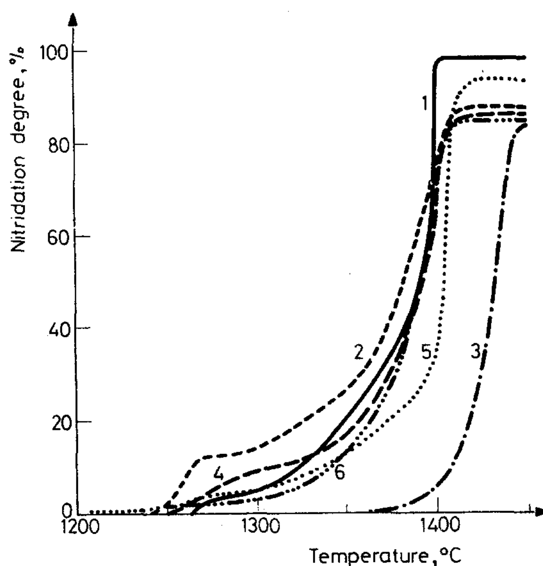

Fig. 4 Nitridation process of various Si-materials.
Curve 1: semiconductor A; curve 2: semiconductor B; curve 3: flying dust f; curve 4: flying dust g; curve 5: techn. Si 1; curve 6: techn. Si 2

Table 2 Thermoanalytical test values of the direct nitridation

Substance	React.*	Reaction range, °C	mass increase, mass-%	Fin. prod. + Nitrid. degree at 1450 °C	%
Semiconductor A	1	1260–1270	1.8		
	2	1300–1410	62.1	$Si_3N_{3.93}$	98.3
Semiconductor B	1	1245–1290	8.2		
	2	1295–1415	48.8	$Si_3N_{3.52}$	88.0
Flying dust f	2	1365–1450	56.6	$Si_3N_{3.41}$	85.2
Flying dust g	1	1250–1295	5.7		
	2	1310–1410	50.6	$Si_3N_{3.44}$	86.1
Technical Si 1	1	1205–1280	2.0		
	2	1285–1420	60.6	$Si_3N_{3.75}$	93.8
Technical Si 2	1	1225–1275	4.5		
	2	1290–1410	55.1	$Si_3N_{3.64}$	90.9

* Reaction 1: prereaction; reaction 2: main reaction

Table 3 Kinetic parameters and mechanisms of the direct nitridation

Substance	Mechanism	n	E_a, kJ/mol	$\ln k_0$ min^{-1}	Model n
Prereaction (reaction 1)					
Semiconductor A	Kinetics 2nd order	1.9	8149 ± 28	640	2
Semiconductor B	Phase boundary reaction	1.3	2867 ± 5	220	3/2
Flying dust g	Phase boundary reaction	0.8	1881 ± 4	140	3/2
Technical Si 1	Kinetics 2nd order	2.0	1840 ± 90	140	2
Technical Si 2	Kinetics 2nd order	(1.2)	1375 ± 122	110	2
Main reaction (reaction 2)					
Semiconductor A	2-dimens. diffusion	—	1682 ± 11	120	−1
Semiconductor B	Kinetics 1st order	0.9	959 ± 1	70	1
Flying dust f	Phase boundary reaction	0.2	1054 ± 4	70	1/3
Flying dust g	Kinetics 1st order	1.2	1597 ± 1	120	1
Technical Si 1	Phase boundary reaction	0.3	825 ± 3	60	1/2
Technical Si 2	Kinetics 1st order	1.0	1375 ± 1	100	1

n = reaction order, E_a = activation energy, $\ln k_0$ = preexponential factor

The incomplete nitridation is caused by the inhibition of nitrogen access to the silicon if a stable oxide layer is formed on the surface of the silicon particles due to the oxygen content of the silicon or that in the reaction chamber of the thermoanalyzer. Furthermore, at advanced temperatures the increasing condensation of the first nitrided near-surface layers and the increasing sintering of the silicon particles hinder the diffusion of nitrogen through the decreasing free sample surface in the thermoanalytical nitridation, and lead to a long reaction time.

The kinetics of the nitridation differs with the basic material. These differences are visible from the shapes of the reaction curves in Fig. 4. The nitridation process was kinetically analyzed by various methods [4–6], and the activation energies were determined. The kinetic parameters and the appropriate reaction mechanisms selected from 10 models are listed in Table 3. The mechanisms of the prereaction and the main reaction generally correspond to phase boundary reactions, but with very different reaction orders. The main reaction of nitridation of semiconductor A (the sample with the highest nitridation degree) is diffusion-controlled. The activation energies of the prereaction and the main reaction differ very strongly depending on the basic material.

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Zusammenfassung — Die direkte Nitridierung von verschiedenen Siliciumpulvern wurde thermogravimetrisch verfolgt. Die chemische Zusammensetzung des unter optimalen Nitridierungsbedingungen hergestellten Endprodukts lag zwischen $Si_3N_{3,41}$ und $Si_3N_{3,93}$ in Abhängigkeit vom Ausgangsmaterial. Die Gründe für die teilweise unvollständige Nitridierung werden diskutiert.
Die Kinetik der Nitridierung wurde analysiert, ihre Aktivierungsenergien wuvden bestimmt. Der Mechanismus sowohl der Vor- wie auch der Hauptreaktion entspricht einer Phasengrenzreaktion mit unterschiedlichen Reaktionsordnungen.

Резюме — Методом ТГ изучено прямое азотирование различных порошков кремния. Химический состав конечного продукта азотирования в зависимости от исходного материала изменяется между $Si_3N_{3,41}$ и $Si_3N_{3,93}$. Обсуждены причины различного стехиометрического состава образующихся продуктов. Исследована кинетика реакций азотирования и определены их энергии активации. Механизм как предварительной, так и основной реакции, в общем, соответствует реакции на границе раздела фаз с различным порядком реакций.