JOURNAL OF MATERIALS SCIENCE 29 (1994) 1041–1044

Si-rich surface layer of photochemically deposited silicon nitride

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The etching reaction of a photochemically deposited silicon nitride film with F_2 has been observed *in situ* using polarization-modulation infrared spectroscopy and quadruple mass spectrometry. The infrared spectrum of the silicon nitride film before etching exhibited two bands at 1030 and 975 cm^{-1}, arising from Si–N vibration. Exposure of the film at 423 K to F_2 led to an intensity decrease of the lower-frequency band, while the higher-frequency band increased. Simultaneous mass analysis revealed that the etching products evolved into the gas phase were SiF_4 and H_2. However, a further admission of F_2 resulted in a slight decrease in intensity of the 975 cm^{-1} band as well as a slight evolution of SiF_4. These results strongly suggest the presence of a metastable Si-rich layer on the surface of the silicon nitride film prior to reaction with F_2. Infrared measurements have also been made in the Si–H stretching region, the results of which are described and discussed.

1. Introduction

In situ molecular vibrational study of the dynamic behaviour of both surface and gaseous species under chemical vapour deposition (CVD) and dry etching conditions is quite important for a comprehensive understanding of the fabrication processes of thin-film devices. Such an understanding further gives us a useful guide in developing new advanced devices. However, little information has been obtained concerning CVD and etching processes on the molecular level because at present only a few techniques are applicable to the *in situ* analysis of such processes. For instance, polarization-modulation infrared spectroscopy (PM-IR) has been demonstrated to be a powerful tool for the *in situ* observation of surface species (see [1, 2] and references therein) and the deposition process of photo-CVD hydrogenated amorphous silicon films [3].

We have previously carried out PM-IR measurements to investigate the growing process of photo-CVD silicon nitride (SiN_x) films [4, 5]. The results obtained show that the film contains two kinds of Si–N bond; one corresponds to the metastable Si–N bond formed in the surface layer and another to the stable Si–N bond forming the bulk network. Further, upon u.v. illumination or by reaction with F_2 the former changed into the latter. Although this variation of film composition should have a strong influence on device performance, the bonding characteristics of the metastable surface layer are still unclear.

In the present work, the F_2 etching process of photochemically deposited SiN_x thin films has been investigated *in situ* using PM-IR and quadruple mass spectrometry (QMS). In the i.r. spectrum of the as-deposited SiN_x film, two bands appeared at 1030 and 975 cm^{-1} due to Si–N vibration. Upon admission of F_2 into the cell, the lower-frequency band decreased in intensity whereas the intensity of the higher-frequency band increased. Simultaneous QMS analysis revealed that the main etching products were SiF_4 and H_2. An additional admission of F_2, however, resulted in a slight decrease of the 975 cm^{-1} band and a faint QMS signal due to SiF_4 evolution. These results suggest that Si is in excess at the growing surface of the photo-CVD SiN_x, but it can easily be etched by F_2, thereby resulting in a stable silicon nitride network. Additional results from measurements in the Si–H stretching region are also discussed in this paper.

2. Experimental procedure

The photo-CVD set-up and PM spectrophotometer used in the present study have been described elsewhere [3, 6]. Source gases (Si_2H_6 and NH_3) were introduced into the cell at constant flow rates (Si_2H_6/NH_3 = 10/150 ccm) and activated with u.v. light (185 and 254 nm in wavelength) from a low-pressure Hg lamp (40 W). The i.r. windows were purged with pure N_2 in order to avoid the deposition of SiN_x. An SiN_x film was deposited at 373 K on to a thick Au film formed on a Pyrex glass plate (ϕ75 $\times$ 2 mm). The total pressure during the deposition was maintained at 130 Pa. F_2 (diluted to 5% by He) was admitted into the cell just after 60 min deposition. During the exposure to F_2 (60 Pa), etching products evolving into the gas phase were monitored with a differentially pumped quadruple mass spectrometry (QMS) instrument attached to the cell [7]. Changes in

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the ion current of etching products were recorded after removal of the background.

3. Results and discussion

The i.r. reflection spectra of the photo-CVD SiN_x film deposited at 373 K were measured in the regions of 3450–3250, 2300–2000 and 1150–850 cm^{-1}. A strong absorption occurred at 1030 cm^{-1}, whereas there were medium to weak absorptions at 2160 and 975 cm^{-1} and a very weak absorption at 3355 cm^{-1}. The incorporation of hydrogen into CVD silicon nitride films has already been reported in the literature [8–12]. The observed frequencies 3355 and 2160 cm^{-1} are in good agreement with those reported for CVD silicon nitride films. Thus, we assign the bands at 3355 and 2160 cm^{-1} to N–H and Si–H stretching vibrations, respectively.

Changes in the i.r. reflection spectra of the film in the regions 2300–2000 and 1150–850 cm^{-1} upon exposure to F_2 are shown in Fig. 1. The film temperature was 423 K. The corresponding changes in the 3450–3250 cm^{-1} (N–H stretching) region were not obvious in such spectra because of the very weak absorption feature in that region, as described above.

In Fig. 1, spectrum A was obtained from the as-deposited SiN_x film. As can be seen from the 1150–850 cm^{-1} region, there are two bands at 1030 and 975 cm^{-1}. These frequencies are much higher than in the transmission i.r. spectra of CVD silicon nitride films, in which a strong Si–N stretching vibration is located at about 850 cm^{-1} [8–12]. It is known that a blue shift of bands takes place in the reflection i.r. spectrum of a film on a metal surface, as a result of the anomalous dispersion of the refractive index (n) of the film compound [13]. We have investigated the film deposition process of photo-CVD SiN_x [4, 5] using the *in situ* i.r. reflection method and found that the main absorption band was located at around 1000 cm^{-1}, which is about 200 cm^{-1} higher than in the transmission spectrum. On the basis of a comparison between the observed and calculated reflection spectra of the silicon nitride films, we ascribed the band at around 1000 cm^{-1} to the Si–N stretching vibration [4, 5]. The bands at 1030 and 975 cm^{-1} in Fig. 1 can thus be assigned to the Si–N stretching vibration.

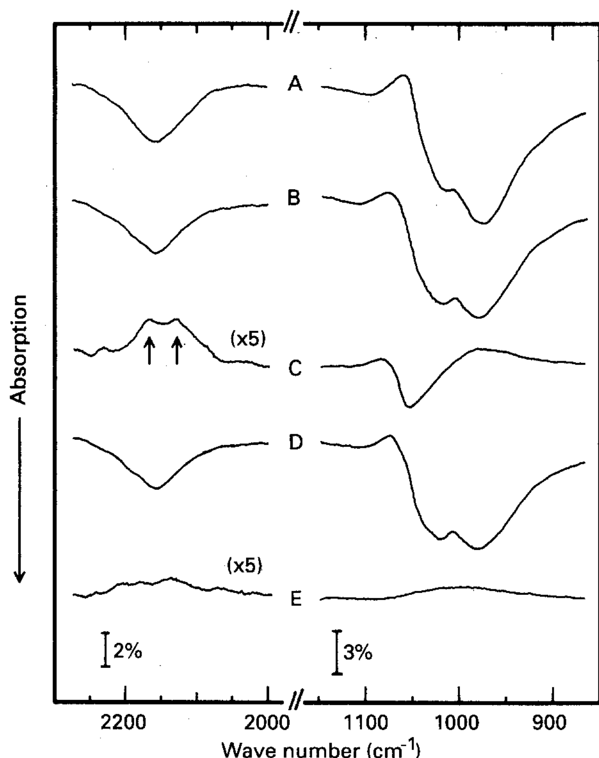

Figure 1 Changes of i.r. spectra of SiN_x film in the region of Si–N and Si–H stretching modes upon the admission of F_2 at 423 K: (A) as-deposited film, (B) spectrum recorded after 3 min of F_2 exposure (60 Pa), (C) difference spectrum (A − B), (D) spectrum recorded after additional 3 min of F_2 exposure, (E) difference spectrum (B − D).

Spectrum B was recorded after 3 min (60 Pa) of F_2 exposure. The difference between A and B is shown in spectrum C. Upon the first F_2 exposure, the 975 cm^{-1} band decreases in intensity with an intensity increase of the 1030 cm^{-1} band. Spectrum D was recorded after the second exposure to F_2 (60 Pa, 3 min) and the difference spectrum of B and D is shown in E. As can be seen from spectrum E, the intensities of the Si–N and Si–H bands decrease only slightly after the second exposure.

Our previous *in situ* i.r. study on the deposition process of photo-CVD SiN_x [4, 5] has shown that bands observed at 1030 and 965 cm^{-1} arise from vibrations of the Si–N bonds, forming a silicon nitride network and a metastable surface layer, respectively. Thus, the i.r. spectral changes upon the first F_2 exposure indicate conversion of the metastable layer to a stable network of silicon nitride. On the other hand, the slight change in the spectrum upon the second F_2 exposure suggests that the stable Si–N network has been almost completed before the additional exposure.

The major spectroscopic change accompanying the first F_2 exposure in the region of Si–H stretching modes (2300–2000 cm^{-1}) is the reduction of the 2140 and 2160 cm^{-1} features, as shown in the difference spectrum C. The peak positions of the Si–H stretching bands are higher than those in hydrogenated amorphous silicon as reported in the literature (see [3, 14] and references therein). Highly electronegative groups or atoms such as F, O and N on the same silicon could cause a blue shift of the Si–H stretching modes accompanying an increase in intensity [15]. Further, the magnitude of the blue shift is in proportion to the sum of electronegativity of the substituent atoms bonded to the Si atom [16]. Since the electronegativity of N ($x = 3.0$) is larger than that of H ($x = 2.1$) or Si ($x = 1.8$), the bonding of N atoms to the Si should result in upward frequency shifts of the Si–H stretching vibrations.

The feature peaking at 2160 cm^{-1} probably corresponds to the Si–H bonds present in the silicon nitride network because this band still remains even after the second F_2 exposure. The intensity reduction of the 2140 cm^{-1} band, on the other hand, was only observed upon the first F_2 exposure (Fig. 1, curve C) and no reduction is observed in the second difference

spectrum E. In our own PM-IR study on the deposition process of photo-CVD SiN_x [4, 5] the peak due to Si–H stretching shifted to a higher frequency ($\sim 2160\ cm^{-1}$) with an increase in the deposition time, i.e. with an increase in the film thickness.

The Si–H bonds in the metastable layer should be different in bonding state from those in the network. It is then most likely that the feature appearing at the low-frequency side ($2140\ cm^{-1}$) probably stems from Si–H bonds in the metastable surface layer. Based on the electronegativity summation rule described above, it can be deduced that N atoms are less bonded to Si in the surface layer than in the bulk network.

The results of *in situ* gas-phase analysis by QMS, carried out concurrently with the above-mentioned i.r. measurements, will be described next. The mainly investigated mass signals (*m/z*) from the reaction products evolving into the gas phase were 85 (SiF_3^+) and 2 (H_2^+). Ion intensity changes for SiF_3^+ as a function of the exposure time are shown in Fig. 2. The exposure-time dependence of the ion current of H_2^+ (not shown in this figure) was similar to that of SiF_3^+. Fig. 2a and b were recorded during the first and the second exposure to F_2, respectively. As can be seen from the figure, the mass signal due to SiF_3^+ appeared just after the first admission of F_2.

In the dry-etching reaction of Si with fluorine-containing compounds (CF_4, XeF_2, SF_6 etc.), SiF_4 is a main reaction product [17]. SiF_3^+ is the major fragment of SiF_4 [18] and the results obtained by us imply that the photo-CVD SiN_x film is etched by F_2, accompanied by the evolution of SiF_4 and H_2. The evolution of the products (SiF_4 and H_2) is apparently limited to an initial short time period (about 15 s). This evolution behaviour gives strong support to the suggestion that the concentration of Si–Si bonds at the growing surface layer is higher than in the hardly etched silicon nitride network. In addition, the change in the evolution behaviour of SiF_3^+ upon F_2 exposure corresponds well to that in the chemical composition of the film deduced from the i.r. results. It can therefore be concluded from the *in situ* PM-IR and QMS measurements that a silicon-rich layer is present on the growing surface of photo-CVD SiN_x films.

An F_2 etching scheme for the photo-CVD SiN_x film is depicted in Fig. 3. The first F_2 exposure should result in etching of the excess Si in the metastable surface layer (Fig. 3b). It is likely that the bond-breaking reaction of Si–Si and/or Si–H by F_2 brings on the formation of dangling Si bonds, accompanied by the evolution of such reaction products as SiF_4 and H_2 into the gas phase. The reaction between dangling Si bonds and neighbouring N atoms in the metastable layer probably leads to the formation of stable Si–N bonds. As a result, the second exposure to F_2 yields no evolution of SiF_4 at 423 K, as shown in Fig. 2.

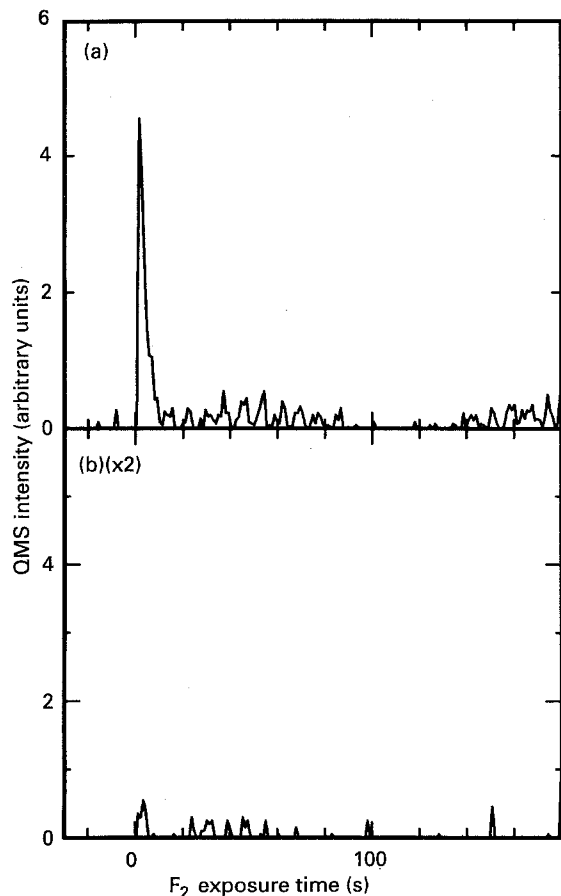

Figure 2 F_2 exposure time dependence of QMS SiF_3^+ (85) signal: (a) the first 3 min of F_2 exposure to the as-deposited film, (b) the second exposure after recording (a).

4. Summary

In the present work we have mainly studied the F_2 etching process of photochemically deposited SiN_x using *in situ* i.r. and mass spectroscopies. Upon the first F_2 exposure, the changes in the i.r. spectra of Si–N and Si–H stretching regions show that the metastable surface layer is easily etched by F_2 and is partly

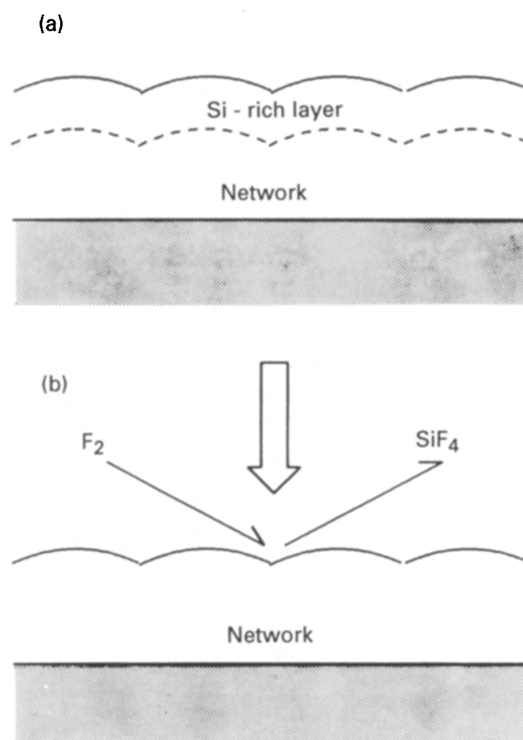

Figure 3 Etching scheme of photo-CVD SiN_x film by F_2: (a) as-deposited film, (b) reaction of F_2 with the Si-rich surface layer.

incorporated into the stable silicon nitride network. The Si–N network which has already been formed in the as-deposited film, on the contrary, is hardly etched by exposure to F_2. From the mass analysis, significant evolution of SiF_4 as well as H_2 into the gas phase was observed immediately after the first F_2 exposure, while the second exposure resulted in a very weak mass signal due to SiF_4. These results indicate that a metastable layer with an excess of Si is present on the as-deposited SiN_x film.

Acknowledgement

One of the authors (T.W.) expresses his cordial thanks to the Nissan Science Foundation for financial support of this work.

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Received 23 March
and accepted 24 August 1993