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LOW-TEMPERATURE EPITAXY AND IN-SITU DOPING OF SILICON FILMS

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Abstract - The B\textsubscript{2}H\textsubscript{6} and PH\textsubscript{3}-partial pressure dependence of the doping concentration of in-situ doped silicon films, deposited in the temperature range between 600 and 750°C by low pressure chemical vapor deposition has been investigated for two different substrate orientations. In addition, the influence of B\textsubscript{2}H\textsubscript{6} and PH\textsubscript{3} and their partial pressure on the silicon growth rate has been studied. It is found that the doping concentration can be controlled over a wide range, and that in the presence of PH\textsubscript{3} as well as B\textsubscript{2}H\textsubscript{6} the silicon growth is reduced. In the case of boron doping, the in-situ doping has been used to fabricate delta-doped silicon layers.

1.-Introduction.

The epitaxial growth of in-situ doped Si films at low temperatures is becoming increasingly important for the fabrication of novel ULSI device structures. Low pressure chemical vapor deposition (LPCVD) at low temperatures allows the growth of high quality silicon layers\cite{1,2} of various thicknesses and doping concentrations, e.g. for abrupt steps in the doping profile, needed for the fabrication of novel devices. For this purpose, the control of the doping profile is a key point for the design and the performance of these devices. In this paper, we report on the investigations of the partial pressure dependence of in-situ doped silicon films epitaxially grown at low temperatures. For the doping B\textsubscript{2}H\textsubscript{6} and PH\textsubscript{3} have been used. The influence of the substrate orientation on the resulting doping concentration and on the deposition rate of silicon has been studied. In addition, the influence of hydrogen partial pressure and the substrate temperature on the doping concentration and the growth rate has been investigated. As an application of the in-situ doping with boron, delta-doped silicon layers have been fabricated.

2.-Experimental.

The experiments have been carried out in a hot wall LPCVD reactor using ultra-pure SiH\textsubscript{4}-H\textsubscript{2} gas mixtures and a process sequence, by which a low-contamination epitaxial growth can be achieved\cite{1,2}. The in-situ doping has been performed by introducing B\textsubscript{2}H\textsubscript{6} and PH\textsubscript{3} gases. The reactor is combined with a N\textsubscript{2}-purge box to avoid air contamination during the loading of the wafers. The reactor with the N\textsubscript{2}-purge box is shown

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\end{itemize}
schematically in Figure 1. The system is UHV-compatible due to its oil-free turbo molecular pump. The moisture level of the gases was less than 10 ppb at the point of use.

As substrates for the boron doping, (100)- and (111)-oriented n-type silicon wafers with a diameter of 33 mm and a resistivity of 3.5-7 and 0.05-0.1 Ω cm have been used, and for the phosphorous doping p-type wafers with a resistivity of 10-15 and 10-20 Ω cm, respectively. The wafers have been cleaned in three cycles, each consisting of a treatment in H₂SO₄ : H₂O₂ (4:1) followed by rinse in DI water. The native oxide had been removed before the wafers were loaded into the N₂-purge box by an HF-dip in 2% diluted HF, followed by a rinse in DI water for 5 min and drying in a N₂-blow.

The N₂-purge was carried out for 15 min before transferring the wafers into the reactor. The reactor was permanently purged with H₂ during evacuation to the deposition pressure. After deposition, the reactor was purged again with N₂. After the transfer into the purge box, the wafers were cooled down in a N₂-flow. By this procedure the contamination with oxygen and carbon can be minimized. The experiments have been repeated for several deposition temperatures in the range between 600 and 750 °C.

The sheet resistance of the epitaxial layers has been measured by the four-point probe method and their thickness determined by Tencor alpha step. From these values, the resistivity has been calculated and the electrically active doping concentration obtained from tabulated values/3/.


The resulting doping concentration in the epitaxial layer is shown as a function of the B₂H₆-partial pressure for the deposition temperature of T=650 °C in Figure 2. The boron concentration in the film can be controlled within the wide range between 10¹⁶ and 10²⁰ cm⁻³, which is important for the fabrication of steep gradients in the doping profile. The boron concentration varies for both crystal orientations approximately with the power 1.5 of the B₂H₆-partial pressure, with a slightly different slope for the two curves. The doping concentration in (111)-oriented films is higher by a factor of about 2.5 compared with (100)-oriented layers. We also observe for the (111)-orientation a tendency to saturate for higher partial pressures. In the high partial pressure regime, the boron concentration in the (111)-oriented direction tends to saturate and becomes smaller than that in the (100)-direction. The RHEED measurements showed a good crystal quality.
of the films, even for a boron concentration of $10^{20} \text{cm}^{-3}$.

![Graph](image1)

**Fig. 2.** - Boron concentration as a function of the B$_2$H$_6$-partial pressure

The influence of B$_2$H$_6$ on the deposition rate of silicon is illustrated in Figure 3 for the same process conditions as in Figure 2. The growth rate decreases slightly with increasing B$_2$H$_6$-partial pressure for both crystal orientations. However, the orientation-dependence exhibits two interesting features. First, the silicon growth rate is higher in the (100)-direction which is in contradiction to what we would expect from the different adsorption site densities in (100)- and (111)-direction, and second, the decrease in the higher B$_2$H$_6$-partial pressure regime is much more pronounced for the (111)-orientation. The decreasing deposition rates are in contradiction to previously published results for polysilicon in-situ doped with B$_2$H$_6$/4,5/. To understand this surprising behavior we consider the following surface reactions for SiH$_4$ and
BzHs or the resulting hydrides. For the undoped silicon growth by decomposition of SiH₄, we assume the following two reactions:

\[ \text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \quad (1) \]

and \[ \text{SiH}_2 \rightarrow \text{Si} + \text{H}_2 \quad (2) \]

at the surface, and in the gas phase:

\[ \text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2 \quad (3) \]

The reactions in which BzHs is involved, are more complicated. The deposition conditions in our experiments suggest that BzHs is decomposed in the gas phase/6/ into:

\[ \text{BzH}_8 \rightarrow \text{BH}_3 + \text{BH}_3 \quad (4) \]

However, only little is known about the following surface reactions of the resulting boron hydrides. There may occur competitive reactions between silicon and boron hydrides, as well as polymerization of decomposed molecules. These effects may also depend on the temperature and the BzHs-partial pressure. Our results suggest that there exists some mechanism which inhibits the silicon growth for these process conditions. They also indicate that the growth mechanisms in the presence of BzHs are not as simple as previously assumed/4,7/. However, at the present stage we cannot yet decide on the origin of this inhibition.

The deposition rate of silicon and the incorporation rate of boron is also influenced by the hydrogen partial pressure. By increasing the H₂-partial pressure we have found that the deposition rate as well as the boron concentration decrease. This indicates that addition of hydrogen leads to a retardation of the complete decomposition of BzHs and SiH₄, or their adsorption is inhibited.

Lowering the deposition temperature results in a decreased deposition rate and a higher boron concentration for both substrate orientations. The temperature-dependence of the boron concentration for one typical deposition condition is shown in Figure 4. However, we observe a different behavior for the two orientations. The shape of the temperature-dependence for the (100)-orientation is complementary to that for the (111)-orientation.

The temperature-dependence of the deposition rate is shown in Figure 5. The process conditions are the same as in Figure 4. The increase of the growth rate with the temperature is larger for the (100)-orientation.

As an application of the in-situ doping with BzHs we fabricated an epitaxial silicon layer on a (100)-oriented p-type silicon wafer with a thin and highly-doped boron spike. The deposition conditions were taken from the results of uniform doping at 650°C. In addition, we modified the process before and after the deposition with respect to the reactor temperature/1,2/ in order to suppress any oxygen and carbon contamination below the background level. The boron spike is sandwiched between two low-doped epitaxial layers on the substrate and on top of the delta-doped layer. Figure 6 shows the resulting doping profile as deposited, obtained from SIMS-measurements. The thickness of the epitaxial layer is about 0.8µm. The lower value of the boron concentration in the film is about 2.5x10¹⁸ cm⁻³ and the peak value at the
location of the spike is somewhat smaller than the true spike value of $2 \times 10^{18} \text{cm}^{-3}$. The intended thickness of the spike was about 100Å. However, SIMS cannot accurately resolve the spatial dimension of such thin layers. We have found that the shape depends sensitively on how the doping gas $\text{B}_2\text{He}$ is switched from the heavy-doped to the low-doped regime. The symmetric shape of the delta-doped layer indicates that autodoping can be avoided at temperatures as low as 650°C. Such an in-situ doped epitaxial film with a boron spike has been used to fabricate a delta-doped n-channel MOS-transistor/8/.
4. Phosphorous Doping.

For the case of phosphorous doping the results exhibit for both crystal orientations a very similar behavior. The phosphorous concentration varies proportionally to the PH₃-partial pressure, as shown for a deposition temperature of $T=650^\circ C$ in Figure 7. The phosphorous concentration is higher for (100)-oriented films over the whole partial pressure regime than for (111)-oriented ones.
is shown in Figure 8. The process conditions are the same as in Figure 7. Increasing the PH₃-partial pressure reduces the deposition rate for both crystal orientations in the same way. These results are in agreement with those found in the literature.

5.-Conclusions.

The partial pressure dependence of the boron and phosphorous concentration and of the deposition rate has been investigated for the two substrate orientations (100) and (111). We have found that the doping concentration can be controlled over a wide range. The surprising result is that in the presence of BₓHₓ the silicon deposition rate is reduced, which indicates that the growth mechanisms under the influence of BₓHₓ are not yet fully understood and more complicated than previously assumed. As an interesting application of the in-situ doping a delta-doped boron layer has been fabricated, sandwiched between two low-doped epitaxial layers. This proves that low-temperature LPCVD and in-situ doping can be used to fabricate advanced device structures with complicated profiles.

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