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PURIFICATION TECHNIQUES AND ANALYTICAL METHODS FOR GASEOUS AND METALLIC IMPURITIES IN HIGH-PURITY SILANE

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Silane has long been used by semiconductor manufacturers to form thin films of silicon or its compounds. In the future, denser and more complex integrated circuits, as well as new devices such as photovoltaic cells, will require silane of very high purity with impurities specified at parts per trillion levels. A review of manufacturing processes, purification techniques, and analytical methods is presented, with critical attention to the issue of metallic impurity measurement versus resistivity as the preferred method for determination of actual product purity.

1. Introduction

Today's electronics industries are discovering more and varied uses for silicon and its compounds. Silicon gases, and especially silane, have been used for more than 20 years by semiconductor manufacturers to form thin films. Today, silane is also used to fabricate such diverse devices as photovoltaic cells, photocopier drums, silicon carbide, and flat panel displays. These new products, as well as denser and more complex integrated circuits, often require gases of exceptional purity.

To provide the required purities, silane manufacturers have resorted to several generic purification schemes. Selection of the proper method depends on a number of factors: manufacturing process (e.g., batch or continuous), levels of raw material impurities, target levels of final material impurities, amounts of gas to be purified, and cost.

At all purification points, acceptable analytical methods must be employed to monitor real-time impurity levels. Because end-user requirements are driving impurities to constantly lower levels, and manufacturers are responding with ever-purer silane, analytical sensitivities must be improved continuously. At Union Carbide, for example, new techniques with improved sensitivities for ten different critical impurities in silane have all been developed over the past two years.

Metals impurity reduction and analysis represent a real challenge to silane manufacturers. The industry historically has specified metals indirectly through resistivity measurement of an intrinsic epitaxial film. The inherent problems of minimizing reactor contamination, of autodoping, out-diffusion, and compensation, and of measuring the resulting film were of little concern as long as resistivity specifications remained at 100 Ω cm. However, today's users expect a higher level of quality and are, we believe, mistakenly equating quality with increased resistivity specifications.

Instead, new analytical techniques such as Deep Level Transient Spectroscopy or Photoluminescence Spectroscopy allow suppliers and users actually to specify metallic impurity levels. Sensitivities ranging down to 10 parts per trillion are now routinely reported. But even these levels may prove inadequate, as one authority predicted in 1980 that heavy metal contamination would need reduction to less than 1 ppt [1].

Much of the following material was discussed at a workshop sponsored by the American Association for Crystal Growth from September 28 to October 1, 1987 [2].

2. Use of silane in fabrication of electronic devices

Commercial uses for silane began during the mid-1960s with the development of the semiconductor industry. An early paper by Joyce and Bradley [3] discussed its use in growth of epitaxial layers, but it also was the silicon source gas chosen for chemical vapor depositions (CVD) of silicon dioxide and, later, silicon nitride and polycrystalline silicon.

State-of-the-art integrated circuits might be fabricated with a thin epitaxial layer, a field oxide, a film of silicon nitride serving as a dielectric and another Si_3N_4 film as a passivation layer, and one or more layers of a silicide serving as interconnections – all made from silane. Other devices might include layers of doped polysilicon, also as interconnects. Amorphous silicon films, deposited usually through Plasma Enhanced CVD techniques, are now used to fabricate photovoltaic cells [4,5], photocopier drums [6], photoreceptor cells in facsimile machines [7], and experimentally, flat panel displays [8]. Thousands of metric tons of silane are also used in industrial applications as a precursor to polysilicon manufacture by Union Carbide, Ethyl Corporation, and Japan's Komatsu [9]. Britain's Pilkington Glass has been forming anti-reflective coatings with silane [10]; in the future, silane may find large industrial applications in silicon carbide manufacture [11].

3. Manufacturing and purification of silane

This discussion first will briefly review the four silane manufacturing schemes, and then describe in some detail the variety of methods proposed to purify the resulting "raw" silane.

Table 1 summarizes silane manufacturing methods. The lithium hydride method was patented in 1957 and today is used, in somewhat modified form, by all but three producers. Its attractions are high yield (98–99%), relatively low cost (perhaps $0.10–0.12 per gram), and high throughput (batches of up to 50,000 g). Problems with this method include high electrical costs and significant impurity contributions from alkali metals.

The tetrahydrofuran method is less electricity-intensive, and alkali metal contamination is reduced, but the THF solvent might add carbon.

Table 1
Silane manufacturing methods

Batch processes

Lithium hydride

(1) $LiCl(45\%)/KCl(55\%) \xrightarrow{400-500\,°C} 4\,Li + 4\,Cl$

(2) $4\,Cl + Si \xrightarrow{\text{anodic reduction}} SiCl_4 + 4\,e$

(3) $4\,e + 2\,H_2 + 4\,Li \xrightarrow{550-625\,°C} 4\,LiH$

(4) $SiCl_4 + 4\,LiH \xrightarrow{390-430\,°C} SiH_4 + LiCl$

Sundermeyer Patent 1957
Used by majority of manufacturers
Batch size: maximum 50,000 g

Tetrahydrofuran

(1) $SiCl_4 + LiAlH_4 \xrightarrow{THF/heat} SiH_4 + LiCl + AlCl_3$

Used by one US manufacturer

Magnesium silicide

(1) $Mg_2Si + 4\,NH_4Cl \xrightarrow{0\,°C} SiH_4 + 2\,MgCl_2 + 4\,NH_3$

Used by Komatsu

Continuous process [a]

Union Carbide catalytic redistribution of chlorosilanes

Hydrogenation

(1) $Si(98\%) + 3\,SiCl_4 + 2\,H_2 \rightarrow 4\,HSiCl_3$

Disproportionation/distillation

(2) $2\,HSiCl_3 \rightarrow H_2SiCl_2 + SiCl_4$

(3) $3\,H_2SiCl_2 \rightarrow H_3SiCl + 2\,HSiCl_3$

(4) $2\,H_3SiCl \rightarrow SiH_4 + H_2SiCl_2$

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[a] Ref. [9] has complete flow diagram.

The magnesium silicide method chosen by one large Japanese manufacturer was used originally for laboratory preparation of silanes. Negatives of this process include the problems of impurities from the salt, as well as high electrical and environmental costs.

All the above are batch processes (although the Mg_2Si method has been commercialized in a semi-continuous operation). As such, they all share the inherent problem of variable impurity levels batch-to-batch. In fact, variation in purity levels often has ben cited as more of a concern than actual impurities. Process control is impossible when, for instance, the CH_4 content of SiH_4 used for amorphous solar cells varies from 1 ppm to 5 ppm – even though 5 ppm is really quite low. Many users in this case would prefer to receive 5 ppm consistently than accept variability between 1 and 5 ppm.

The Union Carbide silane manufacturing method, on the other hand, is a continuous process. Basically, the method involves a catalytical redistribution of chlorosilanes. Starting with metallurgical grade Si plus $SiCl_4$, the process proceeds through a series of distillations and redistributions, with appropriate pressure and temperature conditions, eventually to form very high purity SiH_4 ($>$ 99.995% purity).

Impurities in SiH_4 can be attributed to several sources: the raw starting materials, the process materials such as piping, distillation columns and control equipment, and air or water vapor from poor techniques in transfer and storage.

The most common starting material is metallurgical Si – either used directly as in the continuous method or indirectly in all other methods (in that it is the starting material for all chlorosilanes production). Lorenz [12] has identified no less than 25 possible elemental impurities in metallurgical (98%) Si, including 2000 ppm Al, 6000 ppm Fe, 1000 ppm Ca, 100 ppm P, and 50 ppm each of B, As, Sb, and Sn. Lithium hydride is available commercially at 96.5% purity, with appreciable amounts of C and alkalis [13], and potassium chloride, at 98.8% purity, has as much as 9000 ppm NaCl, and lesser amounts of Br, Ca, and S [14].

An interesting evaluation of impurity sources for the Union Carbide continuous process appears in a 1979 report [15]. On a molar volume basis compared to silane, impurities entering the process could range from 2.01% for N_2, to 1.0% Cu, 0.3% Fe and Al, 0.1% C, 0.01% B, 0.02% P, and 2 to 4 parts per million Sb and As.

It is obvious that any manufacturing method must purify the resulting "raw" silane to remove impurities derived from the precursors. "Raw" silane has been reported to contain 1–2% H_2, 1000 ppm chlorosilanes, 500–1000 ppm $SiCl_4$, 1000–2000 ppm higher silanes and siloxanes, CH_4 (200 ppm) and active metals in the form of hydrides of As, P, and B (10 ppm) [12].

Thus, without purification, silane could be expected to contain unacceptable levels of carbons which could lead to poor crystalline formation [16,17] or uncontrollable resistivity for polysilicon interconnects [18]; it could have many times more chlorosilanes, siloxanes, O_2, N_2, PH_3, or metals than specified for good photovoltaic or photoreceptor performance [19–21]; or it could have more than the several parts per million H_2O or O_2 which lead to SiO_2 formation [22]. Additional impurities of concern include chlorosilanes when used for Si_3N_4 passivation, N_2 for epitaxial depositions, and even excessive H_2 which could lead to unacceptable and variable deposition rates [23].

But information on impurity effects on specific device performance is very difficult to find [24]; undoubtedly, additional effects can be expected for as-yet unknown impurities.

Twenty-one different purification techniques are discussed in the Lorenz work [12]. They can be divided into two basic areas: those methods which distill the product to remove gaseous impurities, and those adsorption techniques required to remove metallic impurities affecting resistivity and other electrical characteristics.

Runyon [25] mentioned the use of "synthetic zeolite beds at $-78°C$ ... to remove any arsenic and phosphorus compounds", and several other sources are quoted as recommending molecular sieves.

Yusa, Yatsurugi, and Takaishi [26] discuss purification quite extensively, claiming that, "In a generation process of monosilane, boron hydrides are completely removed from silane by the chemical reaction $=B + :NH_3 \rightarrow \equiv B:NH_3$ ... According to our experience, boron content in silicon ... ranges between 0.02–0.01 ppb in atomic ratio." However, they do acknowledge that their magnesium silicide production method could lead to as high as 10 ppm phosphorus incorporation. This, then, is the impurity of concern. They describe an ion-exchanged modification of molecular sieve A, in which 30.83% of the ions are replaced by potassium and 16.66% of the exchangeable calcium is replaced by divalent ions from among Mg, Zn, Ca, Pb or Mn.

Perhaps the most interesting method of purification described in open literature to date is a 1978 patent [27] in which the impure silane is passed through six zones in series, to remove $SiCl_4$, chlorosilanes and other silicons, PH_3 and

AsH_3, low boilers and lights, and B_2H_6 and higher silanes.

A Japanese silane manufacturer describes a similar scheme in a recent patent [28] in which SiH_4 containing 1% $SiCl_4$, 900 ppm SiH_3Cl, and 1000 ppm C_2H_4 was purified to less than detectable limits.

Another Japanese patent [29] describes the use of Zeolite 4A ion-exchanged with Ag. 100 ppb PH_3 impurity in silane was reduced to < 0.2 ppb, while 100 ppb AsH_3 was reduced to < 0.5 ppb.

The Union Carbide silane plants also use extensive methods to purify silane, most of which involve a variety of proprietary catalysts [15,30].

Recently, several companies have offered purifiers for end-user removal of contaminants [31]. While adsorptive methods have been used extensively by manufacturers for silane purification, the level of impurity reduction required – to parts per trillion for metals and sub parts per million for gases – makes end-user purification problematical. And since many of these products are based on ion exchange or synthetic zeolite technology, one real concern not yet addressed is whether impurities are simply exchanged; i.e., in the process of removing one metal, are others introduced from the purifier? Such questions must be fully answered before use of such systems becomes widespread.

4. Analysis of gaseous impurities in silane

As the specialty gas industry has learned to remove gaseous impurities in silane to levels below 1 ppm, analytical techniques have had to be developed to keep pace.

Mitchell surveyed "Chemical Analysis of Electronic Gases and Volatile Reagents for Device Processing" in a 1985 article [32]. He supported his claim that "Silane has been investigated thoroughly" through citations from numerous Russian articles about impurity analyses for H_2, O_2, N_2, CO_2, NH_3, B_2H_4, GeH_4, PH_3, and AsH_3. But little information was given about sensitivities and, since these references all are from five to ten years old, it is probable that they do not meet today's sensitivity requirements. Other references to analysis of silane gaseous impurities are scarce, including only mass spectrometric methods [20,33].

Therefore, the remainder of this section will be devoted to Union Carbide's silane analytical methods. Our laboratories have developed new analytical methods for CO, CO_2, CH_4, O_2, N_2, Ar, H_2O, Si_2H_6, chlorosilanes, and siloxanes in silane during the past two years. The following will detail these techniques; these and proposed alternative methods are summarized in table 2.

Bradley has reported on a method for detection of CO, CO_2, and CH_4 in silane to levels below 0.5 ppm each [34]. The method selected involves a methanizer and a flame ionization detector. Specifically, a Carle Series 400 Gas Chromatograph with a 10 foot $\frac{1}{4}$ inch Porapak Q 80/100 mesh copper column with constant 50 °C temperature is used to separate the components of interest. The CO and CO_2 are converted to CH_4 as they pass through the methanizer. The methanizer, maintained at a constant 400 °C, does not affect the CH_4 component. In the analysis, a 2 cm^3 sample size is used and a flow rate of 30 cm^3/min He carrier gas is maintained. A backflush valve is activated immediately after elution of the CO_2 peak, flushing SiH_4 to vent. If the SiH_4 is not directed away from the Flame Ionization Detector, SiH_4 dust particles will interfere with its operation. Sensitivities are reported at approximately 0.2 ppm for each impurity, upon reconditioning of the methanizer.

Gas chromatography, using a Thermal Conductivity Detector, has long been used by the industry for measurement of O_2 plus Ar. Sensitivities range down to 3 ppm, but separation into individual components was not possible with ordinary columns and conditions. In early 1985 [35], Shrewsbury reported successfully analyzing for O_2 through a modification of the Bradley carbon method. He added a carbonizer prior to the methanizer; the O_2 reacted to form CO_2 which then was analyzed as above. Sensitivities to less than 0.5 ppm were claimed.

Ar ($+O_2$), He, and N_2 historically have been analyzed by a Thermal Conductivity Detector; best sensitivities were around 3 ppm. Today, the Union Carbide Analytical Services group is exploring two new detectors. The Discharge Ioniza-

Table 2
Analytical methods; gaseous impurities

Impurity	Comments	Sensitivities
H_2O		
– Dew point detector		1–2 ppm
– Electrolytic cell P_2O_5	Meeco	0.5 ppm
– Piezoelectric sensor	du Pont 560 or 5700	0.1 ppm
O_2		
– GC, FID with carbonizer and methanizer, special columns	O_2 only	0.5 ppm
– GC, TCD	O_2 + Ar	3 ppm
Hydrocarbons (CH_4)		
– GC, FID with methanizer		0.2 ppm
– GC, TCD		1–10 ppm
$CO+CO_2$		
– GC, FID with methanizer		0.2 ppm Ea.
– GC, TCD		3 ppm Ea.
Ar, He, N_2		
– GC, TCD		3 ppm Ea.
– GC, DID		0.1 ppm
– GC, TCD	Microvolume TCD	1 ppm
H_2		
–GC, TCD		5 ppm
Chlorosilanes (SiH_3Cl, SiH_2Cl_2, $SiHCl_3$)		
– GC, TCD		3 ppm Ea.
– Hydrolyzable chloride electrodes	Total Cl	0.1 ppm
– Mass spectrometer		1 ppm Ea.
Disilane		
– GC, TCD	Microvolume TCD	0.5 ppm
– GC, ultrasonic detector		1 ppm
Siloxanes		
– GC, PID		1 ppm
– GC, TCD	Microvolume, TCD	0.5 ppm
– Mass spectrometer		1 ppm

DID = discharge ionization detector
FID = flame ionization detector
GC = gas chromatography
TCD = thermal conductivity detector

tion Detector and Microcell TCD are both expected to provide sensitivities below 1 ppm [36].

Just as O_2 has been identified as a critical impurity, causing SiO_2 formation with resulting haze and poor crystallinity [37,38], water, too, can be critical to device performance and yield. Union Carbide, in conjunction with du Pont, has successfully modified a du Pont Model 5700 detector to analyze H_2O in silane to levels below 0.1 ppm [39]. Obtaining a dry reference of SiH_4 was crucial to successful evaluation, as was modification of the cell to exclude all traces of O_2 or H_2O.

Chlorosilane impurities ranging to over 1000 ppm were common in silanes produced only a few years ago, but many vendors claim levels below 10 ppm today. One important question to ask of vendors is "just what chlorosilanes are you analyzing?", as it is especially difficult to produce a calibration standard for SiH_3Cl [40]. Partly due to this difficulty, gas chromatographic methods have recently been replaced by wet chemical methods whereby a measured amount of SiH_4 is bubbled through a solution which then is measured by titration [41] or an ion-selective electrode [42]. The titration method needs accurate standards, fresh reagents, complete hydrolysis, and quantitative transfers followed by accurate titration to end points; its lower limit is reported at 1 ppm. The ion-selective electrode method, on the other hand, requires easily obtainable calibration standards, does not require quantitative transfer, and can be adjusted to deliver any sensitivity required, dependent only on sample size.

Finally, photovoltaic cell manufacturers have identified a need to minimize Si_2H_6 and especially siloxane (oxysilane) impurities. Several of these users have developed analytical methods for these impurities, and, in a joint development project with Union Carbide, have proven the validity of their method through a round-robin comparison program [43].

A concern of both our customers and Union Carbide was how to standardize the instrument and test the method for accuracy, reliability, and reproduceability. The method chosen involves analysis using a Hewlett Packard 5890A Gas Chromatograph, with a Micro Volume Thermal Conductivity Detector, a 6 foot long by $\frac{1}{8}$ inch diameter stainless steel Porapak PS-AW column at 80 ° C, with a 30 cm^3/min flow of He carrier gas, and a 1 cm^3 sample. Customers used different detectors and columns, but correlation was good: siloxanes were analyzed at < 1, 1.2, 2.5, and 2.5 ppm; and disilane analyzed at 20, < 0.5, < 0.5, < 0.5 ppm. Sensitivities for both siloxanes and disilane were at 0.5 ppm.

Mitchell [32] provides an appropriate summary for this section: "Commercial suppliers have made significant progress in making chemicals of greater purity available. However, it is important to re-emphasize that a high purity label does not indicate the quality of the product. Purity can be established only by accurate determination of deleterious impurities...".

5. Epitaxial resistivity as a measurement of silane quality?

The specialty gases industry historically has specified silane gas quality through measurement of the resistivity of SiH_4-produced epitaxial layers. This made sense years ago, for there was no measurement capability for metallic contamination at required sensitivity levels; the effect of impurities on device performance and yield was poorly, or not at all, understood; epi films often were, in fact, deposited from silane; and the quality requirements for the semiconductor industry were for epi layers with intrinsic resistivity on the order of no more than a few ohm centimeters, and, as a result, poor film quality leading to inaccurate resistivity determinations was rarely a problem.

Today, however, there are numerous reasons to eliminate this industry standard:

There are several metallic measurement techniques with sensitivities in the sub ppb levels (more on these later).

As we have seen [16–23,37,38], gaseous impurity effects on device performance are now better recognized. While the effects of metallic contamination are not yet so apparent, some generalizations are possible: especially to achieve high lifetimes, heavy metallic contamination must be reduced to concentrations below 10^{11} [44]; mobile alkali metals must be eliminated especially for future MOS devices [45]; deposition and etching rates are strongly affected [46,47]; oxidation-induced stacking faults are often caused by metals [48]; and conversion efficiency of solar cells can be drastically affected [21].

Since the mid-1970's, technical [49] and safety [50] concerns have led users away from silane for epitaxial depositions to the point that it is almost never used commercially.

Difficulties in depositing and then measuring high resistivity films were recognized very early. Patrick of IBM in 1965 [51] described an apparent dependence of resistivity upon measuring current, leading to poor reproducibility and accuracy. Passoja et al. [37] described epitaxial depositions where increasing haze caused by SiO_2 formation led to increased resistivity. On the other hand, Donahue and Reif [52] described deposition of intrinsic epitaxial silicon whose resistivity is apparently limited to 40 Ω cm by the presence of electrically active O_2. And Sachitano and Kannan [53] stated that the normal background resistivity of typical epitaxial reactor systems might be 50–150 Ω cm.

The autodoping phenomenon was studied extensively by Ackermann and Ebert [54], who also discussed out-diffusion. Numerous other researchers also have mentioned the problems of autodoping, out-diffusion, and compensation [12,51,52,55]. Bell Laboratories researchers [48,56] described the many potential metallic impurity sources in reactors, in starting Si substrates, and introduced during device fabrication. And finally, Lorenz [12] pointed out that there are differing absorption coefficients for the metallic impurities so that, say, 20 ppt As in the gas phase does not imply 20 ppt As in the deposited layer.

All the above point to the need for a new standard for metallic impurity levels in silane. This will be discussed in the next section.

6. Analysis of metallic impurities in silane and silicon

Measurement of metallic impurities in gaseous SiH_4 is difficult and unrewarding, for even the most sensitive methods have minimum detection limits ranging from parts per billion to tens of parts per million [57]. And Graphite Furnace AA, the most sensitive direct method, is slow and tedious. Table 3 compares these direct measurement techniques.

To obtain the required sensitivities, copious amounts of SiH_4 must be bubbled through aqueous media which must then be concentrated. It is assumed that collection efficiency is 100%, i.e., that all elements are 100% soluble, and that no contaminants are added during the sample concentration procedure – most dubious assumptions, indeed.

Because of these problems with direct SiH_4 analysis, most impurity measurements are taken from silane-derived intrinsic single crystal silicon. Specific analysis for surface contaminants is possible using Auger spectroscopy [58–60], Secondary Ion Mass Spectroscopy [61,62], and techniques with electron microscopes [63–65]. There are, however, only four techniques with the required sensitivities for sub ppb metals determination [66]: Deep Level Transient Spectroscopy, Infrared Spectroscopy, Neutron Activation Analysis, and Photoluminescence Spectroscopy. Table 4 summarizes reported sensitivities for each of these methods.

Deep Level Transient Spectroscopy has been used by many laboratories since its introduction in 1974 [67]. DLTS provides a fairly complete characterization of deep level impurities [62] at sensitivities around 10^{11} carriers/cm^3.

Table 3
Typical instrumental detection limits; direct measurement of metals in silane (ppm) [a]

Element	Inductively coupled plasma emission spectroscopy	Standard atomic absorption spectrophotometry	Graphite furnace atomic absorption spectrophotometry
Al	2	6	0.03
As	30	300	0.1
B	5	500	14
Ca	0.5	1	0.01
Cr	3	6	0.04
Co	3	5	0.7
Cu	1	3	0.04
Fe	2	6	0.03
Pb	40	10	0.05
Mg	0.05	0.3	0.003
Mo	4	20	0.1
Ni	10	10	0.1
P	30	40,000	0.6
K	80	3	0.007
Na	20	0.2	0.003
S	20	–	–

[a] Source: ref. [57].

Table 4
Typical sensitivities – selected elements; indirect measurements of metals in silane (ppba)

Element	Deep level transient spectroscopy (ref. [67])	Neutron activation analysis (ref. [71])	Fourier transform infrared spectroscopy (ref. [70])	Photoluminescence spectroscopy (ref. [76])
Al		500	0.2	$\lesssim 0.01$
Sb		0.002	0.003	$\lesssim 0.01$
As		0.007	0.0028	$\lesssim 0.01$
B			0.0034	$\lesssim 0.01$
Ca		1150		
Cr	×	0.5		
Co	×	0.05		
Cu	×	0.2		
Ga			0.028	$\lesssim 0.01$
Au	×	0.00007		
In			0.14	$\lesssim 0.01$
Fe	×	28		
Mo	×			
Ni	×	860		
P			0.0008	$\lesssim 0.01$
K		65		
Na		0.09		
Ti		550		
Zn	×	0.4		
Zr		150		

DLTS: × implies values for deep energy levels in silicon are well-established, and $\gtrsim 0.1$ eV (ref. [62]).
PL: Current capabilities show sensitivities per analysis around 0.01 ppb, but with analysis of impurities first in epi layer, then in substrate, difference can be < 0.01.

Infrared spectroscopy techniques often are conducted at room temperature for measurement of C and O in single crystal Si [68], at reduced temperatures [69], or with FT-IR at reduced temperatures [57]. Shallow donors and acceptors can be seen at typical sensitivities of 10^{11}–10^{13} atoms/cm^3 Si. These detection limits assume about a 1% transmission for baseline noise; reduction to 0.3% noise levels will provide a significant enhancement [70].

Neutron Activation Analysis is sensitive to levels akin to those of low temperature IR [48,56,71]. It covers many transition metals.

Photoluminescence Spectroscopy offers high sensitivity ($< 10^{10}$ carriers/cm^3) and selectivity [72]. Recently the technique has been expanded to epitaxial layers, thus reducing the extra preparation steps required for a high purity single crystal sample, and increasing the sensitivity, since the measurement of impurities now is the difference between those in the epi layer and those in the substrate. It is non-destructive, not restricted in sample size, and insensitive to surface contamination [73]. Another benefit of PL is its ready availability, with at least one company offering a production-line unit.

There are problems with these methods. All of them require the conversion of gaseous SiH_4 to a solid single crystalline Si – either an epitaxial layer or an actual crystal boule – and the preparation skills and cleanliness requirements are demanding. The differing absorption coefficients make correlation between impurities in the gas and solid questionable. Individually, each method also has problems:

- DLTS has a very high sensitivity, but cannot detect electrically inactive atoms or precipitates [74]; it also requires fabrication of devices, which not only complicates the analysis, but also could further introduce metallic contamination. It is sensitive to only a small cross-sectional area [75].

– Infrared is similarly restricted in that the sample must be small enough to be penetrated by IR light [73].
– NAA gives an average concentration, without regard to electrically active or inactive centers [74], and generally requires that the samples be sent to an outside laboratory for irradiation and analysis [75]. It cannot be used for detection of some dopant impurities such as B, or P, and detection limits are relatively high for Al, Ti, Ni, and Ca [71].
– PL can be used only for selected dopant impurities.

It is apparent that no method for metallic analysis – whether in gaseous SiH_4 or deposited intrinsic crystalline Si – is entirely satisfactory. Some combination of methods is therefore indicated, with photoluminescence and DLTS providing analyses for the widest range of critical impurities.

7. Conclusion

We have reviewed manufacturing methods and their relationship to purification techniques. The quality of silane available commercially probably has made end-user purification of questionable value, due to the potential for added impurities from the gettering device.

Analytical methods for gaseous impurities to sub ppm sensitivities have been developed over the past two years. More than 15 critical impurities can be characterized in a typical commercial silane analytical laboratory.

Resistivity measurements of an intrinsic epitaxial layer historically have been used to qualify SiH_4 quality. But high quality epi films require a very clean reactor and handling techniques (to avoid particulates or dopants), well-controlled flow rates and temperatures (to avoid polysilicon formation), and an absence of leaks or ambient residual air or water (to avoid SiO_2 formation). Diffusion from the substrate and autodoping and reactor memory from previous depositions cause unintended dopant incorporation, leading to false low values if the dopants are of the same type as predominate in the SiH_4, or false high if they are opposite type leading to compensation. Gaseous impurities such as C or O lead to poor crystalline formation, causing false resistivity values. Furthermore, even if a perfect crystal is deposited, with no added impurities due to the reactor, substrate, or gaseous impurity incorporation, adsorption coefficients for the metallic impurities are not well known. And resistivity does not provide an evaluation of specific metallic contamination, but only indicates the difference between net donors and net acceptors.

Instead, future SiH_4 specifications should include a listing for critical metallic impurity levels to sub parts per billion sensitivities.

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