Quantum chemical studies on initial surface process in *a*-Si:H plasma CVD

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Abstract. The surface morphology of *a*-Si:H is strongly dependent on substrate material and temperature, especially in the initial stage of deposition. Furthermore, some surface treatments could induce a drastic change in the initial growth mode. For example, the hydrogen plasma treatment of highly oriented pyrolytic graphite (HOPG) surface prior to *a*-Si:H deposition changed the growth mode from inhomogeneous to homogeneous one. In order to elucidate this surface chemical process, molecular orbital calculations were performed and compared with the experimental observation of the surface by AFM and STM. The calculation verified hydrogen addition to sp^2 carbons on HOPG to facilitate the bonding of SiH₃ to neighbouring carbons, which correspond to the nucleation or pinning of precursors as the origin of homogeneous growth of *a*-Si:H film.

Keywords. Quantum chemical studies; *a*-Si:H; initial surface process.

1. Introduction

In order to improve the performance of *a*-Si:H solar cell, it is important to improve the *a*-Si:H film quality which should be definitely influenced by the film deposition mode. The deposition of *a*-Si:H has been extensively studied by *in situ* infrared reflection absorption spectroscopy (IRRAS) (Toyoshima *et al* 1990), high resolution electron energy loss spectroscopy (HREELS) (Sasaki *et al* 1989), polarized light reflection (Takano *et al* 1993a, b), spectroscopic ellipsometry (Drevillon 1989) and Raman scattering (Tanino *et al* 1992) to draw microscopic mechanism on the surface reaction. From these studies, the surface migration of adsorbed precursors (mainly SiH₃ radical) was presumed to play a key role for controlling the film quality (Ganguly and Matsuda 1993). However, there had been no direct evidence for the enhanced surface migration of adsorbed precursors in real space by the substrate temperature increase until our recent AFM study on the initial growth mode of *a*-Si:H on various substrates (Matsuse *et al* 1994, 1996). We have investigated the initial growth mode and surface morphology of *a*-Si:H on Corning #7059 glass, Si wafer, SnO₂ coated glass, and HOPG. For example, when *a*-Si:H was plasma deposited on bare HOPG(0001) surface, islands were formed both at step edges and terraces at low temperatures ($\leq 110^\circ\text{C}$), but exclusively along high-step lines at high temperatures. The hydrogen plasma treatment of HOPG prior to *a*-Si:H deposition drastically changed the growth mode to homogeneous from inhomogeneous one. This change was observed to accompany a difference in the surface morphology of subsequently grown films till the film thickness reached 100 nm, which exceeds the thickness of doped layers in *a*-Si:H solar cell. Hence, this

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hydrogen plasma treatment could influence photoelectrical properties of a -Si:H and attracted our interest for chemical analysis.

The above phenomenon was presumed to come from the enhanced nucleation or pinning of a -Si:H forming species on the hydrogen-treated surface. In order to verify this speculation of hydrogen addition to HOPG surface to facilitate the nucleation of a -Si:H, we have performed both experimental and theoretical studies by STM and molecular orbital calculations, respectively.

2. Experimental

A capacitively-coupled rf (13.56 MHz) plasma was used to deposit a -Si:H films from pure SiH_4 gas. The growth conditions employed were rf power density: 40 mW/cm^2 , SiH_4 gas flow rate: 3 sccm, reaction pressure: 100 mTorr, and substrate surface temperature: $100\text{--}250^\circ\text{C}$. Corning #7059 glass, polished SnO_2 -coated glass, and HOPG were used as substrates. Prior to the film deposition, HOPG substrate was cleaved under high vacuum and the other substrates were treated with argon plasma to prepare fresh surface. Bare HOPG substrate surface was exposed to hydrogen radicals in the chamber generated with H_2 rf glow discharge plasma. AFM observation (Seiko SPA300) was performed in air for thin (4 nm thick) a -Si:H films deposited on the above substrates. The hydrogen plasma-treated HOPG substrate was characterized by UHV-STM (Omicron, UHV-STM Compact-Lab). STM images were taken at a constant tunneling current of 0.2 nA.

3. Method

As a HOPG surface model for total energy calculation, we used coronene ($\text{C}_{24}\text{H}_{12}$). Geometry optimization with an energy gradient method (McIver and Komornicki 1972; Pulay 1977) was performed by using the restricted open shell Hartree-Fock theory (ROHF) (Roothan 1951) with a 3-21G basis set. The total energies at the optimized structures were calculated for the reactants and products by using the second-order Møller-Plesset perturbation theory (Møller and Plesset 1934) in which electron correlations were taken into account with the same basis set as the geometry optimization (ROMP2/3-21G//ROHF/3-21G). $\text{C}_{150}\text{H}_{30}$ was also used as HOPG surface model for evaluating the change in electronic structure by the reaction with hydrogen. The calculations were performed by using AM1 semi-empirical molecular orbital method. The Gaussian 94 program (Frisch *et al* 1995) was used for all the calculations conducted on a Cray C916/12256 at the Computer Centre, Tokyo Institute of Technology.

4. Results and discussion

The AFM images of a -Si:H films deposited on various substrates at a low temperature (100° or 110°C) and a high temperature (230°C) are shown in figure 1. On Corning #7059 glass, the film surface was not sensitive to the deposition temperature between 30° and 230°C and as smooth as the substrate surface. SnO_2

substrate gave an apparent homogeneous flat surface of the film grown at 100°C, but heterogeneous islands in ~ 50 nm diameter and 5 nm roughness at 230°C. A similar shift in the growth mode from less to more heterogeneous was observed

Figure 1. a, a'.

Figure 1. b, b'.

Figure 1. The AFM images of $a\text{-Si:H}$ on Corning #7059 glass substrate at 100°C (a) and 230°C (a') ($400 \times 400 \text{ nm}^2$), on SnO_2 coated glass at 100°C (b) and at 230°C (b') ($400 \times 400 \text{ nm}^2$), and on HOPG at 110°C (c) and 230°C (c') ($2 \times 2 \mu\text{m}^2$).

Figure 2. The AFM images of α -Si:H deposited on H_2 plasma-treated HOPG substrate. (a) Scan area: $2 \times 2 \mu\text{m}^2$ and (b) scan area: $400 \times 400 \text{ nm}^2$. The deposition temperature was 110°C .

Figure 3. The STM images of HOPG ($5\text{ nm} \times 5\text{ nm}$). (a) bare HOPG surface and (b) HOPG surface treated with H_2 plasma for 0.5 sec.

Figure 4. The stable structure of hydrogen added coronene (*ab initio* method ROHF/3-21G).

for the deposition on HOPG substrate with increasing temperature. In order to interpret this result, we proposed a nucleation and growth mechanism (Matsuse *et al* 1996). Due to the presence of sharp step lines, which should work as nucleation centres, *a*-Si:H deposits (≥ 1 nm high) arrayed along the steps at 230°C, as in the step flow growth in epitaxial films. Presumably, surface migration is enhanced in the high temperature deposition on SnO₂ and HOPG by weak interactions of film precursors (mainly SiH₃) with ionically bonded SnO₂ and delocalized π electron clouds on HOPG to facilitate the heterogeneous growth.

Figure 2 shows the AFM image of *a*-Si:H deposited at 110°C on HOPG treated with H₂ plasma. By comparing with figure 1c, we can see smoother and more homogeneous coverage of HOPG by *a*-Si:H overlayer. Thus, the initial growth mode is extremely sensitive to the chemical state of substrate surface. STM analysis exhibited electronically distinguishable spots in about 20 Å diameter on the plasma-treated terraces in the increasing density with the exposure time (figure 3). This spot indicates either the covalent bond formation between H radical and a conjugated *sp*² carbon on the HOPG surface or a defect (pit) formation by the surface etching with H radical.

The six-membered ring at the centre of coronene (C₂₄H₁₂) is topologically similar to the ring in graphite surface. The length of carbon-carbon bond in the six-membered ring at the centre of coronene was 1.42 Å by the calculation of *ab initio* HF/3-21G, being the same as the carbon-carbon bond length of graphite (experimental value is 1.42 Å). A stable energy minimum was found for the C-H bond formation between H and a *sp*² carbon in coronene (figure 4). The ΔH value for the hydrogen addition reaction

was -0.26 eV. The hydrogen addition induced a deformation of coronene molecular surface to minimize the total energy of the hydrogen added product. Thus, the hydrogen addition to HOPG is presumed to be energetically preferable and deform the flat HOPG surface.

Then, we investigated the perturbation of electronic structure at carbons in the vicinity of hydrogen added carbon. The semiempirical AM1 calculation on C₁₅₀H₃₀ as a model of HOPG indicates that the perturbation extends as far as 20 Å by the hydrogen addition. This range corresponds well with the spot size observed by UHV-STM measurement. Subsequent to the hydrogen addition, the following reaction are expected to take place, since the hydrogen addition should generate a dangling bond at an adjacent carbon.

These reactions are feasible in view of negative ΔH values, -1.78 eV and -1.44 eV, respectively. The latter reaction can be regarded as nucleation or pinning of precursor to induce homogeneous growth of *a*-Si:H film.

5. Conclusion

The initial growth mode on HOPG and the surface morphology of a -Si:H were elucidated by the STM observation of change in the surface electronic state as well as by the theoretical molecular orbital calculations. Hydrogen radicals bond to graphitic carbon to form free radicals on the adjacent carbons, to which SiH_3 radicals are spontaneously bonded. This $\text{H}_3\text{Si-C}$ bond formation can be a nucleation of homogeneous growth of a -Si:H film. Chemical state of substrate surface can play a significant role for controlling the initial growth mode of a -Si:H.

References

- Drevillon B 1989 *J. Non-Cryst. Solids* **114** 139
Fritsch M J *et al* 1995 (Pittsburgh, PA: Gaussian, Inc.)
Ganguly G and Matsuda A 1993 *Phys. Rev.* **B47** 3661
Matsuse M, Kawasaki M and Koinuma H 1994 *IEEE First world conf. on photovoltaic energy conversion, Hawaii* p. 425
Matsuse M, Tshuboi S, Kawasaki M and Koinuma H 1996 *Phys. Rev.* **B53** 12585
McIver Jr J W and Komornicki A 1972 *J. Am. Chem. Soc.* **94** 2625
Møller C and Plesset M S 1934 *Phys. Rev.* **46** 618
Pulay P 1977 in *Modern theoretical chemistry: Applications of electronic structure theory* (ed.) H F Schaefer III (New York: Plenum) Vol. 4, Ch. 4
Roothan C C J 1951 *Rev. Mod. Phys.* **23** 69
Sasaki H, Deguchi M, Sato K and Aiga M 1989 *J. Non-Cryst. Solids* **114** 672
Takano A, Naito N, Kawasaki M and Koinuma H 1993a *J. Non-Cryst. Solids* **164-166** 115
Takano A, Kawasaki M and Koinuma H 1993b *J. Appl. Phys.* **73** 7987
Tanino H, Ganguly G and Matsuda A 1992 *Phys. Rev.* **B46** 15277
Toyoshima Y, Arai K, Matsuda A and Tanaka K 1990 *Appl. Phys. Lett.* **57** 1028