Vapor Pressure Measurements for Dichlorosilane, Trichlorosilane and Tetrachlorosilane[1]

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[1]Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22 - 27, 1997, Boulder, Colorado, U.S.A.

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Key Words: vapour pressure, dichlorosilane, experimental measurement

Abstract

The preparation of elemental silicon of sufficient purity for the fabrication of electronic devices is accomplished by first converting silicon oxide to silicon-hydrogen-chloride compounds, purifying the material as a fluid mixture, and then converting the product back to solid silicon. During the purification process, dichlorosilane (SiH_2Cl_2), trichlorosilane ($SiHCl_3$), and silicon tetrachloride ($SiCl_4$) all are present in significant quantities. Models which describe the vapor-liquid equilibrium behavior for the mixtures are necessary to design the appropriate separation and purification processes. Pure fluid properties form the starting point for most mixture models, hence the importance of vapor pressures for the pure materials.

In this work we report measurements of the vapor pressures for three of the most important fluids in the silicon production process: SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$. Our results agree well with measurements reported previously for $SiCl_4$, thereby providing verification of the experimental accuracy estimates. The accuracies in all cases are better than ± 0.1 %, with the largest uncertainties introduced by the reactive nature of the fluids.

The reactive nature of these fluids complicate the experimental procedures because of the corrosive nature of the products formed, and in the case of SiH_2Cl_2, the potential for self-ignition upon exposure to moist air. The experimental procedures used to minimize the hazards and to avoid contamination of the fluids are described.

Introduction

Silanes are a group of silicon compounds containing silicon along with hydrogen or chlorine, or both. Silanes most commonly are associated with applications requiring precise control of the placement and thickness of layers of pure silicon. A group of silanes that contain chlorine can be referred to as chlorosilanes. Some of the more common chlorosilanes are dichlorosilane, trichlorosilane, and silicon tetrachloride (sometimes referred to as tetrachlorosilane). Although commonly associated with the semiconductor industry, silanes are widely used in various other applications throughout other industries.

Pure silicon for semiconductor applications is manufactured by reaction of silanes or chlorosilanes to deposit pure silicon. The stringent purity requirements of the semiconductor industry require extremely high purity levels in both the manufactured silicon and the intermediate silanes. Design of the silane purification processes requires information about the vapor pressures of the pure materials as well as mixture properties.

Information about the vapor pressure of some silanes is sparse, and the most current work on pure chlorosilanes is either dated or insufficient. The data is especially scarce for dichlorosilane. An extensive search of the literature located only five sources of vapor pressure data for dichlorosilane [1-3]. In this paper we present the results of vapor pressure measurements made using an isochoric method for high-purity dichlorosilane between 300 and 400 K.

Experimental

Apparatus

The isochoric measurements were made in an apparatus which has been described in detail previously [4,5]; only a brief description will be given here. Figure 1 presents a schematic diagram of the apparatus. The sample cell is made of 316 stainless steel. The inner surfaces of the cell were polished to minimize adsorption. A built-in differential pressure transducer (DPT) is located at the top of the cell. The temperature of the cell is

measured with a platinum resistance thermometer with a precision of ±0.001 K and an accuracy (relative to the ITS-90) of ±0.010 K. Temperature gradients across the cell are less than 0.003 K. The cell temperature is controlled to ±0.002 K using a proportional-integral control algorithm implemented with a microcomputer.

The equilibrium vapor pressure causes a force on the bottom of the DPT that is counterbalanced by an inert gas (argon) on the top side. A linear variable differential transformer detects deflections of the 0.05 mm thick stainless steel diaphragm, which is the functional component of the DPT. A calibration for the null position is to be performed immediately prior to each series of experiments, however the null position shift has been shown by repeated tests to be stable to better than ±0.1 kPa [5]. The pressure of the counterbalancing inert gas is measured with a force-balance piston pressure gauge, certified by the manufacturer to be accurate to ±0.005%.

Materials

Research grade dichlorosilane of purity 99.999+% (as specified by the distributor), was purchased from Sigma Aldrich Chemicals. The dichlorosilane was transferred from the original container to a one liter stainless steel sample cylinder for degassing. Prior to transfer, the degassing cylinder was purged with argon and evacuated. The transfer was completed with a combination of pressure and temperature differential driving forces. The pressure differential was caused by the vacuum as discussed earlier, and the temperature differential was caused by submerging the degassing cylinder into liquid nitrogen.

All connections were tested regularly for leaks because dichlorosilane has violent reactions with the water in the atmosphere. Actually it is the water content of the air that initiates the reaction, which is why the sample cylinder had to be purged with a dry gas. Leak testing was performed by pressurizing with argon then probing all connections with a Matheson® Gas Products leak detector, which compares the thermal conductivity of a reference ambient stream of air to the atmosphere in which a probe is submerged.

To ensure the purity of the sample, the dichlorosilane was subjected to an extensive degassing procedure before being transferred to the sample cell in the isochoric apparatus. First, the sample cylinder was submerged in a liquid nitrogen bath to be frozen. Next, a valve at the top of the cylinder was opened to a vacuum to remove the gaseous impurities. Finally, the sample was allowed to thaw completely. This cycle was repeated a total of four times, which was how long it took to achieve a pressure of less than 1 Pa above the frozen sample. After this process, the sample was allowed to thaw partially before it was exposed to a vacuum for approximately two seconds. This second procedure was repeated three times. Both methods involve freezing and thawing, but each has unique significance. The first method may eliminate impurities with freezing points which are lower than the boiling point of nitrogen, but some gases may be trapped in the liquid during the freezing process. The second method is intended to remove trapped gases from within the partially thawed liquid.

All intermediate tubing between the degassing cylinder and the sample volume in apparatus were rinsed with a small amount of dichlorosilane. A valve was then opened to the cold trap to allow the dichlorosilane to be condensed, then closed. The degassing cylinder then was heated with a bath of warm tap water, while the cell was cooled by a chilled water loop. The valve connected to a dipstick in the liquid was opened, and the distillation transfer process was allowed to proceed for approximately two hours.

After disassembling the transfer set-up, great care was taken to purge all external lines of tubing with argon. Exposed surfaces also were cleaned with a highly absorbent lab towel designed especially for chemical clean-up. Acetone also was used to help polish the surface. Over a period of approximately three days, a corrosion layer was evident on all exposed surfaces; however, internal surfaces remained visibly clean. The conclusion is that dichlorosilane tends to be highly adsorbed on stainless steel. Copper or brass fittings are not an option because copper will react with dichlorosilane. There is no current literature

on dichlorosilane removal, or clean-up. The disadvantage here is that valves and tubing that have had contact with dichlorosilane are destined for corrosion, unless extraordinary means are employed to shield them from exposure to air. Even so, no other gas can be used with this equipment because of the risk of contamination.

Results

Measurements were made on dichlorosilane samples from two different lots and two different manufacturers. The experimental values for Sample 1 are given in Table 1, and the values for Sample 2 in Table 2. For sample 2, eight isochores were measured at temperatures ranging from 300 to 400 K. Because the sample volume in the apparatus was filled to a density greater than the critical density of dichlorosilane, the sample volume became entirely filled with liquid as the temperature increased. The end of each isochore is representative of the final point before the DPI experienced a hydraulic pressure. Some sample was discharged from the cell to reduce the average density, and a new isochore measured. This method allowed for multiple replications of several points along each isochore to verify the internal consistency of the results. The experiment was terminated after the series of expansions from the cell lowered the density below the critical density

Mathematical Model

We have chosen to use the equation proposed by Iglesias-Silva, *et al.*, [6] to describe the measured values. This equation has the form:

$$p(t) = \left[p_0(t)^N + p_\infty(t)^N\right]^{\frac{1}{N}} \tag{1}$$

where

$$p(t) = 1 + (P - P_t)/(P_c - P_t)$$

$$t = (T - T_t)/(T_c - T_t)$$

$$p_0(t) = a_0 + a_1(a_3 t + 1)^{b_0/R} \exp\left[(-a_2 + b_0/R)/(a_3 t + 1)\right]$$

$$p_\infty(t) = 2 - a_4(1-t) + a_5(1-t)^{2-q} + a_6(1-t)^3 + a_7(1-t)^4$$

$$a_0 = 1 - P_t/(P_c - P_t)$$

$$a_1 = (1 - a_0)\exp(a_2 - b_0 / R)$$

$$a_2 = b_1 / RT_t$$

$$a_3 = (T_c - T_t) / T_t$$

$$a_5 = -0.11599104 + 0.29506258\ a_4^2 - 0.00021222\ a_4^5$$

$$a_6 = -0.01546028 + 0.0897816\ a_4^2 - 0.05322199\ a_4^3$$

$$a_7 = 0.05725757 - 0.06817687\ a_4 + 0.00047188\ a_4^5$$

$$N = 87\ T_t / T_c$$

$$q = 0.2$$

where T_t is the triple point temperature, T_c is the critical temperature, P_t is the triple point pressure, and P_c is the critical pressure.

Comparison of Results

Previous measurements of dichlorosilane vapor pressures have been reported by Olson [2] and by Stock, *et al.* [3]. The measurements of Stock *et al.* all were below 280 K and at pressures below 1 bar. The measurements reported by Olson lie within the range covered by this work. The Matheson Gas Data Book [1] also provides values for dichlorosilane, but it does not present information about the source or accuracies of the values presented. Figure 2 shows a comparison of our results, those of Olson and those reported in the Matheson Gas Data Book. We have used a simple background equation to provide a reference with which to compare the various measurements. The four points from sample TAMU Sample 2 which have large positive deviations (~5% or larger) illustrates the behavior after the sample container fills with liquid. The pressure rises away from the vapor pressure curve vaery rapidly in that case. Due to the reactive nature of the sample, the internal consistency of these measurements is not comparable with those achieved for nonreactive fluids such as pentafluorethane (R-125). In general, our resulets are internally consistent to about ±1%, and they agree at about the same level with the points measured by Olson [3] using ebulliometry. The agreement between the ebulliometry

results (a dynamic method) and the current results (static method) suggests that the accruacy of the current results is of the order of ± 1% at the 95 % confidence level.

References

1. Matheson Gas Data Book, Dichlorosilane, 1979.
2. J. D. Olson, Fluid Phase Equilib., 52 (1989) 209.
3. A. Stock, C. Somieski and R. Wintgen, Ber. Dtsch. Chem. Ges., 50 (1917) 1754.
4. L. Yurttas, Ph.D. Dissertation, Texas A&M University, College Station, TX, 1986.
5. L. Yurttas, J. C. Holste, K. R. Hall, B. E. Gammon and K. N. Marsh, J. Chem. & Eng. Data, 39 (1994) 418.
6. G. A. Iglesias-Silva, J. C. Holste, P. T. Eubank, K. N. Marsh and K. R. Hall, AIChE J., 33 (1987) 1550.

Table 1. Experimental measurements - sample 1.

T/K	*P*/kPa
323.01	407.79
343.01	672.63
362.99	1052.10

Table 2. Experimental measurements - sample 2.

Isochore #1		Isochore #2		Isochore #3	
T /K	*P*/kPa	*T* /K	*P*/kPa	*T* /K	*P*/kPa
300.001	216.49	299.994	214.54	299.999	214.22
309.990	299.80	319.983	377.60	319.996	377.34
319.998	380.37	339.992	625.63	339.991	625.28
330.017	492.15	349.989	789.00	359.983	981.88
339.994	695.45				

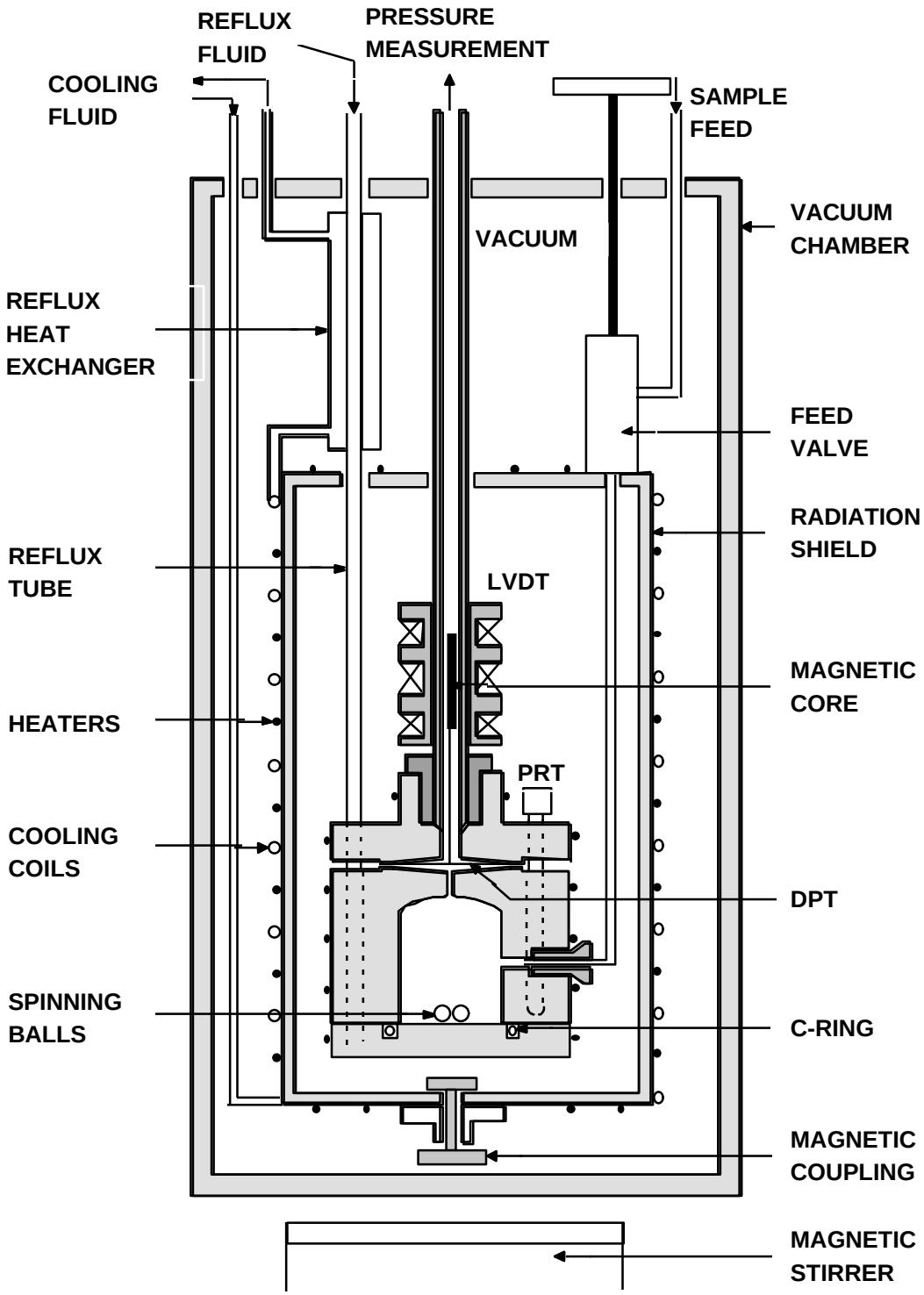
Isochore #4		Isochore #5		Isochore #6	
T /K	*P*/kPa	*T* /K	*P*/kPa	*T* /K	*P*/kPa
329.994	485.76	349.996	785.00	299.999	212.04
349.990	784.65	369.992	1204.95	309.992	284.33
359.988	978.02	379.985	1468.96	349.992	786.36
369.984	1205.16	390.022	2193.15	359.992	982.17
				369.992	1209.08
				379.989	1473.84
				389.994	1778.60

Isochore #7		Isochore #8		Isochore #8	
T /K	*P*/kPa	*T* /K	*P*/kPa	*T* /K	*P*/kPa
299.993	214.37	299.988	213.33	299.993	216.53
319.993	377.90	339.991	626.44	319.995	381.43
339.998	628.55	379.990	1475.90	339.991	631.57
359.991	985.93	389.990	1780.57	359.991	990.31
379.990	1476.96	399.989	2098.64	379.992	1483.51
389.991	1783.63	410.004	2533.88	399.992	2138.36
399.989	2299.44			409.984	2559.11
				419.991	3016.05

Figure Captions

Figure 1. Schematic diagram of isochoric apparatus

Figure 2. Comparison of current results for dsichlorosilane with those of other workers.



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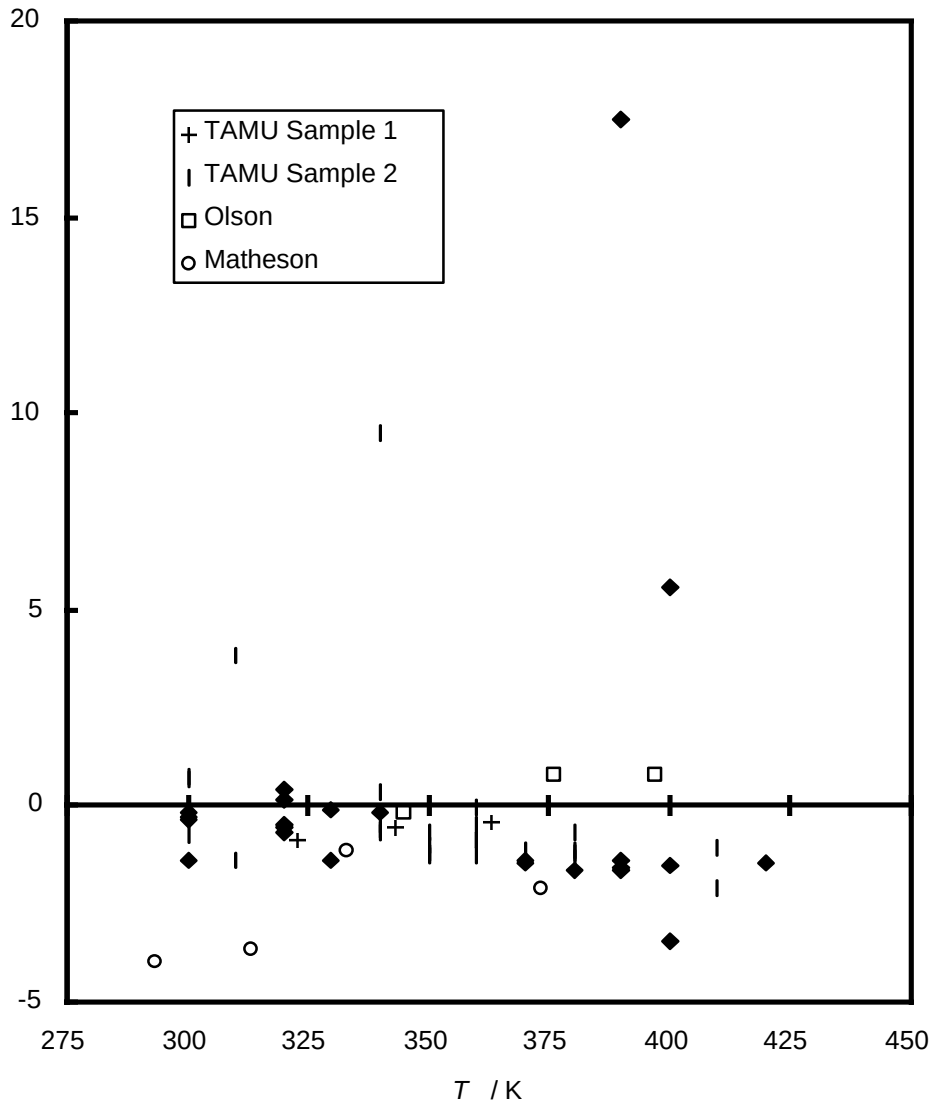

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