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In situ infrared and mass spectroscopic study of the reaction of WF_6 with hydrogenated amorphous silicon

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The reaction process of tungsten hexafluoride (WF_6) with photochemically deposited hydrogenated amorphous silicon was studied by polarization modulation infrared spectroscopy and quadruple mass spectrometry. Infrared absorption bands due to species (SiH_3 and SiH_2) incorporated in the hydrogenated amorphous silicon were decreased in intensity during exposure of WF_6 . The reduction rate was faster for the SiH_3 species than for the SiH_2 species. The mass spectrometric analysis revealed that evolution of hydrogen into the gas phase took place prior to that of silicon fluorides. These results strongly suggest that WF_6 reacts preferentially with the SiH_3 species present in the hydrogen-rich surface layer.

In very large-scale integrated (VLSI) circuit fabrication processes, the deposition process of tungsten (W) on silicon (Si) substrates is an active area of research, because W shows good properties as a gate material, i.e., high resistance to electromigration with relatively low resistivity.¹ The reaction of tungsten hexafluoride (WF_6) with a Si crystal, used as a substrate, leads to deposition of W on it.²⁻⁴ The deposition of W depends on the electronic properties of the Si substrate (*p* or *n* type).⁴ Furthermore, in the selective chemical vapor deposition (CVD) of W⁵⁻¹⁰ using WF_6 and hydrogen (H_2) or monosilane (SiH_4), the deposition of W can only occur on Si substrates or on metals, and not on SiO_2 . The results suggest that reduction of WF_6 is quite sensitive to the properties of substrates. Thus, to make an *in situ* survey of the deposition process of W from WF_6 , especially in its initial stage, is of importance in obtaining reliable contacts between W and Si-based semiconductors used in VLSI. Although a number of investigations have been carried out on the deposition process of W, dynamic behavior of chemical species present at the substrate surface is unclear.

In the present letter, we have investigated the dynamic behavior of the species incorporated in hydrogenated amorphous silicon (*a*-Si:H), as well as reaction products evolving in gas phase by polarization modulation infrared spectroscopy (PMIR) and quadruple mass spectrometry (QMS). We will demonstrate the usefulness of these techniques for providing a deeper insight into the deposition process.

The PMIR spectrophotometer and the CVD cell for the IR measurements used in the present study have been described elsewhere.^{11,12} Films of a *a*-Si:H were deposited photochemically from disilane (Si_2H_6) gas onto vacuum-deposited Au films on Pyrex glass plates ($\phi 75 \times 2$ mm) at 323 K. Si_2H_6 was introduced at a flow rate of 10 ccm into the cell and activated with UV light from a low-pressure Hg lamp (40 W). A total pressure during the deposition was maintained at 1.0 Torr. After 90 min of deposition, WF_6 was admitted into the cell at a constant flow rate of 2 ccm. The reaction products were monitored by a differentially pumped QMS attached to the cell. Changes in the ion

current of reaction products were recorded after removal of the background.

Figure 1 shows the IR spectral change of the *a*-Si:H film on WF_6 exposure at 503 K in the region of deformation modes of the hydrogenated silicon species. Spectra A, B, C, D, E, and F were recorded after 30, 150, 270, 390, and 510 s admission of WF_6 , respectively. The deposition of W onto the *a*-Si:H was confirmed by Auger electron spectroscopy (AES). By comparing the infrared absorption features of the deformation [Fig. 1 spectrum (A)] and the stretching modes [located around 2100 cm^{-1} (not shown in the figure)] of the hydrogenated silicon with the literatures,^{12,13} it is apparent that both SiH_3 and SiH_2 species are incorporated in the film deposited at 323 K. Each gives rise to two deformation bands in the spectral region of Fig. 1. It is then quite likely that spectrum A arises due to the superposition of the four absorption bands. A four-Lorentzians fit was, thus, applied to the spectrum A, the result of which is shown by dotted lines in Fig. 1. The dotted lines centered at 915 and 870 cm^{-1} with a full width at half maximum (FWHM) of 25 cm^{-1} correspond to the asymmetric and symmetric deformation modes of SiH_3 species and those at 895 and 850 cm^{-1} with a FWHM of 30 cm^{-1} correspond to the asymmetric and symmetric modes of SiH_2 species, respectively. The same fitting procedure was used for the spectra B, C, and D so as to follow the change of the SiH_3 and SiH_2 species. The results obtained are also shown in dotted lines in the spectra.

The gas-phase analysis during the exposure at 503 K, in which we monitored the mass signals (m/z) of $2(H_2^+)$, $20(HF^+)$, $68(SiF_2H_2^+)$, $85(SiF_3^+)$, and $86(SiF_3H^+)$, was carried out concurrently with the IR measurements. The results revealed that evolution of the signals due to H_2^+ , SiF_3^+ [derived from silicon tetrafluoride (SiF_4)], and SiF_3H^+ species into gas phase takes place under the given conditions. A time dependence of ion current of SiF_3H^+ at an ionization energy of 20 eV was similar to that of SiF_3^+ . Kobayashi, Goto, and Suzuki⁸ reported *in situ* gas-phase study of the selective W deposition process with Fourier-transform infrared spectroscopy (FTIR) and the results showed that SiF_3H is a main product in the process. The reaction of WF_6 with *a*-Si:H probably gives rise to evolu-

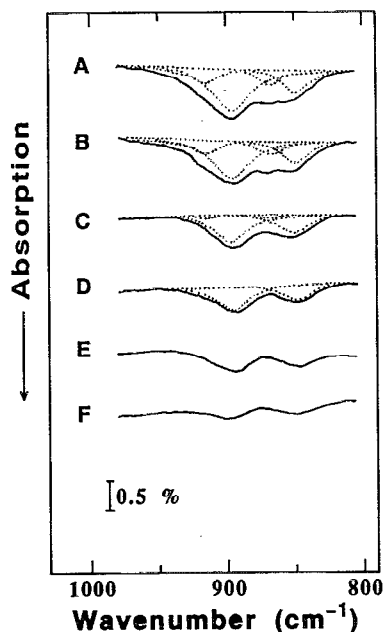


FIG. 1. IR spectral change of the deformation modes of the hydrogenated silicon during WF_6 exposure at 503 K. (A) before the exposure; other spectra recorded after (B) 30, (C) 150 (D) 270, (E) 390 and (F) 510 s.

tion of SiF_3H in the present study. However, by electrons emitted from the filament of the mass spectrometer, SiF_3H is easily decomposed, forming SiF_3^+ . We discuss, in the present study, the evolution of silicon fluorides (SiF_4 and SiF_3H) on the basis of the time-dependent signal of SiF_3^+ .

The IR band intensity change of the SiH_3 (915 and 870 cm^{-1}) and SiH_2 (895 and 850 cm^{-1}) bands as well as the time dependence of each ion current due to H_2^+ and SiF_3^+ during the exposure of 503 K are shown in Fig. 2. The H_2^+ evolution signal peaks at 10 s after the admission of WF_6 and then decays to the noise level after 50 s. The evolution behavior of hydrogen (H_2) is not clear after 50 s because of the relatively high noise level of H_2^+ , which is probably caused by residual H_2 in the present system. There are two stages in the time-dependent signals due to SiF_3^+ : the first stage is a component with a main peak at 20 s and the second stage corresponds to an almost constant value after 250 s. This evolution behavior of the silicon fluorides will be discussed later.

The IR band intensities due both to SiH_3 and SiH_2 incorporated in the film decreased with WF_6 exposure as shown in Figs. 1 and 2. The deposition of W on the film may decrease in infrared reflectivity of the sample (deposited $W/a-Si:H/Au$). The decrease in reflectivity should lead to the reduction of absorption intensity to an equal extent in each band, irrespective of species. The reduction rate of the band intensity of the SiH_3 species, however, is fast in comparison to that of SiH_2 species, as shown in Fig. 2. Thus, the decrease in reflectivity seems to be unessential to the time-dependent change of the IR absorption bands.

Sasaki *et al.*¹⁴ showed with a high-resolution electron energy loss spectroscopy (HR-EELS) that there is a hydrogen-rich layer consisting of multiple hydrides on the growing surface of $a-Si:H$. Our previous PMIR work¹² of

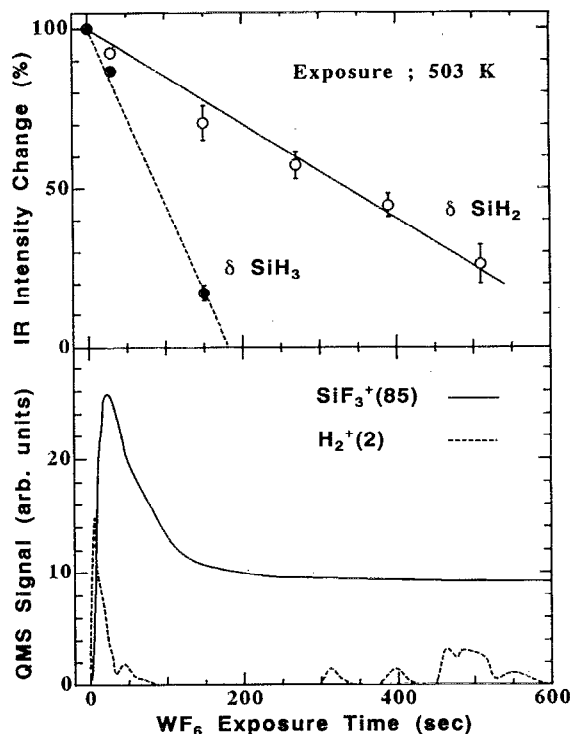


FIG. 2. The WF_6 exposure time dependence of IR and QMS signals at 503 K.

the deposition process of photo-CVD $a-Si:H$ revealed that the band intensity of SiH_3 species in the film tend to saturate when the film grows beyond 1.5 nm in mass thickness. Toyoshima *et al.*^{13,15} found similar saturation behavior of

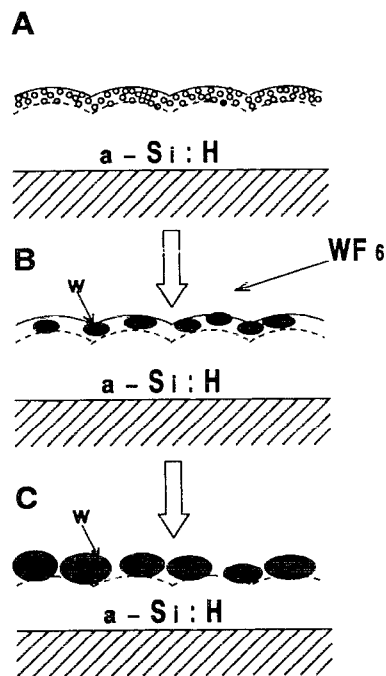


FIG. 3. Deposition scheme of W onto $a-Si:H$ (A) before the exposure (small circle represents the hydrogenated silicon species in the hydrogen-rich layer); (B) reaction of WF_6 with the hydrogen-rich layer; (C) reaction of WF_6 with the bulk.

the absorption intensity due to the higher hydrides in the α -Si:H, deducing that the higher hydrides layer exists at both the growing surface of the film and at the film/substrate interface. The presence of the hydrogen-rich layer, which consists mainly of SiH_3 species, on the growing surface of our film is, therefore, plausible. As can be seen from the time-dependent mass signals in Fig. 2, the evolution of H_2 into gas phase took place prior to that of the silicon fluorides. Further, infrared intensity reduction of the SiH_3 band is about 30% at 50 s when the H_2 evolution mass signals becomes the noise level, while that of SiH_2 is less than 10%. Based on the results obtained and the discussion mentioned above, we conclude that WF_6 reacts preferentially with SiH_3 species present in the hydrogen-rich layer accompanying the evolution of H_2 .

The deposition scheme of W onto the α -Si:H layer is depicted in Fig. 3. Exposure of WF_6 to the film leads to a rapid nucleation of W on the film with consumption of Si present in the hydrogen-rich layer. As the deposition progresses, the amount of Si in the layer should decrease, resulting in the decline of the silicon fluorides evolution. The first component (maximum at 20 s) of the SiF_3^+ signal in Fig. 2 thus corresponds to the reaction of WF_6 with Si present in the hydrogen-rich surface layer [Fig. 3(B)]. On the contrary, the almost constant value of the ion current of SiF_3^+ after 250 s (the second stage) probably arises from the continuous reaction of WF_6 and Si present below the hydrogen-rich layer, i.e., bulk of α -Si:H [Fig. 3(C)].

In summary, we studied the deposition process of W on the α -Si:H film with the *in situ* infrared and mass spectroscopies and deduced that WF_6 reacts preferentially with SiH_3 species present in the hydrogen-rich layer.

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