Effect of hydrogen on adsorbed precursor diffusion kinetics during hydrogenated amorphous silicon deposition

K. R. Bray, A. Gupta, and G. N. Parsons[a)]
Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695

(Received 12 December 2001; accepted for publication 11 February 2002)

Fractal analysis of the surface topography is used to study the effects of hydrogen dilution on the surface transport kinetics during the plasma deposition of hydrogenated amorphous silicon. Images obtained from atomic force microscopy are examined using dimensional fractal analysis, and surface diffusion lengths of growth precursors are estimated from the measured correlation lengths. The addition of small amounts of hydrogen (H_2/SiH_4 ratios $<10/1$) during deposition leads to a decrease in the diffusion length, but larger hydrogen dilutions result in increased diffusion length. Moreover, the measured surface diffusion activation barrier is reduced from 0.20 eV for deposition from pure SiH_4 to 0.13 eV with high hydrogen dilution. Results are consistent with recent models for precursor surface transport during low-temperature deposition, and give insight into critical processes for low-temperature silicon crystallization.
[DOI: 10.1063/1.1467616]

Plasma deposition of hydrogenated amorphous silicon (*a*-Si:H) results in very smooth, conformal surfaces and nonthermally activated growth rates over temperatures ranging from <25° to 400 °C.[1–4] Typical models for *a*-Si:H growth presume that radical precursors generated in the gas phase adsorb and diffuse on the surface with low thermal barriers, giving rise to the observed smooth conformal surface coverage.[2,3,5] The evolution of surface roughness as a function of process conditions during film growth can be used to characterize transport processes on *a*-Si:H surfaces[6–8] and analyze kinetics of adsorbed precursor diffusion.[9–11] Experimental characterization of precursor diffusion is important because it can be used to evaluate and expand models of film growth, which are important to optimize and improve material quality. Moreover, because silicon plasma deposition involves only two elements (Si and H), it is an important model system to help advance understanding of low-temperature activated film growth processes in general.

Critical parameters from the surface roughness evolution include the static and dynamic scaling coefficients, α and β, and the lateral correlation length, L_c, and measurement of these parameters allow surface transport mechanisms, including viscous flow, evaporation/condensation, bulk diffusion, and surface diffusion, to be differentiated and identified. For self-similar surface structure, the lateral correlation length is related to the distance over which a connection in surface roughness extends, and L_c is related to the precursor diffusion length. Therefore, under correct conditions, the effect of deposition temperature on L_c gives insight into precursor transport kinetics.[3,6,8,11]

In this letter, the lateral correlation length is determined as a function of hydrogen dilution for amorphous silicon films deposited by plasma enhanced chemical vapor deposition (PECVD) from mixtures of silane, helium, and hydrogen using temperature between 25 °C and 350 °C in two different reactor systems.[12,13] Surface topography of the deposited films was characterized by atomic force microscopy, and frequency and dimensional analyses were used to extract correlation length from the topography data.

Results of dimensional analysis is shown in Fig. 1, where the root-mean-square (rms) roughness is plotted versus length scale for 1000 Å thick amorphous silicon films deposited with $SiH_4/He/H_2$ ratios of approximately: (a) 1/50/0, (b) 1/100/0, (c) 1/50/50, and (d) 1/150/50. For each sample, the roughness increases with measurement length, then saturates at a value σ_{sat}. The lateral correlation length, L_c, is the distance at which the surface roughness first reaches its saturation value, and is ~50 nm for samples

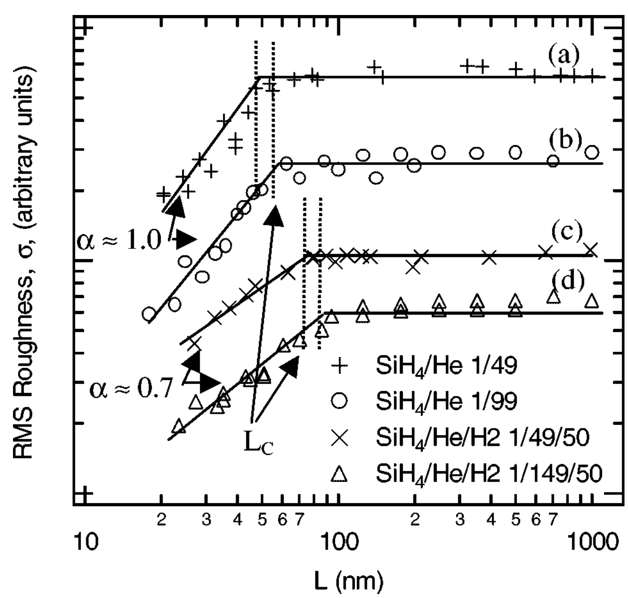

FIG. 1. Fractal analysis of 1000 Å *a*-Si:H films deposited with varying helium and hydrogen dilutions. (a) SiH_4/He 1/49, (b) SiH_4/He 1/99, (c) $SiH_4/He/H_2$ 1/49/50, (d) $SiH_4/He/H_2$ 1/149/50. The correlation length, L_c, where the rms roughness saturates with length, increases with hydrogen dilution. The curves are offset of clarity. Lines are guides for the eye.

[a)]Electronic mail: gregory_parsons@eos.ncsu.edu

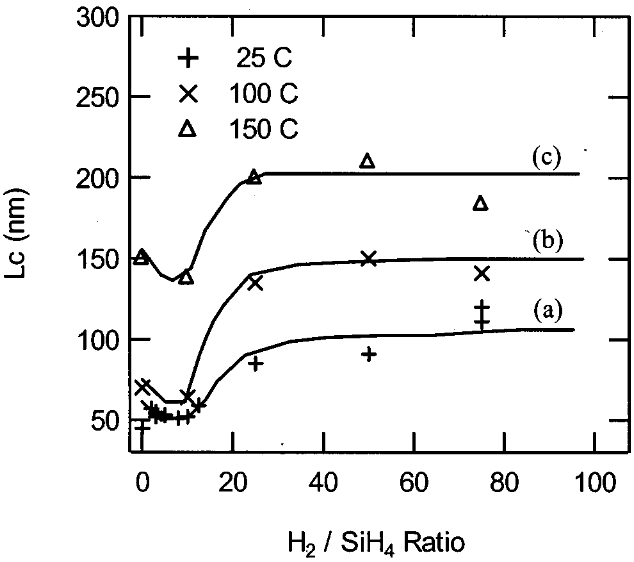

FIG. 2. The correlation length, L_c vs the H_2/SiH_4 ratio. L_c remains constant with low H_2 dilutions, then increases with high hydrogen dilutions for films deposited at (a) 25 °C, (b) 100 °C, and (c) 150 °C. The lines are guides for the eye.

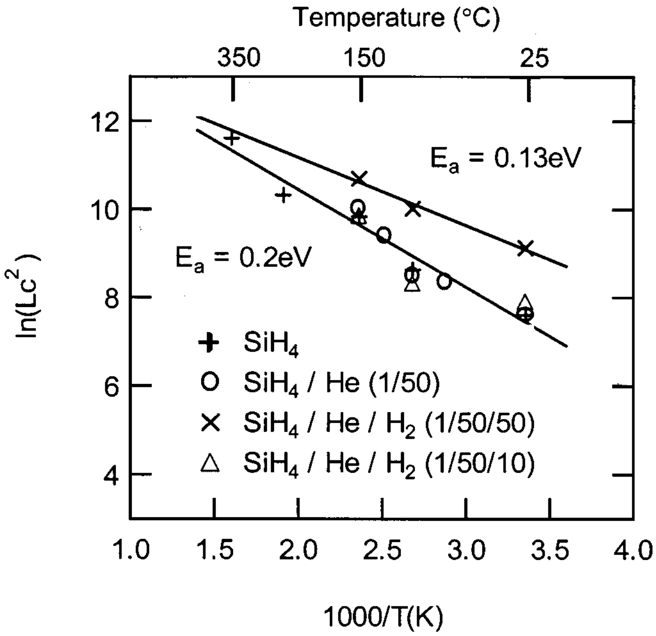

FIG. 3. Arrhenius plots of $\ln(L_c{}^2)$ vs $1/T$ for *a*-Si:H films deposited from SiH_4 (from reactor two), SiH_4/He, and SiH_4/He/H_2 mixtures (from reactor one).

deposited without hydrogen, and is larger (~80 nm) for samples deposited with hydrogen under these conditions. The scaling analysis result in $\alpha=1$ and $\beta=0.26$ for films deposited with only SiH_4 and He, and $\alpha=0.7$ and $\beta=0.22$ for films deposited with additional H_2 dilution. The difference in the scaling coefficients indicates a distinct difference in surface transport with hydrogen dilution, but the scaling parameters for all conditions studied are consistent with surface diffusion dominating surface transport.[14] It is important to note that not all conditions for silicon plasma deposition lead to surface transport dominated by diffusion. For example, parameters obtained from films deposited with argon dilution show nonself-similar scaling, so transport mechanisms cannot be simply evaluated.[11]

The lateral correlation length was measured for films deposited at several H_2/SiH_4 ratios at various temperatures, and the results are shown in Fig. 2. For all temperatures studied, as the H_2/SiH_4 ratio increases from 0–10, the correlation length is observed to decrease slightly. As the H_2/SiH_4 ratio increases further, there is a rapid increase in the correlation length, which then saturates at a constant value. It was speculated that the observed change in lateral correlation length with hydrogen dilution could be simply due to gas phase dilution and a decrease in precursor flux. To test this possibility, the effect of gas dilution on L_c was measured using helium/silane mixtures. The data in Fig. 1 shows that as He dilution increases from 50/1 to 100/1 [samples (a) and (b)], the correlation length increases slightly, consistent with a small dilution effect. However, sample (c) with a 50/50 He/H_2 ratio has the same relative silane concentration as sample (b), but a significant increase in L_c is observed. Similarly, when the helium flow is again increased from 50 to 150 sccm, only a small change in L_c is observed. These results indicate that the changes in correlation length are primarily due to hydrogen and not due to changes in relative precursor flux to the surface.

The correlation length was measured for a series of *a*-Si:H films deposited over a range of substrate temperature (25 °C–350 °C), and the diffusion activation barrier (E_a) was estimated from an Arrhenius plot of $L_c{}^2$ versus $1/T$. Figure 3 shows $L_c{}^2$ versus $1/T$ for a set of films deposited with pure SiH_4, a set deposited with SiH_4/He, and two sets deposited with SiH_4/He/H_2 mixtures. The data shows the same surface diffusion activation barrier (0.20 eV) for films grown with pure SiH_4 and SiH_4/He mixtures. These two sets of films were deposited in different reactor systems, and the similarity in the two data sets indicates the robustness of the analysis. When H_2 is added to the SiH_4/He mixture, an interesting trend in E_a is observed. For small amounts of H_2, ($H_2/SiH_4\sim10$) E_a remains at 0.20 eV, but for larger amounts of H_2 a marked decrease in E_a to 0.13 eV is observed.

We can understand the trends in correlation length, adsorbed precursor diffusion length, and diffusion activation energy as follows. The diffusion distance is generally a function of the species residence time on the surface, the distance per "hopping" step, and the energetic barrier to hopping. When relatively small amounts of hydrogen are used, the precursor diffusion length is observed to decrease, and the activation energy is not significantly affected. This reduction in the diffusion length is attributed to the reduced residence time of the growth precursors on the surface due to additional flux of incident H radicals that increases the direct abstraction of adsorbed silyl precursors from the surface. Under larger flux conditions, however, the diffusion length is observed to increase, and the barrier for diffusion is observed to decrease. The decrease in E_a and increase in L_c are ascribed to a change in dominant surface hydride bonding. Hydrogen exposure will remove higher surface hydrides by abstraction, and promote more monohydride surface bonding. It has been proposed that the monohydride surface presents a smaller barrier for precursor diffusion as compared to di- and trihydride bonded regions.[15] This surface hydrogen dependent transport model is fully consistent with widely known experimental results describing the growth rate,[16,17] bonded hydrogen distribution,[18,19] surface reaction probabilities,[16] and with predicted trends in diffusion activation barriers based on a detailed kinetic analysis of dominant reaction processes that occur during deposition.[15]

We believe that results presented here have important implications for understanding silicon deposition, as well as crystallization during PECVD. While it is possible that the observed reduction in precursor diffusion barrier upon hydrogen dilution results from a transition from amorphous to microcrystalline structure, it is important to note that the explanation presented herein does not specifically rely on surface crystallization. In this picture therefore, the increase in precursor diffusion length upon hydrogen dilution could occur before significant crystallization of the growth surface. This means that the increased surface diffusion length could be a condition that promotes crystallization, rather than a resulting product of the crystallized surface structure.

This work was supported under NSF Grants CTS-9624612 and 0072784.

[1] A. Matsuda, J. Non-Cryst. Solids **59**, 767 (1983).
[2] J. Perrin, M. Shiratani, P. Kae-Nune, H. Videlot, J. Jolly, and J. Guillon, J. Vac. Sci. Technol. A **16**, 278 (1998).
[3] J. Robertson, J. Appl. Phys. **87**, 2608 (2000).
[4] A. Matsuda, Plasma Phys. Controlled Fusion **39**, 431 (1997).
[5] G. Ganguly and A. Matsuda, J. Non-Cryst. Solids **164**, 31 (1993).
[6] D. M. Tanenbaum, A. L. Laracuente, and A. Gallagher, Phys. Rev. B **56**, 4243 (1997).
[7] M. Kondo, T. Ohe, K. Saito, T. Nishimiya, and A. Matsuda, J. Non-Cryst. Solids **227**, 890 (1998).
[8] W. M. Tong, E. J. Snyder, and R. S. Williams, Surf. Sci. **277**, L63 (1992).
[9] L. Bardotti, C. R. Stoldt, C. J. Jenks, M. C. Bartlet, J. W. Evans, and P. A. Thiel, Phys. Rev. B **57**, 12544 (1998).
[10] B. Reinker, M. Moske, and K. Samwer, Phys. Rev. B **56**, 9887 (1997).
[11] K. R. Bray and G. N. Parsons, Phys. Rev. B **65**, 035311 (2002).
[12] E. Srinivasan, D. A. Lloyd, and G. N. Parsons, J. Vac. Sci. Technol. A **15**, 77 (1997).
[13] C. S. Yang, W. W. Read, C. Arthur, E. Srinivasan, and G. N. Parsons, IEEE Electron Device Lett. **19**, 180 (1998).
[14] A. L. Barabasi and H. E. Stanley, *Fractal Concepts in Surface Growth* (Cambridge University Press, Cambridge, UK, 1995).
[15] A. Gupta and G. N. Parsons (unpublished).
[16] A. Matsuda and T. Goto, Mater. Res. Soc. Symp. Proc. **164**, 3 (1990).
[17] M. C. M. van de Sanden, W. M. M. Kessels, R. J. Severens, and D. C. Schram, Plasma Phys. Controlled Fusion **41**, A365 (1999).
[18] W. M. M. Kessels, A. H. M. Smets, D. C. Marra, E. S. Aydil, D. C. Schram, and M. C. M. van de Sanden, Thin Solid Films **383**, 154 (2001).
[19] D. C. Marra, E. A. Edelberg, R. L. Naone, and E. S. Aydil, Appl. Surf. Sci. **133**, 148 (1998).