Thermal Decomposition of Dichlorosilane Investigated by Pulsed Laser Powered Homogeneous Pyrolysis

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ABSTRACT

Results of the SF\textsubscript{3} sensitized infrared pulsed laser powered homogeneous pyrolysis of dichlorosilane are reported. Pyrolyses at temperatures of 1350 to 1700 K and pressures of 150 to 230 Torr with reaction times around 7 \( \mu \)s were carried out in the presence and absence of molecules that could potentially scavenge the primary decomposition products (SiHCl and/or SiCl\textsubscript{2}). We were unable to irreversibly trap the reaction products, but obtained upper limits for the unimolecular decomposition rate constant under these conditions by measuring reactant loss. The observed rates are consistent with the high activation energy for dichlorosilane decomposition, near 75 kcal/mol, that is predicted by \textit{ab initio} calculations.

Introduction

The homogeneous thermal decomposition of dichlorosilane is potentially important in the high temperature chemical vapor deposition (CVD) of epilatinal silicon because it can produce reactive species (SiHCl, SiCl\textsubscript{2}) that can contribute to film growth with much higher probability than the parent molecule. However, the rate and dominant reaction path for the decomposition remain uncertain. The two lowest energy pathways for decomposition are:

\[
\begin{align*}
\text{SiH}_2\text{Cl}_2 & \rightarrow \text{SiCl}_2 + \text{H}_2 \quad \Delta H_{\text{f}298} = 36 \text{ kcal/mol} \\
\text{SiH}_2\text{Cl}_2 & \rightarrow \text{SiHCl} + \text{HCl} \quad \Delta H_{\text{f}298} = 67 \text{ kcal/mol}
\end{align*}
\]

High level \textit{ab initio} calculations by Schlegel and co-workers\textsuperscript{1}\textsuperscript{1} predict comparable barriers for the two reactions. Calculated barriers (electronic plus zero point energy) range from 73 to 80 kcal/mol for elimination, and 74 to 76 kcal/mol for SiCl\textsubscript{2} elimination, with the latter channel consistently 2 kcal/mol lower.\textsuperscript{2} This, combined with a larger predicted pre-exponential for SiCl\textsubscript{2} elimination leads to dominance of that path by a factor of 20 at 600°C. In IR multiphoton dissociation experiments, Sausa and Ronn\textsuperscript{3} detected electronically excited SiCl\textsubscript{2}. Walker et al.\textsuperscript{4} decomposed dichlorosilane in both static pyrolysis experiments and using a single-pulse shock tube. They concluded that the decomposition products were SiCl\textsubscript{2} and H\textsubscript{2}. Krupa et al.\textsuperscript{5} found that SiCl\textsubscript{2} and HCl were the primary products of vacuum flash pyrolysis of SiCl\textsubscript{2}. Ban and Gilbert\textsuperscript{6} observed SiCl\textsubscript{2} by mass spectrometry under silicon chemical vapor deposition (CVD) conditions, but Ho and Brieland\textsuperscript{7} observed SiHCl by laser induced fluorescence in a silicon CVD reactor. Ho et al.\textsuperscript{8} observed that 193 nm photolysis of SiCl\textsubscript{2} produced SiHCl. Two detailed kinetic models of epitaxial silicon CVD from dichlorosilane postulated decomposition mechanisms and adjusted the rate parameters for dichlorosilane decomposition to fit the observed decomposition rates. Hierlemann et al.\textsuperscript{9} assumed the reaction was in the low pressure limit and fit rate parameters of \( A = 10^{10} \text{ molec/cm}^3 \text{-s}^{-1} \) and \( E_a = 40.0 \text{ kcal/mol} \). Knutson et al.\textsuperscript{10} treated the reaction as first order, and fit an activation energy of \( E_a = 60.0 \text{ kcal/mol} \) with \( A = 1.38 \times 10^9 \text{ cm}^3 \text{-s}^{-1} \). Both of these expressions have activation energies that are much lower, and hence decomposition rates that are much higher, than would be predicted based on the \textit{ab initio} calculations.

In this work, we decomposed dichlorosilane via SF\textsubscript{3} photosensitized infrared pulsed laser powered homogeneous pyrolysis (LPHP), incorporating probe laser measurement of reaction time and temperature.\textsuperscript{11} This technique allows us to achieve high reaction temperatures with short reaction times, which minimizes the effects of secondary reactions in the gas phase. No heterogeneous reactions occur in these experiments because only the gas is heated, while the reactor walls remain at room temperature. Effective rate parameters were obtained from measurements of overall reactant loss after a large number of laser pulses. We were unable to chemically trap the reactive products, and therefore cannot conclude which reaction path, if either, was dominant. However, the observed rate coefficients do allow us to obtain an upper limit for the decomposition rate at the experimental conditions. These results support a high activation energy, near 75 kcal/mol, as predicted by the \textit{ab initio} calculations.

Experimental

These experiments were carried out using the same equipment and techniques we have described previously.\textsuperscript{12} Briefly, a Lumonics Model TEA 101-2 pulsed CO\textsubscript{2} laser was used to heat reaction mixtures containing reactants, bath gas, and sulfur hexafluoride as a photosensitizer. The laser was tuned to the P(16) line of the CO\textsubscript{2} transition, with a wavelength of 10.55 \( \mu \)m. Dichlorosilane absorbs at this wavelength, which is the same one used for IR multiphoton dissociation of SiH\textsubscript{2}Cl\textsubscript{2} by Sausa and Ronn.\textsuperscript{3} However, they observed no detectable dissociation at fluences comparable to those used in these experiments. The extinction coefficient for absorption by SF\textsubscript{3} is about 150 times that for SiH\textsubscript{2}Cl\textsubscript{2} at this wavelength at room temperature, so clearly the vast majority of energy transferred into the mixture is absorbed by SF\textsubscript{3} and absorption by SiH\textsubscript{2}Cl\textsubscript{2} will have a negligible effect. The reaction cell was constructed from 1 in. od Pyrex tubing, and had a length of 3.05 cm between the windows and a volume of 4.83 cm\textsuperscript{3}. NaCl windows were used in some of the preliminary experiments, but it appeared that reaction of SiH\textsubscript{2}Cl\textsubscript{2} with water adsorbed on the windows might be occurring. All kinetic data were obtained with ZnSe windows on the reactor, which eliminated this problem. The reaction time was determined by monitoring the thermal lens effect of the reactor contents on a HeNe laser aligned coaxially with the CO\textsubscript{2} laser, as described previously.\textsuperscript{13} The temperature was calculated from the speed of sound, which was determined from the thermal lens signal, as also described previously.\textsuperscript{15} Due to the high activation energy for decomposition and significant fall-off effects, these experiments required temperatures in the range of 1350 to 1700 K. These are higher temperatures than we have previously used in the LPHP experiment.

At such high temperatures we must consider the possibility that higher energy decomposition paths could be important. The silicon hydrogen bond has a bond dissociation energy of about 92 kcal/mol. The simple bond breaking reaction

\[
\text{SiH}_2\text{Cl}_2 \rightarrow \text{SiHCl}_2 + \text{H}
\]

would be expected to have a large pre-exponential factor (10\textsuperscript{14} to 10\textsuperscript{15}) and an activation energy close to the bond dissociation energy. At high pressures, this reaction could start to contribute significantly at temperatures near 1700 K. However, in the unimolecular falloff regime where these
experiments were conducted, this high energy path is slowed much more than the lower energy paths. Multichannel Rice-Ramseberger-Kassel-Marcus theory for unimolecular reactions (RRKM) calculations indicate that this reaction is roughly 1000 times slower than SiHCl elimination under reaction conditions used here. Breaking of the silicon chlorine bond, with a bond dissociation energy near 110 kcal/mol, will clearly be even slower.

Chemicals used were dichlorosilane (Aldrich, 99.99%), sulfur hexafluoride (Matheson, CP grade), and nitrogen (Air Products, ultrahigh purity grade). Product analysis was by Fourier transform infrared spectroscopy (FTIR) using a Nicolet Magna 740 FTIR. Spectra were taken before and after the LPHP experiment. Quantitative measurement of reactant loss was obtained by comparison of these spectra utilizing the sharp dichlorosilane Si-H stretching peak at 2237 cm⁻¹. Product analysis by gas chromatography (Shimadzu Model 14A with thermal conductivity detector) was also attempted, but due to the small sample quantity and high reactivity of dichlorosilane with adsorbed water, it was difficult to fully eliminate hydrolysis of dichlorosilane. Reasonable results were obtained on a 12 ft by 1/4 in. Teflon column packed with 20% SP-96 on Chromosorb P-AW. Careful pretreatment of the sampling system with dichlorosilane to remove adsorbed water was required. Measurements of reactant loss by gas chromatography (GC) would not allow us significantly greater precision than determination by FTIR, so all kinetic data presented here were obtained from reactant loss measured by FTIR.

We carried out several experiments with a trapping agent added to the reaction mixture in an attempt to reversibly capture the SiHCl or SiCl₂ produced by dichlorosilane decomposition. Trapping agents used were D₂, DCl, ethylene, 1,3-butadiene, and methane. Identification of a single final product produced would have allowed us to identify the dominant reaction channel. Additionally, the ability to identify and measure small quantities of a product would have allowed us to make measurements at much lower conversions of reactant than was possible when measuring reactant loss. This would have allowed us to work at lower temperatures where the LPHP experiment is better established. However, none of these species was successful in trapping the SiHCl or SiCl₂, to give a single, stable, identifiable compound. Nonetheless, we can glean some information from the results of these experiments.

Results and Discussion

The infrared spectra of reaction mixtures after the LPHP experiment showed the presence of multiple products which were neither firmly identifiable nor quantifiable. This was true both in the presence and absence of additional species which might have scavenged the reactive SiHCl or SiCl₂ produced. Figure 1 shows the infrared spectrum in the Si-H stretching region before and after reaction, and with the addition of several other compounds. Differences in peak size are primarily due to differences in extent of reaction. The peak at 2237 cm⁻¹ is the Si-H stretch of dichlorosilane. The product peak at 2280 cm⁻¹ is most likely the corresponding mode in trichlorosilane. The corresponding peaks for monochlorosilane at 2211 cm⁻¹ and silane at 2189 cm⁻¹ were not observed. The other product peaks at 2244, 2252, 2276, and 2294 cm⁻¹ are not readily assigned to a Si-H-Cl compound, although they could be due to higher partially chlorinated silanes. The IR spectroscopy of the chlorinated disilanes is not well known, but spectra of the mono-, di-, and trichlorodisilanes and ab initio calculations for all of the chlorinated disilanes indicate that their Si-H stretches should all be at smaller wave numbers than the Si-H stretches in dichlorosilane. No peaks are observed in that region. HCl was observed in the product spectra but was not proportional to the amount of dichlorosilane lost. No additional peaks other than those of Si₂HCl₃ and Si₂Cl₃ were observed in the IR spectrum from 600 to 4000 cm⁻¹. GC analysis of reaction products with thermal conductivity detection indicated the presence of compounds that had residence times consistent with HCl, monochlorosilane, and trichlorosilane. These peaks were not quantified, but were clearly too small to account for the amount of dichlorosilane which had reacted away. No other product peaks were observed in the GC analysis, although compounds with boiling points substantially higher than trichlorosilane could have eluted in small quantities with peaks so broadened as to be undetectable.

Molecular deuterium and deuterium chloride were independently added to the reaction mixture as scavengers in 10 to 20-fold excess over dichlorosilane. SiHCl or SiCl₂ could potentially insert into these diatomics to give deuterated chlorosilanes. As seen in Fig. 1, the product peaks were the same as without any scavenger. More important, none of the Si-D stretching frequencies in the 1600 to 1700 cm⁻¹ range that would be expected from the deuterated chlorosilanes were observed. We can therefore conclude that no significant amount of insertion into D₂ or DCI occurred, and these insertions must be slower than competing processes that occur in their absence. Insertion into D₂ and DCI would have approximately the same rate parameters as insertion into H₂ and HCl, respectively (modified by isotope effects). Therefore we can conclude that insertions into H₂ and HCl, which are the reverse reactions of the primary decomposition steps, do not occur. These observations are consistent with ab initio calculations predict significant barriers for insertion of SiHCl and SiCl₂ into both H₂ and HCl. Methane, ethylene, and butadiene were also tried as scavengers. Methane appeared to have no effect on the product spectrum. Both ethylene and butadiene addition resulted in an identical small peak at 730 cm⁻¹, but no other qualitative differences from the results in their absence. The product peaks from 2240 to 2300 cm⁻¹ were unchanged. Thus, the decomposition products may have reacted with C-C double bonds at a rate comparable to the other processes occurring, but this was not the dominant process and did not give a single stable quantifiable product.

Likely reactions for SiHCl or SiCl₂ to undergo after eliminating from dichlorosilane is insertion into dichlorosilane and dimerization. Ab initio calculations predict barriers (electronic plus zero point energy) of 2 and 10 kcal/mol for insertion of SiHCl and SiCl₂, respectively, into dichlorosilane. We would expect the dimerization reactions to occur with a barrier. Under the conditions of these experiments, the average conversion, per laser pulse, in the laser heated region ranged from 0.02 to 0.35%. So, after a laser pulse, dichlorosilane concentrations are of order 10⁶ molecule/cm³, while SiHCl and SiCl₂ concentrations are of order 10⁸ molecule/cm³. Rate con-
stant for insertion into dichlorosilane can be estimated from the *ab initio* energies and structures\(^{13}\) using conventional transition state theory. Dimerization rates should be near the gas kinetic collision frequency. At 1550 K, a typical reaction temperature, we estimate rates to be

\[
\text{SiHCl} + \text{SiH}_4\text{Cl}_4, k = 1 \times 10^{-13} \text{ cm}^3/(\text{molecule s}),
\]

rate = \(1 \times 10^9 \text{ molecule/cm}^3\text{s} \)

\[
\text{SiCl}_4 + \text{SiHCl}, k = 5 \times 10^{-15} \text{ cm}^3/(\text{molecule s}),
\]

rate = \(5 \times 10^6 \text{ molecule/cm}^3\text{s} \)

\[
\text{SiHCl} + \text{SiHCl}, k = 1 \times 10^{-10} \text{ cm}^3/(\text{molecule s}),
\]

rate = \(1 \times 10^7 \text{ molecule/cm}^3\text{s} \)

\[
\text{SiCl}_2 + \text{SiHCl}, k = 1 \times 10^{-16} \text{ cm}^3/(\text{molecule s}),
\]

rate = \(1 \times 10^8 \text{ molecule/cm}^3\text{s} \)

So, under these conditions, the dimerization rate is much faster than insertion of \(\text{SiCl}_2\) into dichlorosilane and comparable to insertion of \(\text{SiHCl}\) into dichlorosilane. Very little of either process occurs during the 7 µs or so that the mixture is at the reaction temperature. The maximum amount of \(\text{SiHCl}\) insertion into dichlorosilane, for example, is

\[
(1 \times 10^{18} \text{ molecule/cm}^3\text{s}) \times (7 \times 10^{-5} \text{ s}) = 7 \times 10^{12} \text{ molecule/s}
\]

\[
= \text{7% of SiHCl produced}
\]

This tells us that no significant amount of dichlorosilane can be consumed by secondary reactions during the initial reaction time of a few microseconds.

The temperature drop across the expansion wave that initially cools the reactive region is 150 to 200 K under these conditions. This quenches the unimolecular decomposition to a rate that is negligible in comparison to its rate before cooling. However, the lower activation energy secondary processes can continue to occur as additional cooling takes place. The temperature history after the initial expansion cooling is not known quantitatively. Additional acoustic waves propagate on the same microsecond timescale as the initial expansion and mix the hot gas with the surrounding cool gas. Complete mixing would lead to a temperature around 400 K, because only about 8% of the gas in the reactor is heated, while the rest remains at room temperature. Estimates of conductive cooling for the beam diameter and gas mix used in these experiments indicate that significant cooling at the center of the heated region due to conduction occurs on a time scale of 0.2 to 1 ms. So, secondary chemistry could continue to occur for several hundred microseconds after the initial reaction period. As the temperature drops, insertion of \(\text{SiHCl}\) and \(\text{SiCl}_2\) into dichlorosilane will slow down, while dimerization will not, since it has no barrier. Thus, the dominant bimolecular reactions during the cooling period will be dimerization. At high temperatures, the dimers can fall back apart to reproduce the chlorinated disilanes, and could also possibly isomerize to chlorinated silsynlenes and subsequently insert into dichlorosilane, but as the temperature drops, these processes will slow down, and the dimers will only be able to recombine with each other to give higher polychlorosilanes.

The most likely final fate for the \(\text{SiHCl}\) or \(\text{SiCl}_2\) produced by the unimolecular decomposition then seems to be combination to give polychlorosilanes which may then deposit on the walls, explaining the scarcity of observable reaction products. Before combining, these reactive molecules may consume some dichlorosilane through chain processes involving insertion of \(\text{SiHCl}\) and \(\text{SiCl}_2\) into dichlorosilane. The time scale of these experiments, however, is too short for long chains to occur. Suppose, for example, that \(\text{SiHCl}\) continued to insert into dichlorosilane at the rate of \(10^{18}\) molecule/(cm^3 s), as estimated above at the reaction temperature, for 100 µs. Then the amount of dichlorosilane consumed by this secondary reaction would be

\[
(10^{12} \text{ molecule/cm}^3\text{s}) \times (10^{-4} \text{ s}) = 10^8 \text{ molecule/cm}^3
\]

This is an amount equal to the amount of dichlorosilane consumed by the initial unimolecular decomposition, corresponding to a chain length of 2. This assumes that subsequent steps regenerate the \(\text{SiHCl}\) so that its concentration remains constant and that the insertion of \(\text{SiHCl}\) into dichlorosilane consumes dichlorosilane irreversibly. In fact, *ab initio* calculations\(^{13}\) indicate that the fastest reaction of the \(\text{HCl}_2\text{SiHSiHCl}\) produced by \(\text{SiHCl}\) insertion into dichlorosilane is decomposition back to \(\text{SiHCl}\) and \(\text{SiCl}_2\). Since insertion of \(\text{SiCl}_2\) into dichlorosilane is 20 or more times slower than insertion of \(\text{SiHCl}\) into dichlorosilane, \(\text{SiCl}_2\) insertion can consume negligible amounts of dichlorosilane compared to \(\text{SiHCl}\) insertion.

We, therefore, believe that while some dichlorosilane may be consumed in secondary reactions, the amount consumed can, at most, be an amount comparable to that produced by the initial unimolecular decomposition.

Results of decomposition of dichlorosilane in the absence of any scavenging species are presented in Table I. The reaction time is the time required for the expansion wave induced by the laser heating to reach the axis of the laser-heated region. The temperature is calculated from the speed of this wave, which is the speed of sound at the laser-heated temperature. The rate constant is calculated from the fraction of reactant remaining, the number of pulses, and the reaction time. The rate constants have been corrected for reactions occurring during and after the expansion wave cooling. These calculations and corrections are described in detail in our previous work.\(^{13}\) Briefly, the rate constant is given by

\[
k = f (3/t_x) \left( V_{\text{V}}/V_{\text{T}} \right) \left[ 1 - (1 - x)^{1/2} \right]
\]

where \(x = \text{measured reactant conversion, } V_{\text{V}} = \text{total reactor volume, } V_{\text{T}} = \text{volume irradiated by the infrared laser, } t_x = \text{reaction time (per pulse), and } f = \text{a correction factor for reaction occurring during and after the initial expansion wave cooling.}\)

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<th>(p_{\text{V}}) (Torr)</th>
<th>(p_{\text{final}}) (Torr)</th>
<th>Number of pulses</th>
<th>Reaction time (µs)</th>
<th>C/C_0</th>
<th>Calculated T (K)</th>
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Partial and total pressures are given at the reaction temperature after laser heating. C/C_0 is the fraction of initial reactant remaining after the total number of laser pulses. T and \(k\) are calculated as described in the text and in Ref. 11 and 13.
Under experimental conditions, the reaction is well into the unimolecular falloff regime. Pressure, temperature, and mixture composition all vary from data point to data point, as seen in Table I. We have, therefore, corrected all of the data to the high pressure limit. Falloff effects were calculated by solving the master equation for the conditions of each data point. All of these calculations were carried out using programs from the UNIMOL suite of codes by Gilbert et al. The microcanonical rate constants were obtained from RRKM calculations using energies and structures from the published ab initio calculations. Barriers of 73.1 and 75.1 kcal/mol were used for SiHCl and SiCl₂ elimination, respectively. Reactant and transition state geometries and frequencies were those calculated at the MP2/6-31G(d,p) level. Mixture averaged molecular weights and Lennard-Jones parameters were used in calculating the collision rates and energy transfer. Energy transfer parameters were estimated using the biased random walk model of Lim and Gilbert. This gave values of the average energy removed per collision (ΔElower) of 750 to 970 cm⁻¹, and corresponding collision efficiencies that were nearly constant at β = 0.13. These values are reasonable when compared to data on similar systems at comparable temperatures.

The data corrected to the high pressure limit as described above are shown in Fig. 1. The line through the data was obtained by holding the pre-exponential factor fixed at 10¹⁴ s⁻¹ and fitting the activation energy. This is the value of the pre-exponential factor predicted based on reactant and transition state structures from the ab initio calculations. This gives a reasonable fit to the data, showing that our measured rate constants are consistent with the predictions from the ab initio calculations. A slightly better fit could be obtained with a lower activation energy and lower pre-exponential factor. Since some dichlorosilane may be consumed by secondary reactions, as discussed above, our rate constants are upper limits for the actual unimolecular rate constant at these conditions. The amount of dichlorosilane consumed by secondary reactions, relative to that consumed by the unimolecular decomposition, should decrease with increasing temperature since the secondary chemistry is much less temperature dependent than the unimolecular decomposition. This would lower the apparent activation energy. The other most likely source of error is the temperature measurement. The temperatures used here are higher than we have previously used in the LPHF experiment, and there may be complications that were not observed at lower temperatures.

Even with these uncertainties, it is clear that our data is much more consistent with the ab initio predictions than with the dichlorosilane decomposition rate parameters that have previously been used in modeling silicon epitaxy from dichlorosilane. For example, the rate parameters used by Knutson et al. give rate constants roughly 100 times larger than those in Fig. 2 at these temperatures, and the difference becomes even greater at lower temperatures. This illustrates the hazards inherent in attempting to obtain rate parameters for individual reaction steps from film growth rates using a detailed reactor model, as was done in Ref. 9 and 10. The rates obtained in that way are dependent on the rates of many other chemical and physical processes occurring in the reactor, and on the reaction mechanisms in the gas phase and at the surface. Since these are generally not completely known, the rate parameters obtained by fitting can exhibit large and unpredictable errors. This means that, while the resulting model may work well over the range of conditions used in the fitting, it will have limited predictive capability over a wider range of conditions. Independent studies of key reaction steps, such as the one presented here, are needed to obtain rate parameters for elementary reactions that can be used in reactor models that are predictive over a wide range of operating conditions.

Conclusions

Dichlorosilane decomposition was investigated by pulsed infrared laser powered homogeneous pyrolysis. Upper limits on the rate constant for the unimolecular decomposition at 1350 to 1700 K were obtained from measurements of reactant loss. The reactive products of decomposition could not be quantitatively and irreversibly trapped. The observed rate constants were roughly consistent with ab initio predictions and were much smaller than those used in previously published models of silicon epitaxy from dichlorosilane.

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Oxygen Permeation Properties of Dense Bi$_{1.5}$Er$_{0.5}$O$_3$-Ag Cermet Membranes

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ABSTRACT

Oxygen permeation experiments were performed on dense mixed-conducting ceramic-metal composite membranes (thickness 0.2 to 2 mm) Bi$_{1.5}$Er$_{0.5}$O$_3$-Ag with 10.0, 27.3, and 40.0 volume percent (v/o) silver, respectively, in the temperature range 875 to 993 K and oxygen partial pressure range 10$^{-4}$ to 1 bar O$_2$. The oxygen fluxes increased with increasing silver content. In the cerments with a nonpercolative silver phase (10.0 and 27.3 v/o), the increased oxygen flux relative to that of pure Bi$_{1.5}$Er$_{0.5}$O$_3$ was attributed to faster kinetics of surface oxygen exchange in the presence of silver. Percolativity of the silver phase in the 40 v/o Ag composition enhances the ambipolar diffusion of oxygen ions and electrons. High oxygen fluxes (~0.25 mmol m$^{-2}$ s$^{-1}$ at 873 K) were observed with the latter composition, which were shown to be fully limited by the surface exchange kinetics. The activation energy for oxygen permeation in the temperature range 848 to 1003 K is about 95 to 100 kJ/mol for the compositions without percolativity of silver and 115 kJ/mol for the composite with 40 v/o Ag, which reflects a change of the rate-limiting step upon passing the percolation threshold. Results from both permeation and isotopic exchange measurements on the composition with Ag percolativity indicated the kinetic order of the surface process in oxygen to be 1/4, indicating a process fundamentally different from that on pure Bi$_{1.5}$Er$_{0.5}$O$_3$.

Introduction

The high-temperature face-centered cubic (fcc) 6-phase of the defect fluorite-type Bi$_2$O$_3$ is the best oxygen ion conductor known. Its anomalously high ionic conductivity is related to the cubic crystal structure, the nature of the bismuth, and the intrinsically large concentration of vacant sites in the oxygen sublattice, which equals 28% of the total number of crystallographic sites available. The temperature range in which the 6-phase is stable is rather narrow (1002 to 1097 K), and the transition from the 6-phase to the low-temperature 6-phase is accompanied by a conductivity decrease of two to three orders of magnitude. The more conductive cubic phase can be stabilized down to room temperature by partial doping with rare earth elements or yttria, although the conductivity decreases with increasing dopant concentration. The maximum conductivity below the transition temperature of 6-Bi$_2$O$_3$ is therefore obtained at the minimum doping level necessary to stabilize the fcc phase. Doping with erbium or yttria has shown the best preservation of ionic conductivity. The conductivity of compositions Bi$_2$,Y(25)Er(75)O$_3$ have been investigated extensively. In the Bi$_2$,Er$_x$O$_3$ system, the maximum conductivity is reached at 20 to 25 mole percent (m/o) Er (x = 0.4 to 0.5). The ionic conductivity of Bi$_{1.5}$Er$_{0.5}$O$_3$ (denoted as BE25) has an activation energy of 72 ± 4 kJ/mol above 873 K and reaches an absolute value of 25 I$^{-1}$ m$^{-1}$ s$^{-1}$ at 973 K. The ionic conductivities of several compositions Bi$_{1.5}$Y$_x$O$_3$ have been shown to be independent of oxygen pressure.

The partial electronic conductivity of Bi$_{1.5}$Y$_x$O$_3$ at elevated temperatures has been investigated by Takahashi et al. The electronic conductivity, $\sigma_e$, is predominantly p-type at high oxygen pressures and has an activation energy, $E_{a_{el}}$, of 106 kJ/mol. In Kröger-Vink notation, the oxygen incorporation reaction under these conditions can be written as

$$\frac{1}{2}O_2 + V'_0 \leftrightarrow O'_0 + 2h^+$$  \hspace{1cm} [1]