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Existence of surface region with high dangling bond density during a-Si:H film growth

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Abstract

In-situ electron-spin-resonance measurements have been made on the growth of hydrogenated amorphous silicon (a-Si:H) film using a remote hydrogen plasma technique. Dynamic changes of the Si dangling-bond signal intensity were observed during and after the deposition of the film, which confirms the existence of a surface region with a large spin density only during the deposition process due to the interaction with reactive species of SiH_3 and H in the gas phase. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Dangling bond; a-Si:H; Surface region

1. Introduction

Electron-spin-resonance (ESR) technique has been applied to the study of a variety of hydrogenated amorphous silicon (a-Si:H) films, and provided us with important information on the defect structure in the bulk and on its surface. On the other hand, for the growth of a-Si:H, dangling bonds in the surface region would play a crucial role as reacting sites for precursors to make bonding to the surface. It is widely accepted from the measurement of film thickness dependence of the dangling bond signal that there exists a larger density region of dangling bonds close to the surface [1,2]. This density might be the indication of the surface reaction during film growth. However, there had been no information on dangling bonds during deposition until our recent report of the first success of in situ ESR study of a-Si:H film growth [3].

Several groups have reported on the surface morphology and bonding configuration during a-Si:H film growth. Collins et al. [4] studied the nucleation and initial growth process of a-Si:H on different substrates by means of real-time spectroscopic ellipsometry, and discussed its microstructural evolution using a two-layer model. Using ultrahigh vacuum scanning tunneling microscopy, Ikuta et al. [5] reported on a direct subnanometer scale observation of the initial growth of a-Si:H. Using infrared absorption reflection spectroscopy, Toyoshima et al. [6] reported that a hydrogen-rich surface exists during

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the film growth. In situ ESR measurements during deposition should give us the dynamic chemical reactions governing the film growth.

We have reported the first successful in situ ESR measurement during film growth using a remote hydrogen plasma and showed that it is possible to observe the dangling bond ESR signal during film growth in addition to the gas-phase ESR signals [3]. In this paper, we present the dynamic changes of the dangling bond signal intensity during and after growth, and discuss the nature of the film surface during deposition.

2. Experimental procedure

For in-situ ESR measurements of a-Si:H film growth, a remote hydrogen plasma system was used, which is schematically shown in Fig. 1. The hydrogen plasma discharge was sustained within a microwave cavity (2.45 GHz), which was located at the upstream position with respect to the X-band ESR cavity [7]. Hydrogen molecules flowing through a silica tube, with an outer diameter of 6 mm, were dissociated into hydrogen atoms when passing through the discharge cavity. A T-shaped discharge tube was used to avoid incidence of hydrogen plasma light into the deposition space in the ESR cavity. The silane gas was mixed with the atomic hydrogen in the ESR cavity and the primary reaction taking place was $SiH_4 + H \rightarrow SiH_3 + H_2$ [8]. As a result, an a-Si:H film was deposited on the inner wall of the outer silica tube having an inner diameter of 8 mm. The substrate temperature of deposition shown in this paper was room temperature. The ESR measurements were made using an X-band Cavity (BRUKER ESP 300E). To get time-resolved change of dangling bond ESR intensity, the magnetic field was set at the peak position on the lower field side of the spectrum before deposition, the peak position being calculated from the ESR microwave frequency. By using the T-shaped tube, we could suppress the noise level arising from the hydrogen plasma system. As a result, the noise level in the plasma-on state became almost the same as that in the plasma-off state. The change of thickness was monitored by measuring an interference fringe of transmitted He–Ne laser light.

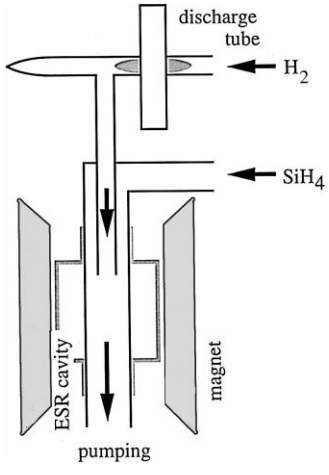

Fig. 1. Sketch of experimental setup. The T-shaped discharge tube was used to avoid incidence of hydrogen plasma light into the deposition space in the ESR cavity.

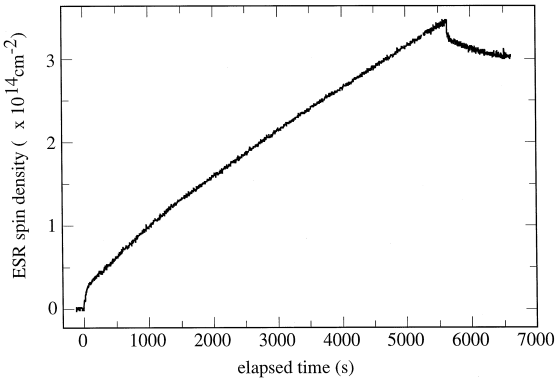

Fig. 2. The dangling bond ESR signal as a function of time. The vertical scale is calculated the number of spins per square centimeters, N_s.

The number of hydrogen atoms in the gas phase can also be measured by the ESR technique [9], which is one of the advantages of this in-situ ESR system. For the deposition conditions used here, an atomic hydrogen signal of $\sim 2 \times 10^{12}$ cm^{-3} was detected. This number is considered as the upper limit in the reaction region, because hydrogen atoms inside the inner tube are also included in the total atomic hydrogen signal.

When we used the experimental setup having a straight inner tube, the hydrogen plasma light illuminates the deposition space in the ESR cavity, and the signal originating from photo-excited SiH_4 related

species was observed [10]. This signal is thought to be caused by chemically-induced dynamic electron polarization (CIDEP) [11], which arises from species that are formed with non-equilibrium spin state populations. However, for the present setup, this signal was not observable due to no incident light from the hydrogen plasma.

The deposition conditions were a gas pressure of 5 Torr, a silane flow rate of 10 SCCM (standard cubic centimeters per minute), a hydrogen flow rate of 100 SCCM, and a discharge microwave power of 20 W. The deposition time was 5640 s and the film thickness was 510 nm. Due to the spatial distribution of film thickness and of the sensitivity in the ESR cavity, the dangling-bond density is estimated. The deposition area was 2.5 cm^2.

3. Results

ESR signal intensity of the dangling bonds was measured as a function of time, which is shown in Fig. 2. The vertical scale represents the number of ESR spins per square centimeters, N_s. As shown in the figure, an increase of the signal intensity is observed when the deposition starts, followed by a relatively slower increase of signal intensity over the whole deposition time with increasing film thickness. A decrease of the signal intensity occurs when the deposition is terminated by stopping the plasma.

The initial change is shown in Fig. 3 on a short time scale. Up to $t \sim 60$ s, the signal intensity increases to around 2×10^{13} cm^{-2} with a steeper slope than that of a following increase for $t > 60$ s. This density is larger than the surface spin density observed after deposition by around one order of magnitude [1,2]. If we assume a constant deposition rate for the initial stage of deposition, a deposition time of 60 s is equivalent to a film thickness of around 5 nm. The dangling bond density is calculated to be 4×10^{19} cm^{-3}.

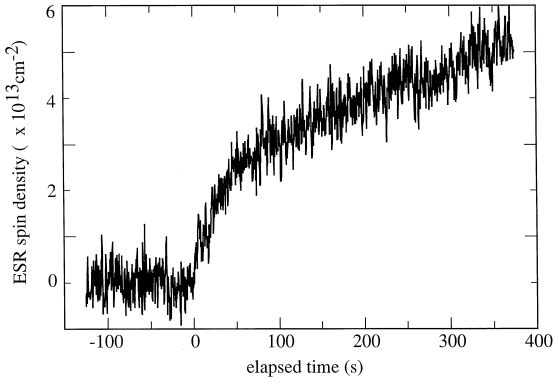

Fig. 3. The initial change of the dangling bond ESR signal on a short time scale. At $t \sim 0$ s, the deposition is started.

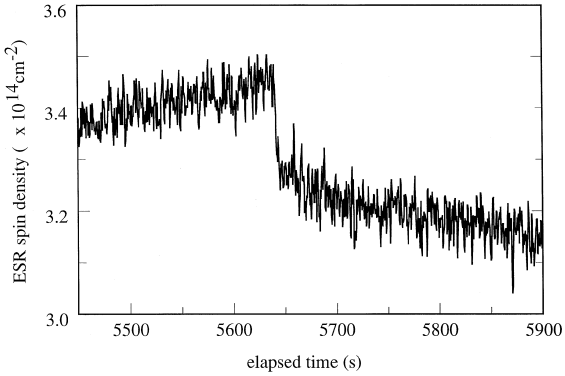

Fig. 4. The final stage of deposition. At $t = 5640$ s, deposition is stopped.

Spin density at the final stage of deposition is shown in Fig. 4, where deposition stopped at $t =$ 5640 s. The signal intensity decays with two distinctly different time constants after stopping the plasma; a decrease just after stopping the plasma, followed by a slower decrease due to a slow structural relaxation of the deposited bulk film. The spin density, N_s, of the film reached $\sim 2 \times 10^{14}$ cm^{-2} (equivalent to $\sim 4 \times 10^{18}$ cm^{-3}) at 10 h after the deposition is stopped, but is still unsaturated. The magnitude of the faster decrease in the spin density at the end of the deposition was almost the same as that of the initial increase. From the measurements for different deposition times, the amount of contributing to the faster decay is almost independent of the deposition time, namely, thickness.

4. Discussion

As the film structure is known to be affected by the substrate during the initial film growth, one possible candidate of a larger spin density region might be the film–substrate interface. However, this

region is not the case, because it is then not possible to explain why the film–substrate interface keeps being affected by reactive species in the gas phase even after the film is 100-nm thick. Eventually, the above data suggest that the high spin-density region created at the beginning of deposition is always located near the surface-region during the film growth independent of the film thickness, and disappears immediately when the plasma is turned off. It is noticeable that the larger density region is located at the two-dimensional top-surface but also at the subsurface region with a thickness of around 5 nm in this experimental condition.

A change of N_s was also observed when hydrogen-plasma treatments were made on a-Si:H films. The plasma conditions were 100-SCCM H_2 flow, 5-Torr pressure, and 2-W discharge power. When the hydrogen plasma was ignited after the growth of a-Si:H film, the surface starts to interact with reactive species in the gas phase and, as a result, N_s increases immediately with a time constant less than 1 s, which is shown in Fig. 5. The increased dangling bond signal decreased after the H_2-plasma was turned off. This experiment also shows that the 'active region' with a high dangling bond density originates from the surface region. It should be noted that the active region with the largest N_s is formed after the H_2 plasma being ignited.

During either deposition or hydrogen-plasma treatment, various radicals, mostly SiH_3 and H, reach the surface and react with it. The fact that the hydrogen plasma induces the N_s region near the top surface suggests that H is at least one of the species determining the N_s region. Branz et al. [12] reported from the deuterium (D) tracer measurements of a-Si:H that the distance D travels before retrapping is around $\sim$15 nm, being determined by an exchange process of free D with trapped H. Beyer and Zastrow [13] reported that D–H exchange in the a-Si:H network takes place even over a distance of $\sim$100 nm by D_2 plasma treatment. Although an estimated depth of the high-N_s-region is around 5 nm in the present study, and a lower than the above two cases, some H-mediated reaction in the surface region in the present study might be the origin of the high N_s state.

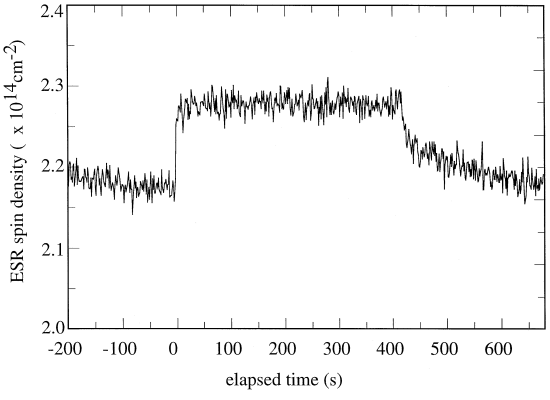

Fig. 5. The change of N_s for hydrogen plasma treatments without SiH_4 flow. The plasma conditions were 100-SCCM H_2 flow, 5-Torr pressure, and 2-W discharge power.

An et al. [14] studied the nucleation and initial growth process of a-Si:H by means of the real-time spectroscopic ellipsometry and observed that a low density layer of $\sim$20 Å was first formed, which was followed by the growth of a denser bulk layer under the low-density surface layer. The high-spin density surface region observed in the present study is thought to be closely related with the low density layer observed in spectroscopic ellipsometry. Although their low density surface layer is thinner than the high N_s region observed in this work, this might be understood by taking into account a difference in systems between two groups.

5. Conclusions

The experimental results clearly showed the existence of a subsurface region during the growth process, where the dangling bond density is dynamically much larger than that in the bulk region.

Acknowledgements

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