Gaseous Thermal Conductivity of Silane, Dichlorosilane, Trichlorosilane, Tetrachlorosilane, and Tetrafluorosilane in the Temperature Range from 28 to 350 °C

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Gas phase thermal conductivities for silane, dichlorosilane, trichlorosilane, tetrachlorosilane, and tetrafluorosilane are reported between 28 and 350 °C using a differential hot-wire technique with helium as the reference gas. Thermal conductivity data for argon and hydrogen are also determined over the entire temperature range to verify the experimental method used. The results are compared with the available literature data. The reproducibility of the values is within 4%.

Introduction

Silane and halogenated silanes have been the most important intermediates in the large scale production of solar cell grade silicon. The chlorosilanes are the most commonly used chemical intermediates in semiconductor industries. The values of thermal conductivity, λ, are needed in such processes. A search of the literature indicated the availability of experimental gaseous thermal conductivity data of silane and halogenated silanes by different techniques (*1–3*). In the present paper, we report the experimental thermal conductivity data for silane, SiH_4, dichlorosilane, SiH_2Cl_2, trichlorosilane, $SiHCl_3$, tetrachlorosilane, $SiCl_4$, and tetrafluorosilane, SiF_4, in the temperature range 28–350 °C using a differential hot-wire technique. The measured values are compared with the available literature results.

Experimental Section

Materials. Trichlorosilane (99.9 mol %) and tetrachlorosilane (99.0 mol %) were obtained from Ventron Inc., and used without further purification. Silane, dichlorosilane, and tetrafluorosilane (99.6 mol %) were purchased from Matheson and used as received. The specific purity of silane was not given, but it was reported to contain less than 5 ppm oxygen and more than 2 ppm water. The purity of dichlorosilane was reported as semiconductor grade. The argon (99.9 mol %) and hydrogen (99.5 mol %) were used as supplied.

Measurements. The hot-wire thermal conductivity apparatus described earlier in some detail in the literature (*4, 5*) has been used in this work. The thermal conductivity cell or catharometer used in this study is the thermal conductivity detector of a Tracor 560 series gas chromatograph. The power supply and bridge current were also supplied with the instrument. The circuit response was monitored by a Soltec recorder, model BC 82000.

The hot-wire cell utilized consists of two identical pairs of matched tungsten–rhenium filaments mounted in cavities in a stainless steel block into which gases can be introduced. The filaments are connected as elements of a constant current Wheatstone bridge. The cell is heated electrically, and the temperature is controlled by a digital temperature controller to within ±0.1 °C. The temperature is measured by calibrated thermocouples mounted on the cell.

The cell is divided into two parts: a reference side and a sample side. The λ values were determined from the response of the cell with a reference gas of known thermal conductivity in the reference side of the cell and the gas whose thermal conductivity is to be measured in a sample side of the cell. The cell responds to the reciprocal of thermal conductivity (*4, 5*) according to eq 1, where E is

$$E - E_{\mathrm{ref}} = b(1/k - 1/k_{\mathrm{ref}}) \qquad (1)$$

the unbalanced voltage with the sample gas on one side and the reference gas on the other side of the thermal conductivity cell and k and k_{ref} are the thermal conductivity values of the sample gas and reference gas, respectively. The characteristic constant or cell constant, b, of the apparatus is determined from eq 1 using a gas of known λ and determining the voltage, E, with respect to the reference gas. Prepurified helium (99.6 mol %) was used as the reference gas for all measurements, and prepurified nitrogen (99.5 mol %) was used as the standard gas to find the value of b. The cell constant, being sensitive to temperature, was determined at all the temperatures.

While measuring the thermal conductivity, it was noticed that the gas may not be at a uniform temperature due to the temperature difference between the cell wall and the filament wire. This temperature difference is minimized by operating the apparatus at a sufficiently low filament current. This required a means of monitoring the temperature of the filament wire. This was accomplished by using the filament as a resistance thermometer. Thus, the filament resistance was calculated by monitoring the current through the filament, and the potential across the filament was calculated by the product of filament current (A) and filament resistance (Ω). The temperature corresponding to a particular filament resistance was obtained from a knowledge of the temperature coefficient of resistance. The temperature coefficient of resistance for the filament used in this study was determined, and the results are presented in Figure 1. During data acquisition, the

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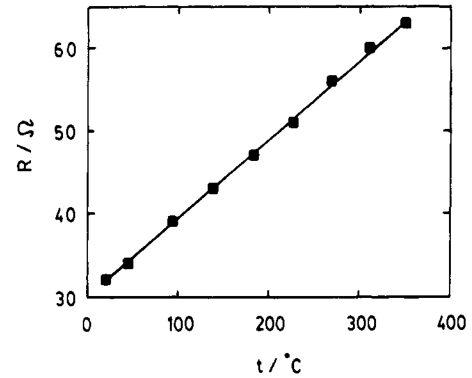

Figure 1. Filament resistance as a function of temperature.

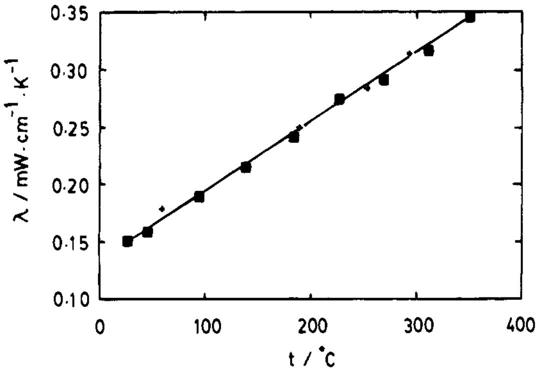

Figure 2. Comparison of thermal conductivity data for argon: (■) present study; (+) ref 5.

filament current was adjusted such that the difference in the temperature of the cell wall and the filament was kept at a minimum, i.e., within 3%.

Results and Discussion

In order to evaluate the accuracy of the apparatus, thermal conductivities of argon and hydrogen were determined. These gases were chosen because of the ready availability of the literature data (*6–10*) at the temperature ranges used in this study. Another reason to select these gases is that hydrogen has a relatively high thermal conductivity while argon has a thermal conductivity nearly the same as those of silanes. This helped in the evaluation and validation of the experimental method over a wide range of λ values.

The literature values of λ have been published over a wide range of temperatures and pressures, making it difficult for direct comparison (*3*). Generally, thermal conductivity increases by 1% or less per atmosphere (*11*). Thermal conductivities for argon and hydrogen from 28 to 350 °C are compared with the literature values in Figures 2 and 3, respectively. For argon, good agreement between the present data and those of Touloukian et al. (*6*) is observed. The agreement is within ±2% up to 300 °C and ±4% from 300 to 350 °C. Thermal conductivities of hydrogen obtained in this study agree with the literature results (*3, 12, 13*) within ±4% up to 300 °C and ±10% from 300 to 350 °C (see Figure 3). However, the percentage difference between the λ values of hydrogen in this study with the recommended values is somewhat high probably because the values for hydrogen are close to those of the reference helium. Thus, the unbalanced voltage was about 0.03–0.04 mV, which was small enough to introduce such a large percentage error.

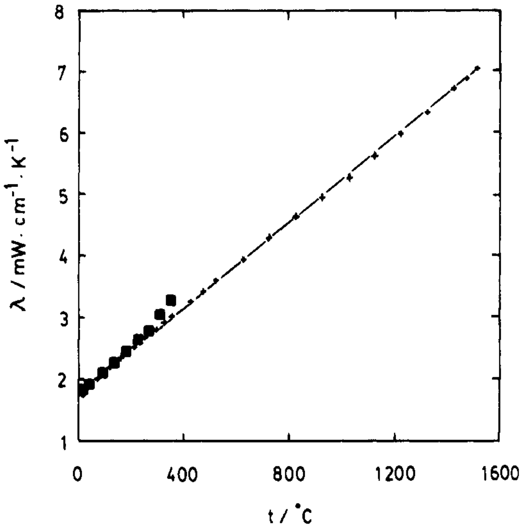

Figure 3. Comparison of thermal conductivity data for hydrogen: (■) present study; (+) ref 5.

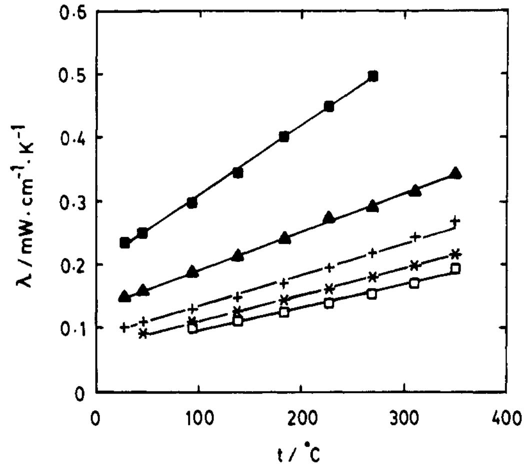

Figure 4. Gaseous thermal conductivity data for silane and halogenated silanes: (■) SiH_4; (▲) SiF_4; (+) SiH_2Cl_2; (*) $SiHCl_3$; (□) $SiCl_4$.

The gaseous thermal conductivities of silane and halogenated silanes as a function of temperature are presented in Table 1 and graphically displayed in Figure 4. It is observed that the thermal conductivities of silane and

Table 1. Gaseous Thermal Conductivity, λ, of Silane and Silane Compounds

	λ/(mW cm^{-1} K^{-1})					$SiCl_4$ (*3*)		SiF_4 (*3*)	
t/°C	SiH_4	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$	SiF_4	*t*/°C	λ	*t*/°C	λ/(mW cm^{-1} K^{-1})
28.0	0.234	0.102			0.150				
45.7	0.249	0.108	0.093		0.158			47	0.168
94.7	0.297	0.129	0.110	0.100	0.189	100	0.086	97	0.197
139.4	0.345	0.148	0.126	0.111	0.215	150	0.101	137	0.220
184.1	0.400	0.169	0.144	0.124	0.241	175	0.108	187	0.248
227.4	0.449	0.194	0.161	0.138	0.274	225	0.123	227	0.271
269.5	0.497	0.217	0.180	0.153	0.291	250	0.129	267	0.293
311.3		0.243	0.198	0.169	0.316	300	0.144	307	0.316
350.6		0.267	0.216	0.193	0.345	350	0.160	347	0.338

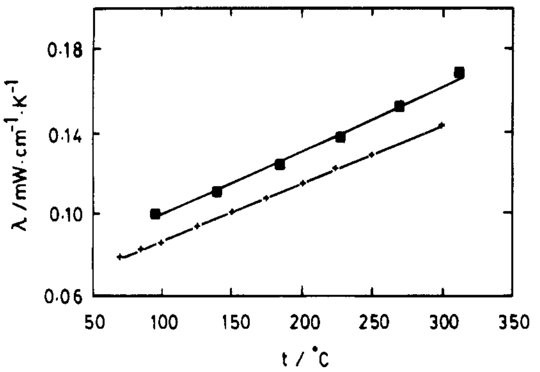

Figure 5. Comparison of thermal conductivity data for tetrachlorosilane: (■) present study; (+) ref 1.

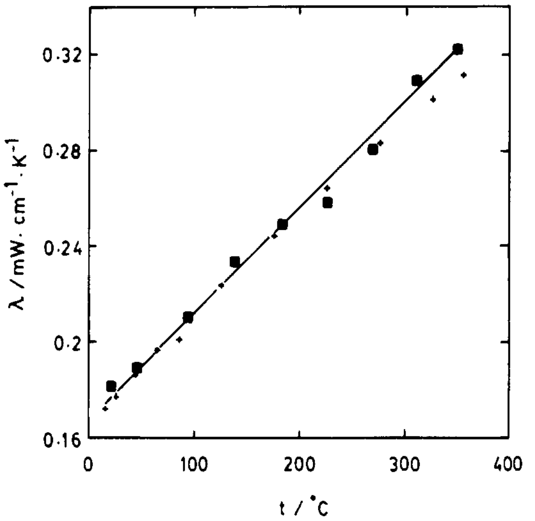

Figure 6. Comparison of thermal conductivity data for tetrafluorosilane: (■) present study; (+) ref 2.

tetrafluorosilane are higher than those of the chlorosilanes. The lowest λ is observed for tetrachlorosilane. Generally, a systematic trend of increase of conductivity with temperature is observed in all cases. Thermal conductivity of silane was not measured above 300 °C as silane began to decompose and elemental silicon was found to be deposited (*14*). Silane was heated further in order to determine the temperature of decomposition. At 300 °C, no deposition of silicon occurred, while at 350 °C, a slight deposition of silicon and, at 400 °C, a heavy deposition of silicon were observed. Thermal conductivities of trichlorosilane below 50 °C and tetrachlorosilane below 100 °C were not measured because of problems associated with the condensation of these gases around 33 and 58 °C, respectively (*14*).

There have been some reports in the literature (*1*, *14*, *15*) of calculated and estimated thermal conductivities of silane and halogenated silanes. A comparison of the present results with literature values is given in Figures 5 and 6, respectively, for tetrachlorosilane and tetrafluorosilane. It is noticed that the literature values are lower than the present results for tetrachlorosilane by about 12% at 100 °C and about 10% at 300 °C (Figure 5). On the other hand, the values for tetrafluorosilane as reported by Choy (*2*) are in agreement with the present values (see Figure 6). However, the recently available data of $SiCl_4$ and SiF_4 are compared in Table 1 wherein the agreement is found to be better, i.e., within 3%.

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