# Real-space investigation of initial growth process of hydrogenated amorphous silicon on a graphite substrate

Mitsutaka Matsuse, Seiji Tsuboi, Masashi Kawasaki, and Hideomi Koinuma
*Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku Yokohama 226, Japan*

Masaaki Eguchi and Hironobu Sakata
*Department of Industrial Chemistry, Tokai University, 1117 Kitakaname, Hiratsuka, Kanagawa 259-12, Japan*
(Received 11 April 1995; revised manuscript received 22 November 1995)

Initial growth of hydrogenated amorphous silicon ($a$-Si:H) from silane plasma on a cleaved surface of highly oriented pyrolytic graphite (HOPG) has been investigated by means of *in situ* x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). At a substrate temperature of 110 °C, island nuclei were formed on atomically flat terraces as well as along the steps of the HOPG surface. At an increased substrate temperature of 230 °C, the nucleation occurred only along the steps. Hydrogen plasma treatment of the HOPG surface prior to the $a$-Si:H deposition drastically changed the growth mode to a homogeneous coverage of the surface from the beginning of film deposition at both temperatures. In order to understand and analyze these results, we propose a mechanism, from analogy to epitaxial film growth, that consists of the adsorption, migration, and fixation (pinning) of precursors on the surface and of subsequent nucleation and growth of film. [S0163-1829(96)05919-X]

## I. INTRODUCTION

For the development of hydrogenated amorphous silicon ($a$-Si:H) devices such as solar cell and liquid crystal display, not only the structure of the bulk $a$-Si:H film itself but also the structure of heterointerfaces between $a$-Si:H and other components must be adjusted to yield optimum properties. For controlling the heterointerface, the initial growth of $a$-Si:H on various materials should be understood. *In situ* surface-sensitive analyses such as x-ray photoelectron spectroscopy (XPS),[1] infrared reflection absorption spectroscopy,[2] and spectroscopic ellipsometory[3] were employed for the investigation of interface formation processes. The results obtained by these optical methods, where the information was averaged out for the macroscopic area on the surface, yielded a model of the initial $a$-Si:H growth composed of homogeneous nucleation on the entire surface, subsequent coalescence, and resulting uniform film coverage.[4] The film growth mechanism is expected to be understood in more detail by using real-space observation methods as scanning probe microscopies. Few studies, however, were reported and they were focused on the surface morphology of thick films to show that the surface roughness increased with increasing film thickness (100–400 nm).[5] We recently reported that the initial growth mode of $a$-Si:H was strongly dependent on the substrate temperature[6] and material.[7] The growth on Corning 7059 glass was homogeneous as observed by *in situ* XPS and *ex situ* atomic force microscopy (AFM). Such a growth mode was constantly observed at substrate temperatures ranging from 30 to 230 °C. On the $SnO_2$ substrate, the growth mode changed from homogeneous to island growth with an increase of the deposition temperature from 30 to 230 °C.

For studying the initial growth stage of $a$-Si:H in detail, we chose highly oriented pyrolytic graphite (HOPG) as one of the substrates well defined in an atomic scale. The growth behavior analyzed by AFM and XPS is discussed from the viewpoints of thermal and chemical effects. We also show the change of initial growth mode of $a$-Si:H due to the surface treatment with hydrogen plasma.

## II. EXPERIMENT

A capacitively coupled rf plasma chemical vapor deposition (CVD) apparatus was directly connected to an XPS (JEOL JPS-80) system with a gate valve so that the surface could be analyzed *in situ* by transferring the sample with a magnetically coupled transfer rod. More detail of the sample preparation chamber was described elsewhere.[7] The graphite substrate (Panasonic graphite PGX04) was cleaved *in situ* prior to the film deposition in an ultrahigh vacuum ($3\times10^{-6}$ Pa). The growth conditions were an rf power density of 40 mW/cm$^2$, a $SiH_4$ gas flow rate of 3SCCM (SCCM denotes cubic centimeter per minute at STP), a reaction pressure of 13.3 Pa, and a deposition temperature varied between 30 and 230 °C. The value of self-bias was constant ($-50$ V) at $a$-Si:H deposition conditions used in our experiments. We did not use a plasma trigger (induction coil) because the initial growth mode turned out to be sensitive to the use of a plasma trigger as described later. $a$-Si:H film deposition was conducted for various durations (4–30 sec) to measure *in situ* XPS. After the XPS measurement, the sample was taken out of the chamber and subjected quickly to the observation by AFM (SEIKO-SPI-3700) in air. The AFM was operated in a noncontact mode. The thicknesses of ultrathin films were nominally evaluated as products of deposition periods and the rate that was determined from the deposition of thick films.

## III. RESULTS AND DISCUSSION

First we checked the deposition rate and the properties of thick (~1 $\mu$m) $a$-Si:H films deposited on Corning No. 7059

 © 1996 The American Physical Society

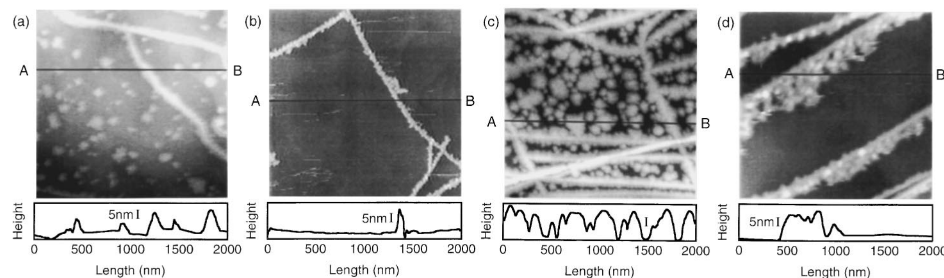


FIG. 1. The AFM images ($2\times2$ $\mu m^2$) of $a$-Si:H films (0.5 and 2 nm thick) deposited on HOPG substrate at temperatures of 110 °C [(a), (c)] and 230 °C [(b), (d)]. The deposition time is (a) 5.0, (b) 4.2, (c) 26.4, and (d) 15.8 sec, respectively.

glass and crystal silicon substrates. As reported previously,[6] the increase in deposition temperature from 30 to 230 °C decreased the hydrogen content from 18% to 9% and improved the photoconductivity ($2\times10^{-7}$–$1\times10^{-4}$ S/cm). The deposition rate at 110 and 230 °C were 0.073 and 0.13 nm/sec, respectively.

AFM images ($2\times2$ $\mu m^2$) of the cleaved HOPG surface showed atomically flat terraces and several steps. The step height ranged from 0.34 nm (one atomic layer of graphite) to 2 nm. On the terraces, atomic resolution was clearly observed by STM. Figures 1(a) and 1(b) show the AFM images ($2\times2$ $\mu m^2$) of deposits at temperatures of 110 and 230 °C. Nominally 0.5-nm-thick (more than one atomic layer) $a$-Si:H films should be formed under the conditions, but the surfaces are covered only partially by islandlike deposits of about 150 nm in diameter. The *in situ* XPS analysis indicated that the islands were composed of silicon, presumably $a$-Si:H. At substrate temperatures of 110 °C and lower, islands were formed on the atomically flat terraces as well as along the steps [Fig. 1(a)]. The density of islands on the atomically flat terraces was 30–40/$\mu m^2$, which corresponded to 150–200 nm average spacing between two adjacent nuclei. By increasing the substrate temperature, the island density on the terraces decreased and lined up along the steps. At 230 °C, $a$-Si:H is deposited only along the steps as shown in Fig. 1(b).

It must be noted that the area free from the deposits is composed not only of terraces, where the atomic image of graphite can be seen, but also of steps with their heights less than 1 nm (1–3 atomic layers height). Thus, at this high substrate temperature, silicon containing precursors adsorbed on the HOPG surface can migrate on the atomically flat terraces as well as across the steps with heights as high as 1 nm until they encounter such strong pinning sites as steps higher than 1 nm. Silicon containing radicals as precursors to $a$-Si:H are presumed not to interact so strongly with the $\pi$ electron of the graphite surface as to form a Si-C chemical bond.

The AFM image of nominally 2-nm-thick $a$-Si:H film deposition at 110 °C is depicted in Fig. 1(c). The density of islands in this film scarcely changed and the relative coverage increased in comparison with the nominal 0.5-nm-thick films shown in Fig. 1(a). Thus, the nucleation of islands seems to be saturated at the stage of the 0.5-nm film depicted in Fig. 1(a). In the subsequent deposition period, the growth of nuclei takes place. Figure 1(d) shows the AFM image of nominally 2-nm-thick $a$-Si:H film deposited at 230 °C. The deposition occurs only along the steps and the width of $a$-Si:H deposits is larger than that observed for the deposition of nominal 0.5-nm $a$-Si:H [cf. Fig. 1(b)].

The nominal thickness dependences of the coverage and island structure of $a$-Si:H are depicted in Fig. 2. The island height was evaluated by AFM to be increasing at 110 °C from 1 to 4 nm with the nominal thickness increase from 0.3 to 2 nm and to stay constant at 230 °C in this nominal thickness range at about 5 nm. It is presumed that $a$-Si:H grows around the homogeneously prefixed islands at 110 °C and along the islands aligned to high steps with keeping the height constant at 230 °C. Silicon containing precursors adsorbed on the bare HOPG surface migrate until they encounter $a$-Si:H islands, which are also strong pinning sites for precursors migrating on the surface. Since the coverage is low, the existing $a$-Si:H islands grow due to the radical flux migrating from the adjacent bare HOPG surface. The increase in the deposition temperature should increase the migration length to allow the adsorbed radicals to diffuse on the surface until they encounter strong pinning sites. All the steps, point defects on the terrace, and $a$-Si:H islands are pinning sites at 110 °C, whereas only high (>1 nm) HOPG steps and $a$-Si:H islands are pinning sites at 230 °C.

The following two explanations are plausible for the island formation at 110 °C on the atomically flat terraces. One is heterogeneous nucleation at crystal defects or adsorbed impurities on the HOPG surface. These nucleation sites should act as weak pinning sites; precursors are not pinned at these sites for the high temperature (230 °C) deposition. The other is homogeneous nucleation from supersaturation phase. Once a group of supersaturated molecules or radicals are condensed into a deposit (cluster) on the surface directly or indirectly from the gas phase, it cannot sublime to the gas phase and acts as a sink (pinning site) of migrating precursors.

The results described above appear to be quite different

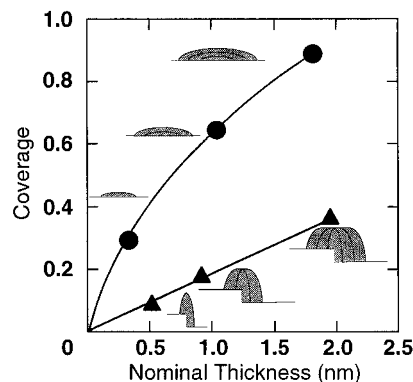


FIG. 2. The film thickness dependences of the coverage fraction at 110 (●) and 230 °C (▲). The growth images of $a$-Si:H is shown in the inset.

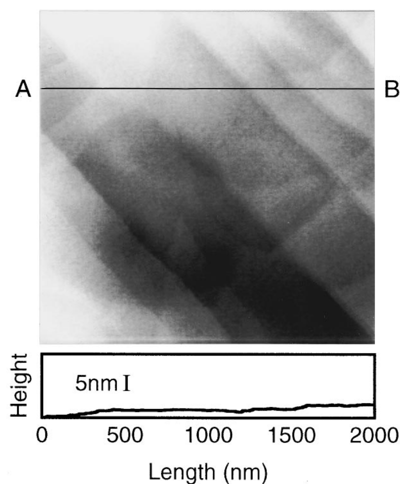


FIG. 3. The AFM image (2×2 $\mu m^2$) of $a$-Si:H (2 nm thick) film deposited on HOPG substrate treated with hydrogen plasma at temperature of 110 °C.

from the results reported recently by Ikuta *et al.*[8] They investigated $a$-Si:H deposition on HOPG by STM and observed essentially no change in growth mode depending on the temperature ranging from room temperature to 300 °C. Very small clusters (about 0.5 nm) were reported to be homogeneously nucleated on the entire HOPG surface in the initial stage regardless of the temperature. Subsequently, coalescence occurred between the nuclei (clusters) to increase the cluster size with the increase of film thickness, resulting in a coverage of close to unity. As described above, we observed a strong dependence of initial growth mode on the deposition temperature as well as very small coverage of the $a$-Si:H island. We conclude the difference between their results and ours should be attributed to whether or not a plasma trigger was used prior to the deposition to start the glow discharge.[8,9] We presume that a pulsed high voltage applied to trigger the glow discharge plasma could generate a lot of hydrogen radicals by decomposing pure $SiH_4$ to a large extent. The hydrogen radicals then generate pinning sites on a graphite substrate as in the same case of hydrogen plasma treatment discussed later. By using the plasma trigger in our system, the initial growth mode of $a$-Si:H on HOPG substrate was found to change drastically; the surface morphology turned out to be very smooth as compared with the case without using the trigger. HOPG surface modification by the trigger plasma is apparently responsible for this change. The change in the initial growth mode by the use of a plasma trigger was also confirmed by *in situ* XPS analysis. At the same nominal $a$-Si:H thickness, the $C_{1s}$ photoelectron intensity from the underlying HOPG was lower when the film was deposited on HOPG using the plasma trigger. This result indicates that the bare HOPG surface is covered less effectively due to inhomogeneous $a$-Si:H deposition without using the plasma trigger and that the HOPG surface is homogeneously covered with $a$-Si:H in the case of using the plasma trigger.

In order to elucidate the plasma treatment effect on the HOPG surface as well as on the growth mode of $a$-Si:H in more detail, we treated the as-cleaved HOPG surface with hydrogen plasma (66.7 Pa, 40 mW/$cm^2$) for 50 msec to 10 sec prior to $a$-Si:H film deposition under the same conditions

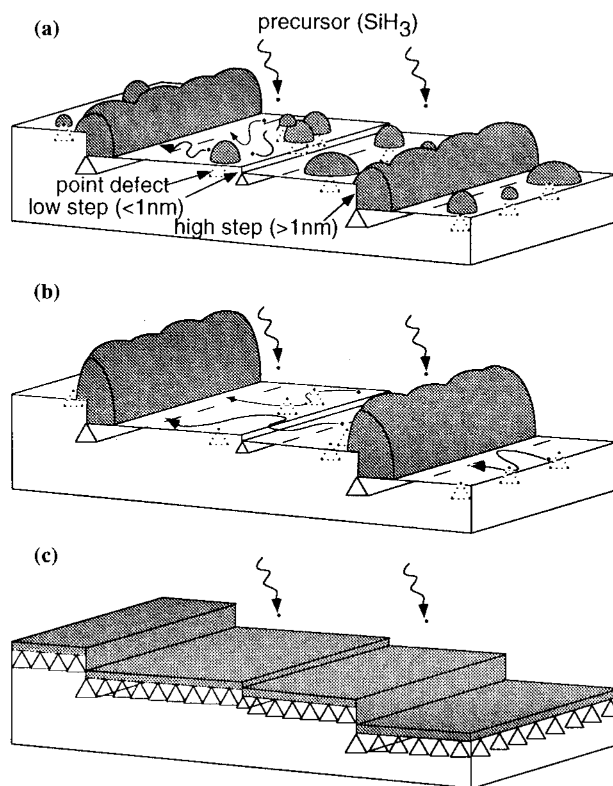


FIG. 4. Schematic illustration of the precursor hopping mechanism for the initial growth of $a$-Si:H on HOPG substrate. The film formation process consists of the adsorption, migration, and fixation (pinning) of precursors on the surface. The nucleation and growth of $a$-Si:H islands should take place at the pinning sites (see text) located at atomically flat terraces as well as along steps (>1 nm), where the pinning energy is larger than the thermal energy of the migrating precursors. At low deposition temperature (110 °C) $a$-Si:H islands were formed on the atomically flat terraces as well as along the steps (a). At high deposition temperature (230 °C) $a$-Si:H was deposited only along the steps (b). When the HOPG surface was treated by hydrogen plasma, the homogeneous coverage of $a$-Si:H took place (c).

as the case of Fig. 1(c). Figure 3 shows the AFM image of a nominal 2-nm-thick $a$-Si:H film deposited on HOPG treated with the hydrogen plasma for 10 sec. The surface was homogeneously covered with $a$-Si:H to conserve quite smooth step and terrace patterns of the HOPG surface. Similar results with uniform coverage of $a$-Si:H were also obtained in the deposition at 230 °C. The hydrogen plasma treatment for 1 sec gave the same results. The effect of plasma treatment remained in the surface of $a$-Si:H films deposited as thick as 50 nm.

Two possible explanations exist for the change of initial growth on the plasma treated HOPG substrate. One is hydrogen attachment of the HOPG surface and the other is the generation of surface defects with hydrogen plasma treatment. Hydrogen radical was indicated to form a C-H bond on the graphite surface.[10] If the C-H bond is once formed, the $SiH_3$ radical should easily react with the dangling bond on the adjacent carbon atom on the graphite terrace. Atomic hydrogen is also known to etch $sp^2$ carbon in CVD diamond film growth.[11] Even in this etching reaction, the hydrogen

attachment on the carbon atom discussed above should be considered as the first elementary reaction. Etch pits produced by the hydrogen plasma on HOPG could work as nucleation or pinning sites of *a*-Si:H, since the etching of a carbon atoms from the graphite substrate surface generates steps on the surface, which were shown to act as pinning sites. Thus, it is hard to specify if either of the above mechanisms is more plausible at present.

When we take the UHV STM image for the HOPG substrate treated by hydrogen plasma for 50 msec, we observed many bright spots (3 nm in diameter and $4\times10^2/\mu m^2$ in density) on an atomically flat surface.[12] The spot density was found to increase in proportion to the period of the hydrogen treatment. When the hydrogen plasma treatment was performed more than 1 sec, we speculate that the density of the pinning site became so large that the resulting *a*-Si:H film looked homogeneous in appearance. Further study is in progress to identify what gives these spots in STM image and to specify the origin of the drastic change in the *a*-Si:H growth mode on HOPG by the plasma surface treatment.

Based on these results, we propose the precursor hopping mechanism, which consists of the adsorption, migration, and fixation (pinning) of precursors on the surface and of subsequent nucleation and growth of film. The mechanism is schematically illustrated in Fig. 4. There are several pinning sites with different pinning energies on HOPG with atomically flat terraces. Steps higher than 1 nm high and preexistent *a*-Si:H islands, for example, have high pinning energy, whereas steps of 1 nm high or less and point defects, if they exist, on the terraces work as weak pinning sites. In Fig. 4, these pinning sites are marked by triangles with its size proportional to the pinning energy. At low deposition temperature, thermal energy of adsorbed precursors is not high enough to let the precursors escape from the weak pinning sites on the surface to give *a*-Si:H islands on atomically flat terraces as well. When the thermal energy of adsorbed precursors exceeds the pinning energy at the weak pinning sites, the precursors can migrate on the surface until they are fixed at strong pinning sites to give an inhomogeneous rough surface in appearance. The change of growth mode for the case of hydrogen plasma treatment and the use of plasma trigger can be interpreted if these procedure generate high density of strong pinning site on the surface.

## IV. CONCLUSION

Plasma CVD of *a*-Si:H films on clean HOPG started with both island growth on the terraces and one-dimensional growth at the steps at 110 °C due to the nucleations both at strong and at weak pinning sites. At an elevated deposition temperature of 230 °C, *a*-Si:H lined up only along steps, due to the nucleation only at strong pinning sites such as high steps. Hydrogen plasma treatment drastically changed the initial growth mode of *a*-Si:H to the uniform coverage of the surface with *a*-Si:H film. We showed that the initial growth process of the *a*-Si:H film deposition is determined by the pinning of precursors migrating on the substrate surface.

## ACKNOWLEDGMENTS

We thank Mitsui Toatsu Chemicals Inc. for supplying silane gas. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture and Iwatani Foundation.

[1] M. Kawasaki, Y. Matsuzaki, and H. Koinuma, Phys. Rev. B **39**, 13 316 (1989).
[2] Y. Toyoshima, K. Araki, A. Matsuda, and K. Tanaka, Appl. Phys. Lett. **57**, 1028 (1991).
[3] A. M. Antonie, B. Drevillon, and Rocal Cabarrocas, J. Appl. Phys. **61**, 2501 (1987).
[4] R. W. Collins and J. M. Cavese, J. Appl. Phys. **61**, 1869 (1987).
[5] G. C. Stutzin, R. M. Ostrom, Alan Gallagher, and D. M. Tanenbaum, J. Appl. Phys. **74**, 91 (1993).
[6] M. Kawasaki, M. Matsuse, M. Eguchi, M. Sumiya, H. Sakata, and H. Koinuma, in *Proceedings of the 2nd International Conference on Reactive Plasmas and 11th Symposium on Plasma Processing*, *Yokohama, Japan*, *1994*, edited by Toshio Goto (Japan Society of Applied Physics, Nagoya, 1994), p. 637.
[7] M. Matsuse, M. Kawasaki, and H. Koinuma, in *Proceedings of the First World Conference on Photovoltaic Energy Conversion*, *Waikoloa, Hawaii*, *1994*, edited by Dennis J. Flood (IEEE, New York, 1995), p. 425.
[8] K. Ikuta, K. Tanaka, S. Yamasaki, K. Miki, and A. Matsuda, Appl. Phys. Lett. **65**, 1760 (1994).
[9] K. Ikuta (private communication).
[10] D. Neumann, G. Meister, U. Kurpick, A. Goldmann, J. Roth, and V. Dose, Appl. Phys. A **55**, 489 (1992).
[11] Y. Saito, K. Sato, H. Tanaka, and H. Miyadera, J. Mater. Sci. **24**, 293 (1989).
[12] M. Matsuse, S. Tsuboi, T. Arakane, M. Kawasaki, and H. Koinuma, J. Non-Cryst. Solids (to be published).