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Advances in Remote Plasma-enhanced Chemical Vapor Deposition for Low Temperature *In Situ* Hydrogen Plasma Clean and Si and $Si_{1-x}Ge_x$ Epitaxy

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Remote plasma-enhanced chemical vapor deposition (RPCVD) is a low temperature growth technique which has been successfully employed in *in situ* remote hydrogen plasma clean of Si(100) surfaces, silicon homoepitaxy and $Si_{1-x}Ge_x$ heteroepitaxy in the temperature range of 150–450° C. The epitaxial process employs an *ex situ* wet chemical clean, an *in situ* remote hydrogen plasma clean, followed by a remote argon plasma dissociation of silane and germane to generate the precursors for epitaxial growth. Boron doping concentrations as high as 10^{21} cm^{-3} have been achieved in the low temperature epitaxial films by introducing B_2H_6/He during the growth. The growth rate of epitaxial Si can be varied from 0.4Å/min to 50Å/min by controlling the *rf* power. The wide range of controllable growth rates makes RPCVD an excellent tool for applications ranging from superlattice structures to more conventional Si epitaxy. Auger electron spectroscopy analysis has been employed to confirm the efficacy of this remote hydrogen plasma clean in terms of removing surface contaminants. Reflection high energy electron diffraction and transmission electron microscopy have been utilized to investigate the surface structure in terms of crystallinity and defect generation. Epitaxial Si and $Si_{1-x}Ge_x$ films have been grown by RPCVD with defect densities below the detection limits of TEM (~10^5 cm^{-2} or less). The RPCVD process also exploits the hydrogen passivation effect at temperatures below 500° C to minimize the adsorption of C and O during growth. Epitaxial Si and $Si_{1-x}Ge_x$ films with low oxygen content (~3×10^{18} cm^{-3}) have been achieved by RPCVD. Silicon and $Si/Si_{1-x}Ge_x$ mesa diodes with boron concentrations ranging from 10^{17} to 10^{19} cm^{-3} in the epitaxial films grown by RPCVD show reasonably good current-voltage characteristics with ideality factors of 1.2–1.3. A $Si/Si_{1-x}Ge_x$ superlattice structure with sharp Ge transitions has been demonstrated by exploiting the low temperature capability of RPCVD. *In situ* plasma diagnostics using single and double Langmuir probes has been performed to reveal the nature of the RPCVD process.

Key words: Plasma chemical vapor deposition, low temperature Si epitaxy, low temperature $Si_{1-x}Ge_x$ epitaxy, hydrogen plasma clean

INTRODUCTION

The study of low temperature semiconductor processes for achieving future-generation Ultra Large Scale Integration (ULSI) devices and Si-based heterostructures has been driven by a need to reduce the redistribution of dopants and hetero-interfacial intermixing, minimize thermal-expansion-mismatch-induced strain, and to open up new materials opportunities. One of the major challenges in the drive towards low temperature processing is low-temperature Si epitaxial growth. Epitaxial growth requires sufficient energy to drive the reactions occurring in the gas phase and on the substrate surface. The epitaxial process includes cleaning the surface prior to epitaxial growth, creation of a precursor molecule from the source gas, providing adequate adatom mobility, and removal of reaction byproducts such as hydrogen from the Si surface. A variety of low temperature techniques have been reported for Si homoepitaxy in the temperature range of 250–800° C.[1–5] In our work, remote plasma-enhanced chemical vapor deposition (RPCVD) has been developed to achieve Si homoepitaxy and $Si_{1-x}Ge_x$ heteroepitaxy in the temperature range of 150–450° C. RPCVD is a low temperature technique in which plasma excitation is employed in order to reduce the thermal energy required to drive reactions for epitaxial growth.[6,7] The key features of RPCVD which make it different from conventional plasma CVD are: (1) In most cases the plasma glow discharge is remote from the substrate, *i.e.* the substrate is not immersed in the plasma; therefore, plasma-induced surface damage can be minimized; (2) The process is performed in a clean UHV environment using ultra clean gases; (3) The growth rates are generally much less than those of conventional

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Si plasma deposition processes. The reactant gases, 2%SiH_4/He (99.999% purity) and 2%GeH_4/He (99.999%) are introduced into the system through a gas dispersal ring located between the plasma and the substrate, dissociated by plasma-excited species such as Ar metastables, Ar ions or energetic electrons, and transported to the substrate, resulting in epitaxial growth.

Achieving and maintaining a clean Si surface at low temperatures prior to an epitaxial process is very critical for successful Si and $Si_{1-x}Ge_x$ epitaxy. Surface contaminants such as carbon and oxygen must be removed or sufficiently minimized to ensure a high quality epitaxial film. An *in situ* remote hydrogen plasma clean has been employed in this work to clean the Si surface prior to RPCVD growth.[8,9] During cleaning, hydrogen gas is flowed through the plasma column and excited by a 13.56 MHz *rf* source to produce atomic hydrogen which can chemically etch the Si surface and remove carbon, nitrogen and oxygen.

Surface modification of the Si(100) surface by a remote hydrogen plasma clean under various plasma powers and substrate temperatures was examined using Auger electron spectroscopy (AES), reflection high energy electron diffraction (RHEED), and transmission electron microscopy (TEM) for optimization of the cleaning conditions. Subsequent epitaxial growth was investigated using RHEED, TEM and secondary ion mass spectroscopy (SIMS) to determine the crystalline quality and impurity concentration in the epitaxial films grown in the range of 150–450° C by RPCVD as a function of process parameters. The growth kinetics were investigated as a function of process parameters and the results were correlated with Langmuir probe measurements of electron and ion temperature and density in the *rf* glow discharge. The results help provide an improved understanding of the nature of the RPCVD process.

EXPERIMENTAL

The schematic of the RPCVD system used for the *in situ* remote hydrogen plasma clean and low temperature epitaxial growth is shown in Fig. 1. The system consists of three interconnected ultra high vacuum (UHV) chambers: a load lock chamber for sample loading which has a base pressure of 1×10^{-9} Torr, a surface analysis chamber with a base pressure of 1×10^{-10} Torr, equipped with an AES system for *in situ* monitoring of surface contamination, and a process chamber with a base pressure of 1×10^{-9} Torr equipped with an *rf* plasma source in which the remote hydrogen plasma clean and low temperature epitaxial growth are carried out. The deposition chamber is equipped with a residual gas analyzer (RGA) to monitor the background levels of oxygen and water in the ambient, as well as to mon-

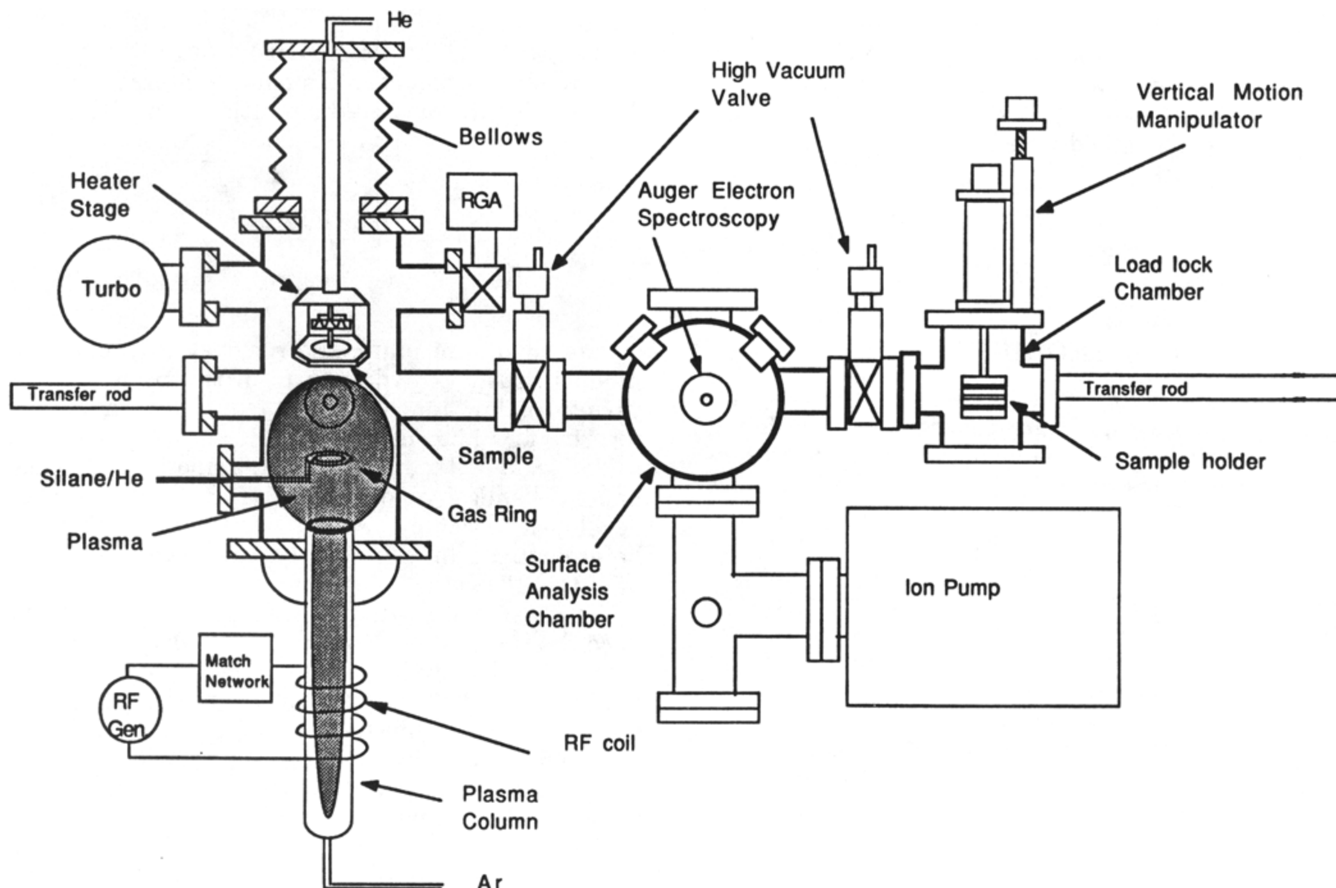

Fig. 1 — Schematic of the RPCVD system.

itor the various species during processing using a differential pumping scheme. A RHEED system is installed in the process chamber for *in situ* diagnostics of surface crystallinity. A Langmuir probe in the deposition chamber allows measurement of electron and ion density and temperature in the plasma. The deposition is carried out using ultra-high purity gases (99.9999%) in the process chamber, in which the partial pressures of water and oxygen are 1×10^{-9} Torr and 5×10^{-11} Torr, respectively. To further reduce the oxygen and water vapor in the processing gases, all gas lines are equipped with resin-based gas purifiers which reduce the oxygen and water vapor to the parts-per-billion level.[10] The total chamber pressure is maintained through a feedback-controlled throttle valve. Substrate temperature is controlled by two quartz lamps inside the chamber. Unlike in a conventional plasma CVD chamber, a noble gas (argon) *rf* plasma is generated remotely from the wafer so that the plasma-induced damage is minimized or avoided. The plasma generated excited species, such as long-lived noble gas metastables and energetic electrons, are transported to the substrate where they interact with and selectively excite the reactant gases (2% SiH_4/He, 2% GeH_4/He, and 91 ppm B_2H_6/He) which are introduced through a gas ring between the substrate and the plasma column. Therefore, in this technique the downstream plasma excitation rather than elevated temperature is used to provide the energy needed for the deposition reaction and to increase adatom mobility on the surface of the substrate. This allows greatly improved control over the reaction pathways and therefore, the crystal morphology, layer thicknesses, and sharpness of interfaces and doping transitions.

The wafers used in the experiment are 3″ Czochralski Si(100). The *ex situ* cleaning process includes an ultrasonic degreasing step and a modified RCA clean, followed by a final HF dip. For degreasing prior to RCA clean, the wafers are ultrasonically cleaned in TCA, acetone, methanol and de-ionized water for 5 min each. The modified RCA clean consists of a 10 min clean in a 5:1:1 $H_2O:H_2O_2:NH_4OH$ solution, an intermediate 40:1 H_2O:HF(49%) dip, and another 10 min clean in a 5:1:1 $H_2O:H_2O_2$:HCl solution. A final 10:1 H_2O:HF(49%) dip is performed to etch the native oxide and provide a H-terminated Si surface.

In situ remote hydrogen plasma cleaning is performed prior to epitaxial growth to further reduce the surface contamination. To investigate the cleaning capability as well as possible defect generation on the Si surface by the cleaning step, the substrate temperature and plasma power during cleaning were varied. Substrate temperature was varied from room temperature to 305° C. RHEED and AES analyses were performed before and after the remote hydrogen plasma clean under various conditions to examine the surface reconstruction patterns and effectiveness of the clean. TEM analysis was also employed to investigate defect generation in the Si near-surface region.

Si and $Si_{1-x}Ge_x$ epitaxial growth were performed in the temperature range of 150–450° C by RPCVD. During growth, typically at 200 mTorr, 250 sccm Ar flow is *rf* plasma-excited which, in turn, dissociates the 2%SiH_4/He, 2%GeH_4/He, and 91 ppm B_2H_6/He reactant gases flowing between the substrate and the plasma glow discharge. *In situ* RHEED and *ex situ* TEM analyses were employed to examine the crystallinity and defect microstructure of the epitaxial Si films grown at different temperatures.

The boron-doped epitaxial Si and Si_xGe_{1-x} films were grown on *n*-type, phosphorus-doped Si(100) substrates in order to form *p-n* junctions for electrical characterization. The fabrication process of the mesa diodes involved a wet chemical etch to define the mesa area and a thermal oxidation at 850° C for 6 min followed by a deposition of 2000Å low temperature oxide (LTO) at 450° C for side-wall passivation. The LTO process was used to minimize the thermal budget of the low temperature epitaxial films.

A superlattice structure with 24 pairs of Si(60Å)/$Si_{0.8}Ge_{0.2}$(60Å) layers was grown by periodically introducing 2% GeH_4/He into the chamber during growth. SIMS analysis was employed to determine the impurity levels in the epitaxial Si films and Ge profiles in the $Si_{1-x}Ge_x$ films. During Langmuir probe measurements, the deposition conditions were simulated as closely as possible except that 100% He was substituted for 2% SiH_4/98% He in order to prevent Si deposition on the probe.

RESULTS AND DISCUSSION

Remote Hydrogen Plasma Clean

AES analysis results of the Si surface before and after a 45 min remote hydrogen clean at 305, 250, 150° C and room temperature with all other parameters fixed (45 mTorr chamber pressure, 12 W plasma power, and 200 sccm hydrogen flow rate) are shown in Fig. 2. The as-loaded Si surface is observed to be quite clean with low levels of oxygen and carbon as the only detectable vestiges of contamination. Upon *in situ* remote hydrogen plasma clean, the oxygen and carbon KLL peaks at 509 and 2·72 eV, respectively, are drastically reduced, and the Si LMM peak (91 eV) and KLL peak (1618 eV) are increased. From the results, it seems that the capability of the remote hydrogen plasma clean in terms of removal of oxygen from Si surface decreases with decreasing temperature, since less reduction of the oxygen peaks (KLL:511 eV) was observed at lower cleaning temperatures. The oxygen concentration is below the detectability limit of AES analysis (0.1–1 at. %) at cleaning temperatures above 250° C as shown in Fig. 2(b), (c). Removal of carbon is effective at all temperatures since no carbon was observed, within the sensitivity of 0.1%–1%, after the plasma clean in all cases. The remote hydrogen plasma is believed to be a source of atomic hydrogen which has a slight etching tendency on silicon and silicon dioxide.[11] It, furthermore, hydrogenates the Si surface and pro-

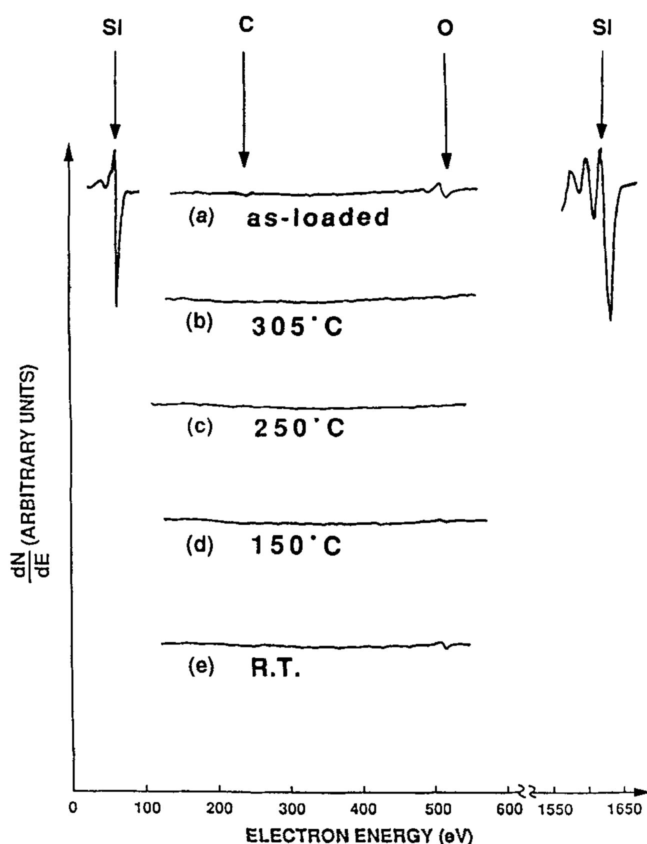

Fig. 2 — AES analysis of a Si(100) surface after (a) a 40:1 H_2O:HF(49%) dip, and a 12 W remote hydrogen plasma clean at (b) 305° C, (c) 250° C, (d) 150° C, and (e) room temperature for 45 min.

vides a chemically inert hydrogen passivation layer which inhibits readsorption of contaminants from the ambient.[9]

RHEED analysis of the Si surface before/after the hydrogen plasma treatment at the various temperatures shows that the surface is converted from (1 × 1) to (3 × 1) hydrogen termination. The conversion of the Si(100) surface from (1 × 1) to (3 × 1) is believed to be due to a change in the Si-H bonding configuration from dihydride termination to a alternating monohydride/dihydride termination on the Si surface by the remote hydrogen plasma clean. The hydrogen tends to passivate the Si surface, where the degree of passivation is believed to increase with hydrogen coverage.[12,13] At cleaning temperatures lower than 250° C the one-third order streaks tend to be "washed out." The very faint one-third order streaks shown on the surface cleaned at 150° C and the complete disappearance of the one-third order streaks on the sample cleaned at room temperature may indicate an increase of hydrogen coverage on the Si surface as a result of lower cleaning temperatures. For cleaning temperatures above 350 C, half-order streaks are observed, which are symptomatic of silicon monohydride coverage.

To examine defect generation on the Si surface due to the hydrogen plasma clean, TEM analysis was performed on Si surfaces cleaned at the different temperatures mentioned earlier. Highly defected Si surfaces were observed in the samples cleaned at room temperature-250° C, while the defect density was found to have been greatly reduced to below the sensitivity of TEM analysis (~10^5 cm^{-2}) at 305° C. The type of defect is predominantly dislocation loops or faulted dislocation loops which have thickness fringes associated with them. From the comparison of defect size and density on Si surfaces cleaned at different temperatures, it appears that the defect density increases and the defect size decreases at lower temperatures. Since the formation of dislocation loops is primarily due to agglomeration or coalescence of vacancies or interstitials, as proposed by Seitz,[14] the TEM results suggest that the hydrogen plasma, for 12 W *rf* power, etches Si atoms from the surface, leaving vacancies on the surface, which, in turn, migrate and agglomerate forming dislocation loops. Depending on the substrate temperatures, the dislocation loops grow to different sizes due to temperature-enhanced surface mobility. Therefore, a lower density of larger size defects results at higher temperatures. No defects were observed on the Si surface cleaned at 305° C, indicating that thermal energy at this temperature (305° C), in addition to plasma excitation, is high enough to provide adequate surface mobility for "healing" the Si surface, possibly by dislocation climb out of the substrate to the surface, under these plasma conditions (12 W). It is believed that the lower the plasma power used for cleaning, the lower the temperature required to heal the surface. Indeed, from TEM analysis of the Si surface cleaned at lower plasma power (9 W), 250° C substrate temperature is found to be sufficiently high to achieve a defect-free Si surface. Excessive plasma power seems to cause more defects during cleaning. The sample cleaned at 250° C and 15 W shows a higher defect density than samples cleaned at 12 or 9 W, although the cleaning capability of the higher power plasma is better.

MICROSTRUCTURAL ANALYSIS OF EPITAXIAL SILICON FILMS

Figure 3 shows RHEED patterns of intrinsic Si films grown at 305, 220, 150, and 125° C with all the other parameters fixed (200 mTorr chamber pressure, 6.6 W plasma power, and 15 sccm 2%SiH_4/He flow rate). It is very clear that epitaxial growth can be sustained at temperatures down to 150° C as indicated by the streaky RHEED patterns in Fig. 3(a), (b) and (c). For the Si films grown at 125° C, a diffuse RHEED pattern results, indicating an amorphous film. TEM analysis was employed to study the defect microstructure of the epitaxial Si films grown at 305, 220, 190 and 150° C, and the results are shown in Fig. 4. The defect density, estimated from TEM analysis seems to be a strong function of growth temperature. It increases from ~10^6 to ~10^9 cm^{-2} as the temperature is decreased from 305 to 150° C. For growth temperatures slightly higher than 350° C, the defect density in the epi-

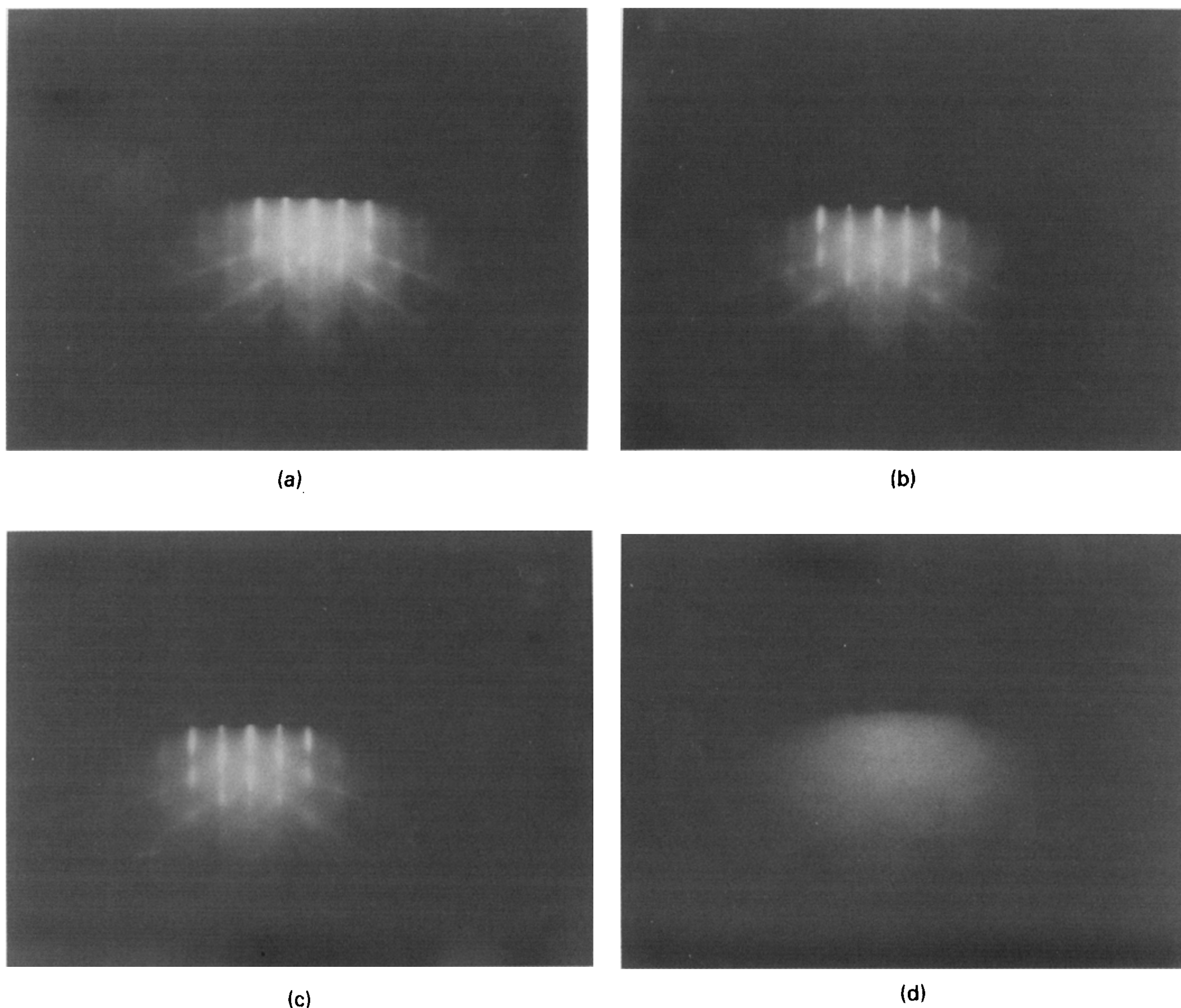

Fig. 3 — RHEED analysis of the epitaxial Si films grown at 6.6 W plasma power, 200 mTorr chamber pressure, and (a) 305° C, (b) 220° C, (c) 150° C, and (d) 125° C substrate temperature by RPCVD.

taxial films is reduced to below the sensitivity of the TEM analysis (~10^5 cm^{-2}). Also, with different growth conditions, films grown at 150° C exhibited defect densities ≤10^5 cm^{-2}.[6] On the other hand, the defect size in the epitaxial Si films appears to be smaller at lower growth temperatures. This temperature dependence of defect characteristics is similar to what has been observed for TEM analysis of the substrate surface after remote hydrogen plasma cleaning at different temperatures, as discussed earlier. The same argument can be applied for explaining the defect generation behavior in both cases. The fact that the epitaxial Si films grown at higher temperatures tend to have lower defect densities and larger defect sizes suggests that thermal excitation, in addition to plasma excitation, is important in enhancing adatom mobility in RPCVD. This makes the vacancies or extra atoms more likely to coalesce into larger dislocation loops rather than creating scattered, smaller dislocation loops as observed in the films grown at lower temperatures.

SIMS analysis was performed on the epitaxial Si films grown at 305, 220, and 150° C by RPCVD. The oxygen concentration in these epitaxial films is ~4 × 10^{19} cm^{-3} without using the gas purifier in the silane gas line and does not seem to be a function of growth temperature. In order to determine the contribution of oxygen and water vapor in the reactant gas to the oxygen concentration in the epitaxial Si films, epitaxial growth at 150° C was first carried out with 2%SiH_4/He flowing through a Nanochem gas purifier, and then bypassing the purifier in the middle of the growth process. SIMS analysis of this film shows two different oxygen levels in the film as a result of the use of the gas purifier (Fig. 5). The oxygen concentration in the first 300Å deposited layer, when the gas purifier was in use, is more than an order of magnitude lower than

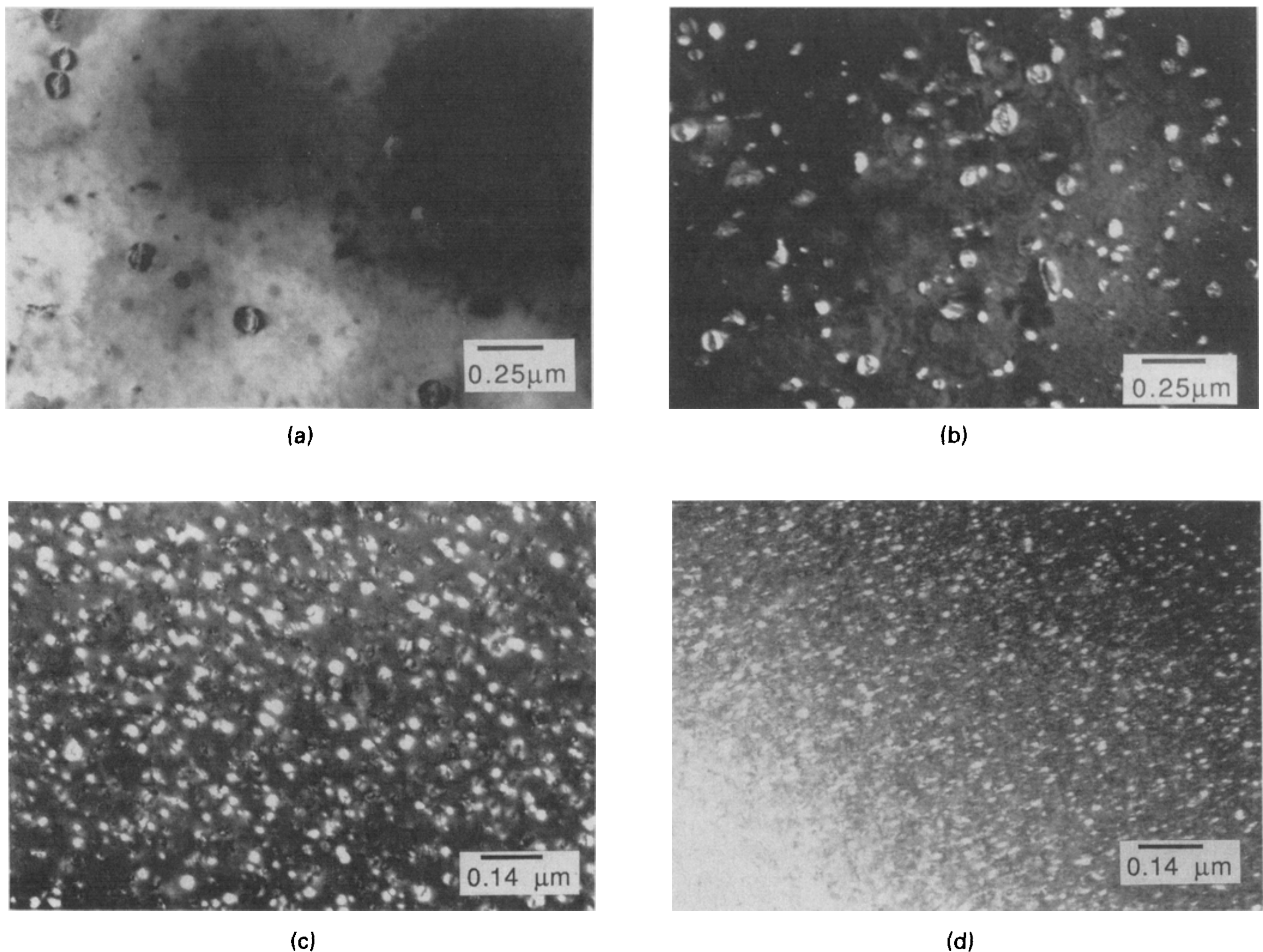

Fig. 4 — TEM micrographs of epitaxial Si films grown at 6.6 W plasma power at (a) 305° C, (b) 220° C, (c) 190° C, and (d) 150° C by RPCVD.

in the case where the gas purifier was not in use. An oxygen concentration as low as 3×10^{18} cm^{-3} has been achieved in epitaxial Si films grown at 150° C by RPCVD. This result suggests that the oxygen and water vapor in the reactant gas are a major source of oxygen in low temperature epitaxial Si films grown by RPCVD.

The hydrogen concentration in the epitaxial Si films, as determined from SIMS analysis, is higher at lower growth temperatures. Hydrogen desorption from the Si surface has been proposed to be an important step, and, perhaps the rate limiting step in low temperature Si epitaxy. The higher hydrogen concentration observed in the Si films grown at lower temperatures suggests that the desorption of hydrogen from the Si surface during growth is enhanced at higher substrate temperatures.

In Situ Boron Doping

Figure 6 shows the boron concentration in epitaxial Si films from SIMS analysis as a function of diborane/silane partial pressure ratio. The boron concentration increases proportionally with the ratio of diborane and silane partial pressure. The solid line in Fig. 6 represents an incorporation efficiency of 0.3. The boron incorporation efficiency is found to be independent of substrate temperature and substrate bias. The sharpness of boron doping profiles was characterized by SIMS analysis on a modulation-doped structure. Figure 7 shows the boron profile of a modulation-doped structure grown at 450° C by RPCVD. The transition width of the boron doping profile is found to be ~50–100Å/decade. This value is comparable to what has been reported by other low temperature CVD techniques.[15,16]

Electrical Characterization

The hole mobility in the epitaxial Si films grown by RPCVD at 450° C has been measured by Hall effect measurements. Hall effect measurements have confirmed 100% electrical activation of the incorporated boron. However, a hole mobility of 80 cm^2/V·s was obtained for a boron concentration of 7×10^{17} cm^{-3}, which is approximately 50% of the theoretical value for bulk Si with comparable boron doping. The films with higher boron concentrations

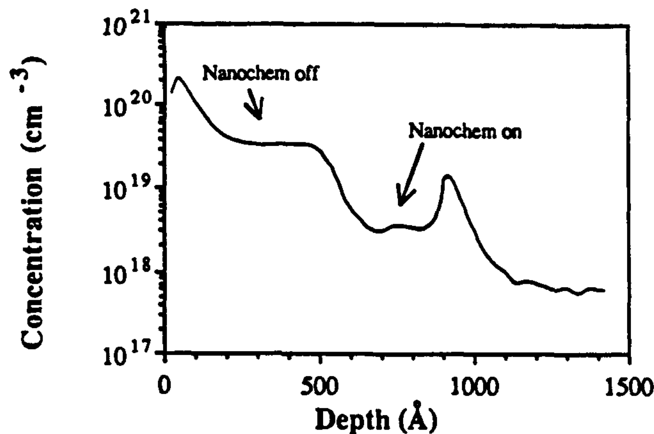

Fig. 5 — SIMS profile of oxygen in RPCVD film grown with and without Nanochem purification of 2%SiH_4/He gas.

(10^{18}–10^{19} cm^{-3}) also show the behavior that hole mobilities are about half of the theoretical values. The carrier mobility as a function of growth temperature is a interesting issue and is currently under investigation. Figure 8 shows the I–V characteristics of the mesa diodes fabricated by RPCVD. Mesa diodes with a range of boron doping concentrations (10^{17}–10^{19} cm^{-3}) show reasonably good characteristics with ideality factors of 1.2–1.3. The leakage current density at −1 V reverse bias for various doping levels is in the range of 0.2–20 $\mu A/cm^2$ for a diode structure with 0.001 cm^2 junction area. Although these values are significantly higher than the state-of-the-art, it is suspected that it is due to the mesa sidewall leakage. The sidewall experiments for devices with different area/perimeter ratios are in progress, and the results will be discussed in a future publication. It has been observed that the epitaxial Si film grown at 16 W shows lower leakage current than the films grown at 6.6 W. It

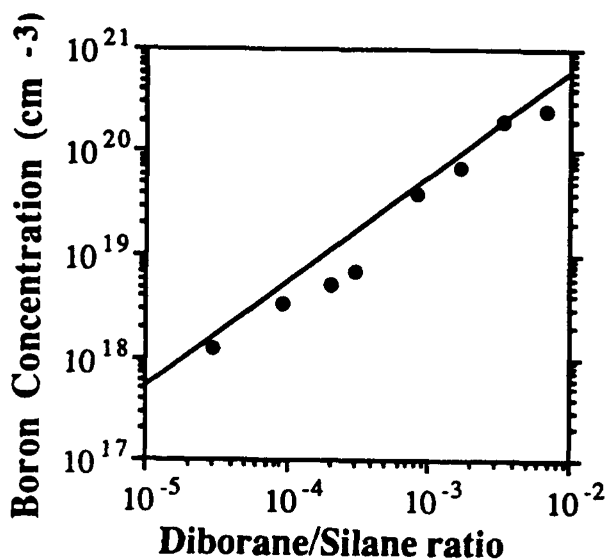

Fig. 6 — Boron concentration in the Si films grown by RPCVD as a function of the ratio of diborane partial pressure to silane partial pressure.

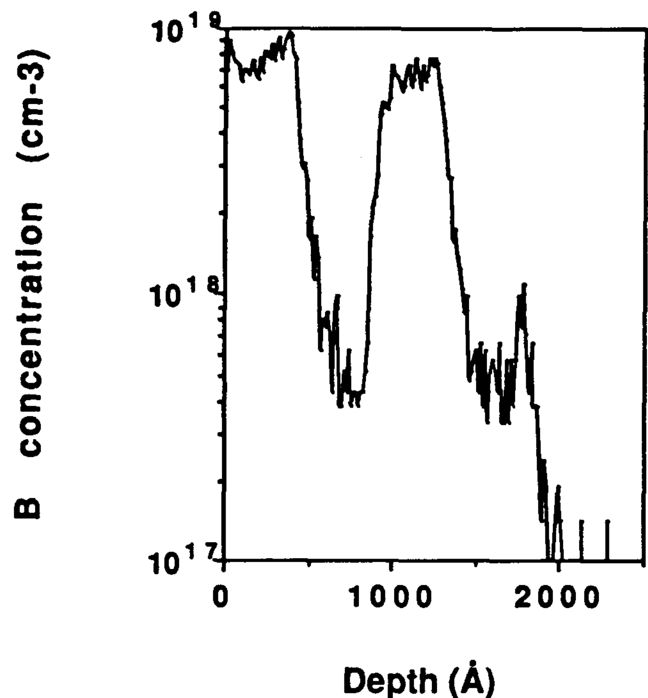

Fig. 7 — SIMS profile of a boron modulation doping structure grown at 450° C by RPCVD.

is believed that higher *rf* powers allow more effective hydrogen desorption because of greater Ar flux. Also, since the plasma potential decreases with increasing *rf* power, the Ar ion bombardment energy, and therefore ion bombardment damage, should be reduced. Both of these factors are expected to improve the RPCVD epitaxial Si electronic properties.

$Si_{1-x}Ge_x$ Heteroepitaxy and $Si/Si_{1-x}Ge_x$ Superlattice Structures

Epitaxial growth of $Si_{1-x}Ge_x$ films with Ge mole fractions as high as 0.7 has been achieved at 450° C substrate temperature by RPCVD. The $Si_{1-x}Ge_x$ films with thickness below the critical layer thickness were confirmed to have excellent crystallinity with defect density below the sensitivity of TEM analysis (10^5 cm^{-2}). It has been reported that the Ge mole fraction in $Si_{1-x}Ge_x$ films grown by thermal CVD may not be easily controlled due to the catalytic reactions between Ge and the Si surface. It has been proposed that Ge can react with the Si surface and reduce the activation energy for hydrogen desorption, which is the rate-limiting step, thereby causing growth rate enhancement.[17] The Ge mole fraction in the $Si_{1-x}Ge_x$ films grown by RPCVD increases linearly with the GeH_4 mole fraction, indicating a well controlled Ge mole fraction in the film. The relative incorporation efficiency of Ge and Si is 1.3:1, presumably due to the weaker Ge-H bond in GeH_4 than the Si-H bond in SiH_4.

A superlattice structure with 24 pairs of $Si/Si_{0.8}Ge_{0.2}$ layers has been grown at 450° C by RPCVD. The thickness of each Si and $Si_{0.8}Ge_{0.2}$ layer is ~60Å, as confirmed by SIMS and cross-sectional TEM analyses. Figure 9 shows the cross-sectional TEM

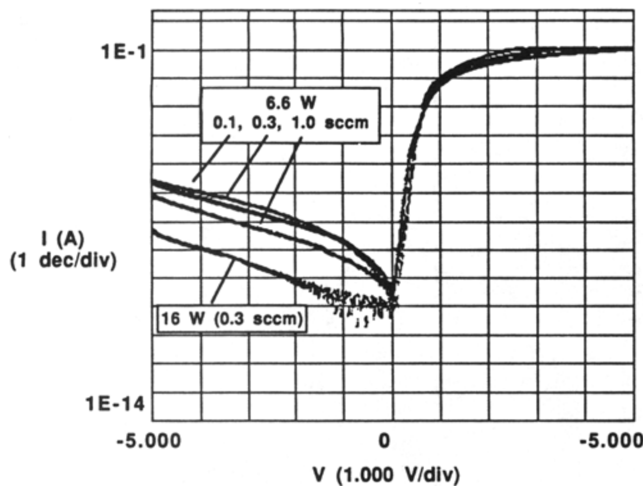

Fig. 8 — Si mesa diode current-voltage characteristics. The epitaxial *p*-type Si films grown at 6.6 and 16 W plasma power, respectively, and 450° C substrate temperature. The boron concentration corresponding to flow rates of 0.1 (6.6 W), 0.3 (6.6 W), 1.0 (6.6 W), and 0.3 (16 W) sccm are 1×10^{18}, 4×10^{18}, 1×10^{19} and $\sim 5 \times 10^{17}$ cm^{-3}.

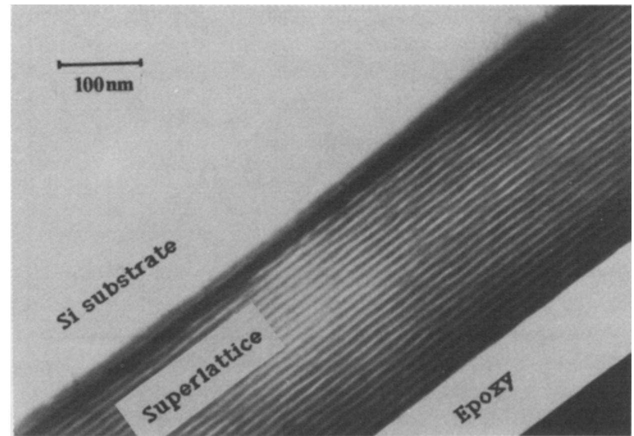

Fig. 9 — Cross-sectional TEM of a superlattice structure with 24 pairs of $Si/Si_{0.8}Ge_{0.2}$ layers.

micrograph of the superlattice structure. No extended defects such as dislocation loops and stacking faults are observed. The interfacial Ge transition layer width at the $Si/Si_{1-x}Ge_x$ interface is 30Å/decade or less, based on SIMS analysis.

Study of Growth Kinetics from Plasma Diagnostics

In Fig. 10, the growth rate is plotted vs 1/T for depositions at 200 mTorr, 15 sccm diluted silane flow rate and 6.6 W *rf* power. Our investigation into the variation of the growth rate with substrate temperature has provided interesting insights into to the details of hydrogen coverage of silicon surfaces. At low temperatures (<300° C), the growth rate is roughly independent of temperature. However, the growth rate exhibits a different temperature dependence at temperatures above ~325° C. This observation is consistent with the assumption that the rate limiting step in RPCVD is hydrogen desorption. Since the stable interatomic spacing of surface hydrogen atoms is greater at higher temperatures, the rate of hydrogen desorption should increase at higher temperatures. The relatively flat segment of the growth rate vs temperature plot below ~300° C corresponds approximately to the temperature range in which the Si surface has mixed monohydride and dihydride surface termination (confirmed by RHEED analysis). The temperature range (300–325° C) where there is a "knee" in the growth rate vs temperature plot corresponds to the temperature range where the nature of the hydrogen coverage changes from a mixed monohydride and dihydride surface termination to a monohydride termination. This is manifested by a change in the surface reconstruction pattern from (3 × 1) to (2 × 1) on the silicon (100) surface.[18,19]

At higher *rf* powers, the glow region is observed to extend closer to the sample. In order to understand the relative contributions of this effect and higher *rf* power *per se* to the enhancement of the growth rate at higher plasma powers, the growth rate was measured as a function of sample position for a fixed *rf* power of 6.6 W. The position of the sample was varied from 2.5 cm closer to the glow region (relative to the nominal position) to 1.8 cm further away from the discharge. The growth rate was observed to vary from 7.6Å/min to 3.6Å/min, respectively. This significant dependence of growth rate on position suggests that a large part of the growth rate enhancement that we have observed as the *rf* power is increased is due to the movement of the glow region closer to the wafer as the *rf* power is increased.

In order to obtain better insight into the RPCVD kinetics and to determine what the excitation pathways might be, the growth rates were determined as a function of *rf* power and substrate bias and correlated with Langmuir probe measurements of electron temperature and density, as well as ion density and flux. For typical deposition conditions of 200

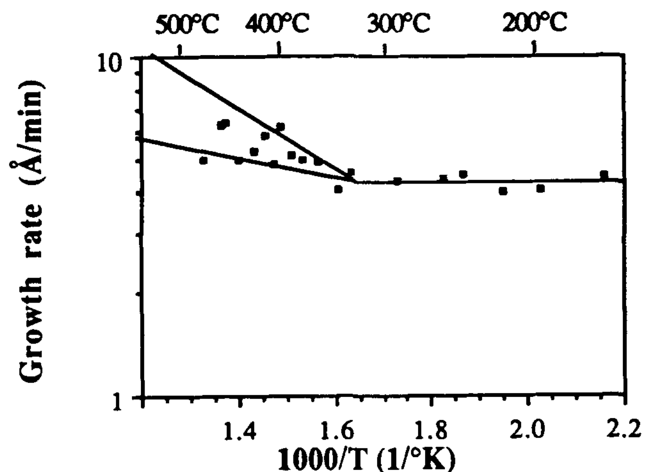

Fig. 10 — Arrhenius plot of growth rate at 200 mTorr chamber pressure, 6.6 W *rf* power, and 15 sccm dilute silane flow rate.

mTorr and 6.6 W *rf* power, the growth rate is found to increase for negative bias and to decrease for positive substrate bias. This suggests that positively charged ions are responsible for driving the deposition reaction which is believed to be surface-reaction-rate limited.[18] The proposed mechanism by which the substrate bias affects growth rate is explained in Fig. 11, which shows qualitatively the variation of electric potential in the plasma with distance from the silicon substrate. In Fig. 11, the potential drop between the glow region and the wafer is divided into two regions. Region II is a quasi-neutral region in which a small electric field exists which assists ions in reaching the wafer. Region I is the sheath region where most of the potential drop between the glow discharge and the wafer occurs. The resultant electric field accelerates ions to the wafer surface. We believe that an increase in the sheath voltage will not result in an increased deposition rate since the energy distribution of ions striking the surface is sufficiently tight such that all ions have sufficient energy to drive the surface reaction. For the above conditions of 200 mTorr, and 6.6 W, and with a grounded substrate, the plasma potential is approximately 30 V so that the voltage drop across region I is in the neighborhood of 30 V. We have previously proposed that H desorption is the rate limiting step for RPCVD.[18,20] The energy required to drive the reaction should be at least equal to the energy required to break a Si-H bond, which is ~2 eV. Therefore, it is proposed that the observed increase in growth rate for negative substrate bias is due to the increase in the potential drop in region II, which in turn increases the ion flux on the wafer surface. The plasma potential is important since it determines the potential drop in the sheath, which in turn, determines the kinetic energy with which ions strike the surface. A small decrease in the plasma potential with *rf* power is observed, which suggests that at higher *rf* powers slightly lower kinetic energy ions are involved in the reaction. Thus, the increase in growth rate at higher *rf* powers cannot be due to an increase in ion energy, but rather must be due to an increase in the ion flux. This supports the hypothesis that negative substrate bias results in an increased potential drop in the quasi-neutral region between the glow and the substrate, which enhances the ion flux on the wafer surface.

The plasma density is defined in terms of the electron or ion concentration in the glow region. These concentrations are approximately equal since the glow discharge is almost space charge neutral, or quasi-neutral. Since we have suggested that the growth rate is proportional to the ion flux, we expect the growth rate to be proportional to the plasma density (ion density). The ion density is found to increase with increased *rf* power as shown in Fig. 12, in which we observe that the plasma density measured using the double Langmuir probe increses with *rf* power. At low *rf* powers (4–8 W), the increase in growth rate with *rf* power is more dramatic than for higher powers (>8 W). This is because, as discussed earlier, the glow region moves closer to the substrate as the *rf* power is increased from 4 to 8 W. This results in a more rapid increase in ion density than would be expected from an increase in *rf* power alone.[18] When the *rf* power is greater than 8 W, the glow extends all the way to the sample, and the increase in growth rate in this regime is due only to the increase in ion density in the glow region with *rf* power. Indeed, for *rf* powers >8 W, the growth rate increases with approximately the same slope as does the ion density measured by using the double probe as seen in Fig. 12. The fact that the plasma density measured in the glow region using the single Langmuir probe in the 4–8 W range shows the same *rf* power dependence as in the 8–16 W *rf* power range where the substrate is engulfed by the plasma, supports the argument that the slow increase of growth rate at higher powers (8–16 W) is due only to the increase in plasma density with *rf* power.

The growth rate at 6.6 W *rf* power is found to increase at lower pressures as expected; however, as

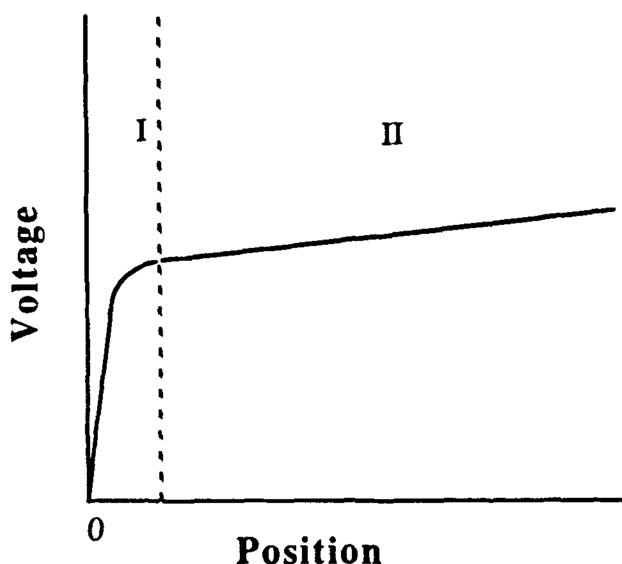

Fig. 11 — Schematic of the variation of plasma potential with position.

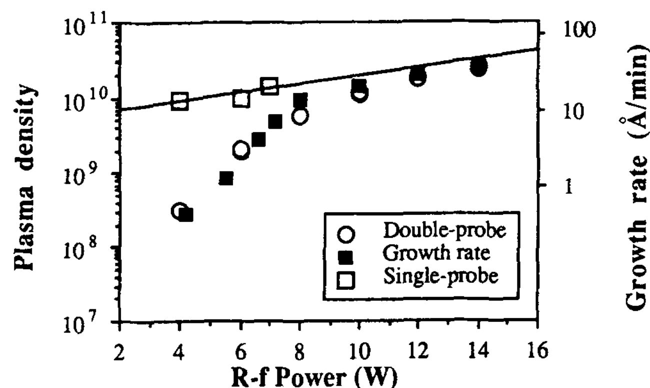

Fig. 12 — Growth rate vs *rf* power for 15 sccm diluted silane flow and 305° C substrate temperature. Results of ion density measurement as a function of *rf* power using Langmuir probe are also plotted.

is observed for the growth rate dependence on *rf* power, the growth rate dependence on pressure is complicated by changes in the glow discharge spatial location with changes in pressure. At reduced pressure, the glow extends closer to the wafer, which is expected to enhance the ion flux on the wafer surface over and above the anticipated ion flux increase due to the measured increase in ion density at lower pressures.

CONCLUSIONS

Remote Plasma-enhanced Chemical Vapor Deposition is a novel, low temperature growth technique which has been successfully employed in silicon homoepitaxy in the temperature range of 150–450° C. The epitaxial process employs an *ex situ* wet chemical clean, an *in situ* remote hydrogen plasma clean, followed by remote argon plasma dissociation of silane to generate the precursors for epitaxial growth. From AES analysis of the Si surface cleaned by a remote hydrogen plasma, it is found that a Si surface with oxygen, carbon and nitrogen contamination below the detectability limit of AES analysis can be achieved at temperatures of 250° C and above. RHEED analysis shows different structures of the substrate surface due to the remote hydrogen plasma clean at different temperatures. The transition of the surface structure from (3 × 1) to (1 × 1) reconstruction is believed to be due to a change in the surface Si-H bonding configuration which may give a different degree of hydrogen passivation. A defect-free, clean Si surface has been achieved at either 250° C for 9 W plasma power or 305° C for 12 W plasma power. Low temperature epitaxial growth by RPCVD was investigated at various temperatures. It is found that 150° C is the lowest temperature at which single crystal growth can be maintained by RPCVD. Epitaxial Si films with defect densities below TEM detectability ($\sim 10^5$ cm^{-2} or less) and low oxygen content ($\sim 3 \times 10^{18}$ cm^{-3}) have been achieved by RPCVD. The *in situ* boron-doped Si films have been successfully grown by addition of diborane during Si epitaxial growth. The electrical properties of the *p*-type Si films grown at 450° C by RPCVD have been shown to be of device quality. From the reaction kinetics, and correlation with Langmuir probe data, it appears that positively charged argon ions may be the dominant species responsible for driving the reaction. The rate limiting step appears to be hydrogen desorption from the hydrogenated silicon surface, which is assisted by argon ion bombardment. The low temperature feature of RPCVD has enabled us to grow $Si/Si_{0.8}Ge_{0.2}$ superlattice structures with minimal layer intermixing.

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