for oxide crystals and some borate and silicate glasses. The horizontal axis of the figure is the calculated optical basicity of the matrix, which was proposed by Duffy and Ingram [7] to estimate Lewis basicity of oxyanionic crystals, glasses and solutions. The emission from 4-co-ordinated Mg^{2+} concentrates in the lower energy (higher $\Delta 2\theta$) region and that from 6-co-ordinated in the opposite region. It is clearly seen in the figure that all the emissions from the phosphate glasses with a composition ranging from $x = 40$ to 58 are located in the higher energy region. This suggests that 6-co-ordinated Mg^{2+} is predominant in the glasses. Since the line shape and the full-width at half maximum intensity (≈ 0.7 eV) were found to be almost identical for all the glasses and MgO (the reference crystal), the contribution from 4-co-ordinated Mg^{2+} seems to be negligible. Therefore, it is inferred that the abrupt change in the physical properties of $MgO-P_2O_5$ glasses around metaphosphate composition should not be attributed to the change in the co-ordination number of Mg^{2+}, as has been postulated. At present we have no convincing alternative explanation.

It may be interesting to note that there is a measurable difference between the peak energies for the metaphosphate glass and crystal, the emission from the crystal being at higher energy. This fact reveals that Mg–O bonding is stronger in the glass than in the crystal [6]. A similar phenomenon was also observed in the ESR spectrum of Cd^+ in CaP_2O_6 glass and β-CaP_2O_6 crystal [8].

References

1. E. KORDES, W. VOGEL and R. FETEROWSKY, *Z. Elektrochem.* **57** (1953) 282.
2. E. KORDES and R. NIEDER, *Glastech. Ber.* **41** (1968) 41.
3. E. KORDES and J. NAVARRETE, *ibid.* **46** (1973) 113.
4. L. D. BOGOMOLOVA, V. A. JACHKIN, V. N. LAZUKIN, T. K. PAVLUSHKINA and V. A. SHMUCKLER, *J. Non-Cryst. Sol.* **28** (1978) 375.
5. H. HOSONO, H. KAWAZOE and T. KANAZAWA, *ibid.* **37** (1980) 427.
6. H. KAWAZOE, H. KOKUMAI, T. KANAZAWA and Y. GOHSHI, *J. Phys. Chem. Sol.* in press.
7. J. A. DUFFY and M. D. INGRAM, *J. Non-Cryst. Sol.* **21** (1976) 373.
8. H. HOSONO, H. KAWAZOE, J. NISHII and T. KANAZAWA, *ibid.* in press.

Received 17 November
and accepted 12 December 1980

K. ISOZAKI
H. HOSONO
H. KOKUMAI
H. KAWAZOE
T. KANAZAWA
Department of Industrial Chemistry,
Faculty of Technology,
Tokyo Metropolitan University,
Fukasawa,
Setagaya-ku,
Tokyo 158,
Japan
Y. GOHSHI
Department of Industrial Chemistry,
Faculty of Engineering,
University of Tokyo,
Hongo,
Bunkyo-ku,
Tokyo 113,
Japan

The removal of surface silica and its effect upon silicon nitridation kinetics

It is well established that a thin (typically ~ 3 nm) native oxide layer covering the surface of silicon particles has a pronounced retarding effect on nitridation kinetics and that pretreatment of the powder with the object of removing the film leads to accelerated kinetics [1–3]. This letter presents the results of a brief study of the effects of pretreatments on the nitridation kinetics for high-purity silicon.

Silicon powder (~ 99.99 Si; Fe,Al ~ 100 ppm: < 8 μm) prepared from ingot was isostatically compacted (200 MPa) into cylinders (~ 1 cm diameter x 1 cm length) and nitrided in a controlled-atmosphere thermogravimetric balance. Both the powder preparation method and the balance are

0022–2461/81/082319–03$02.30/0

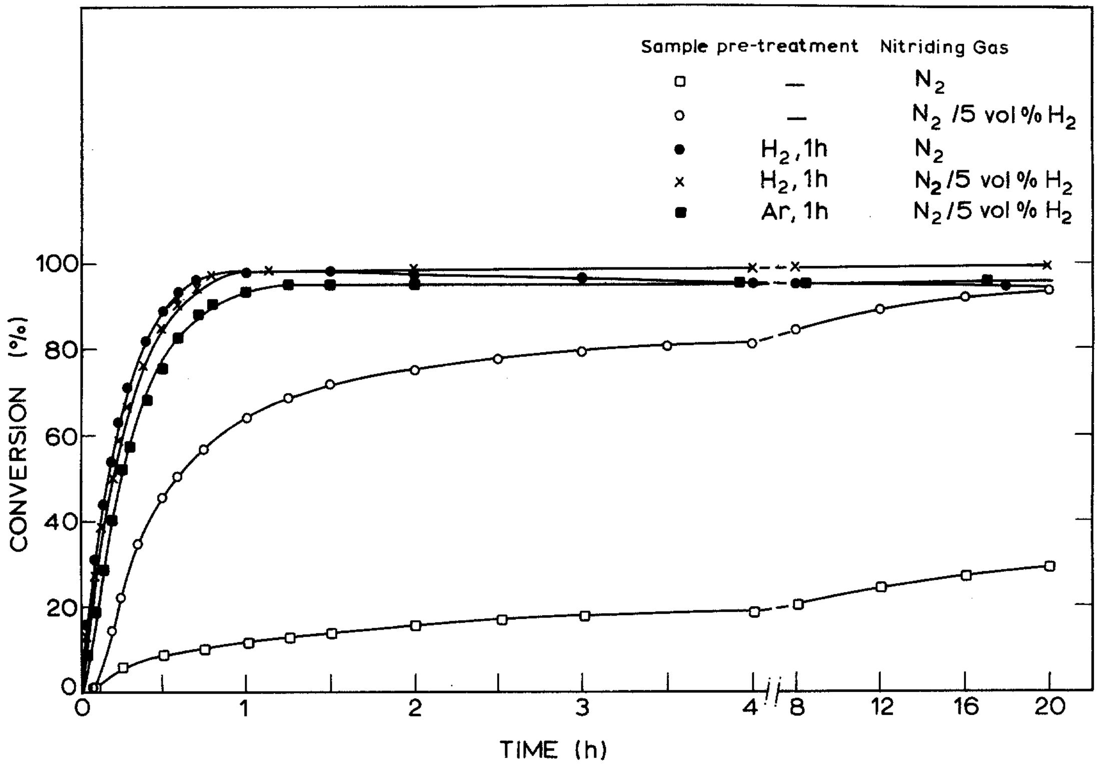

Figure 1 Silicon nitridation kinetics.

described elsewhere [4]. The O_2 and H_2O contents of the various pretreatment and nitriding gases were monitored and were typically close to 10 ppm. The balance incorporated a facility for raising or lowering the sample which was contained in a small perforated alumina crucible.

The schedule for a typical pretreatment and nitridation run was as follows. With the hot zone of the furnace adjusted to the reaction temperature (1350° C) a sample was positioned high in the balance where its temperature was less than 100° C and the system pumped down to a pressure of $\sim 10^{-2}$ mm Hg. The pretreatment gases (Ar or H_2) were then passed into the balance and a flow rate of $\sim 100\,\text{ml min}^{-1}$ established. This gas flow was maintained for ~ 6 h after which the sample was lowered into the hot zone for a pretreatment of 1 h. After the pretreatment the sample was raised to a higher point in the system where its temperature was ~ 850° C. The pretreatment gas was then replaced, over a period of about 2 h, with the nitriding gas (either N_2 or $N_2 + 5\,\text{vol}\%\,H_2$) after which the sample was lowered into the hot zone when the weight gain was continuously monitored. The nitridation curves are shown in Fig. 1 together with details of the pretreatment and nitriding conditions. Fracture surfaces of the nitrided samples were examined in the SEM and the $\alpha:\beta$ nitride ratios, determined by XRD following the procedure described by Gazzara and Messier [5], were, in all cases, close to 5.1.

The experiments confirm that high-purity silicon powder, usually regarded as relatively unreactive, can be rapidly nitrided to nearly complete conversion following pretreatments designed to remove the silica layer. It is especially significant that the Ar-pretreatment is effective since such a stage might readily be incorporated into existing procedures for the commercial production of reaction-bonded silicon nitride (RBSN).

The micrographs shown in Fig. 2 are essentially indistinguishable from those for the other pretreatment and nitriding conditions. The microstructures, and particularly the morphology of the "transgranular" fracture surfaces, are not readily reconciled with the "thickening whisker" hypothesis

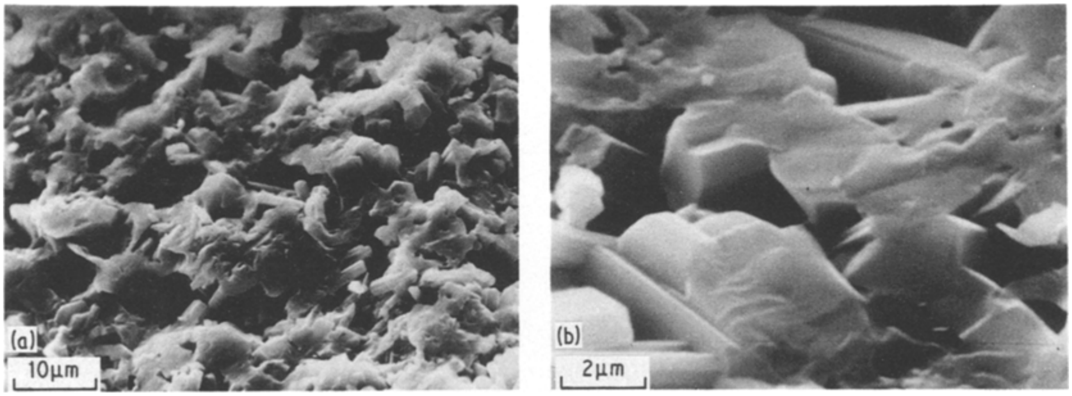

Figure 2 (a and b) Scanning electron micrographs of the fracture surface of a sample pre-treated in H_2 for 1 h and nitrided in N_2.

for the formation of RBSN but rather with the deposition of "massive" CVD-Si_3N_4, as discussed elsewhere [6].

References

1. A. ATKINSON and A. J. MOULSON, *Sci. Ceram.* 8 (1976) 111.
2. W. A. FATE and M. E. MILBERG, *J. Amer. Ceram. Soc.* 61 (1978) 531.
3. D. CAMPOS-LORIZ and F. L. RILEY, *J. Mater. Sci.* 14 (1979) 1007.
4. A. ATKINSON, A. J. MOULSON and E. W. ROBERTS, *J. Amer. Ceram. Soc.* 59 (1976) 285.
5. C. P. GAZZARA and D. R. MESSIER, *Bull. Amer. Ceram. Soc.* 56 (1977) 777.
6. A. J. MOULSON, *J. Mater. Sci.* 14 (1979) 1017.

*Received 19 November
and accepted 12 December 1980*

M. N. RAHAMAN
A. J. MOULSON
*Department of Ceramics,
University of Leeds,
Leeds, UK*

X-ray studies on the high pressure behaviour of some rare-earth formates

As part of a programme of high pressure X-ray studies on some solids, the results of the high pressure behaviour of Hg_2Cl_2 [1] and K_2SnCl_6 [2] have previously been reported. Results of a similar study on the formates of lanthanum, cerium and gadolinium [$La(O_2CH)_3$, $Ce(O_2CH)_3$ and $Gd(O_2CH)_3$] rare-earth elements will be presented in this note. These compounds are isomorphous and crystallize in the trigonal system, space group $R3m$, with one molecule per unit cell [3–6]. Recently Hamann [7] studied the infrared (i.r.) spectra of these solids under pressure and reported pressure induced phase transitions. A perusal of the literature shows that no X-ray studies on the high pressure behaviour of these solids seem to be available. In an effort to study the structural changes that occur under pressure, *in situ* X-ray diffraction studies were carried out. This note presents the detailed results of this investigation.

The samples used in the present study were kindly supplied by Dr D. Hamann of CSIRO Applied Chemistry Laboratories, Australia. The details of the growth and purity of these compounds are given by Hamann [7]. The lattice parameters of these compounds determined from the powder patterns on the basis of a rhombohedral lattice with a hexagonal cell are listed in Table I along with the earlier reported values for comparison. The values of the lattice parameters in the present study are slightly higher than the reported ones.

X-ray diffraction data of these compounds at room temperature and at different pressures were obtained using a diamond anvil apparatus

0022–2461/81/082321–03$02.30/0