

STUDIES OF $\text{SiH}_2\text{Cl}_2/\text{H}_2$ GAS PHASE CHEMISTRY FOR SELECTIVE THIN FILM GROWTH OF CRYSTALLINE SILICON, c-Si, USING REMOTE PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

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ABSTRACT

Conventional high temperature, $>800^\circ\text{C}$, CVD processes, utilizing SiH_2Cl_2 promote selective deposition of c-Si onto c-Si, but not on SiO_2 surfaces. We show that low temperature, 300°C remote PECVD, with rf-excited He plasmas, and SiH_2Cl_2 and H_2 injected downstream, also selectively deposits c-Si on c-Si and not SiO_2 surfaces. This preliminary study employs *in-situ* mass spectrometry, MS, to determine the species responsible for selective deposition process reaction pathways. These MS studies suggest that species responsible for film deposition are Si-containing fragments of the SiH_2Cl_2 molecule, e.g., SiH_2Cl , SiCl_2H , etc., while the species responsible for inhibiting deposition on the SiO_2 surfaces are by-products of the break-up of the SiH_2Cl_2 molecule in the gas phase, e.g., H-atoms, HCl and H_2Cl^+ ions.

INTRODUCTION

Selective homoepitaxial growth of silicon is an important technique that creates unique opportunities for fabrication of high density circuits, and reduction of some photolithographic processing steps. For example, self-aligned techniques for polycrystalline silicon can eliminate the masking step sequence required for producing gate electrodes. A variety of thermal CVD techniques in the temperature range from 850 to 1100°C , based on various combinations of H_2 , HCl, and partially halogenated silane compounds, have been used for selective epitaxial growth of Si [1,2]. Much of the work on the chemistry of the Si/H/Cl system for thermal CVD processes show that there are competing deposition and etching reactions occurring simultaneously [3,4]. However, the high processing temperatures ($> 850^\circ\text{C}$) are undesirable for technologies where dopant diffusion and thermally induced stress must be minimized, or for heterojunction devices where compound semiconductors have already been incorporated into the structure [5,6]. There have been extensive studies of low temperature epitaxial growth of Si [7-9]. For example, by remotely exciting SiH_4 and H_2 with species extracted from a remote He plasma, Tasch et al. have deposited epitaxial Si on Si at temperatures as low as 150°C for thicknesses up to 100\AA , and significantly larger film thickness at temperatures of $\sim 300^\circ\text{C}$ [7]. There are two plasma techniques, other than what we discuss in this paper, by which Si has been selectively grown. Baert et al. have employed a glow discharge to deposit microcrystalline, high conductivity n+ silicon gate electrodes for CMOS devices, utilizing an SiH_4 and SiF_4 source gas mixture, that also includes the dopant source gas, PH_3 [8]. Yew and Reif have used an H_2 plasma with an alternating SiH_4 flow cycle, to switch between Si deposition and etching, in order to obtain selective Si epitaxial films at 600°C [9]. There are two reasons why remote PECVD is being investigated for low temperature selective deposition studies: i) it intrinsically affords good control over gas phase reaction chemistries; and ii) it minimizes substrate damage associated with bombardment by energetic ions, as in conventional PECVD utilizing capacitively coupled reactors.

In order to understand how the selective process operates, it is necessary to understand and separate those chemical reactions that occur in the gas phase, e.g., the formation of deposition and etching precursors, and at the specific substrate surfaces, e.g., c-Si and SiO_2 . The primary goal of this work is to determine the species that contribute to selective silicon deposition using remote PECVD. We start by determining what the species are formed in the gas phase by the break-up of the SiH_2Cl_2 molecule in the presence of H_2 . By studying the effect of the H_2 flow rate for a constant flow rate of SiH_2Cl_2 , we can identify the way SiH_2Cl_2 is fragmented in the gas phase by interaction with plasma generated species from a H_2 and He discharge. We then discuss the way that these species can react at the respective Si and SiO_2 surfaces to either promote or inhibit Si deposition.

EXPERIMENTAL TECHNIQUES AND RESULTS

The chamber used for this study embodies all of the attributes of a remote PECVD system, and in addition it provides in-situ analysis of the gas species in the chamber by MS, and non-intrusive analysis of radiating species by optical emission spectroscopy, OES. The

inner diameter of the chamber is 14.9 cm, and the length is 56 cm (see Fig. 1). One end of the chamber is connected to a fused silica plasma generation tube with an inner diameter of 3.2 cm. This tube is positioned along the central axis of the chamber.

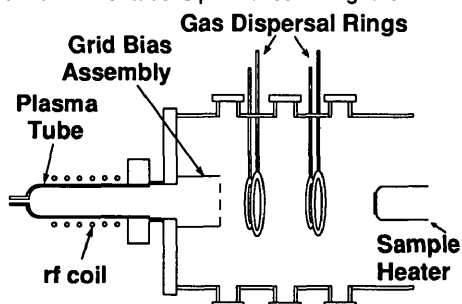


Figure 1: Schematic diagram of the Deposition/Analytical System

Plasma excitation is achieved at a frequency of 13.56 MHz. There is a grid assembly at the end of the plasma tube that connects to the deposition chamber region of the apparatus. A 400 l/s turbomolecular pump is used to attain a base pressure of $\sim 5 \times 10^{-8}$ Torr. A load-lock assembly located at the other end of the deposition chamber is designed to accommodate an electrically floating piston driven substrate holder/heater assembly. Inside the chamber, at 10.2 cm and 35.6 cm from the plasma tube flange, there are two sets of double gas rings for downstream injection of process gases. There are sampling stations located along the gas stream in three strategic locations: one between the plasma tube flange and the

first gas ring, and the other two, 3.8 cm downstream from the each set of gas dispersal rings. These consist of two horizontally aligned pyrex windows for OES, and a vertical port to accommodate the sniffer tube for the MS. The mass spectrometer is an Extrel C-50 3/8" quadrupole mass spectrometer with a mass range of 0-280 m/z, and an independently operated ionizer, so that both neutral and ionized species may be studied.

A series of films were grown on partially oxidized wafers to examine the selectivity of the deposition process. Each wafer is (100) oriented Si and was patterned with 1200 Å of SiO₂, grown by remote plasma CVD. The plasma power is 75W. 100 sccm He is injected through the plasma tube, and 10 sccm of 1% SiH₂Cl₂ in He, and between 0 to 50 sccm of H₂ are injected into the first set of downstream gas dispersal rings. The sample is mounted on a Si-coated copper block heater that is held at 300°C, and is kept 3.8 cm downstream from the first gas dispersal ring. The plasma grid assembly is kept electrically floating, and in this configuration does not block the plasma afterglow from extending into the deposition region of the chamber. After deposition, samples are examined under SEM to determine selectivity and growth morphology, and by RHEED to determine the degree of film crystallinity. Mass spectrometry is used to identify the gas phase species. We have used D₂ for H₂ substitutions in order to determine the parentage of the H-atoms in the various H-containing deposition and etching precursor species.

Figure 2 shows SEM micrographs of the boundaries between the oxide, and the grown c-Si layer. For the samples grown with less than 50 sccm of injected H₂, there is no selectivity, while for the sample grown with 50 sccm of H₂ flow, selectivity is apparent. However, for this case there are a significant number of isolated Si nuclei on the oxide surface. Figure 3 shows RHEED patterns for the samples grown with 0, 20 and 50 sccm of injected H₂. The rings of the 0 sccm sample indicate a microcrystalline Si, and a randomly oriented morphology, while the 20 and 50 sccm films, exhibit a spot pattern associated with a preferred orientation of polycrystalline film growth. At the present state of our research effort, film growth is limited by the low effective flow rate of the Si-source gas species, 1% SiH₂Cl₂ in He. To achieve selective film growth the films must be grown in a sequence that loads the chamber walls with active deposition, and also possible etchant species. This is accomplished by a 10 hour flow of sccm H₂, 10 sccm 1% SiH₂Cl₂ + He, and 100 sccm He, with remote excitation of the He at 75 W. Using this pre-deposition process, we achieve reproducible selective film growth.

Figures 4 through 6 show the results of the MS in-situ monitoring. Figure 4 shows the cracking pattern of SiH₂Cl₂ in He, for masses 0-110, by a 70 eV electron beam energy in the MS ionizer. The electron-initiated cracking of SiH₂Cl₂ produces di- and mono-chlorosilane groups at 98-103, and 63-67 m/z, respectively, an HCl/Cl group with masses 35-38, and a silane group with masses 28-30. Mass 30, corresponding to SiH₂ is mostly absent, and the peaks above mass 31 are actually doubly ionized mono-chlorosilane fragments. Figure 5

shows the change in intensities for these peaks for mass 25 to 110, as the H_2 flow rate increases with the plasma power fixed at 75 W. As the H_2 flow increases, there is an

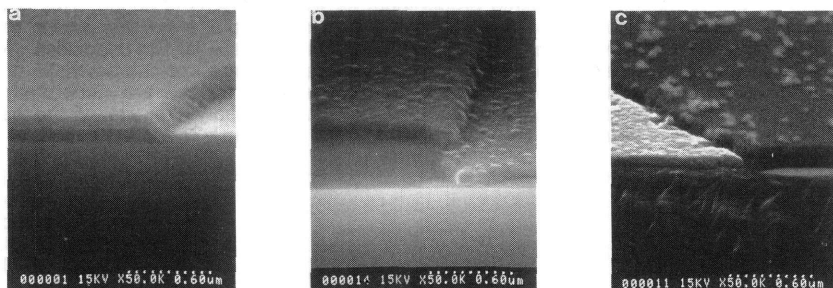


Figure 2: SEM Micrographs of Deposited Films a) 0 sccm H_2 , b) 20 sccm H_2 , c) 50 sccm H_2 . Deposited at 75W, 300°C, 100 sccm He in the plasma tube, 10 sccm 1% SiH_2Cl_2 + He downstream.



Figure 3: RHEED sample of films shown above, a) 0 sccm H_2 , b) 20 sccm H_2 , c) 50 sccm H_2 .

increase in the mono- and di-chlorosilane, silane, and hydrogen chloride peaks. Additional peaks at mass 31 and mass 39 appear, and the peak at mass 37 increases much more than the other HCl peaks. The major contribution to masses 31 (50%) and 37 (99%), and the only contribution to mass 39 are from ions generated externally to the mass spectrometer. This leads to the conclusion, that peaks 37 and 39 are caused by the formation of H_2Cl^+ , otherwise known as the chloronium ion, which has been well-documented as a species produced in

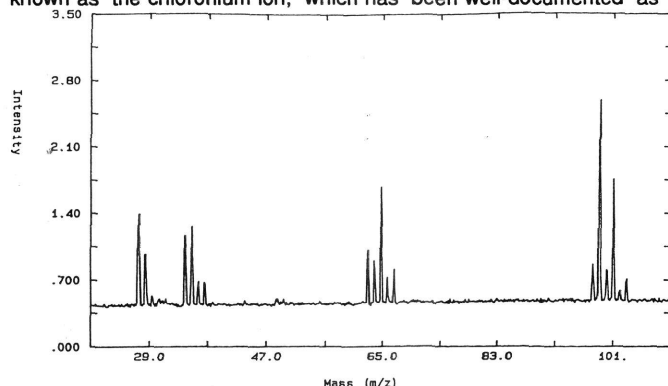


Figure 4: Mass spectrum showing the break-up pattern of SiH_2Cl_2 at 70 eV electron beam.

plasmas of HCl and hydrogen [10]. The mono- and di-chlorosilane peaks are also composed of almost entirely ions. The mono-chlorosilane peak intensities are about twice as large as the di-chlorosilane peaks with the plasma on, whereas in the SiH_2Cl_2 cracking pattern, the mono-chlorosilane peaks are only about half as intense. This is an indication that a Cl stripping reaction occurs under plasma excitation conditions. The silane peaks, particularly masses 30 and 31, associated with SiH_2 and SiH_3 , respectively, do not necessarily come

from the gas phase plasma excited reaction between H_2 and of SiH_2Cl_2 . This is shown by striking a He plasma with only H_2 injected, and noting that the peaks associated with masses 30 and 31 are produced in the same proportional as when SiH_2Cl_2 is added. This is one indication that the chamber walls are a significant source of silane species *under these particular flow conditions*, which are lower than those generally used for film deposition. Note further that the relative peak intensities for masses 30 and 31 are not characteristic of the cracking pattern of silane by the MS ionizer, indicating that these species are generated by H-atom etching reactions at the chamber walls. Figure 6 shows results of the same experiment, in which deuterium, D_2 , was substituted for H_2 in order to tag the source of the hydrogen in the

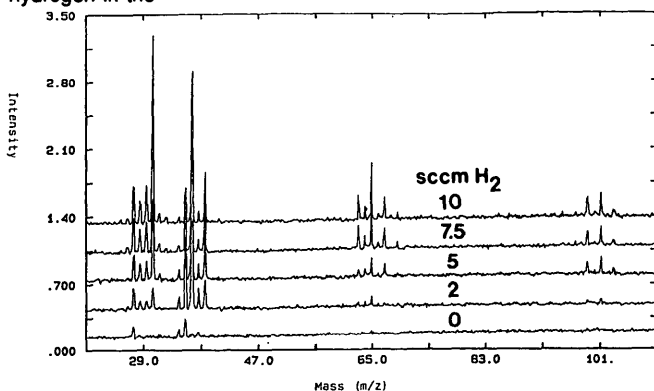


Figure 5: Mass spectra of SiH_2Cl_2 after 75W rf excitation as a function of H_2 flow rate.

same as the injection ratio of the gases, it is evidence that hydrogenation from injected sources is limited. For example, mass 64 can only be from $SiClH$, and mass 65 can be primarily from $SiClD$ and $SiClH_2$.

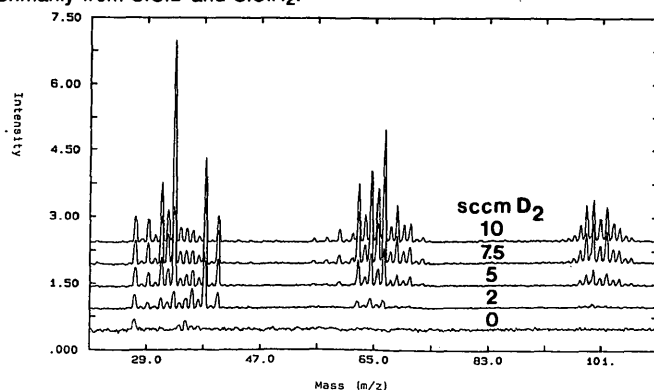


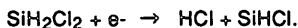
Figure 6: Mass spectra of SiH_2Cl_2 after 75W rf excitation as a function of D_2 flow rate.

larger than for the cracking of SiH_2Cl_2 without the plasma, this demonstrates conclusively that Cl is being stripped from SiH_2Cl_2 in the gas phase. There are two possible mechanisms that may perform the stripping, electron impact dissociation, and H stripping, followed by with ionization. With only SiH_2Cl_2 and a He plasma, or SiH_2Cl_2 in the 70 eV electron beam of the mass spectrometer HCl is formed, with the only source of hydrogen being SiH_2Cl_2 . Since virtually no gas phase collisions occur in the mass spectrometer, the HCl formed is a decomposition product of the reaction,

various species. The additional silane, and mono- and di-chlorosilane peak groups show that D-atoms are substituted for H-atoms. The mass intensities of the entirely deuterated species show the same relative intensities as the same protonated species. But, since the relative peak heights between deuterated and non-deuterated species are not the

DISCUSSION

From the data presented in Figs. 5 and 6, it is clear that the addition of increasing amounts of hydrogen into the chamber, along with its interaction with the plasma, strips Cl from SiH_2Cl_2 . The increase in the Cl and HCl peaks, and disproportionate increase in mass 37 show the production of H_2Cl^+ . Since these peaks are



A similar reaction may occur in the chamber, even though the average electron temperature is much lower than the mass spectrometer ionizing electron beam. In fact, the collision cross section is greatest at electron energies much less than 70 eV. The mechanism would at first seem counter-intuitive with the addition of the downstream H_2 , but the electron temperature decrease in the plasma after-glow is offset by an increase in the electron current. This will increase the efficiency of SiH_2Cl_2 cracking, as long as the total number of electrons with energies over the threshold is high. Any hydrogenation of these cracking species apparently occurs afterwards. A hydrogen-ionization/hydrogenation mechanism appears less likely, since the deuterium substitution shows that the injected hydrogen attaches to stripped chlorosilanes and hydrogen chloride species at a much lower ratio of injected D_2 to SiH_2Cl_2 , e.g. (3:1 for mass 65:mass 64, at a 20:1 D_2 to SiH_2Cl_2 injection ratio). If the injected hydrogen were performing the dissociations and ionizations, the ratio of peak heights would be expected to be more on the order of the ratio of total deuterium to total hydrogen content in the system.

As shown in Figs. 5 and 6, the concentration of monochloro- and silane species increases with the increasing H_2 injection. The largest change in the mass spectrometer signal is the increase in mass 31, which primarily consists of SiH_3 species. SiH_3 increases to a level that is about 5 times greater than SiH_2 , whereas the intrinsic cracking pattern shows that SiH_2 is normally about 15% greater than SiH_3 . The production of SiH_3 could be in the gas phase, but it is likely an etching product, associated with the walls of the chamber. When a discharge of He and H_2 is struck with no flow of SiH_2Cl_2 , SiH_3 species are easily detected. The only source of Si in the system under these conditions are the fixtures and walls of the chamber. The mass 31 species is apparently formed in a surface etching reaction that directly produces SiH_3 . If we assume that mass 30 is due from SiH_4 generation during etching, then at most 15-20% of the SiH_3 can also be attributed to wall-generated SiH_4 , arriving unreacted at the mass spectrometer.

The fact that H_2Cl^+ is found in the gas phase, is very interesting, from the standpoint of it being a possible process active species in inhibiting deposition of the SiO_2 surfaces. H_2Cl^+ is designated among a group of chemical species known as superacids, which are known to be very strong proton donors. The formation of H_2Cl^+ occurs in gaseous discharge systems of H_2 and HCl from the attraction of protons to HCl (proton affinity 6.1 eV) [10,11]. Due to the relatively strong dipole of the HCl molecule, it is easy to see that the proton will naturally be attracted to the net negative charge of the chlorine atom. Since HCl is a product of SiH_2Cl_2 decomposition by plasma excited H_2 , it can clearly be a reaction intermediate in the process which generates H_2Cl^+ .

There are several possibilities through which H_2Cl^+ ions may participate in the selective film deposition process. For example, they can hydrogenate the Si surface and promote etching. Protons are much more reactive than H atoms and H_2 molecules, thus more effective in promoting proton initiated surface reactions. Another possibility, is that the proton may be used to "dehalogenate" the Si surface, and promote crystalline rather than amorphous growth [12]. In addition, selectivity may be enhanced by the etching of Si species attached to the oxide preferentially to the Si species on Si. This can be accomplished by proton donation from the H_2Cl^+ species as well. For example, it will take less energy for a proton to break the donor/acceptor bond between a surface O-atom of the oxide and a Si-atom of an attached silane or di-chlorosilane fragment, than a similar surface Si-atom associated bond on c-Si.

The surface morphology and RHEED patterns show, that at least the surface of the film is polycrystalline, which implicates a secondary etching mechanism, based on arguments of thin film nucleation and growth processes. Assume that both deposition and etching reactions occur on the oxide and the silicon surfaces. The deposition of Si atoms on the c-Si surface can come about in three ways: i) formation of additional nuclei through heterogeneous mechanisms; ii) bonding to existing nuclei; or iii) bonding directly to the substrate. In contrast bonding to the oxide to form a continuous Si layer can only be accomplished by i) and ii), thereby favoring nucleation and growth on the Si substrate over the oxide substrate. Due to the differences in growth morphology, shown in Fig. 2, atoms on the edges and corners of the crystallites on the oxide will be more susceptible to removal by hydrogenation, since they contain more reactive surface bonds. Even though the films shown here are polycrystalline surfaces, there is no reason inherent in this process that would prevent epitaxial film growth. The substrate is on an electrically floating sample stage, which inhibits the formation of a

sheath region about the wafer, thus minimizing any sort of damage that may be produced through ion acceleration. Hsu et. al. have shown that substrate damage sustained by the wafer is primarily from excited hydrogen creation of point defects, but that this technique can grow epitaxial films at 250°C anyway.[13]

As stated in the previous section, it is required that a sequence of "wall loading" depositions be performed in order to achieve selective film growth under these conditions. When this sequence is not followed, the conditions under which selective growth *can* be obtained, yield no significant film growth. It appears that residue from the previous runs is extracted from the surfaces of the chamber to assist in both growth and etching. However, when the H₂ flow rate is kept at less than 5 sccm, a crystalline film may be grown *uniformly* across the entire sample surface including the Si and oxide regions, and regardless of the previous deposition chamber history. By running a He/H₂ plasma, it is possible to remove all of the species that are apparently active in selective depositions. Since the wall loading plays a key role, it implies that the concentration of etchant and deposition species needs to be increased over what is currently available in our source gas mixtures, e.g., by increasing the effective flow rate of SiH₂Cl₂, or by using a source gas mixture with a higher concentration of SiH₂Cl₂. Independent of the deposition reactions studies at high H₂ flow rates, the mass spectrometry studies provide valuable insight into the breakup of di-chlorosilane in a remote plasma system, including the identification of probable deposition and etching precursors, such as mono- and di-chlorosilane ions and SiH₃⁺, and H₂Cl⁺, respectively.

SUMMARY

This paper has demonstrated the effect of the relative H₂ flow rate on the gas phase species produced in the presence of downstream-injected SiH₂Cl₂/H₂ mixtures with respect to an rf-excited He discharge. The SiH₂Cl₂ is stripped of Cl, producing chlorinated silane ions, and H₂Cl⁺ ions. The H₂Cl⁺ ion is likely to be an etchant species, with the chlorinated silane being a possible deposition precursor. SiH₃ in this system is shown to be an etching product from wall interaction, but is none-the-less also a possible deposition precursor as well. It appears that the dissociation/ionization of SiH₂Cl₂ is caused by an electron impact mechanism, rather than proton attachment. It has been shown that this remotely excited process can produce selectively grown crystalline Si films at 300°C, but under special conditions of wall loading. This work raises several research issues as well. What is the effect of the Si:Cl ratio on the selectivity and deposition? Since H₂Cl⁺ is present, and it is known to be a super-acid, how will fluorine substitution affect the degree of selectivity? These questions are currently under investigation. In particular, we will study remote PECVD using: i) a significantly increased flow rate of SiH₂Cl₂; ii) mixtures of down-stream injected SiCl₄, SiH₄ and H₂; iii) mixtures of downstream injected SiH₄, HCl and H₂; and iv) fluorinated as well as chlorinated hydrides and substituted silanes.

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