

STICKING PROBABILITY AND STEP COVERAGE STUDIES OF SiO₂ AND POLYMERIZED SILOXANE THIN FILMS DEPOSITED BY PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

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ABSTRACT

This paper describes a method for estimating the effective sticking probability for plasma enhanced chemical vapor deposition (PECVD) of hexamethyldisiloxane (HMDSO) using SiO₂ and polymerized siloxanes deposited on specially prepared trench structures. Comparison of the data with direct Monte-Carlo simulation curves provides information about the incorporation probability relative to film growth. It is shown that besides variation in gas chemistry, the choice of trench and film dimensions influences the step coverage. The sticking probability is shown to increase with oxygen flow rate by about 30%, from 0:1 to 10:1 O₂:HMDSO flow ratio. This flow rate dependence is found to be consistent with work performed on tetraethoxysilane.

1. INTRODUCTION

The sticking probability is one of the most important parameters for describing film step coverage and developing deposition models. However, due to the lack of knowledge of the flux and surface kinetics of the deposition species for many chemical systems, the sticking probability is difficult to directly quantify. Instead much work has gone into developing models to relate the contour of a deposited film to the sticking probability [1-8]. In particular, several simulations have been created to estimate the sticking probability of CVD processes. For example, Kawahara et al. developed a Monte Carlo model with a single depositing species of constant sticking probability [1]. Watanabe et al., developed a one dimensional analytical model along with a test structure to perform actual measurements [2]. Ikegawa et al., used direct simulation Monte Carlo with finite element analysis techniques to determine film conformality based upon a full reaction model for thermal CVD processes for phosphosilicate glasses in molecular and transitional gas flow regimes [3]. More recently, work has been done to develop PECVD-based models, such as the string model developed by Yuuki, et al. for a-Si:H film growth by SiH₄ decomposition [4]. Predictive models have been used for PECVD processes to determine the relative concentration of multiple deposition components with different sticking probabilities for SiH₄ deposition [4,5]. However, these models have only been used to determine the overall sticking probability for PECVD processes whose chemistries is already well understood. One objective of this work is to apply the results of LPCVD models to PECVD processes, and demonstrate how they may be used as a tool for characterizing CVD systems of less well understood chemistries and processes. The other objective is to show how the sticking probability and conformality change as the ratio of the plasma feedstock gases varies for the HMDSO/O₂ deposition system.

2. EXPERIMENTAL

The films were deposited on (110) Si wafers with trenches of various aspect ratios. The deposition conditions were 250 mTorr, 30 sccm HMDSO, between 0 and 300 sccm of O₂, 300W, 250 kHz rf power, autotransformer-matched impedance at 2450Ω, and no substrate heating. The samples were placed on the grounded bottom electrode of a Plasmatherm PK-1241 parallel plate system with a 2.5 cm electrode gap. (The plasma was confined to the region between the two plates.) The deposition time was varied between 10 and 12 minutes to achieve approximately 3 μm films. Samples were then cleaved and imaged in full cross section in SEM backscatter mode operating at 20 keV. The samples were not coated with a conductive layer.

The test structure used for this experiment was made up of repeating sets of fully rectangular cross section trenches, produced by orientation dependent etching (ODE) of (110) Si [9-11]. The die measured 1.014 cm by 0.512 cm, and consisted of 74 sets of trenches, each set having 5 different widths (nominally 5, 10, 15, 20, and 30 μm) separated by nominally 10 μm wide walls,

for a total trench set width of 130 μm . The trench layout used repeating sets of trenches rather than grouping all trenches of a single width together, in order to minimize the dimension of detectable local chemical variations. The maximum trench width chosen was much smaller than the molecular mean free path length of 200 μm . The minimum Knudsen number (λ/D) for a trench was 7, well above the value of unity that defines the molecular flow limit. Two sets of wafers were fabricated to produce trenches that were 5 and 15 μm deep. These two sets of trenches gave aspect ratios of width:depth of 1:2.5 to 6:1. It should be noted that the 1:1 and 2:1 aspect ratios exist for both trench depths. During deposition, one die of each etched depth was coated, so that 10 different trenches were simultaneously exposed for each data point.

The trenches were formed in (110) Si using ODE with KOH [9-11]. The trench die pattern was transferred to an oxide mask using standard photolithographic and wet etch techniques, such that the trench walls were aligned with the (111). A two-step KOH etching procedure was used to produce a fully rectangular cross section trench with perpendicular sidewalls and flat bases, as shown in Figure 1 [12].

The estimation of the sticking probability for each data point was determined using curves generated by Kawahara et al., and Yuuki et al. [1,4]. The modeled sticking probability data were presented as a plot of isoprobability curves of film coverage as a function of trench aspect ratio. A limiting case equation of sticking probability equal to unity, and minimal topwall film thickness was also stated (for $\beta = 1$, and $d_{\text{max}}/D = 0$, $d_{\text{min}}/d_{\text{max}} = [1 - (W/D)/[1 + (W/D)^2]^{1/2}]/2$) (1) [4]. In order to systematically determine the sticking probability for the measured data, a sticking probability (β) parameterized equation was found by inductive reasoning and regression analysis:

$$d_{\text{min}}/d_{\text{max}} = \left(\frac{1}{1+\beta} \right) \left(1 - \left(\frac{1}{x} \right) \left(\frac{1}{\sqrt{\beta^{-3/2} + x^{-2}}} \right) \right) \quad (2)$$

where, $x = W/D$, W is the trench width, D is the trench depth, d_{max} is the topwall film thickness, and d_{min} is the film thickness at the bottom of the sidewall ($d_{\text{min}}/d_{\text{max}}$ is the fractional step coverage). Equation (2) reduces to equation (1) at unity sticking probability. This equation provided a fit within 5% to the curves for sticking probabilities equal to or greater than 0.1.

3. RESULTS

Figure 2 is a backscattered electron SEM image of a typical deposited film on a trenched surface. The deposition rate for the films is in the range of 3000 $\text{\AA}/\text{min}$. The aspect ratio of the trench is 1:2.5 (width:depth) with portions of a 1:1.5 trench on the right and a 2:1 trench on the left. As can be seen from examining the thickness of the sidewall layers in each trench, the highest aspect ratio trench has the thinnest sidewall material. The texture of the film is featureless in cross section, except for the sidewall material. It appears to have a columnar-like structure of low temperature sputtered films, oriented at 45° relative to the base. Energy dispersive x-ray mapping, and XPS did not detect any compositional differences of the sidewall and topwall material.

Figure 3 is a representative plot of experimental sticking probability data superimposed on a plot by Kawahara et al., and Yuuki et al. to show how the experimental data compare with modeled data [1,4]. The data come from two wafers processed simultaneously; one has 15 μm deep trenches and the other has 5 μm deep trenches. While the data follows the same trend as the modeled material, there are important differences. First, the experimental values for $d_{\text{min}}/d_{\text{max}}$ increase more slowly with increasing aspect ratio compared to the model, instead of following a single sticking probability curve. In addition the data points from the 5 μm deep trenches tend to have a lower step coverage than the 15 μm deep trench of about the same aspect ratio. This difference in step coverage is within the standard error for the data collected from a single deposition, but is evident for every sample. The sticking probability estimation procedure uses Newton's iterative method to solve for β using equation 2, with the values of W/D and $d_{\text{min}}/d_{\text{max}}$.

Figure 4 is a plot of the sticking probability as a function of the O_2 gas flow rate. The data points are collected from trenches with a 2:1 aspect ratio. The sticking probability ranges from 0.39 to 0.78 for this aspect ratio. Overall, the sticking probability ranges from about 0.2 to almost unity. The error bars reflect the uncertainty in estimation of the sticking probability at each point.

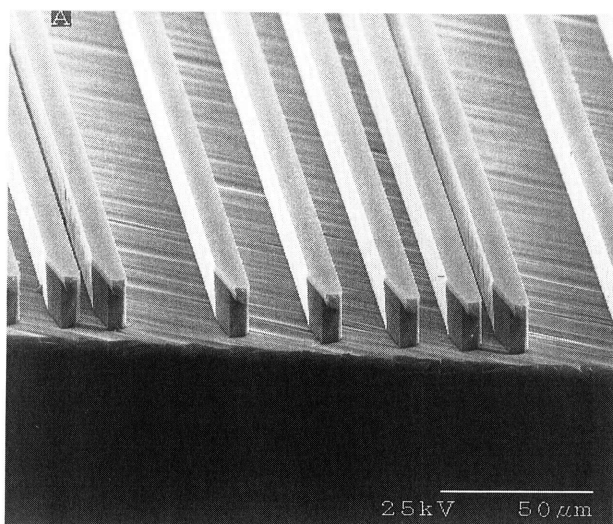


Figure 1: Secondary electron SEM image of edge of fully processed uncleaned (110) Si trench die used in experiments. Trench walls and bases consist of Si. Trench depth is 15 μm .

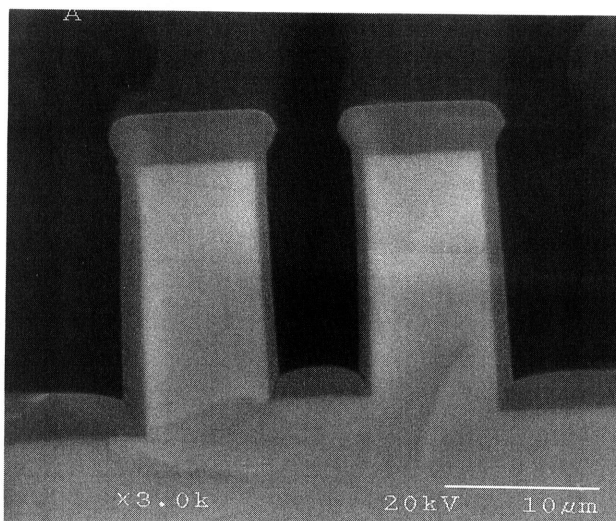


Figure 2: Backscattered electron SEM image of cleaved 6 μm wide x 15 μm deep trench with 3 μm oxide. Deposition conditions include 30 sccm HMDSO and 150 sccm O_2 . Edges of the 30 μm trench to the left, and the 10 micron trench to the right can be seen. Note the differences in sidewall film thickness between all three trenches.

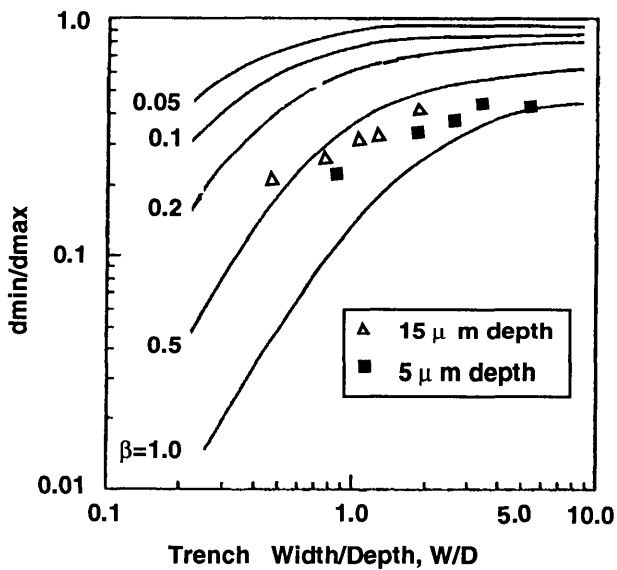


Figure 3: Ratio of film thicknesses as a function of trench aspect ratio. Data comes from the sample shown in Figure 2. The data are super-imposed on a plot of modeled curves by Kawahara et al. for comparison [1].

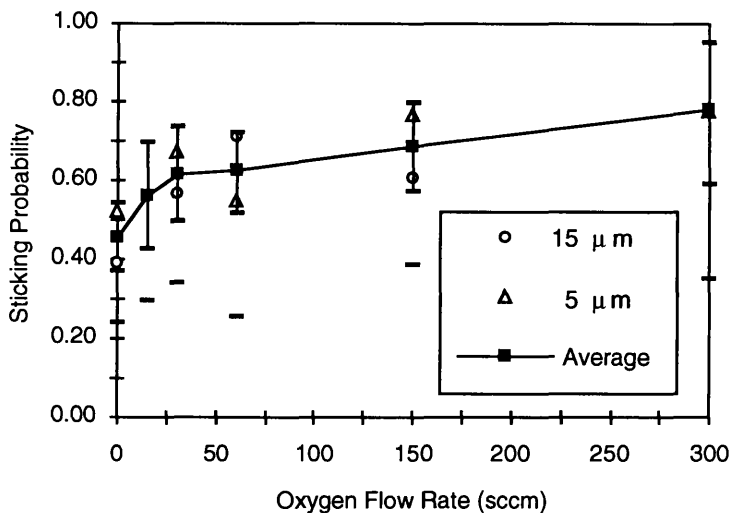


Figure 4: Sticking probability as a function of O_2 flow rate. Trench aspect ratio 2:1, 300W, 30 sccm HMDSO, 3 μm top layer film thickness. The lower set of bars represents the maximum deviation of measured data from plotted values.

The lower bars are data points showing the maximum difference between the 2:1 trench sticking probability and the estimated sticking probabilities for the other trenches. The figure shows that there is a drop in the sticking probability for very low O_2 flow rates, but that it is relatively constant above 30 sccm (1:1 HMDSO: O_2).

4. DISCUSSION

The flatter shape of the measured data relative to the modeled curves is caused by the presence of multiple deposition species. This can be shown by how the model used for deriving the curves is developed [4]. (The measured data in Figure 3 are superimposed upon curves generated by the model of Yuuki et al., and Kawahara et al. [4,1].) The model used is based upon several assumptions, including only one sticking probability that describes all depositing species, and a constant film thickness/trench depth ratio. The measured data in Figure 3, however, more closely match data from experiments by Tsai et al. [4, 13]. They examined step coverage of PECVD a-Si:H films deposited from SiH_4 , a chemical system known to have multiple depositing species. Because of the deviation of the single species model from experimental evidence, Yuuki et al. changed the model by allowing calculations using two sticking probabilities [4]. The calculations are performed on the assumption that the different species do not interact with each other on the surface. The best fit is then made by adjusting the sticking probability and the relative flux of each component. The shape of the multicomponent curve relative to the single component model shows significant deviation, but matches the experimental data [4]. The data from this experiment vary in a similar fashion, which provides experimental evidence for the assumption that the HMDSO/ O_2 PECVD process has multiple deposition species for film growth.

The other important feature to note in Figure 3 is that the d_{min}/d_{max} values from the deeper aspect ratio trenches are slightly higher than the values from the wider aspect ratio trenches, (see, for example, the ~1:1 aspect ratio trenches, for both sets of points in Figure 3). The effect is evident for each sample measured. This effect is due to the occlusion of the trench opening during film growth as shown by Blech, and Ross and Vossen [6,7]. As the film becomes thicker, the trench opening narrows effectively increasing the trench aspect ratio. The cumulative effect of trench occlusion and aspect ratio change is characterized by the ratio of the topwall film thickness over the trench depth (d_{max}/D , occlusion ratio). As d_{max}/D increases, trench occlusion becomes more pronounced. For shallower trenches the effect is more pronounced than for a deeper trench, since a given thickness of deposited material alters the trench cross section more. The increased aspect ratio of the unfilled cross section increases selective filtering of the higher sticking probability precursor. The material on the bottom of the trench will receive a disproportionately higher flux of the lower sticking probability material. This explains the behavior of d_{min}/d_{max} when comparing two trenches with similar aspect ratios but different trench depths. According to the models, d_{max}/D shifts the curve by less than 2% for ratios wider than 2:1 [1,7]. For the presented data, in which the top wall film thickness is the same, for the 15 μm deep trenches d_{max}/D ranges from 0.17 to 0.28, and from 0.42 to 0.92 for the 5 μm deep trenches. It shows that the occlusion effects are relatively greater for shallower trenches. The greater trench occlusion lowers the relative flux reaching the trench walls, thus lowering step coverage within the trench.

When analyzing the measured data from a PECVD system, it is necessary to take into account the effect of multiple deposition species and the difference in trench dimensions. By choosing data from a single aspect ratio, the generalized behavior of the sticking probability will be self-consistent with respect to independent parameters, such as gas flow. In general, it is preferable to select trenches with dimensions close to the size of interest. Since the objective of this work is to understand deposition on a planar substrate, wider trenches are preferable because they receive fluxes that are more representative of the multiple species that a planar surface receives. Deeper aspect ratio trenches receive disproportionately more low sticking probability material on the trench sidewalls and base. Furthermore, wide trenches are relatively less susceptible to occlusion effects of the trench opening. However, the sensitivity of the measurement decreases by more than a factor of 2 for aspect ratios between 1:2 and 5:1, and a sticking probability of ~0.3. The 2:1 aspect ratio trench was selected for data analysis in this experiment because it is the best compromise between estimation sensitivity and minimization of deep trench effects.

Examining the details of the results provides several clues about the nature of the HMDSO/O₂ deposition process. The shape of the step coverage curve in Figure 3 implies that there is more than one depositing species influencing film growth, and that they have widely varying sticking probabilities. Earlier work shows that at low O₂ concentrations, deposited films are essentially polymerized methylated siloxanes, but above a dilution of about 1:5, HMDSO:O₂, films are predominantly oxide [14]. The change in slope for the sticking probability shown in Figure 4 occurred around 1:1 ratio. The direct relationship between sticking probability and oxygen flow rate is consistent with the work of Raupp et al., who examined SiO₂ film growth from TEOS and O₂ using microwave remote PECVD [15]. They attribute the increase in sticking probability to an increase in the surface reaction rate caused by higher atomic O production rates. For this capacitively-coupled system, a similar mechanism tied to the production rate of an excited oxygen species is likely to hold. Therefore, it is probable that surface oxidation reactions of the deposition precursor play a key role in film evolution for this process. Since a change in sticking probability is most often related to changes in surface composition or gas composition, the results imply that the incorporation processes may have relatively little influence on the final film composition.

5. SUMMARY

It has been shown that it is possible to estimate the sticking probability for PECVD processes in which the specific chemical species are not known, by quantifying step coverage of trenches. An equation has been found that fits the single component model curves in the range of 0.1 to 10 aspect ratio to within 5%. The fit of the experimental data with the published isoprobability plots has been attributed to the presence of multiple deposition species and the occlusion ratio, d_{\max}/D . The primary criterion of selecting trench dimensions is to find trench features that approximate actual conditions of interest. In order to make measurements on nominally flat substrates, it is necessary to select a wide trench to minimize occlusion effects. Models that include multiple deposition species will improve the estimation process. For the HMDSO/O₂ PECVD system, it has been demonstrated that the sticking probability decreases as the ratio of O₂ to HMDSO decreases and that this does not coincide with the incorporation of methylated siloxane groups within the film. These findings help demonstrate that 1) there is more than one deposition species, and 2) surface oxidation may play a key role in oxide film growth for this chemistry.

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