The distortion of (111) sub-diffused layers during silicon epitaxial deposition.

Robert P. Deysher
THE DISTORTION OF (111) SUB-DIFFUSED LAYERS DURING SILICON EPITAXIAL DEPOSITION

by

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A Thesis

Presented to the Graduate Committee of Lehigh University in Candidacy for the Degree of Master of Science in Metallurgy and Material Science

Lehigh University 1976
This Thesis is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science.

March 23, 1976

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ACKNOWLEDGEMENTS

The author wishes to acknowledge the advice and helpful discussions with his advisor, Dr. M. R. Notis. He also wishes to thank Mr. W. R. McCormack of the Western Electric Company who allowed the author the time and support necessary to accomplish this investigation.

Finally, the author wishes to thank his wife and family for their patience and encouragement which made this work possible.
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ABSTRACT

The distortion of the sub-diffused buried layer patterns during silicon epitaxial growth results in improper alignment of subsequent mask levels and lower device yields. This pattern distortion was measured after silicon epitaxial growth in a vertical R. F. heated reactor over (111) antimony sub-diffused wafers misoriented at \(3.0^\circ \pm 0.5^\circ\) in the [211] direction. The following silicon sources were used: \(\text{SiH}_4\), \(\text{SiHCl}_2\), \(\text{SiHCl}_3\), and \(\text{SiCl}_4\). The temperature of growth was varied from 950°C (optical) to 1175°C (optical) and the \(\text{H}_2\) mainstream flow rate from 20 to 80 liters per minute. In general, pattern distortion decreased with both increasing deposition temperature and \(\text{H}_2\) mainstream flow rate.

No pattern distortion was observed when \(\text{SiH}_4\) was used as the silicon epitaxial source over all deposition temperatures and \(\text{H}_2\) mainstream flow rates studied. When small amounts of gaseous HCl were added to epitaxial growth with \(\text{SiH}_4\), distortion did occur and increased with increasing amounts of gaseous HCl. At higher deposition temperatures the gaseous HCl additions had less of an effect on pattern distortion. Anisotropic growth rates were observed with increasing amounts of gaseous HCl additions with the (110) planes having
the highest growth rate. Anisotropic growth rates were found to decrease with both decreasing amounts of gaseous HCl and increasing deposition temperature.
INTRODUCTION

The diffusion of an N-type dopant into specific areas of (111) silicon wafers prior to silicon epitaxial deposition significantly reduces the collector series resistance of transistors in integrated circuits. By virtue of the processing required to fabricate these sub-diffused regions, a small step in the silicon wafer is created relative to the undiffused areas. This step is on the order of several hundred angstroms exposing low indice planes, other than the (111) planes, which have anisotropic growth properties. (1-2)

During epitaxial deposition, these sub-diffused regions can become distorted. Since these regions do act as guides in the alignment of subsequent diffusions, the shape distortion of these regions can lead to improper device performance. This is of considerable interest in today's large scale integration technology where packing densities of devices have increased significantly. As the density of devices per unit area increases, the definition of specific regions into which diffusions are required becomes more critical. For this reason, the geometry of the sub-diffused region after silicon epitaxial deposition has to be maintained.

The scope of this investigation covers the pattern
distortion of sub-diffused buried layers in (111) Czochralski wafers during silicon epitaxial deposition. The parameters of deposition temperature and H₂ main stream flow rate are varied using different epitaxial silicon sources (Silane-SiH₄, Dichlorosilane-SiH₂Cl₂, Trichlorosilane-SiHCl₃, and Silicon Tetrachloride-SiCl₄). Differences in the processing characteristics of each source are studied and their relationships to different amounts of pattern distortion are investigated. From a comparison of these results, the role of gaseous HCl on pattern distortion is studied with respect to different crystallographic orientations.
The use of epitaxial deposition is an integral part of the processing necessary in the fabrication of integrated circuits. Epitaxial deposition of silicon is the growth of a silicon layer on a silicon substrate. This layer is single crystal with the same crystallographic orientation as the substrate. The layer's thickness is on the order of microns whereas the substrate has a thickness on the order of mils.

The advantage of this processing step is that the electrical properties of the epitaxial layer can be accurately controlled. Epitaxial layers can be grown with either identical or opposite conductivity types to that of the substrate at dopant levels several orders of magnitude lower than that of the substrate. The resultant structure is one with a very sharp dopant profile between the substrate and epitaxial layer. (3-5) This profile is substantially sharper than those fabricated using diffusion processes. It is into this thin layer of silicon that the collector, base, and emitter of the transistors are diffused with the epitaxial layer acting as the collector. (FIG. 1a).

The epitaxial process is a high temperature
process (>1000°C) carried out in a reducing ambient which is usually H₂. A silicon bearing species plus an appropriate dopant is added to the epitaxial reactor after the silicon substrates are heated to the deposition temperature. The commonly used silicon epitaxial sources are SiH₄(Silane), SiH₂Cl₂(Dichlorosilane), SiHCl₃(Trichlorosilane), and SiCl₄(Silicon Tetrachloride). When a N-type epitaxial layer is required, either AsH₃(Arsine) or PH₃(Phosphine) are used, whereas B₂H₆(Diborane) is used when a P-type layer is desired.

As reported by Theuerer(6), silicon tetrachloride (SiCl₄) was the first silicon source used for epitaxial deposition. The high temperature reaction(Eq. 1) is one of H₂ reduction with the formation of gaseous HCl as a by-product.

\[
\text{SiCl}_4 + 2\text{H}_2 \rightarrow \text{Si} + 4\text{HCl} \quad (\text{Eq. 1})
\]

At temperatures below 1100°C, this reaction is rate limited whereas above 1100°C, the controlling parameter is one of mass transfer. For this reason, the deposition temperature is in the range of 1100°C to 1150°C at a growth rate of approximately 1 micron per minute.

Another commonly used silicon epitaxial source is silane(SiH₄). The advantage of this source is that
its high temperature reaction (Eq. 2) is one of pyrolysis.

$$\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \quad \text{(Eq. 2)}$$

The by-product of this reaction is $\text{H}_2$ and not gaseous $\text{HCl}$. Since the reaction is one of pyrolysis, its deposition rate is not reaction rate limited as that of $\text{SiCl}_4$. Typical deposition temperatures are in the range of $1000^\circ\text{C}$ to $1050^\circ\text{C}$. What limits the use of $\text{SiH}_4$ as an epitaxial source is its processing characteristics. $\text{SiH}_4$ has a tendency to deposit on anything that is at elevated temperatures above $600^\circ\text{C}$. Coating of various reactor parts occurs and not necessarily on the silicon substrates. This limits the deposition rate to less than 1 micron per minute.

Dichlorosilane($\text{SiH}_2\text{Cl}_2$) is a silicon epitaxial source recently made available\(^8\). Like $\text{SiH}_4$, its high temperature reaction (Eq. 3) is one of thermal decomposition, however, its by-product is gaseous $\text{HCl}$.

$$\text{SiH}_2\text{Cl}_2 \leftrightarrow \text{Si} + 2\text{HCl} \quad \text{(Eq. 3)}$$

Typical deposition temperatures are in the $1050^\circ\text{C}$ to $1100^\circ\text{C}$ range. Its processing characteristics are similar to those of $\text{SiCl}_4$ and is capable of deposition rates in excess of 1 micron per minute.

Trichlorosilane($\text{SiHCl}_3$) is a little used silicon epitaxial source. Its high temperature reaction is one of $\text{H}_2$ reduction (Eq. 4)\(^9\). Like $\text{SiCl}_4$, it has...
a reaction rate limited temperature range below $1150^\circ C$ and is capable of high deposition rates greater than 1 micron per minute at deposition temperatures above $1150^\circ C$. Its processing characteristics parallel those of SiCl$_4$ with the high growth rate properties of SiH$_2$Cl$_2$.

During epitaxial growth with any of the chlorosilanes (SiH$_2$Cl$_2$, SiHCl$_3$, or SiCl$_4$), the formation of gaseous HCl as a by-product is unavoidable. With the presence of gaseous HCl in the epitaxial reactor, the reverse reaction (Eq. 5) of etching takes place. Since

$$\text{Si} + 2\text{HCl} \rightleftharpoons \text{SiCl}_4 + \text{H}_2$$  \hspace{1cm} (Eq. 5)

it is possible to remove silicon from the wafer surface by the addition of small amounts of gaseous HCl, it has become a standard procedure to etch, in situ, prior to epitaxial deposition at temperatures greater than $1150^\circ C$. This exposes a clean silicon surface prior to deposition and reduces structural defects that form during epitaxial deposition and are due to surface contamination.

When fabricating transistors in integrated circuits, the three transistor contacts are made on the top of the epitaxial layer (Fig. 1a). Using this structure, the collector series resistance limits the switching speed of the transistor. This resistance
is due to the distance necessary for the current to flow through the lightly doped epitaxial layer. The only way to reduce the collector series resistance is to reduce the distance through which the current flows*.

To achieve this condition, a heavily doped N⁺ buried layer is diffused into the substrate prior to epitaxial deposition (FIG. 1b). By making contact to this sub-diffused buried layer, a low resistance path is provided to the collector region from the collector contact.

The problem associated with this process is that the formation of the sub-diffused buried layer produces a small step in the silicon substrate on the order of several hundred angstroms (FIG. 2a). It is this step that act as guides for subsequent masking operations. During silicon epitaxial deposition the possibility that this pattern may distort exists (FIG. 2b). This will shift the alignment of subsequent diffusions resulting in improper device fabrication and performance.

A considerable amount of work has been done in the area of pattern distortion during silicon epitaxial deposition with emphasis on the elimination of the

*An alternate scheme would be to increase the epitaxial dopant concentration but this would be associated with a decrease in the base-collector breakdown voltage.
FIGURE 1b. SCHEMATIC OF EPITAXIAL TRANSISTOR USING SUB-DIFFUSED BURIED LAYER
FIGURE 2a. CROSS-SECTION OF SUB-DIFFUSED EPITAXIAL WAFER
FIGURE 2b. CROSS-SECTION OF SUB-DIFFUSED EPITAXIAL WAFER WITH PATTERN DISTORTION

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problem. Benjamin and Fatzer\textsuperscript{(11)} have reported that by misorienting wafers more than $2^\circ$ off the (111) plane during wafer shaping, distortion can be reduced. Pattern distortion of the sub-diffused areas was reduced such that pattern geometries are maintained. In comparison to this work, both Drum and Clark\textsuperscript{(12)} and Doss and Doo\textsuperscript{(13)} have indicated that it is important to misorient wafer normals approximately $3^\circ$ of the (111) plane, however, toward the [110] direction. This will reduce the distortion when compared to wafers misoriented toward the [100] direction. From these initial works\textsuperscript{(11-13)} in the area of pattern distortion, it has been a standard processing technique to misorient (111) silicon wafers which are used for epitaxial deposition.

The initial investigations\textsuperscript{(11-13)} into pattern distortion also observed that different deposition temperatures, growth rates, and hydrogen main stream flow rates change the amount of distortion. Epitaxial growth at low deposition temperatures as well as high growth rates increases the severity of distortion. This result was explained by using the data of both Tung\textsuperscript{(1)} and Mendelson\textsuperscript{(2)} who observed an anisotropic growth rate of silicon with respect to orientation. This analysis is consistent with the recent model
of pattern distortion proposed by Juleff(14). He gave qualitative approximations of distortion in (111) silicon from crystallographic considerations. This model does not, however, consider temperature effects and the assumption is made that the higher surface mobilities at elevated temperatures may reduce anisotropic crystalline effects.

All the initial works(11-13) observed the effects of growth rate and deposition temperature on pattern distortion but the only silicon source used for epitaxial deposition was silicon tetrachloride(SiCl₄). Benzing et al(8) has recently pointed out that pattern distortion is substantially reduced using SiH₂Cl₂. Distortion at 1050°C with SiH₂Cl₂ is comparable to the amount of distortion with SiCl₄ at 1150°C. In view of these results, different amounts of distortion might be expected with different epitaxial sources over a wide range of deposition parameters.
EXPERIMENTAL PROCEDURE

This study investigates the effect of different epitaxial parameters on pattern distortion. The parameters of deposition temperature and hydrogen main stream flow rates are varied using four silicon epitaxial sources (SiH$_4$, SiH$_2$Cl$_2$, SiHCl$_3$, SiCl$_4$). From a comparison of the results, the role which gaseous hydrochloric acid (HCl) has on pattern distortion is made. This result is further investigated and confirmed by the growth of silicon epitaxial layers using SiH$_4$ with gaseous HCl additions on wafers with different crystallographic orientations.

All sub-diffused wafers used in this study were cut from a (111), 4-15\hspace{1em}cm, boron doped Czochralski grown silicon crystal. The crystal was centerless ground to a nominal diameter of two inches and sawed into wafers using a diamond I.D. saw. The wafers were cut 3°±0.5° off the (111) plane in the $\{\bar{2}11\}$ direction. To remove damage introduced by the sawing operation, the wafers were chemically etched in a 4-1-3 (nitric-hydrofluoric-acetic) acid mixture and one mil of material removed from each side of the wafer. This was followed by mechanically polishing the wafer with Syton* to a mirror finish. Approximately, *A commercial semiconductor polishing compound
one mil of material was removed at this operation resulting in a wafer with a nominal thickness of 15 mils.

Wafers were cleaned in a hot (95°C) ultrasonic sulfuric-nitric acid mixture, rinsed in de-ionized (D.I.) water, and hot air dried. This was followed by a steam oxidation at 1100°C for one (1) hour where 6000-7000 Å of oxide (as measured by ellipsometry) was grown (FIG. 3 & 4a). Patterns in the oxide were generated by standard photolithographic techniques. The wafers received another mixed acid clean similar to the clean prior to oxidation which was followed by an antimony pre-deposition at 1250°C for two (2) hours (FIG. 4b). Solid Sb₂O₃ was used as the antimony source at 600°C. The sheet resistance (\(\rho_s\)) after pre-deposition was nominally 20Ω/□ as measured by four point probe as per ASTM F-374 and a nominal junction depth (\(x_J\)) of 4 microns as measured by groove and stain per ASTM F-110. After a one minute buffered HF oxide etch to remove any residual Sb₂O₃ glass, the wafers were cleaned using a mixed acid mixture. This was followed by an eight (8) hour drive-in at 1250°C in a N₂-10% O₂ ambient (FIG. 4c). This resulted in a final junction depth (\(x_J\)) of 9μ with a sheet resistance (\(\rho_s\)) of 15Ω/□. The step height relative to the original wafer surface generated by this process was
FIGURE 3.
FORMATION OF SUB-DIFFUSED BURIED LAYER PATTERN

\[
\begin{align*}
\text{SiO}_2 & \quad \text{0.7 \( \mu \text{m} \)} \\
\text{Si} & \quad \text{375 \( \mu \text{m} \)} \\
\hline
\text{PHOTORESIST} & \\
\end{align*}
\]

\[
\begin{align*}
\text{SiO}_2 & \\
\text{Si} & \\
\hline
\end{align*}
\]

\[
\begin{align*}
\text{SiO}_2 & \quad \text{4 \( \mu \text{m} \)} \\
\text{Si} & \quad \text{500 \( \AA \)} \\
\text{Sb} & \quad \text{10 \( \mu \text{m} \)} \\
\hline
\end{align*}
\]
FIGURE 4a. STEAM OXIDATION OF SUB-DIFFUSED WAFERS
FIGURE 4b. PRE-DEPOSITION OF ANTIMONY
SUB-DIFFUSED BURIED LAYER
approximately 500 Å after a HF strip of the oxide.

Prior to epitaxial deposition, the sub-diffused buried layer wafers were acid cleaned in a hot (95°C) ultrasonic sulfuric-nitric acid mixture and rinsed in D.I. water. This step was followed by a mechanical scrub using a mild detergent to remove any particles from the wafers.

Epitaxial deposition was performed on a vertical reactor (AMV-1200*; FIG. 5). The deposition sequence which was followed is given in TABLE 1. All wafers were etched (in situ) with gaseous HCl for 5.0 minutes at 1175°C(optical) where approximately one half micron of material was removed from the wafer surface. All deposition times were kept constant at ten(10) minutes. The temperature of deposition was varied from 925°C(optical) to 1175°C(optical) in 25°C intervals using either SiH₂Cl₂, SiHCl₃, or SiCl₄ as the silicon epitaxial source. In all cases, the H₂ main stream flow rate was kept constant at 80 liters per minute (LPM) except where the effect of main stream flow rate on pattern distortion was studied. For these epitaxial runs, the main stream flow rate was varied from 10 LPM to 80 LPM.

*A commercially available epitaxial reactor
FIGURE 5.
SCHEMATIC OF VERTICAL EPITAXIAL REACTOR

75 KW GENERATOR

SILICON WAFERS

H2

H2

HCl

SiH2Cl2

3%H2SiH4/H2

SiCl4

SiCl3

HIGH FREQUENCY COIL

GAS SCRUBBER

OPTICAL PYROMETER
<table>
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<th><strong>SEQUENCE</strong></th>
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<td>1-(\text{N}_2) FLUSH</td>
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</tr>
<tr>
<td>2-(\text{H}_2) FLUSH</td>
<td>3.0</td>
</tr>
<tr>
<td>3-HEAT TO 1175(\text{C(OIT.)})</td>
<td>5.0</td>
</tr>
<tr>
<td>4-HCl ETCH</td>
<td>5.0</td>
</tr>
<tr>
<td>5-(\text{H}_2) FLUSH</td>
<td>1.0</td>
</tr>
<tr>
<td>6-TEMP. ADJUST &amp; STABLIZE</td>
<td>3.0</td>
</tr>
<tr>
<td>7-DEPOSITION</td>
<td>10.0</td>
</tr>
<tr>
<td>8-(\text{H}_2) FLUSH</td>
<td>1.0</td>
</tr>
<tr>
<td>9-(\text{H}_2) COOL DOWN</td>
<td>10.0</td>
</tr>
<tr>
<td>10-(\text{N}_2) FLUSH</td>
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The effect which gaseous HCl has on pattern distortion was studied using silane (3% SiH₄ in H₂). Deposition was performed at 1000°C (optical) and 1100°C (optical) with additions of integral amounts of gaseous HCl. By adjusting the amount of gaseous HCl additions during deposition, the molar ratios of 1/1, 2/1, 3/1, and 4/1 (HCl/SiH₄) were investigated.

To evaluate the effect of orientation on pattern distortion, differently oriented wafers were used to study what variation exists with respect to gaseous HCl concentrations. One and one half inch diameter wafers with a nominal ten (10) mil thickness were used. The shaping of these wafers was identical to the sub-diffused wafers but with different crystallographic orientations. The orientations studied were (100), (110), and (111). Each epitaxial run contained wafers of each orientation using SiH₄ as the epitaxial source with integral amounts of gaseous HCl. Prior to deposition all wafers received a hot (95°C) ultrasonic sulfuric-nitric acid clean followed by a D.I. water rinse and a mechanical scrub using a mild detergent. The nominal dopant level of these wafers was approximately $5 \times 10^{18}$ carriers/cm³ (boron).

The evaluation of the pattern distortion on the sub-diffused buried layer wafers necessitated the
observation of the epitaxial layers at 280X using phase contrast microscopy. All wafers after epitaxial deposition were photographed using Nomarski interference techniques. The thicknesses of the epitaxial layers was measured using a Digilab FTG-12* interferometer and evaluated per ASTM F-95.

*A commercially available interferometer used in the measurement of epitaxial layer thicknesses
RESULTS

In FIGURE 6 the growth rates for \( \text{SiH}_2\text{Cl}_2 \) (0.47 mole %), \( \text{SiHCl}_3 \) (0.35 mole %), and \( \text{SiCl}_4 \) (0.56 mole %) are given as a function of deposition. All deposition temperatures were measured optically and corrected for emissivity using the data of Allen\(^{(15)}\). The temperature dependence of the growth rate for these sources can be more easily seen in FIGURE 7. In this plot the growth rate was normalized against the maximum growth rate obtained. This data is in agreement with that of Shepard\(^{(5)}\), Bloem\(^{(7)}\), and Benzing et al\(^{(8)}\).

With an increase in the chlorine content of the chlorosilanes, one observes an increase in the temperature dependence of the growth rate at the lower deposition temperatures. It is in this temperature region where the deposition rate is reaction rate limited. Epitaxial deposition using \( \text{SiCl}_4 \) does not become mass transfer limited until a deposition temperature of approximately 1150°C (opt.) is reached. \( \text{SiHCl}_3 \) becomes mass transfer limited at 1100°C (opt.) and \( \text{SiH}_2\text{Cl}_2 \) at approximately 1050°C (opt.). The reason that \( \text{SiH}_2\text{Cl}_2 \) has less of a temperature dependence is due to the nature of its high temperature reaction. It is one of thermal decomposition similar
FIGURE 6.
EPITAXIAL GROWTH RATE VERSUS DEPOSITION TEMPERATURE

TEMPERATURE °C (OPTICAL)

GROWTH RATE (μM/minute)

(Temperature)$^{-1}$ ($^\circ$K)$^{-1} \times 10^3$
Figure 7. Normalized Epitaxial Growth Rate Versus Deposition Temperature

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to SiH₄'s, however, gaseous HCl is the by-product instead of H₂. On the other hand, both SiH₄'s and SiHCl₃'s high temperature reactions are due to H₂ reduction.

If the temperature dependence of SiH₄'s growth rate had been plotted on FIGURE 7, it would have resulted in a curve above that of SiH₂Cl₂'s. This is a direct consequence of the pyrolysis reaction of SiH₄. However, due to its processing characteristics at high deposition temperatures, there is a tendency for silicon to deposit on the walls of the bell jar. This alters the gas phase concentration of silicon and substantially reduces the growth rate. For this reason, SiH₄ is used in a temperature range of 1000°C (opt.) to 1050°C (opt.). At higher deposition temperatures, forced air or water cooling of the bell jar are required.

To quantitatively evaluate the effect of different epitaxial parameters on pattern distortion, a pattern distortion parameter was defined (FIG.8). The parameter is the amount of distortion divided by the epitaxial layer thickness.

\[
PATTERN\ DISTORTION\ PARAMETER = \frac{\Delta l}{\frac{1}{2} - \frac{1}{1}} = \frac{\Delta l}{IR\ EFI\ LAYER\ THICKNESS}
\]
FIGURE 8. DEFINITION OF PATTERN DISTORTION PARAMETER

\[
\text{PATTERN DISTORTION PARAMETER} = \frac{l_2 - l_1}{\text{IR EPITAXIAL LAYER THICKNESS}}
\]

\[
= \Delta l/t
\]
Since the amount of distortion is on the order of a few microns, it can be readily observed on small sub-diffused patterns (FIG. 9). The sub-diffused patterns in FIGURE 9 were photographed using an interference contrast microscope, and with increasing deposition temperature the amount of distortion decreases.

It is a standard processing step to perform an in situ, gaseous HCl etch prior to deposition. This removes surface damage and contamination and exposes a clean surface of silicon on which to deposit. In order to assure that this operation does not contribute to pattern distortion, epitaxial runs were made with and without the gaseous HCl etch. The resulting pattern distortion parameter for these runs remained constant and was independent of the etch. This implies that the etch temperature of 1150°C (opt.) is sufficiently high to eliminate anisotropic etching effects. Also, the time period between the etch and the initiation of epitaxial growth (TABLE 1) is sufficiently long to allow removal of any residual HCl in the gas phase due to the etch.

In FIGURE 10 the pattern distortion parameters for SiH₂Cl₂, SiHCl₃, and SiCl₄ are given as function of deposition temperature. All three sources exhibit a decrease in pattern distortion with
FIGURE 9. PHOTOMICROGRAPHS OF BURIED LAYER PATTERN
FIGURE 10. PATTERN DISTORTION PARAMETER VERSUS DEPOSITION TEMPERATURE
increasing deposition temperature. These results are consistent with previously published data \(^{(11-13)}\). The data with SiH\(_2\)Cl\(_2\), however, is not in agreement with that of Benzing et al \(^{(8)}\). Their data indicated that pattern distortion with SiH\(_2\)Cl\(_2\) is considerably less than with SiCl\(_4\) at equivalent deposition temperatures. The data generated in this study points out that pattern distortion with SiH\(_2\)Cl\(_2\) is identical to that of SiCl\(_4\) at comparable growth rates and deposition temperatures.

In the temperature range above 1000\(^\circ\)C (opt.), the pattern distortion parameter is shifted upward for deposition with SiHCl\(_3\). This result is intriguing since it can not be explained by an increase in the gas phase concentration of the reacting species (i.e. mole % SiHCl\(_3\) < mole % SiH\(_2\)Cl\(_2\) < mole % SiCl\(_4\)). To explain this data, one has to investigate what parameters are controlling pattern distortion.

The pattern distortion using SiH\(_4\) as the epitaxial silicon source was not plotted on FIGURE 10 because at all deposition temperatures studied, it was negligible. This result together with the fact that no chlorine specie is present in the high temperature reaction of SiH\(_4\) (Eq. 2) indicated that chlorine species are responsible for the pattern distortion.
To further illustrate the effect of chlorine species, SiH₄ was used as the silicon source with incremental amounts of gaseous HCl to stoichiometrically simulate different chlorosilane species and the values of the pattern distortion parameter are plotted in FIGURE 11. With an increasing amount of gaseous HCl, the value of the pattern distortion parameter increases at both deposition temperatures of 1100°C (opt.) and 1000°C (opt.). At the higher deposition temperature the value of the pattern distortion parameter is lower and is expected from the results in FIGURE 10.

FIGURE 12 is a plot of the thickness variation for epitaxial growth in different crystallographic directions versus increasing amounts of gaseous HCl added to SiH₄ during epitaxial deposition. The percent thickness variation was calculated using the following equation:

\[
\% \text{ THICKNESS VARIATION} = \frac{T_{\text{max}} - T_{\text{min}}}{T_{111} + T_{110} + T_{100}} \times 100\%
\]

where \( T_{\text{max}} \) = maximum epitaxial thickness of \( T_{111}, T_{110}, \) or \( T_{100} \)

\( T_{\text{min}} \) = minimum epitaxial thickness of \( T_{111}, T_{110}, \) or \( T_{100} \)

\( T_{111} \) = epitaxial thickness of (111) wafers
FIGURE 11. PATTERN DISTORTION PARAMETER VERSUS HCl/SiH₄ MOLAR RATIO

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FIGURE 12. PERCENT THICKNESS VARIATION VERSUS HCl/SiH$_4$ MOLAR RATIO
\[ T_{110} = \text{epitaxial thickness of (110) wafers} \]
\[ T_{100} = \text{epitaxial thickness of (100) wafers} \]

For all epitaxial runs the value of \( T_{\text{max}} \) was equal to \( T_{110} \) with the value of \( T_{111} \) approximately equalling the value of \( T_{100} \). This plot (FIG. 12) indicates that the variation in growth rate with respect to orientation does exist as previously reported by Tung\(^1\) and Mendelson\(^2\) with the (110) orientation having the highest growth rate. The anisotropic growth rates decrease with increasing deposition temperatures as reflected in a decrease in the percent variation in FIGURE 12.

FIGURE 13 is a plot of the \( H_2 \) main stream flow rate versus the pattern distortion parameter. With an increasing \( H_2 \) flow rate, the value of the pattern distortion parameter decreases for all sources. This is due to an increase in the mass transfer of species both to and from the growing epitaxial layer. This is further explained with the use of FIGURE 14.

The growth rate in FIGURE 14 was normalized to a constant concentration in the \( H_2 \) main stream flow using the value of the \( H_2 \) main stream flow of 80 LPM. At a constant concentration in the gas phase, the growth rate will increase with increasing \( H_2 \) flow for this reactor type. This implies that the
FIGURE 13. PATTERN DISTORTION PARAMETER VERSUS MAIN STREAM FLOW RATE
FIGURE 14. NORMALIZED GROWTH RATE VERSUS MAIN STREAM FLOW RATE FOR SiH$_2$Cl$_2$, SiHCl$_3$, AND SiCl$_4$
growth is mass transfer limited over the entire range of \( \text{H}_2 \) main stream flow rates.
**DISCUSSION**

The effect that deposition temperature has upon the distortion of sub-diffused layers is shown in FIGURE 10 and is in agreement with published results (11-13). With an increase in the deposition temperature a decrease is observed in the value of the pattern distortion parameter for the three sources (SiH₂Cl₂, SiHCl₃, and SiCl₄). This result is explained by Drum and Clark (12), Benjamin and Fatzner (11), and Boss and Doo (13) as a decrease in anisotropic growth conditions and can be explained from nucleation theory. At higher deposition temperatures, the formation of three dimensional nuclei is low with an associated increase in surface mobility. Migration of silicon atoms to the buried layer step is dominant resulting in a decreased amount of distortion. At lower deposition temperatures, a larger number of nuclei exist due to an increase in the sticking probability of stable nuclei. This condition results in a lowering of atom mobilities and an increase in pattern distortion.

Below 1000°C (opt.) the value of the pattern distortion parameter decreases for SiH₂Cl₂ whereas for SiHCl₃ and SiCl₄ it is constant at its maximum value. The reason for the drop is due to the high temperature processing characteristics of SiH₂Cl₂ as
well as the definition of the pattern distortion parameter. Dichlorosilane's (SiH₂Cl₂) high temperature reaction is one of thermal decomposition with little drop in the deposition rate at lower temperatures. Also, the pattern distortion parameter is inversely proportional to the growth rate (i.e. epitaxial thickness) and by maintaining a high value of growth rate, the value of the pattern distortion parameter decreases.

The difference in the results of FIGURE 10 and those of Benzing et al (8) is that Benzing's results indicate that pattern distortion with SiH₂Cl₂ is significantly less than with SiCl₄. According to Benzing, distortion with SiH₂Cl₂ at 1050°C is equivalent to distortion with SiCl₄ at 1150°C but the results in this investigation point out that there is no temperature difference above 1000°C. This conflict in results may be due to the deposition apparatus used in each investigation. Benzing used a horizontal type reactor whereas in this investigation, a vertical type reactor was used. Since mass flow characteristics are different for different reactor types, different results might be anticipated. Although different reactors might result in different absolute values of distortion at the same deposition temperature, no
difference should be observed with different epitaxial sources. The differences that are noted by Benzing may be due to the fact that constant growth conditions are not maintained when switching different epitaxial sources. On the identical reactor used by Benzing, higher $H_2$ main stream flow rates are used with $SiH_2Cl_2$ than with $SiCl_4$. As shown in FIGURE 13, increases in the mass transfer characteristics due to higher main stream flow rates will decrease pattern distortion. If the $H_2$ flow rate was higher with $SiH_2Cl_2$ deposition in this study, a decrease in the distortion will be observed as compared to deposition with $SiCl_4$ at the identical deposition temperature.

The intriguing result of the effect of deposition temperature on pattern distortion was that no distortion was observed when $SiH_4$ was used as the epitaxial source. The difference between this source and the other three ($SiH_2Cl_2$, $SiHCl_3$, and $SiCl_4$) is that it does not produce gaseous HCl as a by-product. The role of gaseous HCl was investigated and the results are shown in FIGURE 11. As the gaseous HCl content increases, the amount of distortion increases to values typical of those observed with $SiCl_4$, $SiHCl_3$, and $SiH_2Cl_2$. Also observed in this experiment was a temperature effect on the addition of gaseous HCl to $SiH_4$. With an
increase in deposition temperature, gaseous HCl additions have less of an effect on distortion. This is identical to the results observed with the other chlorosilane epitaxial sources.

The phenomenon of gaseous HCl on pattern distortion has not been considered by the initial investigations in this area \(^{(11-13,18)}\). Their results were correct but their analysis was not. Although such parameters as surface mobilities and nucleation rates are temperature dependent, they can not totally give a qualitative answer to pattern distortion. The gaseous HCl effect has to be investigated since it dominates all other parameters controlling pattern distortion.

To fully understand the effect of gaseous HCl, one has to consider what reactions are possible at the temperature of interest. The most likely reaction is:

\[
\text{Si} + 2\text{HCl} \rightarrow \text{SiCl}_2 + \text{H}_2 \quad (\text{Eq. } 5)
\]

Steinmeier \(^{(16)}\) reports that the equilibrium constant for this reaction is approximately unity at the temperature of 1000°C such that the possibility of forming SiCl\(_2\) exists. This reaction is occurring during the addition of gaseous HCl to SiH\(_4\) in view of the modified processing characteristics. There is little or no coating of the bell jar walls with silicon indicating that the reaction (Eq. 2) is being altered.
Since the formation of SiCl\textsubscript{2} is occurring, it appears that it is associated with an anisotropic etching phenomenon. This leads to the distortion because deposition properties are anisotropic at lower temperatures.

The anisotropy of growth rates is seen in FIGURE 12 where an increase in the amount of gaseous HCl results in increases in growth anisotropy. This result indicates that the growth rate in the [110] direction is the highest and is in agreement with previously published results\textsuperscript{(1-2)}. Since the [110] direction is the one of highest growth rate, distortion would be anticipated in the [110] direction. This result is observed in FIGURE 9 where the pattern distortion was in the [110] direction.

The percentage change in the growth rate as shown in FIGURE 12 is only on the order of several percent and cannot fully explain the magnitude of the distortion. Since distortion of the sub-diffused layers is on the order of the epitaxial layer thickness, small percentage changes in the growth rate are not sufficient to explain the results. Thus, the presence of the chlorine species must modify surface kinetics such as nucleation rates and surface mobilities.

The effect which the chlorine species have on the
pattern distortion is modified by mass transfer characteristics of the reactor. This result is shown in FIGURE 13 where with an increase in the $H_2$ main stream flow rate, a decrease in distortion is observed. The transfer of species to and from the epi-gas interface increases and results in a lower probability of species remaining on the silicon surface. With the decrease in species on the surface, the possibility of an interaction of chlorine species and silicon nuclei is reduced with an associated decrease in distortion.

The effect which the $H_2$ main stream flow rate has on distortion is limited. As the flow increases there is a decrease in the effect and eventually, any increase in $H_2$ flow will have little effect. This result is observed in FIGURE 14 where the rate of change in growth rate decreases at the higher $H_2$ main stream flow rates.

It is a common practice to operate an epitaxial reactor in a temperature range where the growth rate is mass transfer limited. At lower deposition temperatures where growth is limited by surface reaction rates, minor temperature variations result in substantial growth rate fluctuations. From the data of this investigation, this attitude must be altered if distortion of sub-diffused layers is to
be avoided. The obvious example of this result is the use of dichlorosilane (SiH₂Cl₂). Deposition is normally done in the temperature range of 1050°C to 1100°C where the growth rate is mass transfer limited. As the data in FIGURE 6 points out, the value of the distortion parameter is significant in the temperature where SiH₂Cl₂ is normally used.

Since the distortion is on the order of the epitaxial layer thickness and can be minimized, it does not pose a problem in today's technology. Many of the diffused patterns are orders of magnitude larger than the distortion phenomenon and the relative shape distortion is quite small. However, as the state of the art in photolithographic processes improves and requires the definition of small line geometries, distortion effects become more important. Distances between active devices will be reduced and mask alignments to define diffused regions become more critical.
GROWTH MECHANISM

The mechanism which governs the growth of epitaxial layers must satisfy a number of results observed in this investigation. These results include:

1 - The decrease in pattern distortion with increasing deposition temperature for all chlorosilane silicon sources.
2 - The observation of no pattern distortion at any deposition temperature with SiH₄.
3 - The addition of gaseous HCl during SiH₄ epitaxy results in pattern distortion.
4 - The fact that anisotropy in the vertical epitaxial growth rate is not sufficient to numerically satisfy the amount of pattern distortion observed.
5 - The increase in the H₂ main stream flow results in a decrease in pattern distortion.

These results suggest that a nucleation and growth theory must satisfy the above observations with emphasis placed upon nucleation rates and surface mobilities. However, the presence of gaseous HCl has modified the results and must be considered in the analysis. This fact is most evident by the result that pattern distortion only occurs with chlorosilane sources.
The results of this investigation, specifically the fact that at high deposition temperatures pattern distortion decreases for SiH$_2$Cl$_2$, SiHCl$_3$, and SiCl$_4$, agree with the analysis of Nishizawa et al.(18). Their analysis of silicon epitaxial deposition has generated a plot of nucleation sites versus deposition temperature which indicates a decrease in sites with increasing deposition temperature. Thus a condition for decreased pattern distortion corresponds to the decrease in sites necessary for epitaxial growth. The results of Nishizawa et al.(18) agree with the data in this study and further support a nucleation and growth theory.

If the correlation observed between the work of Nishizawa et al.(18) and this investigation is extrapolated to cover the results of silicon deposition using SiH$_4$, a decrease in nucleation sites should be anticipated. Thus, the number of sites that are stable at 1000$^\circ$C (opt.) with SiH$_4$ should be equal to those present at 1150$^\circ$C (opt.) with SiH$_2$Cl$_2$, SiHCl$_3$, and SiCl$_4$. This analysis appears to be correct in view of the results of Farrow(19). The work of Farrow measures the rate of SiH$_4$ decomposition and adsorption at elevated temperatures and finds SiH$_4$ to decompose slowly with poor adsorption on silicon surfaces. Implied from these results is that the nucleation on silicon surfaces
appears to be retarded with a significantly low number of sites.

From the above analysis, a decrease in nucleation sites requires that the surface diffusion rates must increase accordingly. However, the measurement of the diffusion rate is difficult in view of the fact that at 1000\(^\circ\)C (opt.) with SiH\(_4\), the rate is sufficient to allow atoms to diffuse to the step created by the buried layer processing. By decreasing the nucleation sites, the silicon atoms from deposition can not become stable on the silicon surfaces unless the atoms migrate to the buried layer step or evaporate from the surface.

The idea that nucleation sites can be used to explain the pattern distortion phenomenon is implicit but can not be proven from the results in this investigation. What is required to fully investigate the nucleation phenomenon is a controlled experiment similar to the one performed by Nishizawa et al\(^{18}\). This experiment should concentrate on silicon substrates which are oriented exactly on the (111) planes. This will allow facets to grow during epitaxial deposition which correspond to discrete nucleation sites which can be evaluated with respect to various deposition temperatures.
The geometry of the sub-diffused layer should assume a circular shape (FIG. 15) rather than the square form used in this report. This will expose all crystallographic directions and allow the study of anisotropic growth during epitaxial deposition.

The processing parameters which should be investigated are both deposition temperature and the HCl/SiH₄ molar ratio. Deposition times should be kept at a minimum to allow only nucleation processes to occur with little epitaxial growth. Since a facet or pyramid type growth will occur, each facet or pyramid should be assumed to be a nucleation site and plotted versus deposition temperature for various HCl/SiH₄ molar ratios. The anticipated results should be as indicated in FIGURE 16.

The surface mobility of the silicon atoms on the surface can be measured with respect to the distance between nuclei. As distances change with respect to deposition temperature, the value of the surface diffusion coefficient with respect to deposition temperature can be determined. Also, distances at different times with a constant deposition temperature can be evaluated and a mathematical dependence calculated. However, a square root dependence may not be observed in view of surface diffusion measurements made for
FIGURE 15.
PROPOSED GEOMETRY OF SUB-DIFFUSED REGION
PROPOSED EFFECT OF HCl/SiH₄ MOLAR RATIO ON NUCLEATION RATE AT DIFFERENT DEPOSITION TEMPERATURES

FIGURE 16.
different elements\textsuperscript{(21)}.  
This set of experiments should clarify the effect which both nucleation rates and surface diffusion have upon epitaxial growth. However, these results have to be modified by investigating preferred growth directions as the gaseous HCl concentration is increased.
CONCLUSION

In conclusion, the major results of this investigation of pattern distortion of antimony sub-diffused layers during (111) silicon epitaxy are:

1 - Distortion is always present when using chlorosilane epitaxial sources (SiH₂Cl₂, SiHCl₃, and SiCl₄).

2 - High deposition temperatures and high H₂ main stream flow rates reduce pattern distortion.

3 - Silicon epitaxial deposition using SiH₄ does not result in pattern distortion until gaseous HCl is introduced into the deposition cycle.

The reason for these results is that gaseous HCl, which is an unavoidable by-product of the epitaxial deposition process, has modified the mechanism by which epitaxial growth occurs. From an atomistic standpoint, gaseous HCl apparently modifies the number of nuclei on the silicon surface which results in anisotropic growth conditions at low deposition temperatures. Thus, in order to minimize distortion and maintain the integrity of device geometries, silicon epitaxial deposition must be performed at high deposition temperatures and high H₂ main stream flow rates.
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VITA

Robert P. Deysher was born to Lila A. and Paul E. Deysher on November 30, 1948 in Allentown, Pennsylvania. After receiving his high school education from Kutztown Area High School, Kutztown, Pennsylvania, he enrolled in the metallurgy curriculum at Lehigh University. He was active in student affairs throughout his undergraduate career, serving as treasurer of the student metallurgical society and president of Sigma Nu social fraternity. In 1969 he was inducted into Tau Beta Pi and served as chapter treasurer during his senior year. He graduated in June of 1970 with High Honors and a Bachelor of Science degree in Metallurgy and Material Science.

In June of 1970 he started his association with the Allentown Works of Western Electric as an engineer in the Semiconductor Materials Engineering group. In 1971 he was promoted to Planning Engineer and since 1970 has specialized in the areas of semiconductor crystal growth, solid state diffusion, and chemical vapor deposition.

In July of 1972 he married the former Anne Meyer who became mother of his son Seth in 1975.