Kinetics of the Topotactic Formation of Siloxene

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The kinetics of the topotactic transformation reaction of the epitaxial Zintl phase CaSi₂ into the sheet polymer siloxene in aqueous hydrochloric acid solutions have been studied. The effects of acid concentration, temperature, and crystal orientation on the reaction rates have been determined by in-situ electrical conductivity measurements. The reaction rate is found to be anisotropic with the reaction front propagating about 10 times faster in-plane to the CaSi₂ layering than perpendicular to it. The reaction is generally limited by the chemical reaction rate and is thermally activated with an activation energy of 0.40(2) eV. The total reaction rate is significantly influenced by the HCl concentration with a maximum value observed for a concentration of 13 wt %. The implications of the kinetic data obtained are discussed in detail.

Introduction

The kinetics of homogeneous chemical reactions in the gas or liquid phase are well understood. In contrast, reactions involving solids occur heterogeneously so that transport processes may play an important role, in some cases even limiting the reaction progress and rendering a kinetic description more complex.¹ Somewhat easier to describe are reactions which are limited to the surface of the reacting solid, for example etching or dissolution processes. On the other hand, topochemical or topotactic reactions are typically characterized by extended reaction zones and especially by the formation of product layers separating the reactants which have to be overcome by complex diffusion processes. Consequently, no generally valid theoretical concepts exist for a description of such solid-state reactions,² making an unequivocal interpretation of experimental data quite difficult.

The layered sheet polymer siloxene is particularly known for its intense visible luminescence which is unique among silicon based materials. Siloxene prepared according to Wöhler³ is formed by 2-dimensional Si layers, corresponding to the {111} double layers of crystalline Si, which are saturated by H- and OHligands and stacked one upon another.^{4,5} Sheet polymers are obtained from the layered Zintl phase CaSi₂ by a topotactic exchange reaction in hydrochloric acid in which the Ca atoms are replaced by H and OH leaving the Si backbone intact:

$$[\operatorname{CaSi}_2]_n + 2n \operatorname{HCl} + xn \operatorname{H}_2 \operatorname{O} \to n \operatorname{CaCl}_2 + [\operatorname{Si}_2(\operatorname{OH})_x \operatorname{H}_{2-x}]_n + xn \operatorname{H}_2 (0 \le x \le 2)$$
(1)

where, depending on the exact transformation condi-



Figure 1. Crystal structure of the tr6 modifications of CaSi₂ 1 and siloxene Si₂HOH 2.

tions, a varying degree of hydrolysis can occur.^{6,7} Figure 1 shows the crystal structure of CaSi₂ 1 and siloxene $Si_2HOH 2$ in the tr6 modifications.⁸ It is evident that the structure of the substances is highly anisotropic and that therefore the physical and chemical properties should be anisotropic as well.

Although the physical and chemical properties of sheet polymers are well-known,7,9-15 no systematic

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investigation concerning the kinetics of their preparation has been reported so far. On one hand, it can therefore be of fundamental interest to study the kinetics of the topotactic transformation of layered Zintl phases, and to investigate whether anisotropic diffusion in the sheet polymer layer formed leads to an anisotropy in the total transformation kinetics, as could be suggested from Figure 1. On the other hand, sheet polymers are being discussed as a possible active material in electroluminescent devices. It is therefore of tantamount importance for the fabrication of devices based on these substances to know and make use of the characteristic transformation kinetics. Although sheet polymers with pure Si and pure Ge¹⁴ backbone structures, as well as with SiGe alloy structures,¹⁵ have been prepared, we shall focus here on the topotactic preparation of siloxene as the prototype group-14 sheet polymer.

A possible way of monitoring the progress of the topotactic transformation is to detect the amount of hydrogen evolved during the reaction in eq 1,^{16,17} but because this method is extremely sensitive to the degree of hydrolysis taking place, it is not suitable for comparing different reactions. For example, during the formation of polysilyne $[SiH]_n$ (x = 0),¹⁸ no hydrogen would be detectable, although the reaction rate may still be similar to that of the formation of siloxene (x = 1). Kinetic data, therefore, should be determined by monitoring other substances involved in the reaction such as Ca which can be detected as dissolved CaCl₂.¹⁹

We show here that a very suitable way to measure the reaction kinetics of the topotactic formation of Si sheet polymers is by monitoring the amount of remaining CaSi₂ as a function of time. Whereas CaSi₂ is a metal,²⁰ the sheet polymers are undoped wide band gap semiconductors,²¹ and the specific room temperature resistivities differ by many orders of magnitude. Because the sheet polymers, therefore, essentially do not contribute to the overall electrical conductivity of the sample, this physical quantity during transformation directly mirrors the amount of silicide not yet reacted. Measuring the time dependence of the conductivity, in the present study, we systematically investigate the influence of the concentration and the temperature of aqueous hydrochloric acid on the transformation rate of epitaxial CaSi₂ films. Different substrate orientations and sample geometries are used to study the anisotropy of the reaction kinetics with respect to the silicide layering, and the processes determining the overall kinetics are discussed.

Experimental Section

Epitaxial CaSi₂ films with a typical thickness of 400 nm (and in some cases 4 μ m) were grown on Si(111) and Si(110)



Figure 2. (a) and (b) Schematic illustration of the different directions of reaction propagation (propagation paths, PP) used for the topotactic transformation of epitaxial CaSi2 into siloxene. (c) Experimental setup for PP I. The layered structure of CaSi₂, which is oriented differently on the different substrates, is indicated in the epilayers.

substrates by reactive deposition epitaxy. The orientation of the silicide layering with respect to the substrate surface is parallel for Si(111) and inclined with an angle of 35° for Si-(110).⁸ Cleaved fragments with lateral dimensions of 1×4 mm² were mounted on a Teflon holder and contacted with conductive silver paste. The typical resistivity of the films was about $1\cdot 10^{-4}$ Ωcm in good agreement with previous data obtained from bulk CaSi₂.²⁰ The contact areas were then sealed with epoxy resin to prevent electrolytic decomposition of the HCl solutions. Additionally covering the cleaving edges or the film surface with epoxy resin allows the exclusive choice of a certain crystal face to be exposed to HCl and thereby to study the anisotropy of the kinetics. In the case of CaSi₂ on Si(111) (Figure 2(a)), the direction of the reaction propagation may be in-plane (propagation path PP I) or perpendicular (PP III) with respect to the silicide layering. For $CaSi_2$ on Si(110), inplane reaction propagation (PP II) can be realized as well (Figure 2(b)). As an example, the complete experimental setup for an investigation of the kinetics of PP I is shown in Figure 2(c). A constant DC voltage of 5 mV was applied to the contacts, and the time dependence of the current was measured while the films were exposed to 50 mL of different aqueous HCl solutions. The concentration of HCl was varied in the range of 0 to 37 wt %, whereas the temperature of the solutions was varied between -10 and +80 °C using a Peltier element.

Results and Discussion

General Considerations. Surface reactions between a solid and a liquid phase are usually considered as occurring in consecutive single steps describing diffusion and chemical reaction.²² For the topotactic preparation of siloxene, this description has to be modified by two additional diffusion steps (steps 2 and 4) because the product siloxene is not removed or dissolved: (1) reactant (HCl, H₂O) diffusion through liquid to the siloxene/ liquid interface; (2) reactant diffusion through siloxene to the CaSi₂/siloxene interface; (3) reactant adsorption, actual exchange reaction (Ca \rightarrow H, OH), and product desorption; (4) product ($CaCl_2$, H_2) diffusion through siloxene to the siloxene/liquid interface; and (5) product diffusion in the liquid.

As the slowest step determines the overall reaction rate, the entire process can be controlled either by the chemical reaction itself (chemical reaction rate) or by the diffusion processes (physical mass transport). Also, the reaction limiting process can change between chemical and diffusion control depending on the exact reaction conditions.

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Figure 3. Propagation of the reaction zone in a $CaSi_2$ film on Si(111) along to propagation path I. The film surface is photographed through the covering epoxy layer; the black spots are caused by gas bubbles enclosed in the epoxy resin. The propagation front is indicated by the lower arrows.



Figure 4. Time dependence of the current obtained for epitaxial $CaSi_2$ films on Si(111) and Si(110) which were exposed to concentrated HCl at 20 °C. The propagation of the reaction zone was in-plane to the $CaSi_2$ layering (PP I and II).

Zero Order versus Diffusion-Limited Reaction. We first study the kinetics of the topotactic transformation reaction of a CaSi₂ film into a siloxene film using PP I, carried out in concentrated HCl at room temperature, the transformation conditions used most widely to obtain siloxene. Figure 3 shows the propagation of the reaction zone observed directly through the covering epoxy layer. One can see that the reaction front (indicated by the lower arrow in each picture) propagates in a largely homogeneous way and approximately linearly with the reaction time *t* (the upper arrow indicates the position of the front at t = 0). This linear transformation of CaSi₂ with time is confirmed by the time-dependent conductivity measurements shown in Figure 4. The lower curve is obtained from CaSi₂ on Si(111) using PP I, where the current is directly proportional to the extension of the remaining silicide below the transformation front indicated by the bottom arrow in the photographs of Figure 3. The upper curve in Figure 4 is obtained for CaSi₂ on Si(110) using PP II. The plots show that in both cases the conductivity due to the remaining CaSi₂ decreases linearly in agreement with the results obtained from Figure 3. As expected, the reaction rate is identical for both curves, as both PP I and II correspond to reaction propagation in-plane to the silicide layering.

We now turn to the other case of perpendicular reaction propagation (PP III in Figure 2). Figure 5 gives the time dependence of the film conductivity corresponding to the remaining silicide layer thickness for different concentrations of HCl. Apart from the initial phase of the experiment, the conductivity also decreases linearly with time. Thus, from the optical data shown in Figure 3, as well as from the conductivity measure-



Figure 5. Plots of current versus time obtained for a 400 nmthick $CaSi_2$ film on Si(111) which was exposed to HCl solutions of different concentrations at 20 °C. The propagation of the reaction zone was perpendicular to the $CaSi_2$ layering (PP III). The dotted line shows the initially quadratic time dependence attributed to a surface layer.

ments of Figures 4 and 5, we observe that the reaction zone in general propagates homogeneously and linearly with time. This corresponds to a linear decrease of the conducting $CaSi_2$ volume, and is, therefore, equivalent to a constant total reaction rate.

At first sight, a linear reaction progress is surprising if one considers the number of complex reaction and diffusion steps involved. We shall first consider the diffusion in the HCl solution. Etching and dissolution reactions are often limited by the diffusion through a thin depletion layer with a reduced reactant and an enhanced product concentration adjacent to the solid surface. Because the concentration gradient remains approximately constant during such reactions, they can indeed proceed linearly with time.²³ On the other hand, by stirring the liquid, one can increase the gradient and thereby enhance the reaction rate. As no corresponding effect was detected in our experiments, we can exclude diffusion within the liquid to limit the preparation reaction of siloxene.

Therefore, one would rather suppose the diffusion through the siloxene matrix to control the entire reaction. However, one would expect a different time dependence of the reaction rate in this case. Assuming that the reactant concentrations at the siloxene surface and at the CaSi₂/siloxene interface remain constant, the concentration gradient, and consequently the transport and reaction rate, will decrease with the increasing thickness of the siloxene layer formed during the reaction. In this simple diffusion model, the diffusion distance (which here is equivalent to the extension of the formed siloxene layer) will increase with the square root of the reaction time.²⁴ Consequently, the current through the remaining silicide should be proportional to

$$d = d_0 - \sqrt{Dt} \tag{2}$$

where *D* is the diffusion coefficient and d_0 is the original silicide extension. As we have seen so far, eq 2 cannot describe the topotactic transformation of CaSi₂. In contrast, a corresponding behavior is reported for vari-

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Figure 6. Effect of HCl concentration on the transformation rate of 400 nm-thick $CaSi_2$ films on Si(111) as obtained from Figure 4. The line is a guide to the eye.

ous inter- and deintercalation reactions into the layered structure of graphite clearly indicating that these reactions are limited by diffusion.^{24,25} Thus, we have to conclude that the topotactic preparation of siloxene is limited by the chemical reaction itself rather than by diffusion. For a reaction-rate-limited process, the observed constant rate indicates a zero order reaction. In fact, because the respective amount of $CaSi_2$ is constant at the reaction zone and an excess of HCl solution is applied, this is the expected reaction order in the present case.

Returning to Figure 5, we shall briefly discuss the nonlinear behavior in the initial phase of the experiments. Because CaSi₂ is not totally stable toward air and moisture,²⁶ a thin oxidized cap layer is present on the film surface which is slowly being removed by the acid. Assuming the thickness of this cap layer to decrease linearly with the reaction time, the reaction rate of the CaSi₂ transformation below the cap should increase linearly. Because an integration of the reaction rate corresponds to the current measured in Figure 5, we expect an initially quadratic time dependence as indicated by the dotted line in the figure which indeed fits well, e.g., the CaSi2 transformation observed for 15 wt % HCl. As the initial nonlinear behavior is, therefore, caused by a surface effect, the reaction rates obtained for PP III were determined from the linear regime of the I-V curves at long reaction times.

Effect of Acid Concentration. The reaction rate of the topotactic formation of siloxene is obviously expected to depend on the reaction conditions. Plotting the rates obtained from Figure 5 as a function of acid concentration (Figure 6), one observes a well-defined maximum at 13 wt % separating a region at low concentrations, where the reaction rate increases linearly with increasing acid concentration, and a region at higher concentrations, where the rate decreases again. The maximum rate is by about a factor of 4 higher at 13 wt % than for the most commonly used concentrated HCl (37 wt %). A similar behavior is observed in common crystal etching reactions^{27,28} and is usually interpreted as a



Figure 7. Effect of temperature on the transformation rate of $CaSi_2$ films exposed to HCl solutions of different concentration.

transition from a chemically controlled reaction mechanism at low concentrations to a diffusion-controlled mechanism at high concentrations. However, because in our case diffusion does not play a limiting role in the whole concentration range, the decrease of the reaction rate for high HCl concentrations must have a different origin. For this purpose, we separate reaction 1 (eq 1) into the basic ion exchange

$$\operatorname{CaSi}_2_n + 2n \operatorname{HCl} \rightarrow n \operatorname{CaCl}_2 + [\operatorname{SiH}]_{2n}$$
 (3)

and the subsequent hydrolysis reaction

$$[SiH]_{2n} + xn H_2O \rightarrow [Si_2(OH)_xH_{2-x}]_n + xn H_2$$
 (4)

The ion exchange of eq 3 is obviously governed by the amount of reactive HCl molecules, which rationalizes the linearly increasing regime of Figure 7. Although the degree of dissociation of the HCl molecules in aqueous solution drastically decreases at high HCl concentrations, the total number of dissociated Cl⁻ ions remains nearly constant in this concentration range.²⁹ Therefore, this effect cannot cause the decrease of the reaction rate observed at high concentrations. On the other hand, the hydrolysis reaction of eq 4 is determined by the amount of water available for this process which decreases with increasing HCl concentration. Indeed, a significant change in the degree of hydrolysis has already been reported in ref 6. As this reaction is exothermic, the released energy will be significantly higher in dilute solutions compared to that in concentrated HCl solutions. As the entire process is a heterogeneous solid state reaction, the local temperature at the reaction zone is expected to be enhanced with respect to that of the liquid main body. Indeed, we have found that stirring the liquid decreases the reaction rate by cooling the reaction zone. As discussed below (Figure 7), a temperature difference of only 50 °C can change the reaction

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rate by one order of magnitude. Thus, compared to the situation in concentrated HCl, the higher degree of hydrolysis in dilute HCl leads to an enhanced local temperature and a higher reaction rate, which, in addition to the other mechanisms discussed, can qualitatively account for the concentration dependence of the reaction rate shown in Figure 6.

Effect of Temperature. The topotactic transformation of $CaSi_2$ into siloxene is a thermally activated process. The temperature dependence of the reaction rate *R* can be described by

$$R = R_0 \exp(-E_A/kT) \tag{5}$$

where E_A is the activation energy of the limiting process, k is Boltzmann's constant, T is the absolute temperature, and R_0 is the preexponential factor. Figure 7 shows the observed temperature dependence of the reaction rate in an Arrhenius plot for different geometries and acid concentrations. The solid curves were obtained in concentrated HCl with the direction of the reaction propagation corresponding to PP I and PP III, respectively. On the other hand, the dotted curve was measured in dilute (4 wt %) HCl using PP III. Within experimental accuracy, all three curves exhibit an identical linear slope corresponding to a common activation energy $E_A \approx 0.4$ eV, independent of the direction of reaction propagation and of the HCl concentration. This fact confirms the model that the reaction is chemically and not diffusion controlled, because in the latter case one would expect different diffusion paths with respect to the siloxene layering to be characterized by different energetic barriers and, therefore, by different activation energies. Thus, we are led to interpret the observed activation energy of 0.40(2) eV as the chemical activation barrier of the topotactic preparation of siloxene. Assuming this barrier to be given by the energy necessary to remove Ca from CaSi₂, the value is in good agreement with the heat of formation of CaSi₂ which is 0.54 eV/atom.³⁰

Anisotropy of the Topotactic Transformation. In contrast to the activation energies, the preexponential factors and, consequently, the reaction rates at a given temperature differ significantly between the solid curves in Figure 7, with the reaction front propagating by a factor of 10 faster in-plane than perpendicular to the CaSi₂ layering. This behavior is obviously caused by an anisotropic chemical reactivity of the different CaSi₂ crystal faces exposed to the HCl solution. Indeed, typical for a layered material the crystal faces perpendicular to the layering exhibit a more "open" structure than the in-plane faces and, therefore, are more sensitive to the attack of HCl.

The anisotropy factor of 10 obtained from Figure 7 has generally been observed for thin films. However, for the transformation of films with a thickness of $\geq 2 \ \mu m$ or bulk CaSi₂, a different behavior is found. For a 4- μm -thick CaSi₂ film on Si(111), the reaction propagation perpendicular to the layering is only chemically controlled (constant rate) until about 2 μm of the film have been transformed as shown in Figure 8. After that, the rate decreases, approximately following eq 2, clearly

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Figure 8. Remaining thickness as a function of reaction time of a 4 μ m-thick CaSi₂ film on Si(111) exposed to concentrated HCl at 0 °C (PP III). The lines are guides to the eye indicating when chemical control or diffusion control dominates the reaction progress.

Table 1. Reaction Rates of the Topotactic Transformation of CaSi₂ into Siloxene at Some Selected Reaction Conditions

temp. (°C)	solution (HCl in H ₂ O)	reaction rate (nm/sec)
0	concentrated	5
20	concentrated	20
0	concentrated	60
20	13 wt %	90
20	concentrated	200
80	concentrated	2600
	temp. (°C) 0 20 0 20 20 20 80	$\begin{array}{c} \text{temp.} & \text{solution} \\ (^{\circ}\text{C}) & (\text{HCl in }\text{H}_2\text{O}) \\ 0 & \text{concentrated} \\ 20 & \text{concentrated} \\ 0 & \text{concentrated} \\ 20 & 13 \text{ wt }\% \\ 20 & \text{concentrated} \\ 80 & \text{concentrated} \end{array}$

indicating that the reaction is diffusion controlled at longer times. From the remaining $CaSi_2$ thickness at longer reaction times, we can estimate a diffusion coefficient of about 10^{-11} cm²/sec at 0 °C. As expected, this value describing diffusion processes perpendicular to the layered structure of siloxene is significantly smaller than the in-plane diffusion coefficients observed for various intercalation reactions, which, e.g., in graphite typically range between 10^{-4} and 10^{-8} cm²/sec.²⁴

Thus, for a perpendicular reaction propagation (PP III), we observe a transition from chemical to diffusion control, in agreement with the expectation that diffusion through the Si layers of siloxene should be rather difficult. In contrast, the rate for the in-plane reaction propagation remains constant over macroscopic dimensions (Figure 3), indicating that diffusion parallel to the Si layers is generally faster than the reaction itself.

Summarizing the reaction rates obtained under different conditions, we observe a wide range of 3 orders of magnitude. This fact again demonstrates the significant influence the reaction conditions have on the preparation of siloxene. As an overview, the rates for some special reaction conditions are given in Table 1. For the most commonly used concentrated HCl at 0 °C the rates are 60 nm/sec for in-plane and 5 nm/sec for perpendicular propagation of the reaction zone with respect to the CaSi₂ layering.

Conclusions

In this study, we have presented details concerning the reaction kinetics of the topotactic preparation of

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siloxene in aqueous HCl solution using in-situ electrical conductivity measurements to determine the changing amount of CaSi₂ left. The process is in general controlled by the chemical reaction rate and is found to be thermally activated with an activation energy of 0.40-(2) eV. CaSi₂ is transformed anisotropically with the propagation of the reaction zone being about 10 times faster in-plane to the CaSi₂ layering than perpendicular to it. For concentrated HCl at 0 °C, the rates are 60 and 5 nm/sec, respectively. For the perpendicular reaction propagation, we observe a transition from chemical to diffusion control when about 2 μ m of CaSi₂ have been transformed. In contrast, in the case of in-plane reaction propagation, the reaction remains chemically controlled

also over macroscopic distances. Therefore, $CaSi_2$ bulk crystals are preferentially transformed via the crystal edges by in-plane reaction propagation. Finally, in dilute HCl the reaction rate exhibits a well-defined maximum at an HCl concentration of 13 wt % which is linked to a higher degree of hydrolysis taking place under these conditions.

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