Invited

A New Horizon of Plasma Enhanced CVD for Future Electron Devices

M. Hirose, H. Shin and S. Miyazaki

Department of Electrical Engineering, Hiroshima University

Higashi-Hiroshima 724, Japan

This paper reviews recent progress in the research of plasma enhanced CVD from silanebased gas mixtures. Atomic scale characterizations of the deposited silicon/silicon nitride multilayer structures have indicated that the spatially homogeneous, layer-by-layer growth proceeds on the surface. It is also shown that the surface reaction is very sensitive to the impinging ion flux and its energy as well as the substrate temperature. By controlling these parameters, a new deposition chemistry for novel material synthesis has been demonstrated.

1. INTRODUCTION

Plasma enhanced chemical vapor deposition (CVD) is composed of sequential steps of the electron impact dissociation of material gases, transport of the reaction products onto the surface, their surface condensation, network propagation reaction and the desorption of surface products. Recent extensive studies on the gas phase chemistry of a silane plasma have shown that the major stable precursor is most likely to be SiH₃ as directly measured by infrared diode laser absorption spectroscopy 1). The other idea for the reaction pathway is the deposition via higher silanes formed by a fast insertion reaction of silylene (SiH₂) into gaseous silane²). The surface processes during thin film growth from a silane plasma have been investigated by in situ ellipsometry³) and infrared reflection absorption spectroscopy⁴). These results have shown that SiH₃ and/or SiH₂ molecular units are predominantly incorporated in the surface layer. Such an ultra-thin, hydrogen-rich layer is a kind of growth zone where the Si network formation reaction is in progress⁵).

2. DEPOSITION KINETICS — LAYER-BY-LAYER GROWTH

The ellipsometric study of hydrogenated amorphous silicon (a-Si:H) deposited from a silane plasma has revealed the existence of a rather low density surface layer or the possibility of island growth⁶). A question to be answered is whether the island growth or spatially-homogeneous, atomic layer growth is more predominant mode in the plasma deposition. To answer this question, well defined multilayer structures consisting of a-Si:H (10~200Å) and silicon nitride a-Si₃N₄:H (25~200Å) have been deposited from silanebased plasmas⁷). If the island growth is a predominant mechanism, the multilayer will not show clear x-ray diffraction peaks which reflect the periodic superlattice structure. As shown in Fig. 1, the layer spacing determined from the Bragg diffraction angles is in excellent agreement with the layer thickness estimated from the deposition rate of the individual layer. Also, the x-ray interference effect which is clearly observed in the figure is well fitted to the intensity calculated by a dynamical theory in which it is assumed that each of the layers is atomically flat and the interface is atomically abrupt⁷). The further confirmation of the ideal multilayer structure formation or layer-by-layer growth has been obtained by fabricating resonant tunneling diodes with an a-Si:H quantum well (13~40Å) sandwiched by a-Si₃N₄:H (46Å) barriers. The resonant tunneling current bumps are observed at voltages theoretically predicted (Fig. 2)⁸). These results indicate that the a-Si:H/ a-Si₃N₄:H multilayer structure is composed of atomicallyflat, ultra-thin layers parallel to each other. This feature is basically independent of the nature of substrates.



Fig. 1 X-ray diffraction intensity vs diffraction angle for the multilayer with a designed a-Si:H well width of 20Å and an a-Si₃N₄:H barrier thickness of 50Å.



Fig. 2 Resonance voltage vs well layer thickness for a-Si:H/a-Si₃N₄:H double barriers. The solid lines are calculated curves corresponding to the first to fifth quantized states, and open circles are experimental data.

3. ION BOMBARDMENT EFFECT

A conventional plasma enhanced CVD technique employs a diode type reactor with a grounded substrate electrode and a substrate temperature higher than 300K. Therefore, the deposition surface suffers ion bombardment induced by the plasma potential. In order to simulate the interaction of a silane plasma with the growing film surface, a neutral or partially-ionized hydrogen or deuterium beam has been irradiated onto a silicon thin film deposited by the silane radical beam on a cooled (-40°C) substrate where the thermal reactions among adsorbed species are less pronounced. It is shown that the irradiation of partially ionized hydrogen beam causes the evolution of H2 and SiH4 from the surface held at the ground potential, and application of a negative substrate bias dramatically enhances the desorption of Si₂H₆ in addition to H₂ and SiH₄ (see Fig. $3)^{9}$. A chemically inert Ar⁺ beam with energies higher than the plasma potential causes physical sputtering and the desorption of H_2 , SiH₄ and Si₂H₆⁷). These results suggest that the ion flux impinging on the deposition surface remarkably changes the growth kinetics. Also, the lowering of the substrate temperature in a silane plasma has revealed the formation of polysilane at temperatures below -86°C, above which hydrogen rich a-Si:H is deposited¹⁰).

4. A NEW GROWTH MODE

Based on the results in 3, we have investigated CVD processes from a silane plasma by lowering the substrate temperature and by suppressing the ion flux intensity on the surface. Figure 4 compares the deposition profiles of a polysilane film grown at -110°C on a patterned SiO₂ on a Si wafer with and without ion flux control. In the case of Fig. 4 (a), the ion flux intensity and the energy are not controlled



Fig. 3 $Si_2H_x^+$ signal intensities as a function of substrate bias under irradiation of partially ionized hydrogen beam produced by a microwave discharge.

in a diode reactor where no film deposition occurs in the narrow trenches. In contrast to this in Fig. 4 (b) the substrate is biased at +30V in a triode reactor with a grounded metal mesh in order to suppress the ion flux. Hence, very high surface migration capability of deposition precursors is achieved and the selective growth of a polysilane film proceeds from the trench bottoms as if a liquid material moves into the trench to minimize the surface free energy. Note that in the triode reactor the discharge is generated between the powered electrode and the metal mesh. Suppression of the ion flux eliminates the ioninduced reactions which promote the solid network formation accompanied with the desorption of H2, SiH4 and Si₂H₆. A possible thin-film precursor for the case of Fig. 4 (b) is inferred to be higher silanes such as Si_2H_6 as confirmed by the mass spectrometry of surface products emitted from the cooled substrate after interrupting the deposition and evacuating the reactor 10,11). The other implication of the formation of polymeric species on the surface is the substrate bias dependence of growth rate as shown in Fig. 5. The growth rate is significantly reduced by the negative substrate bias although the hydrogen content and its bonding features of the deposited film remain almost unchanged¹¹). This indicates that the ion induced ablation occurs on the surface growth zone while no ion-induced modification takes place in the underlying bulk silicon layer. The condensation rate of the precursor is thought to be highest at the corner edge of the trench bottom¹²). Once the condensation starts from the corner edge, the surface diffusion of the precursor is enhanced because of a high precursor concentration gradient.



Fig. 4 Cross-sectional SEM photographs of silicon deposition profiles with (b) and without (a) ion flux control.



Fig. 5 Growth rate and bonded-hydrogen content as a function of substrate bias.

5. HIGH FLUIDITY CVD AT CRYOGENIC TEMPERATURE

The high-fluidity deposition of SiO₂ has first been done at temperatures of less than -20°C by mixing tetramethylsilane $Si(CH_3)_4$ with microwave excited oxygen¹²). Based on the high-fluidity deposition scheme of polysilane described in the previous section 4, we have attempted to grow SiO₂ from an SiH₄+O₂ gas mixture¹³). As illustrated in Fig. 6 a patterned surface is selectively refilled and finally planarized as in the case of silicon deposition from a silane plasma. The surface reaction products are inferred to be silanols and siloxanes which could be produced through polymerization reactions among silane radicals and activated oxygen on the cooled substrate. The surface migration of such deposition precursors could be enhanced by energy transfer from neutral gas molecules whose temperature is $\sim 500 \text{K}^{14}$). It should be noted that the formation of gas-phase precursors is less important because of a low silane partial pressure of ~5mTorr.

The structure of the deposited film has been evaluated by the infrared absorption spectra (Fig. 7). A significant amount of bonded hydrogen are incorporated in an as-grown film and most of them are effused from the film by 400°C annealing for 60min in an oxygen atmosphere. Also, in situ oxygen-plasma annealing by interrupting the film deposition is effective to reduce bonded hydrogen¹⁵). Even after the 400°C annealing the deposition profile remains unchanged and exhibits no crack. The refractive index of the oxide after the 400°C annealing is 1.42 and the breakdown field strength is higher than $5x10^6$ V/cm. Further improvement of the electrical properties will make it possible to utilize the low temperature oxide as an interlayer dielectric for the multilevel metallization.



Fig. 6 Cross-sectional SEM photographs of the deposition profiles of silicon oxide. $0.2 \,\mu\text{m}$



Fig. 7 Infrared absorption spectra of as-deposited and annealed oxides. The symbols (S), (B), (R) refer to the vibrational modes of stretching, bending, and rocking, respectively.

6. FUTURE PROSPECTS

The incident ion flux and its energy as well as the ratio of ion to neutral species must be controlled in the plasma enhanced CVD. Also, the substrate temperature should be scanned over the wide range below 300K where a new surface chemistry appears to be hidden as already discussed in 4 and 5. Proper selection of a material gas (for example, Si₂H₆ instead of SiH₄) is another key to control the surface reactions. Such view points will offer us more opportunities to synthesize novel organic or inorganic materials for electron devices. As described in 2, atomic layer controlled CVD is the other important issue. Thin film transistors with an a-Si:H/a-Si $_{1-x}N_x$:H multilayer structures have shown a significantly high electron mobility ¹⁶). Also, a boron doped a-Si:H/a-Si_{1-x}N_x:H multilayer has been employed as a ptype window layer in amorphous silicon solar cells to improve the collection efficiency in the short wavelength region¹⁷⁾. More recently a-C:H/a-Si:H or a-Si_{1-x}O_x:H/a-Si:H multilayers are successfully developed for high efficiency solar cells. In addition to this, high-efficiency electroluminescent devices consisting of a-C:H/a-SiC:H multilayers have been fabricated¹⁸). The idea of layer-bylayer growth of SiO₂ has also been proposed and demonstrated by using two remote plasma sources which alternately supply SiH_x radicals and excited oxygen 19 . Since the bonded hydrogen in polysilane is evolved by electron beam irradiation, the three dimensional Si network is formed in polysilane. The unirradiated region is easily oxidized in air, while the irradiated part is chemically stable. This enables us to fabricate the fine silicon pattern with a width of about 0.1 μ m embedded in an SiO₂ matrix²⁰). Wide varieties of approaches described above will open up a new area of research on plasma enhanced CVD for future electron devices.

ACKNOWLEDGMENTS

The author is grateful to K. Okamoto, H. Ichihashi, Y. Kiriki and Y. Inoue for their contributions to current research work and to Prof. Y. Horiike for stimulating discussion. Part of this work was supported by a Grant-in-Aid for Scientific Research on Reactive Plasma in Priority Areas of Ministry of Education, Science and Culture. Also, part of this work has been carried out in Research Center for Integrated Systems, Hiroshima University.

REFERENCES

- N. Itabashi, N. Nishiwaki, M. Magane, S. Naito, T. Goto, A. Matsuda, C. Yamada and E. Hirota, Jpn. J. Appl. Phys. <u>29</u> (1990) L505.
- M. Heintze and S. Veprek, Appl. Phys. Lett. <u>54</u> (1989) 1320.
- N. Blayo and B. Drevillon, J. Non-Cryst. Solids <u>137&138</u> (1991) 771.
- Y. Toyoshima, K. Arai, A. Matsuda and K. Tanaka, Appl. Phys. Lett. <u>56</u> (1990) 1540.
- A. Matsuda, Proc. of the Intern. Seminar on Reactive Plasmas (Nagoya, 1991) p. 405.
- R. W. Collins and J. M. Cavase, J. Non-Cryst. Solids 97&98 (1987) 269.
- M. Hirose and S. Miyazaki, Pure and Appl. Chem. <u>62</u> (1990) 1661.
- S. Miyazaki, Y. Ihara and M. Hirose, Phys. Rev. Lett. <u>59</u>(1987) 125.
- S. Miyazaki, Y. Kiriki, Y. Inoue and M. Hirose, Jpn. J. Appl. Phys. <u>30</u> (1991) 1539.
- H. Shin, S. Miyazaki and M. Hirose, J. Non-Cryst. Solids <u>137&138</u> (1991) 713.
- H. Shin, K. Okamoto, S. Miyazaki and M. Hirose, Jpn. J. Appl. Phys. <u>31</u> (1992) 1953.
- S. Noguchi, H. Okano and Y. Horiike, Extended Abstracts of the 19th Conf. on Solid State Devices and Materials (Tokyo, 1987) p. 451.
- H. Shin, S. Miyazaki and M. Hirose, Appl. Phys. Lett. <u>60</u> (1992) 2616.
- H. V. Boenig, Fundamentals of Plasma Chemistry and Technology (Technomic, Lancaster, 1988) p. 15.
- 15) H. Shin, S. Miyazaki and M. Hirose, unpublished.
- M. Tsukude, S. Akamatsu, S. Miyazaki and M. Hirose, Jpn. J. Appl. Phys. <u>26</u> (1987) L111.
- S. Miyazaki, N. Murayama and M. Hirose, Extended Abstracts of the 17th Conf. on Solid State Devices and Materials (Tokyo, 1985) p. 107.
- M. Yoshimi, H. Shimizu, K. Hattori, H. Okamoto and Y. Hamakawa, Optoelectronics 7 (1992) 69.
- M. Nakano, H. Sakaue, H. Kawamoto, A. Nagata, M. Hiroseand Y. Horiike, Appl. Phys. Lett. <u>57</u> (1990)1096.
- 20) K.Okamoto, H. Shin, K. Shiba, S. Miyazaki and M. Hirose, Digest of Papers of 5th Intern. MicroProcess Conference (Kawasaki, 1992) to be published.