In situ electron-spin-resonance measurements of film growth of hydrogenated amorphous silicon

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In situ electron-spin-resonance (ESR) measurements of film growth of hydrogenated amorphous silicon (*a*-Si:H) using a remote hydrogen plasma technique have been performed. The Si dangling-bond signal in *a*-Si:H during and after deposition has been detected, in addition to the gas-phase ESR signals both of atomic hydrogen and radicals related with silane molecules. Dynamic changes of the Si dangling-bond signal intensity have been observed in real-time, where the signal intensity increases with deposition time and decreases after stopping the deposition due to a structural relaxation. High potentiality of *in situ* ESR techniques for microscopic understanding of film growth and surface reaction has been demonstrated. © *1997 American Institute of Physics.* [S0003-6951(97)03609-7]

In the field of semiconductor technology, various kinds of processing are utilized to fabricate devices. To get good-quality films, surfaces, and interfaces, various probes such as infra-red, visible light, electron beam, scanning probes, etc. have been introduced for monitoring microscopic processes of growing or reacting surfaces. Infra-red reflection absorption spectroscopy,[1] spectroscopic ellipsometry,[2] scanning probe microscopy[3] etc. provide information on film density, bonding configuration, surface atomic arrangement, and others. On the other hand, defect centers, whether they are in the bulk or at surfaces and interfaces, play an essential role in determining final device performances.[4] If one can directly observe the creation and annihilation of defect centers and those dynamic bonding configurations during film deposition and surface reaction in real-time, it will give much more important information for the improvement of device performances. Initial attempts to measure defect centers by electron spin resonance (ESR) technique during film growth were carried out by Johnson *et al.*[5] for a-Si:H deposition using the remote plasma system, and they detected ESR signals associated with hydrogen atoms and E′ centers of the silica-glass tube. However, no Si dangling-bond centers of *a*-Si:H (D centers) could be detected, perhaps, because of paucity of deposited material.

We performed *in situ* ESR measurements during deposition of hydrogenated amorphous silicon (*a*-Si:H) for a wide range of deposition conditions and different geometrical relationships between the ESR cavity and the remote plasma system. We succeeded in depositing a-Si:H film in the ESR cavity and observing D center signals from the film during and after the deposition. In this letter, ESR signals not only from the solid phase but also from the gas phase are presented with a tentative interpretation of their dynamical changes.

For *in situ* ESR measurements of growing *a*-Si:H films, a remote hydrogen plasma system was used.[6] The basic design of the system was adapted for compatibility with the ESR apparatus. The sketch of our experimental setup is shown in Fig. 1(a). The hydrogen plasma discharge was sustained within a microwave cavity (2.45 GHz), which is located upward of the *x*-band ESR cavity. Molecular hydrogen flowing through a high-purity vitreous-silica (HPVS) tube, outer diameter of 6 mm, was dissociated into atomic hydrogen at the position of the discharge cavity. Silane gas was mixed with atomic hydrogen in the ESR cavity and the primary reaction takes place there as follows:[7]

$$SiH_4 + H \rightarrow SiH_3 + H_2. \quad (1)$$

As a result, a thin film of *a*-Si:H was deposited on the inside wall of an outer HPVS tube having an outer diameter of 10 mm, as shown in the figure. The substrate temperature of this setup was room temperature. ESR measurements were made using the BRUKER ESP 300E system.

The distance between the end of the inner tube and the ESR cavity was adjusted so that the *a*-Si:H film was deposited with its thickest point at around the center of the ESR active region, whose thickness distribution with respect to

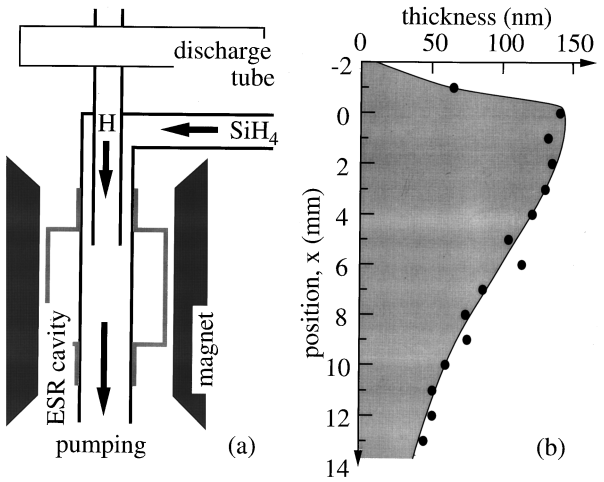

FIG. 1. (a) Sketch of experimental setup. (b) Film thickness as a function of vertical position, *x*. The thickest point is at the end of an inner high-purity vitreous-silica tube. The ESR active region is 0 mm $< x <$ 10 mm.

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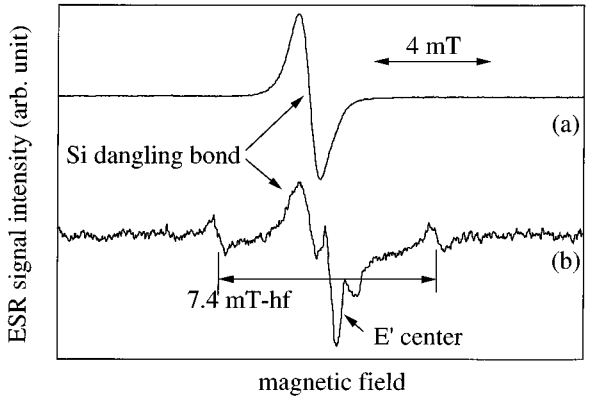

FIG. 2. ESR spectra after film deposition. (a) ESR spectrum of D centers in *a*-Si:H after deposition with pressure of 5 Torr, silane flow rate of 5 sccm, hydrogen flow rate of 50 sccm, discharge microwave power of 20 W. The peak-to-peak width and g-value are 0.7 mT and 2.0055, respectively. (b) ESR spectrum for the case of relatively low pressure deposition. Dangling bond signal in *a*-Si:H, E′ center (dangling bond signal of SiO_2) and hydrogen hyperfine structure with splitting of 7.4 mT related with E′ centers are seen.

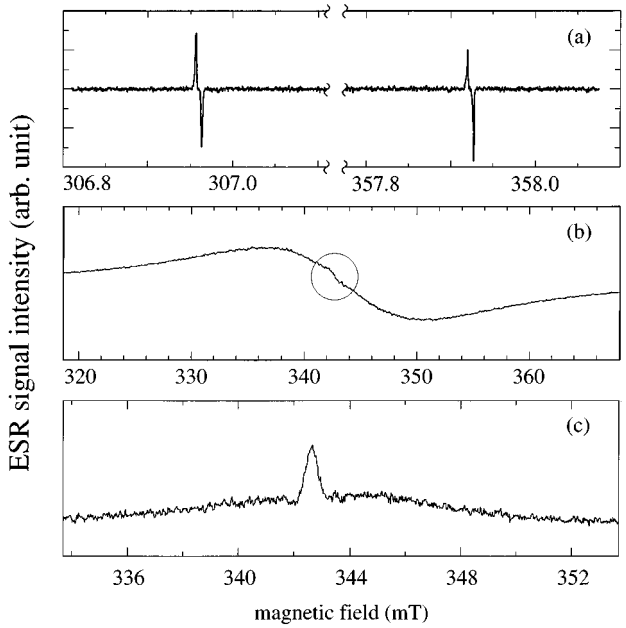

FIG. 3. ESR spectra during deposition (a) a doublet hyperfine structure of atomic hydrogen, and (b) a single peak of spin centers related with silane gas. (c) The second derivative curve of ESR absorption during deposition being the in-phase 2ω component of a modulation. This signal was clearly observed even after stopping deposition and was confirmed to be identical to that of the *D* centers.

the end of the inner tube is shown in Fig. 1(b). The position of $x=0$ mm is referred to at the end of inner tube. A typical ESR spectrum after deposition is shown as curve (a) in Fig. 2. The spin density is around 10^{18} cm^{-3}. The present deposition condition was with a gas pressure of 5 Torr, a silane flow rate of 5 standard cubic centimeter per minute (SCCM), a hydrogen flow rate of 50 SCCM, and a discharge microwave power of 20 W. The spectrum (a) is identified as a D center in *a*-Si:H because its peak-to-peak width and *g* value were found to be 0.7 mT and 2.0055, respectively. This is quite different from the report of Johnson *et al.*[3] They observed spectra of the E′ center associated with a dangling bond of SiO_2 (Ref. 8) as well as a hydrogen hyperfine structure with a splitting of 7.4 mT related with E′ centers,[9,10] and speculated that those signals originated from the film resulting from a reaction between silane–hydrogen plasma and oxygen extracted from a HPVS tube. This difference between the present data and those of Johnson *et al.* might be caused by the difference of plasma conditions, although in their paper, detailed plasma conditions are not given. Actually, we observed almost the same signals as theirs using a plasma condition of much lower gas pressure ($<$ 1 Torr), which is also shown as curve (b) in Fig. 2. Even for this case, D centers were observed in addition to the signal related with E′ centers. This kind of spectrum was also observed from the system after exposure to the hydrogen plasma in the absence of silane flow.

During deposition of the *a*-Si:H film, two kinds of signals were observed, which are shown in Fig. 3; a doublet hyperfine structure of atomic hydrogen, in (a),[11] and a single peak related with silane gas in (b). Both signals are thought to originate from gas-phase, because they are seen only during deposition and their intensity and shape are influenced by plasma conditions. The latter signal intensity increases with an increase of silane gas-flow rate and line shape seems to be dominated by pressure broadening. This signal could be related with SiH_3 radicals, because in this remote plasma system SiH_3 is the main radical of plasma reaction, although we need more intensive research for the final identification.

Another independent structure is also seen at the position of g=2.0055 superposed on the large gas-phase signal of Fig. 3(b), as is marked by a circle in the figure. To see the detailed shape we took a second derivative curve of absorption being the in-phase 2ω component of a modulation, which is shown in Fig. 3(c). This signal was clearly observed even after stopping deposition and was confirmed to be identical to that of the D centers. Since the signal intensity is increased with the increase of deposition time (which is shown in Fig. 4) the ESR signal is considered to originate mainly from the bulk region. After stopping the plasma, a long-lasting decay of *D* center signal was observed in vacuum, as shown in the figure. According to a tentative

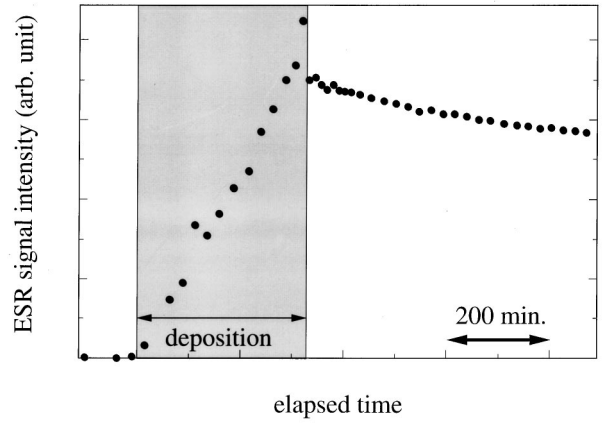

FIG. 4. *D* center ESR intensity as a function of elapsed time during and after film deposition. During deposition the signal intensity increases with an increase of time, while it decreases after stopping deposition.

analysis, the decay curve comprises fast and slow components. It is speculated that the slow decay is related with structural relaxations in a bulk region depending on the depth from the surface and the fast one is due to a relaxation in the vicinity of the surface. Details of the post growth signal intensity decay will be published in the near future.

For this measurement a film with high spin density was deposited to observe the dynamic change of D centers. Even for a device-quarily a-Si:H sample after deposition it is well known that there exists a high spin density region around a surface by $\sim 10^{12}$ cm^{-2}. Since the typical area of this system is ~ 3 cm^2, this spin number is in a detectable range for ESR measurements, although the noise level during deposition is larger than that of plasma-free conditions.

During the growth of a-Si:H film a variety of chemical reactions are expected to occur at the growing surface such as $\equiv$Si-(s)+SiH_3(g)$\rightarrow\equiv$Si–SiH_3(s), $\equiv$Si–H(s)+H(g) $\rightarrow\equiv$Si-(s)+H_2(g), $\equiv$Si–H(s)+$\equiv$Si–H(s)$\rightarrow\equiv$Si-Si$\equiv$(s) +H_2(g), $\equiv$Si(s)+$\equiv$Si-(s) $\rightarrow\equiv$Si–Si$\equiv$(s), etc., where (g) and (s) denote ''gas-phase'' and ''surface,'' respectively, and $\equiv$Si-(s) represents a D center at the surface. For these surface processes, hyperfine interactions between D centers and hydrogen atoms and/or other interactions between Dcenters should be involved. However, as is seen in Fig. 3(c), no discernible characteristic signals except D centers in a-Si:H have been observed. Reasons why such signals as related with hyperfine and/or electron spin–spin interactions are absent might be the fast reaction time of surface processes, because a fast reaction causes lifetime broadening of the ESR spectra, and/or paucity of their density. In order to clarify this, similar experiments at low substrate temperatures will be done in the future.

In conclusion, the ESR signal associated with D centers has been observed from a growing a-Si:H film in addition to the gas-phase signals related with silane and hydrogen. This experiment opens up the possibility of directly observing the dynamic process of defect creation or annihilation, along with its detailed bonding configuration, on the growing surface as well as in the bulk region undergoing structural relaxation. One can also discuss the microscopic reaction processes between the gas phase and the surface.

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