In Situ P-Doped Si and Si$_{1-x}$Ge$_x$ Epitaxial Films Grown by Remote Plasma Enhanced Chemical Vapor Deposition

S. THOMAS, J. FRETWELL, D. KINOSKY, R. QIAN, A. MAHAJAN, P. MUNGUÍA, S. BANERJEE, A. TASCH, and C. MAGEE*

Microelectronics Research Center, University of Texas, Austin, TX 78712
*Evans East Inc., Plainsboro, NJ 08536

Remote plasma-enhanced chemical vapor deposition has been applied to grow *in-situ* doped n-type epitaxial Si and Si$_{1-x}$Ge$_x$ with the introduction of phosphine. Growth rates and dopant incorporation have been studied as a function of process parameters (temperature, rf power, and dopant gas flow). Growth rates remain unaltered with the introduction of PH$_3$ during deposition, unlike in many other low temperature growth techniques. Phosphorus incorporation shows a linear dependence on PH$_3$ flow rate, but has little if any dependence on the other growth parameters, such as radio frequency power and substrate temperature, for the ranges of parameters that were examined. Phosphorus concentrations as high as 4×10^{19} cm^{-3} at 14 W have been obtained.

Key words: *In-situ* phosphorus doping, plasma-enhanced deposition, Si and Si$_{1-x}$Ge$_x$ epitaxy

INTRODUCTION

Phosphorus doping of epitaxial Si and Si$_{1-x}$Ge$_x$ films has been demonstrated by several growth techniques using either elemental phosphorus or gaseous phosphine. Yet for each of these techniques, P doping has been problematic. For Si molecular beam epitaxy (MBE), elemental P has a very high vapor pressure which has led to unacceptable background levels. Hirayama et al. have used PH$_3$ in gas source MBE (GSMBE) to reduce the background levels of P, but a near twofold decrease in growth rate was observed for a PH$_3$ flow rate sufficient to achieve 1×10^{20} cm^{-3} carrier concentration.[1] Friess et al. demonstrated an alternative approach for phosphorus doping in Si MBE by co-evaporating phosphorus doped Si.[2] This technique has been used to demonstrate better control over background P levels, but still suffers from P segregation at temperatures above 400°C. For ultra-high vacuum chemical vapor deposition (UHV-CVD),

Racanelli et al. have reported a factor of two decrease of Si growth rates when PH$_3$ flow rates are increased to achieve 10^{13} cm^{-3} P doping.[3] Yu et al. have proposed that the reduction is due to chemisorbed PH$_3$ blocking adsorption sites for Si adatoms, thereby reducing the growth rate.[4] Temperature programmed desorption (TPD) studies by Colaianni et al. have also shown that hydrogen desorption occurs at higher temperatures from a PH$_3$-adsorbed layer than from a hydrogen-passivated Si surface.[5] The TPD results further show that increasing the growth temperature to account for the higher hydrogen desorption temperature of a phosphine-terminated surface will not be successful. Increasing the growth temperature above 550°C increases desorption of P from the surface, leading to a reduction in the P concentration in the deposited Si layer. Another problem that arises when using PH$_3$ is that large background levels of P are observed in the chamber even after the PH$_3$ flow has stopped, leading to a "memory" effect in terms of P doping of the Si epitaxial films. To achieve sharp doping profiles, it has been necessary to stop deposition until back-
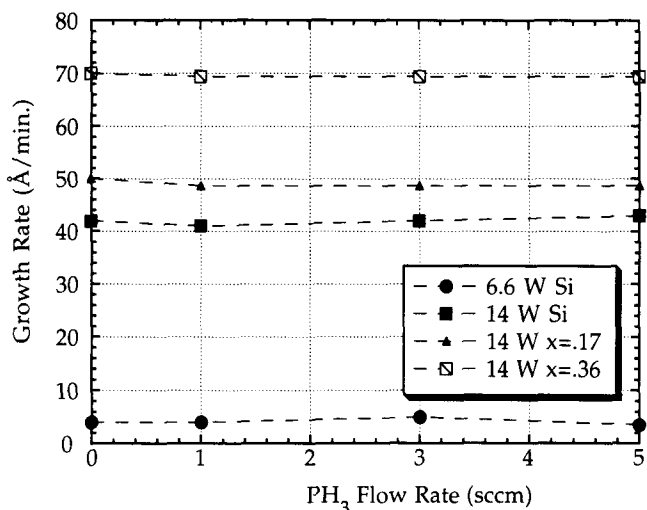
Fig. 1. Growth rates for Si films deposited at 6.6 and 14 W, and $Si_{1-x}Ge_x$ films grown at 14 W. The growth rates remain unchanged with the introduction of PH_3. All samples were grown at 450°C, 200 mTorr, and with a constant 2% SiH_4 flow rate of 1.5 sccm.

ground P levels are reduced sufficiently.[1] Phosphorus doping of remote plasma-enhanced CVD (RPCVD) deposited Si and Si_xGe_{1-x} films has proved to be less problematic. In this technique, argon ions, metastables and energetic electrons generated by a remote inductively coupled argon radio frequency (rf) plasma are used to dissociate the precursor molecules and aid the desorption of hydrogen from the Si surface and, thereby, promote growth. Using this technique, low-temperature Si epitaxial growth has been demonstrated in the range of 150–500°C and Si_xGe_{1-x} heteroepitaxial growth has been demonstrated in the range of 300–450°C.[6,7] In situ boron doping of Si using diborane has also been demonstrated.[8] In this paper, results of in situ P doping of RPCVD deposited Si and $Si_{1-x}Ge_x$ films will be presented.

EXPERIMENTAL

The system configuration and operation have been described previously.[6] Briefly, the RPCVD system is a three chamber ultra-high vacuum (UHV) system that uses ultra-pure gases. The base pressures of the load-lock chamber, the surface analysis chamber, and the deposition chamber are 3×10^{-9} Torr, 1×10^{-10} Torr, and 3×10^{-9} Torr, respectively. The system is equipped with in situ Auger electron spectroscopy (AES) and in situ reflection high energy electron diffraction (RHEED) capabilities as well as a residual gas analyzer (RGA). Czochralski 3″ Si(100) wafers are loaded into the load lock chamber after an ex situ clean consisting of a modified RCA clean and a 30s 5:1 methanol/HF dip. This is followed by a 45 min in situ clean using a hydrogen plasma at 250°C, using 9 W rf power, and 200 mTorr H pressure to remove residual carbon and oxygen from the Si surface.[9] The in situ hydrogen clean leaves the surface hydrogen passivated with a (3×1) surface reconstruction.

The source gas (2% SiH_4/He and/or 2% GeH_4/He) and dopant gases (91 ppm B_2H_6/He and 49 ppm PH_3/He) are introduced through a gas dispersal ring lo-

cated below the Si wafer with flow rates controlled by mass flow controllers. The dispersal ring is located downstream of the Ar plasma, thereby limiting the direct excitation of source and dopant gases. While source gases, dopant gases, and a 100 sccm of He (used to purge the heater assembly) are flowing, growth is initiated when 250 sccm of Ar gas is introduced at 200 mTorr into the chamber and a plasma is inductively generated below the wafer using a 13.56 MHz rf source. The resulting low energy argon ion bombardment, in addition to energetic electrons, aids in the desorption of hydrogen from the wafer surface as well as increases Si adatom mobility. The remote nature of the plasma reduces substrate damage associated with high energy ion bombardment during conventional capacitively coupled plasma-enhanced CVD. Since the thermal growth component at 450°C is negligible, growth may be initiated or stopped by simply turning on or off the rf power supply.

After growth, the crystalline quality of the Si and $Si_{1-x}Ge_x$ films is determined in situ by RHEED. Growth rates and P incorporation are studied in the deposited films as a function of growth temperature (350–500°C), dopant gas flow (1 to 5 sccm of 0.49 ppm PH_3/He), and rf power (6.6–22W) using secondary ion mass spectroscopy (SIMS). Using a patterned wafer consisting of a stacked 1000Å oxide/1000Å polysilicon layer, growth rates are also determined from the change in the thickness of the polysilicon layer following deposition. We have also, on several occasions, measured the step height across the polysilicon/oxide stack using a surface profilometer (Alphastep) and observed that the step height remains unchanged before and after epitaxial growth, thus confirming that the epi growth is equal to the increase of the polysilicon film thickness.

RESULTS AND DISCUSSION

Growth Rate of Single Crystal P-Doped Si

In situ P doping using PH_3 was observed to have little effect on the crystallinity of the deposited layers, as measured by RHEED. Samples grown using process parameters for which single-crystal films had been deposited for the undoped case, also resulted in epitaxial growth after the introduction of PH_3 during growth. Transmission electron microscopy (TEM) analysis of these films verified that the dislocation loop density is below the TEM detection limit of 10^5/ cm^2. Additionally, there are no stacking faults observed in Nomarski pictures of samples exposed to a modified Schimmel etch. The RHEED patterns of the samples had 1/2 order streaks along with integral order streaks at the end of growth. To examine the growth rate dependence on PH_3 flow rate, the thicknesses of Si films deposited using different PH_3 flow rates were compared while keeping the other process parameters constant (200 mTorr, 450°C, 250 sccm of Ar, 100 sccm of He, 15 sccm of 2% SiH_4, and 6.6 or 14 W of rf power). The growth rates remained unaltered with the introduction of PH_3 (Fig. 1). All films were

deposited at rates comparable to undoped film deposition, with deviations being within the uncertainty of the measurement technique used (± 2Å/min). With the introduction of either 4 or 10 sccm of 2% GeH$_4$/He mixture to the chamber during deposition, Si$_{0.83}$Ge$_{0.17}$ and Si$_{0.64}$Ge$_{0.36}$ films were deposited, respectively. Again, the growth rates remained unaltered with the introduction of PH$_3$. The addition of GeH$_4$ during Si epitaxial growth is known to strongly affect the film growth rate. The phenomenon was first reported in 1988 by Meyerson et al. for ultra-high vacuum chemical vapor deposition (UHV-CVD) at 550°C. This increase has been attributed to both an increase in the partial pressure of the reactive gas in the chamber with the introduction of GeH$_4$ and to the reduction of the hydrogen desorption temperature due to the presence of GeH$_4$. This reduction causes adsorption sites to become available more readily which, in turn, increases the deposition rate. Other researchers using thermal CVD techniques have reported similar results.[10] In Fig. 2, Ge$_x$Si$_{1-x}$ film deposition rates are plotted for typical RPCVD deposition parameters (16 W rf plasma power and 450°C) along with the growth data from two UHV-CVD investigations.[10,11] For each of the three processes depicted in Fig. 2, the silane flow rate was held constant while the germane flow was added such that the total amount of reactive gas was not constant, but rather increased with increasing Ge mole fractions in the film. The RPCVD growth rate increases linearly with addition of germane, while the two UHV-CVD depositions show decidedly nonlinear effects. The catalytic-like growth rate enhancement with the introduction of GeH$_4$ is not observed during the growth of Ge$_x$Si$_{1-x}$ films under the typical deposition conditions used in RPCVD, since adsorption sites are created by low energy ion bombardment and are only minimally dependent on temperature for activation.[12]

In situ doped films were also deposited at various rf powers. Again, growth rates were measured and compared to those for undoped films. For the rf power range investigated, no decrease in the growth rate was observed for Si deposition with the introduction of PH$_3$ (Fig. 3). The growth rate was found to increase with increasing rf power for both doped and undoped films, with differences being within the uncertainty of the measurement technique. Similar results have been obtained in this study for *in situ* P doped Si$_{1-x}$Ge$_x$ films.

The increase in growth rate with increasing rf power has been observed before.[13] Using Langmuir probe measurements of the plasma density as a function of plasma power, the growth rate was observed to increase with increasing plasma density. This has led to a growth kinetics model in which hydrogen desorption is stimulated by low energy ion bombardment from plasma generated species. The cause of the leveling off of the growth rate at higher rf powers (greater than 16 W) is unknown at present.

The independence of growth rate on PH$_3$ flow is consistent with the RPCVD growth mechanism de-

scribed earlier. Since deposition occurs at temperatures for which the thermal growth rate using SiH$_4$ is negligible, the Si deposition rate must be dependent on the energy derived from the rf plasma. This energy may be in the form of low energy bombardment by energetic electrons, ions, and/or radicals that subsequently create adsorption sites for growth. In addition, radicals of source gases created by plasma excitation may insert directly into the hydrogen-passivated layer, leading to growth. The growth rate is expected to be independent of the introduction of a low concentration dopant gas, which is consistent with experimental data. In contrast, during UHV-CVD, Racanelli et al. report that the growth rate decreases by nearly a factor of two when a P-doping level of 4×10^{18} cm^{-3} is introduced.[3]

Phosphorus Incorporation During Growth

The P concentration, [P], of films deposited at varying rf powers and varying PH$_3$ flow rates was measured using SIMS. All films were deposited at 200
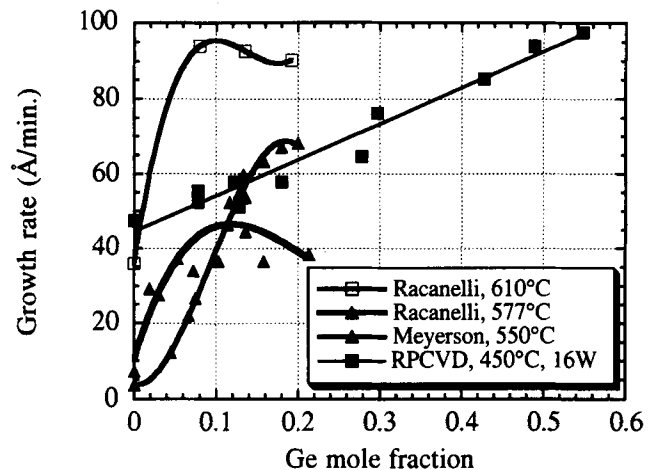

Fig. 2. Growth rates for Si$_{1-x}$Ge$_x$ films deposited at 16 W and 450°C grown by RPCVD compared with growth rates from UHV-CVD studies showing the linearity of the RPCVD growth rates with increasing GeH$_4$ flow rate. The data for the UHV-CVD growth rates are from Refs. 10 and 11.
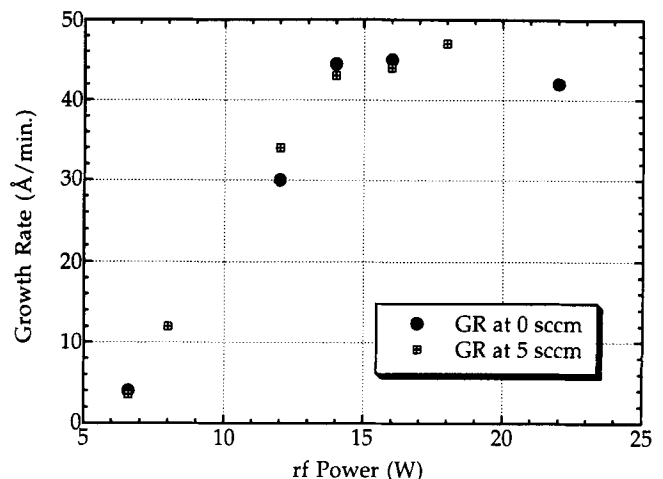

Fig. 3. Growth rates of *in situ* P-doped (5 sccm 49 ppm PH$_3$/He) and undoped (0 sccm PH$_3$) films vs rf power. The films were deposited at 450°C and at 200 mTorr.

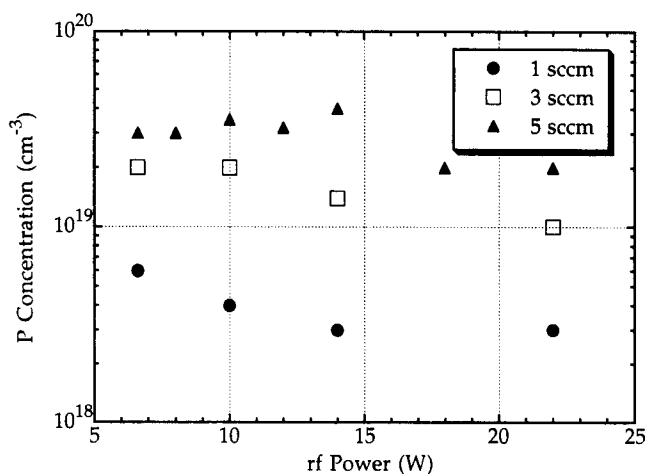Thomas, Fretwell, Kinosky, Qian, Mahajan,
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Fig. 4. Chemical P concentration for 1, 3, and 5 sccm for PH_3 flow rates vs rf power for RPCVD deposited films. The P incorporation decreases with increasing rf power.
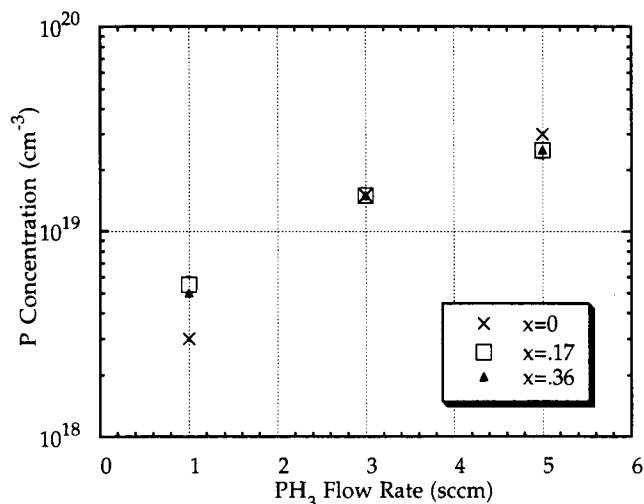

Fig. 6. Phosphorus concentration for RPCVD Si films deposited at different substrate temperatures. The P concentration decreases with temperature.

Fig. 5. Chemical P concentration for $Si_{1-x}Ge_x$ films for different PH_3 flows. The P concentration is independent of GeH_4 flow.

mTorr chamber pressure, 450°C substrate temperature, with 100 sccm of He purging the heater stage assembly and 15 sccm of 2% SiH_4 flowing through the gas dispersal ring while an Ar plasma was excited. The Ar flow rate was 250 sccm through the tube. For a fixed rf power, a near linear dependence on PH_3 flow was observed (Fig. 4). With higher rf powers, however, [P] decreases, particularly for PH_3 flow rates less than 5 sccm. As the rf power increases, the ion density increases. Sufficient energy transfer may occur to the adsorbed P through collisions that P_2 desorption occurs, leading to a reduction in the P concentration at high rf power.

The incorporation efficiency of PH_3 on Si(100) from the gas phase into the deposited film, relative to SiH_4, was calculated to be between 0.8 and 0.9. These values are less than expected. The sticking coefficient of PH_3 has been reported to be 40 X that of SiH_4.[4] If the deposition rate is not altered by the introduction of PH_3, as has been experimentally confirmed, and assuming no gas phase or surface reactions exist that favor the incorporation of certain gases, the incorpo-
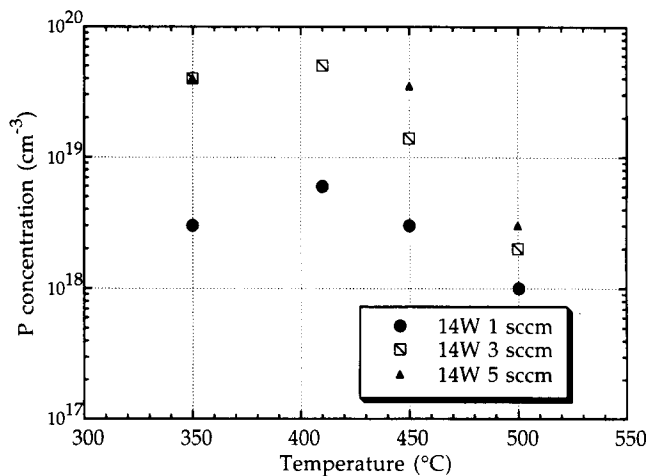
ration efficiency of PH_3 relative to SiH_4 should be greater than 100%. An immediate conclusion that may be drawn is that the RPCVD growth precursors are not simply PH_3 and SiH_4 but more reactive species of these gases which have similar incorporation efficiencies.

For $Si_{1-x}Ge_x$ films deposited at 14 W and 450°C, an approximate linear dependence of [P] on PH_3 flow rate was observed (Fig. 5). No reduction in [P] was observed with increasing GeH_4 flow. The incorporation efficiency of PH_3 relative to the total reactive gas concentration was calculated to be 0.8 for x = 0.2 and 1.0 for x = 0.4. The lack of dependence of [P] on partial pressure of GeH_4 can be explained by the fact that the PH_3 partial pressure only decreases by 1.5% when the GeH_4 flow is increased from 4 sccm to 10 sccm, and all other gas flows are kept constant. This percentage change is not significant enough to effect the [P].

Colaianni et al. have observed that the desorption of P_2 from a Si (100) surface exposed to PH_3 using TPD has a peak at 672°C.[5] The temperature at which this reaction begins is not mentioned. Though the substrate temperatures during RPCVD were below this temperature, the rf plasma may add enough energy for the P_2 desorption reactions to begin, leading to a reduction in the P concentration. In situ P doped films deposited at 14 W and at a variety of substrate temperatures were used to investigate the dependence of P incorporation on temperature. Growth rates were observed to be independent of the substrate temperature for the range investigated. Phosphorus concentration, however, shows a near linear dependence on PH_3 flow rate for a particular deposition temperature, but a reduction in [P] is observed for temperatures greater than 410°C (Fig. 6). The exact mechanism by which P desorbs from the Si surface is unknown at this time.

Electrical Activation of Incorporated P Dopant

Electrically active [P] was measured by comparing both four-point probe and Hall effect combined with

sheet resistance measurements to tabulated values of P doping levels. Though a discrepancy exists between the values obtained by the two electrical activation measurements, both measurements showed a reduction in the active [P] with increasing rf power (Fig. 7). As the growth rate increases for higher rf powers, incorporation of P interstitially as opposed to substitutionally becomes more likely since less time is available for P atoms to find appropriate lattice sites before a subsequent layer is deposited. In addition, if layers are deposited before surface reactions are fully completed, high levels of reaction by-products should also be incorporated into the films. Secondary ion mass spectroscopy measurements do show high concentrations of hydrogen (10^{19} cm^{-3}) in all samples supporting the theory that P is incorporated interstitially. However, further evaluation of films grown at higher powers will have to be made to fully establish the dependence of the concentration of electrically active donors on applied rf power.

Phosphorus Doping Transitions

Since other growth techniques have observed large dopant transition widths with P doping, RPCVD transition widths were studied by depositing films under a variety of conditions with the dopant gas flow modulated (0, 1, 0, 3, 0, 5, and 0 sccm). The doping level transitions were measured using SIMS. For Si layers, P transitions from high to low concentration of 250Å/decade were obtained. However, the [P] in the unintentionally doped layer was strongly dependent on the PH$_3$ flow rate just prior to deposition. Unintentional doping levels ranged from 1×10^{17} to 8×10^{17} cm^{-3}. For Si$_{1-x}$Ge$_x$ films with Ge mole fraction x = 0.17 and x = 0.36, the P transition widths were significantly better (Fig. 8), approximately 110Å/decade. Unintentionally doped layers had P concentrations of 5×10^{17} cm^{-3}, and were independent of prior PH$_3$ flow conditions. Another major difference between the Si and

Si$_{1-x}$Ge$_x$ films is that the H levels were over an order of magnitude higher in the Si films. The interaction of H with P may play a role in the determination of
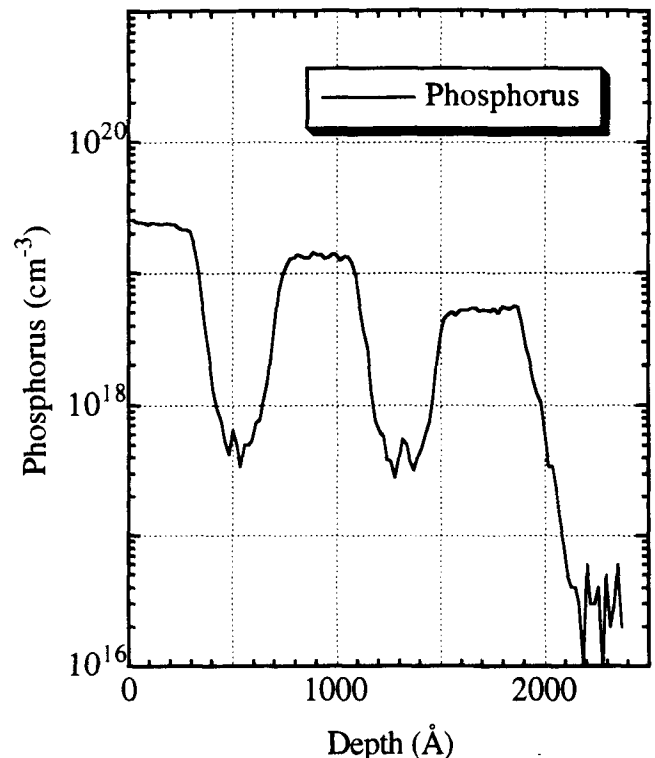
Fig. 8. Secondary ion mass spectroscopy measurements of P doped Si$_{0.63}$Ge$_{0.37}$ films deposited using RPCVD. Transition widths are approximately 110Å/decade. No stoppage of growth was necessary to achieve these transitions.
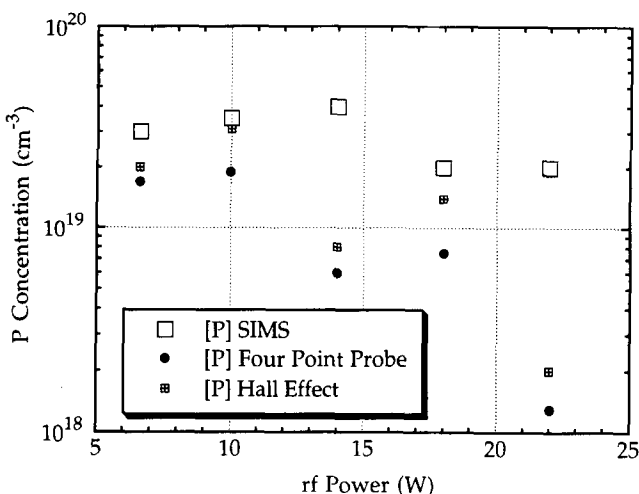
Fig. 7. Chemical and active P concentration for RPCVD deposited films. Secondary ion mass spectroscopy measurements were used to measure the chemical concentration, while sheet resistance measurements from four-point probe or Hall effect measurements were used to measure the active concentration.
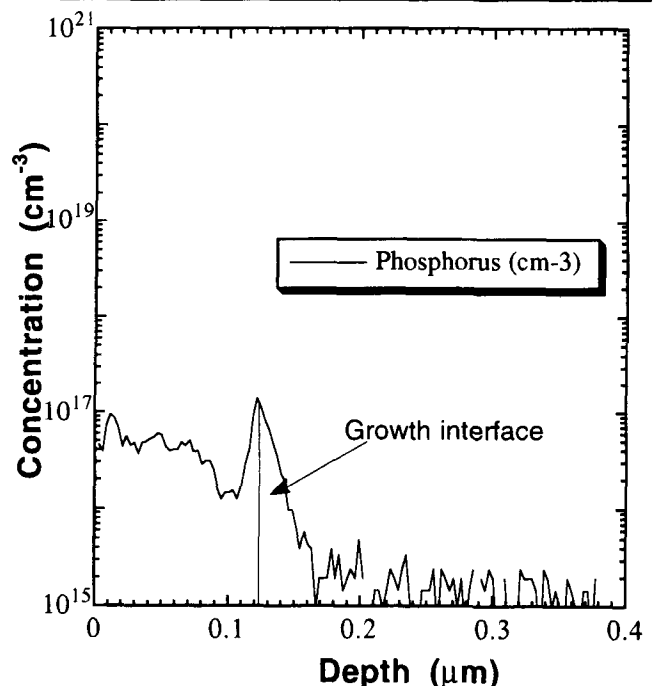
Fig. 9. Background level of P present in the deposition chamber. An undoped RPCVD Si film was deposited two days after P-doped Si deposition. The Si layer was deposited at 6.6 W (15 sccm of 2% SiH$_4$), 14 W (15 sccm of 2% SiH$_4$), and 14 W (30 sccm of 2% SiH$_4$). The P concentration increases as the rf power is increased.

doping transition widths, but the exact mechanism is uncertain. Johnson et al. have observed that P reduces H diffusion in Si, but the effect of H on P diffusion was not considered.[14] Another reason for the high transition widths may simply be related to the design of the gas distribution system. The final PH_3 valve is located several feet from the gas dispersal ring in the present RPCVD system. When the PH_3 flow is stopped, residual PH_3 in the long section of tubing connecting the PH_3 valve to the gas ring, especially in the absence of a gas flow in this section to flush the line, may be responsible for the large transition widths. Modifications that reduce the tube length between the gas valves have more recently been implemented.

Films deposited with no PH_3 flow were used to measure background levels of P present in the chamber. Growth was initiated at 6.6 W at 200 mTorr, 450°C and with a 15 sccm 2% SiH_4 flow rate for 2 h, and then the rf power was raised to 14 W for 10 min. A final layer was deposited at 14 W and 30 sccm of 2% SiH_4. Samples were deposited one day (C220) or two days (B201) after a doped film deposition with no depositions in between. For better sensitivity, the P concentration was measured using magnetic sector SIMS (Fig. 9).[15]

At 6.6 W, [P] was measured to be 3×10^{16} cm^{-3} for C220, while [P] was 1.3×10^{16} cm^{-3} for sample B201. A slight time dependence is observed at 6.6 W, but at 14 W, the P concentration remains unchanged at 6×10^{16} cm^{-3}. No change was observed with increasing SiH_4 flow. Assuming an incorporation efficiency of 0.8, a background partial pressure of P can be calculated. Using sample C220, the P partial pressure increases from 1.23×10^{-10} Torr to 2.46×10^{-10} Torr as the rf power increases.

Since no leaks were detected in the PH_3 gas line, the increase in P partial pressure with increasing rf power suggests that the source of P is the sputtering of P from the chamber walls or the heater stage assembly. Since [P] did not decrease as the undoped deposition continued, P surface segregation may also play a role, even though the temperature of the chamber walls remained less than 100°C. In addition, [P] remained unaltered with the increase of SiH_4 partial pressure. For $Si_{1-x}Ge_x$ deposition, the [P] was found to be independent of source gas partial pressures for the low concentrations of PH_3 used in this study. The results from this section also suggest a mechanism for the incorporation of P that is also independent of SiH_4 partial pressure. Attempts to reduce the P partial pressure must, therefore, focus on reducing P sputtering from chamber walls.

CONCLUSION

N-type doping of RPCVD-deposited Si and $Si_{1-x}Ge_x$ films has been achieved using PH_3 as the dopant gas. No adverse effects on crystallinity or growth rate are observed with the introduction of PH_3. The P chemical concentration, for a fixed rf power and substrate temperature, displays a near linear dependence on the PH_3 flow rate with measured [P] as high as 4×10^{19} cm^{-3}. The P concentration decreases with increasing temperature and rf power in the ranges 410 to 500°C and 6.6 to 22 W, respectively. For these conditions, P_2 desorption from the wafer surface probably occurs leading to a reduction in [P]. The source of the background levels of P present in the chamber during a undoped deposition was determined to be adsorbed P on the chamber walls. The growth rate remains unaltered with the introduction of PH_3 for both Si and $Si_{1-x}Ge_x$. This is unique to RPCVD growth since researchers, using other techniques such as UHV-CVD and GSMBE, have observed a large decrease of growth rate with the introduction of PH_3.[1,3]

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