Obstruction of Si Crystal Growth by Surface Hydrogen Desorption

Yasutake TOYOSHIMA†
Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central-2, Umezono 1-1-1, Tsukuba, Ibaraki 305-8568, Japan
(Received 9 November 2008; Accepted 9 December 2008; Published 20 December 2008)

By monitoring the post-growth behavior of surface bonded hydrogen on the Si films prepared from gas phase discharge of SiH₄, it is shown that thermal desorption of surface hydrogen from multi-hydride (SiH₂ and SiH₃) configurations obstructs crystal formation through a disruption of T₃ symmetry in Si bonding.

[DOI: 10.1380/ejssnt.2008.286]

Keywords: Infrared absorption spectroscopy; Raman scattering spectroscopy; Growth; Silicon; Amorphous thin films; IRRAS; Surface hydrogen; Thermal desorption

I. INTRODUCTION

It is commonly accepted that amorphous Si films are usually grown from the gas phase discharge of SiH₄. When a high dilution of SiH₄ by H₂ is employed, crystalline films (often called as microcrystalline Si or μc-Si) may also grow, which has been experimentally attributed to the atomic H supply onto the growing surface inducing the crystal formation, although its role for crystallization is somewhat controversial [1]. On the other hand, since Si atoms prefer tetrahedral (T₄) bonding and thus form diamond structure in nature, one may assume that crystal formation should be quite natural while amorphous formation would be extraordinary, suggesting that there must be some particular reasons in common amorphous formation from SiH₄ discharge. Based on this way of thinking, we have been investigating the behavior of surface hydrogen by in-situ infrared reflection absorption spectroscopy (IRRAS) to identify such phenomena that may cause amorphous formation. An external reflection setup is employed to be free from spectral limitations that are usually imposed in the internal multiple reflection setup [2]. This feature provides a clear advantage in the Si surface hydride observations since di-hydride (SiH₂) and tri-hydride (SiH₃), absorption bands are observed as distinct peaks in the bending region, which locates below 1000 cm⁻¹. In this report, post-growth behavior of surface hydrogen on both amorphous and μc-Si has been carefully monitored to show that, at elevated temperature (typically above 200 °C), thermal desorption of surface hydrogen is one of such obstructing factor for the crystal formation in Si growth under the SiH₄ plasma.

II. EXPERIMENTAL

The Si film growth, both amorphous and microcrystalline, is performed in a plasma-enhanced chemical vapor deposition (PECVD) reactor equipped with a real time in situ IR observation system, all of which are similar to previously reported one except that the main FTIR instrument is a Mattson RS instead of previous Bomem DA3 [3–6]. A high angle of incidence (81°) is employed to get the absorption signal enhancement on a metal reflector substrate (Al plate, here in our case). In addition, polarization modulation is utilized to remove isotropic absorptions other than the film absorptions on the metal substrate. Finally, surface isotope exchange, replacing surface hydrogen by deuterium by exposing the film surface to D₂ plasma for short time (a few second), is performed to differentiate the surface signals from those in film body. By integrating these techniques, submonolayer sensitivity for surface observation is well established.

Amorphous films are prepared from pure SiH₄ (SiH₄ flow rate of 1.6 ml/min, total pressure of 20 mTorr, rf power of 1 W), while hydrogen dilution is employed for microcrystalline films (SiH₄ and H₂: 0.6 and 50 ml/min respectively, 120 mTorr, 1 W). IR monitoring has been done through the growth as well as for post growth duration of prolonged time up to 6 hrs. Growth duration is adjusted for the film thickness of about 50 nm, since the absorption signal enhancement is dependent on the total film thickness (or optical distance from the metal reflector, to be precise [6]). These growth monitored films on Al substrates are experienced Raman observation (a Renishow system with 633 nm excitation) to identify their crystallinity.

It should be noted here that the growth temperature described in this report is carefully calibrated by monitoring the thermal emission from the residual natural oxide on the Al substrate by using an infrared radio-thermometer (Minolta IR-308) with the estimated error of about 10 °C, including the positional distribution in a relatively large substrate of 10 cm square. Care should be taken that the growth temperature denoted in some of conventional reports was actually the susceptor (substrate holder) temperature or the temperature bottom of the substrate and thus not the real temperature of growing films.

III. RESULTS AND DISCUSSIONS

At first, the temperature dependence of (micro-) crystalline film formation is investigated. Figure 1 displays the Raman scattering spectra of films prepared under hydrogen dilution. It is seen from the crystalline peak at 520 cm⁻¹ that these films contain crystallites, with the most favored temperature range between 100 and 200 °C. To quantify this temperature dependence, a peak height

*This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-5), Waseda University, Japan, 9-13 November, 2008.
†Corresponding author: y.toyoshima@aist.go.jp
FIG. 1: Raman scattering spectra obtained for the films prepared under the hydrogen dilution condition at various temperature.

FIG. 2: Summary of temperature dependent crystallization as shown in the Raman ratio of crystalline peak to amorphous feature, for films prepared under the hydrogen dilution condition.

The IR absorption spectra of surface hydrogen obtained at during-growth and post growth are displayed in Fig. 3 for amorphous films prepared from pure SiH$_4$ (Figs. 3(a)-3(c)) as well as those from hydrogen dilution (Figs. 3(d)-3(f)). In every couple of spectra, left hand side is for stretching region (where mono-, di- and tri-hydride bands are overlapped) and right hand side for bending region (where tri-hydride and di-hydride appear as separated bands, while there is no monohydride absorption). Also, bottom two spectra in each set are observed “during the growth” and “at 2 min. after growth”, respectively, while the observation time after growth for top two spectra is varied from 8 min. to 6 hrs, depending on the degree of spectral change. It is seen from these spectra that at around 200°C and above, spectral changes are observed, most evident in the tri-hydride band in the bending region (the 870 cm$^{-1}$ one). Although careful examination on the shape change also seen in the stretching bands prevails corresponding changes in the surface hydrides, observing the bending region is most straightforward to identify these changes in each multi-hydride (di- and tri-hydrizes). At higher temperature typically in Fig. 3(a) at 320°C, di-hydride band (the 910 cm$^{-1}$ one) also starts to decrease, leaving almost no features in the bending region while there stays a sharp feature in the stretching region, indicating that only monohydride is stable against thermal desorption at these high temperatures. In addition, the peak height of monohydride band has evidently increased with these multi-hydride desorptions, suggesting that the surface termination has transformed from multi-hydrides to monohydride, with some modification of surface structure.

To understand these rather-complicated features of thermal desorption in di- and tri-hydrizes observed, we introduce a concept of “excess hydrogen” on the growing surface of these Si films. First, we assume that monohydride is the thermally stable species on these surfaces. Then, a di-hydride has one H atom to desorb, and a tri-hydride has two H atoms to desorb, both leaving monohydride on the surface as the final (stable) state. Accordingly, the number of excess hydrogen on the surface can be obtained by addition of number of di-hydride and doubled number of tri-hydride. For simplicity, the number density of di- and tri-hydrides on the growing surface is assumed to be represented by the each peak height in the bending region. Then we obtain

$$I_{\text{(excess hydrogen)}} = I_{\text{(di-hydride peak)}} + 2 \times I_{\text{(tri-hydride peak)}}$$

Now, by numerically fitting the exponential decrease of this “excess hydrogen” as a function of post-growth duration time, the hydrogen desorption lifetime can be obtained and plotted in Fig. 4. By comparing this Fig. 4 with Fig. 2, it can be readily seen that there is a quite good correlation between the onset of surface multi-hydride desorption and the onset of crystallinity degradation.

This correlation can be explained in the following way. As mentioned earlier, we assume crystalline structure in the beginning of Si growth. When the growing surface is (111)-like and is fully terminated by hydrogen, the top surface would be similar to the one schematically described in Fig. 5(a). On such a structure, crystal Si growth is expected to proceed as shown in Fig. 5(b). However, when the temperature is high enough for hydrogen desorption, the H atom bonded in both tri-hydrides may recombine each other to form H$_2$ molecule and then desorb, leaving another Si-Si bonding created with di-hydride termination, as described in Fig. 5(c). In this structure after hydrogen desorption, Si atoms that form 5-membered ring are no longer in the T$_d$ symmetry and thus terminate the crystal growth. Similarly on the (001)-like growing surface (Fig. 6(a)), H$_2$ molecule desorption from the couple of surface di-hydrizes may also leave 5-membered Si rings with T$_d$ symmetry destroyed (Fig. 6(c)). This surface modification is essentially iden-
FIG. 3: Post-growth behavior of surface hydrides on the growing Si films prepared from pure SiH$_4$ ((a)-(c)) and from hydrogen dilution ((d)-(f)).

tical to the well known reconstruction of Si(001)1 × 1:di-hydride to 2 × 1:monohydride [2]. Of course these surface multi-hydride desorptions are observed in the post-growth durations, we have no reasons that these surface modifications are not taking place during the Si growth, possibly in a more complicated manner. So, these desorption models that accompany surface structural modifications can explain the essential part of correlation between hydrogen desorption and crystallinity deterioration. We name this modeling as “ring contraction” after 5-membered Si ring formation that terminates the crystal growth; whereas Si crystal is consist of 6-membered Si rings.

Then, the role of H atom for crystal formation can be readily explained since H atom can etch [8] and thus may break the contracted Si–Si bond (it is just like reversing the reaction from (c) to (a), both in Figs. 5 and 6), retrieving the T$_d$ symmetry to the top surface Si atoms.

This “ring contraction” scheme, where thermal stability of surface hydrides plays an essential role in the continuous formation of crystalline structure, has an additional advantage in explaining the preferred crystallite orientation commonly found in the PECVD grown µc films. That
FIG. 4: Surface “excess” hydrogen desorption lifetime plotted as a function of growth temperature.

FIG. 5: Hydrogen terminated Si(111) surface models; (a) with tri-hydride termination, (b) a single Si atom growth with sustaining the crystal structure (all the Si atoms stay in Td symmetry), (c) after H2 desorption leaving new di-hydride termination with creating Si–Si bond that composes 5-membered Si ring (some of the Si atoms are no longer in Td symmetry).

is; at lower temperature, (111) is the preferred orientation and at higher temperature, it is (110), while (001) is usually not the major orientation [7]. In an ideal surface termination, (111) surface needs alternate termination of tri- and monohydrides, so only in the lower temperature range where tri-hydride can survive, it may grow; (110) only needs ‘zig-zag’ monohydride termination (Fig. 7) so that this should be most temperature resistant and thus will appear as the preferred orientation at higher temperature. The (001) surface, meanwhile, need always di-hydride termination, which is expected to modify its surface structure easily to lower symmetry in a way as described in Fig. 6, since the di-hydride species on Si(001) is reported to disappear even at 475 K anneal [2, 8], at which temperature a considerable amount of di-hydride is surviving in our observations (suggesting these observed di-hydrdes are not on the (001)-like surface).

Si crystal growth taking place on fully hydrogen terminated might sound curious since such surfaces are quite inert for growth reactions. We only have a simple concept that, like many other free radicals, the silyl radical, the dominant growth precursor [1], can be expected to attach on the growing surface by substituting the one of the surface terminating H atoms.

Finally, we have to comment on the other factors that may disturb the crystal formation in PECVD since even at the desired temperature range, crystal formation will not occur without hydrogen dilution. A possible origin would be ions (mainly proton due to its lighter mass) coming onto the growing surface. However, since it is common that these film growth is done on the anode, those ions will not be highly accelerated even the film growth is performed under the electric discharge. We are currently working on the effect of non-energetic ions which may destroy the Si crystal (Td) structure by computer simulations [9]. In the lower temperature, where higher stability is expected for surface hydrides, the reasons why no µc growth is found in spite of hydrogen dilution are totally open question at this stage.

IV. CONCLUSIONS

By carefully monitoring the post-growth behavior of surface hydrides, the higher temperature limit for crystal formation observed in PECVD growth can be understood by the hydrogen desorption induced “Si ring contraction”, that accompanies a modification of Si bonding from Td

http://www.sssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
symmetry to lower ones, and thus terminates the crystal growth. The role of H atom supplied to the growing surface, which contributes to the $\mu_3$ formation, should be understood as breaking the such-contracted Si bond, and retrieving the $T_d$ symmetry to the top surface Si network. This contraction scheme has additional advantage to explain the preferred crystallite orientation commonly found in the PECVD grown films.

Acknowledgments

The author is grateful to Dr. T. Miyazaki of AIST, Dr. K. Miki of NIMS, and Dr. S. Watabnabe of Fujitsu Labs, for their stimulating discussion, and also to Prof. M. Suemitsu of RIEC, Tohoku Univ. and his lab’s members for their continuous interest throughout this work.

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