

Fictive temperature measurement of amorphous SiO₂ films by IR method

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Abstract

The structure and properties of amorphous materials, in general, change with their thermal history. This is usually explained using the concept of fictive temperature, i.e., the temperature at which the super-cooled liquid state turned into a glassy state. In earlier studies, a simple IR method was used to determine the fictive temperature of silica glasses, both bulk and fiber. In the present study the applicability of the same technique for thin amorphous silica films on silicon was examined. It was found that the IR absorption as well as reflection peak wavenumber of the silica structural band can be used to determine the fictive temperature of amorphous silica films on silicon with an unknown thermal history. Specifically, IR absorbance spectra of an amorphous silica film of thickness greater than 0.5 μm grown on silicon can be taken before and after etching a thin surface layer of 20–30 nm and the peak wavenumber of the difference signal can be compared with the pre-determined calibration curve to convert the peak wavenumber to the fictive temperature. For a film thicker than ~2 μm, IR reflection peak wavenumber can be converted directly to the fictive temperature of the film by using the calibration curve. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Amorphous silica film is an important material being used as dielectric in microelectronics and microelectronic mechanical systems (MEMS). Consequently, extensive research has been performed on various aspects of amorphous silica films including their growth kinetics, structure, and properties. For example, the classical work [1] on amorphous silica film growth kinetics by oxidation of silicon established that the film thickness grows more rapidly in wet atmosphere than in dry atmosphere and that at a constant temperature and under a given atmosphere the film grows linearly with time initially followed by the parabolic growth. The linear growth is attributed to the reac-

tion rate-controlled process at Si/SiO₂ interface while the parabolic growth is attributed to a diffusion-controlled process. It is recognized that amorphous silica properties change slightly with the growth temperature.

Although they are made by different processes and called by different names, amorphous silica and silica glasses are the same material having the same chemical composition, SiO₂, and same random network structure. One of the unique characteristics of amorphous materials or glasses is that they acquire slightly different structures and properties depending upon the manufacturing processes and the subsequent heat-treatment, even if the chemical composition is identical. This characteristic is attributed to the different temperature, called fictive temperature in glass science, at which a glassy state is expected to be in metastable equilibrium [2]. This definition of the fictive temperature can also be applied to glasses made by vapor deposition or oxidation. In this case, glasses with the identical structure as

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the glass which reached the metastable equilibrium at a given temperature can be considered to have the same fictive temperature.

Knowing the fictive temperature of amorphous silica is important because it enables one to predict the properties of the material. Effects of fictive temperature on various glass properties have been investigated extensively for many glasses including silica glasses. For example, silica glass with a higher fictive temperature has higher hardness, [3,4] higher density [5], higher mechanical strength [6], lower viscosity [7], and poorer chemical durability [3,4].

In previous studies, a simple IR method, either absorption or reflection, was found to determine the fictive temperature of bulk silica glasses [8] or silica glass fiber [9,10]. The method relies on the fact that the fictive temperature of silica glasses correlates with the IR peak wavenumber of silica structural bands. In the present study, a similar method was explored to determine the fictive temperature of amorphous silica films grown on silicon. IR spectroscopy has been used to investigate various characteristics of amorphous silica films grown on silicon [11–14]. In particular, Devine found a good correlation between IR peak wavenumber and density as well as Si–O–Si bridging bond angle for amorphous silica [14].

2. Experimental procedure

The thin amorphous silica films were obtained by oxidation of silicon. An n-type (100) oriented silicon wafer, ~ 0.6 mm thick, with low doping concentration (ShinEtsu Corp. Japan, product, resistivity 2–3 Ω -cm) was chosen for the substrate of silicon oxidation. A low doping concentration is necessary to ensure an adequate transmission of the IR beam through silica film on silicon in the wavenumber range near 1100 cm^{-1} where the strongest silica structural band is observed [15]. The silicon wafer was cut into a plate approximately $10\text{ mm} \times 10\text{ mm}$ and thermally oxidized at $1000\text{ }^\circ\text{C}$, $1100\text{ }^\circ\text{C}$ and $1200\text{ }^\circ\text{C}$ for various lengths of time in a wet atmosphere. The wet atmosphere with water vapor pressure of 22.7 kPa (170 Torr) was generated by passing air through a hot water bath kept at $65\text{ }^\circ\text{C}$ and then introduced into a tube furnace where the silicon wafers were heat-treated. Water can enter in amorphous silica films during the heat-treatment, the amount of hydroxyl being proportional to the square root of water vapor pressure. The hydroxyl content in the film produced in the present study is estimated to be ~ 800 ppm in weight [16]. But it was confirmed that even the higher hydroxyl content produced under a higher water vapor pressure, 44.7 kPa (335 Torr), did not affect the fictive temperature measurement by the IR method [8,16].

At various stages of heat-treatment, the samples were taken out of the furnace and IR absorption spectra were obtained using a Nicolet magna 560 Fourier transform infrared (FTIR) spectrometer with the beam size of 6 mm in diameter, performing 512 scans at the resolution of 4 cm^{-1} . In order to eliminate the effect of the silicon sub-

strate, the absorbance from the IR background reference sample, which was prepared by removing native oxide from the surface of a silicon wafer using a dilute HF acid etch solution, was subtracted from the absorbance of amorphous silica film on silicon. The silica structural band peak position located at $\sim 1100\text{ cm}^{-1}$, which represents the Si–O–Si asymmetric stretching vibrational mode, was determined as a function of the film thickness and the film growth temperature. The silica film thickness was measured by an ellipsometer and was also estimated from the absorbance of the silica asymmetric stretching band using the relationship established by Wong [11].

It is known that the IR peak wavenumber of a silica structural band can change with the non-stoichiometry, which is observed at Si/SiO₂ interface [12,17], as well as by stress in the film [18,19] and the fictive temperature [8]. Since the IR absorbance spectra reflect the characteristic of the entire film including the Si/SiO₂ interface, the difference signal of the IR absorption spectra between successive heat-treatment times was also obtained. The difference signal would represent, then, the characteristic of the thin layer corresponding to the film growth during the time period, since the rest of the film could be assumed to have an identical structure at the two successive heat-treatment times.

Using the same samples, IR reflection spectra were also obtained. For this purpose, the FTIR with a Spectra-Tech IR Plan Advantage microscope attachment was used. The beam size of 4 mm in diameter and 1024 scans were used in the similar manner to our previous work [18].

3. Results

Examples of IR absorption spectra are shown in Fig. 1. Fig. 1(a) shows IR absorption spectrum of HF etched silicon wafer without oxide film, which constitutes the background of the oxide spectra. Fig. 1(b) shows an example of IR spectrum of silicon wafer oxidized at $1100\text{ }^\circ\text{C}$ for 40 min under 22.7 kPa (170 Torr) water vapor, before the background subtraction. Fig. 1(c) shows IR spectra for amorphous silica films formed by oxidation of silicon at $1100\text{ }^\circ\text{C}$ in wet atmosphere of 22.7 kPa (170 Torr) water vapor pressure for various length of time, after subtraction of the background signal. The absorbance value increases with increasing heat-treatment time, corresponding to the growth of the silica film. IR spectrum for zero time corresponds to zero absorbance. As the thickness of Si wafer decreases slightly with the progress of oxidation, the baselines of the spectra in Fig. 1(c) do not remain fixed. In order to evaluate the absorbance of silica structural bands, e.g., peak at $\sim 1100\text{ cm}^{-1}$, therefore, a common tangent line is usually drawn as the baseline of each spectrum [11,20]. Fig. 1(d) shows an example of typical IR reflection spectra of the amorphous silica sample. In this case no background subtraction was necessary.

Fig. 2 shows the calculated amorphous silica film thickness from the measured absorbance using the relation

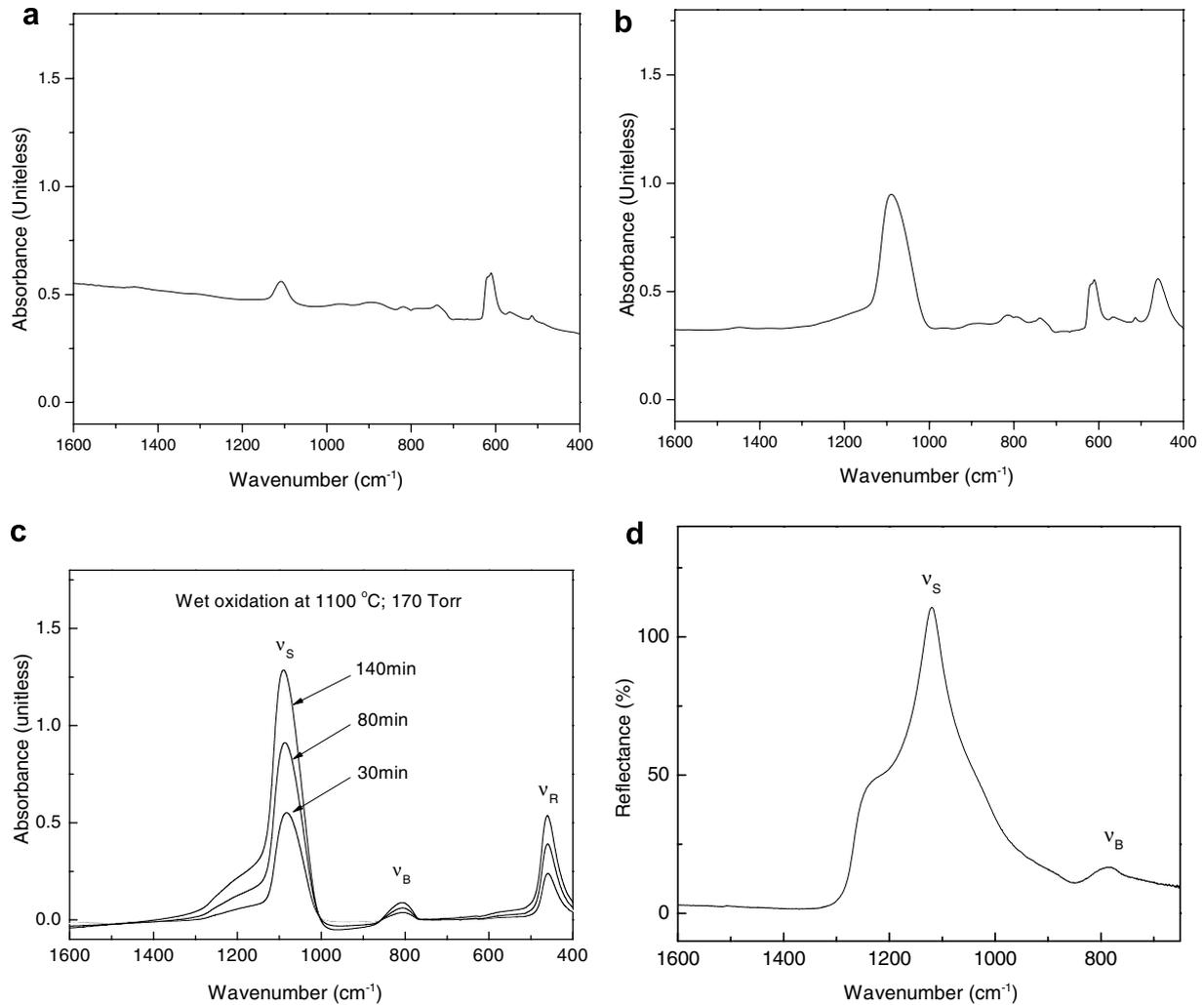


Fig. 1. (a) IR spectrum of silicon wafer without oxide film (background), (b) IR spectrum of silicon wafer + oxide film formed by wet oxidation at 1100 °C, for 40 min. under 22.7 kPa (170 Torr) water vapor, (c) IR absorption spectra of thin amorphous silica film formed by oxidation of silicon as a function of heat-treatment time at 1100 °C in wet atmosphere of 22.7 kPa (170 Torr) water vapor. Background from silicon wafer was subtracted and (d) IR reflection spectra of 2.1 μm thick amorphous silica film formed by silicon oxidation. ν_s : Si–O–Si asymmetric stretching vibration band, ν_B : Si–O–Si bending vibration band, ν_R : Si–O–Si rocking vibration band.

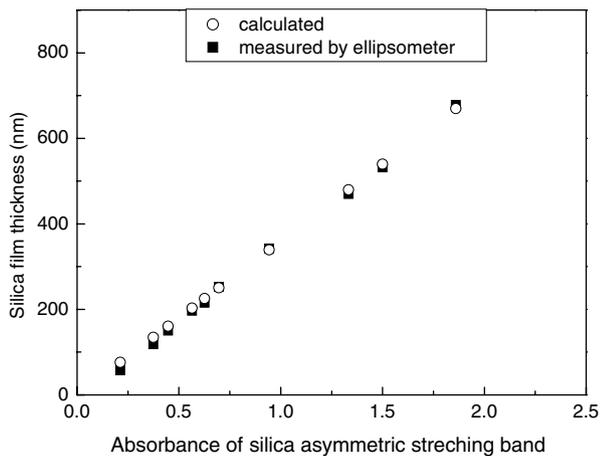


Fig. 2. Thickness of amorphous silica film grown on silicon vs. IR absorbance of silica asymmetric stretching band. \circ : calculated thickness using the relation reported by Wong [11]. \blacksquare : thickness measured using an ellipsometer.

reported by Wong [11] and thickness measured by an ellipsometer. There is good agreement between the thicknesses obtained by the two methods. The error of the film thickness measurement by an ellipsometer is known to be less than ± 0.5 nm [21]. The error of the film thickness obtained from IR absorbance measurement is about the size of the symbols in Fig. 2.

The IR peak of the silica asymmetric stretching band and its wavenumber as a function of the film thickness are shown in Fig. 3 for the film grown at 1200 °C in the wet atmosphere of 22.7 kPa (170 Torr) water vapor pressure. Here both the peak wavenumber of the spectra of the entire film thickness as well as the peak wavenumber of the spectra of the thin layer are shown. The latter was obtained by taking the difference spectrum between the two successive spectra corresponding to two successive heat-treatment times (or two successive thicknesses). Fig. 3(a) shows an example of two successive spectra and

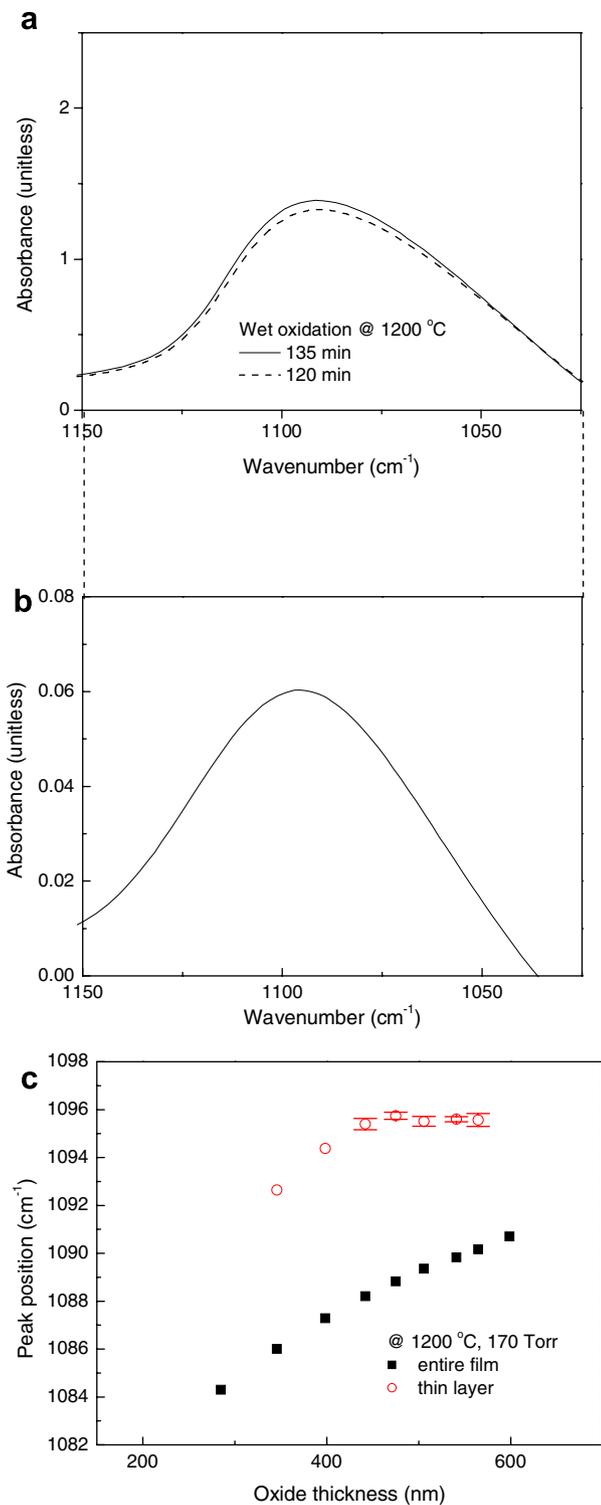


Fig. 3. (a) IR absorption spectra of two heat-treatment times at 1200 °C in wet atmosphere, (b) the difference IR signal of the two spectra shown in Fig. (a) and (c) IR absorption peak wavenumber variation of amorphous silica film grown on silicon at 1200 °C in wet atmosphere as a function of film thickness. ■: asymmetric stretching band peak wavenumber of the entire thickness of the amorphous silica film. ○: peak wavenumber of the spectra obtained by taking the difference of two absorption spectra of successive heat-treatment times (or corresponding thicknesses). The error bars in (c) represent \pm one standard deviation of the multiple measurements. The error range of the filled square symbols is approximately same as the size of the symbols.

Fig. 3(b) shows the difference spectrum. Fig. 3(c) shows the IR peak wavenumbers of the entire film (filled symbols) as well as the wavenumber from the difference spectra (open symbols), corresponding to the thin film grown between two successive heat-treatment times, plotted against the thickness of the film. It can be seen that the IR peak wavenumber of the difference spectrum becomes constant at the film thickness greater than $\sim 0.5 \mu\text{m}$ while the IR peak wavenumber of the entire film continuously increases with film thickness. Similar trends were obtained at other heat-treatment temperatures, i.e., 1000 °C and 1100 °C, and the constant IR peak wavenumbers of difference spectrum at various heat-treatment temperatures were considered as equilibrated or stabilized values of amorphous silica thin films at the growth temperature.

In Fig. 4, the equilibrated absorption peak wavenumbers of amorphous silica thin films formed by silicon oxidation at various heat-treatment temperatures, which are equal to the fictive temperatures, are compared with those of silica thin films, prepared by ion milling and etching, reported by Tomozawa et al. [22]. It can be seen that thin amorphous silica films on silicon exhibit a similar trend to thin films made from bulk silica glass in terms of IR peak wavenumber variation with fictive temperature, although there is some difference in the absolute magnitude of the wavenumber. The lines in the figures were drawn choosing the slope to be same as that of the reflection peaks of silica glasses since absorption and reflection are coupled and extensive reflection data of silica glasses are available [22].

The obtained relation between the equilibrated IR absorption peak wavenumber and fictive temperature for silica films on silicon, shown in Fig. 4, can be represented by

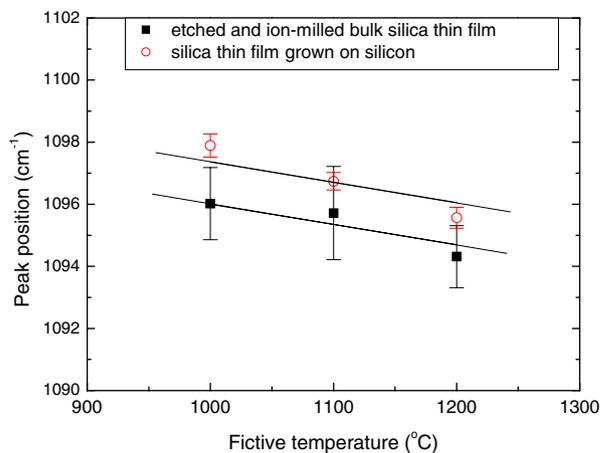


Fig. 4. The IR absorption peak wavenumber at equilibrium of silica asymmetric stretching band as function of heat-treatment (or fictive) temperature. ○: measured absorption peak wavenumber of thin amorphous silica films grown on silicon. ■: measured absorption peak wavenumber of ion-milled and etched silica glass thin films. The error bars represent \pm one standard deviation of multiple measurements. The slope of the lines were chosen to be same as that of reflection peak of bulk silica glass [22].

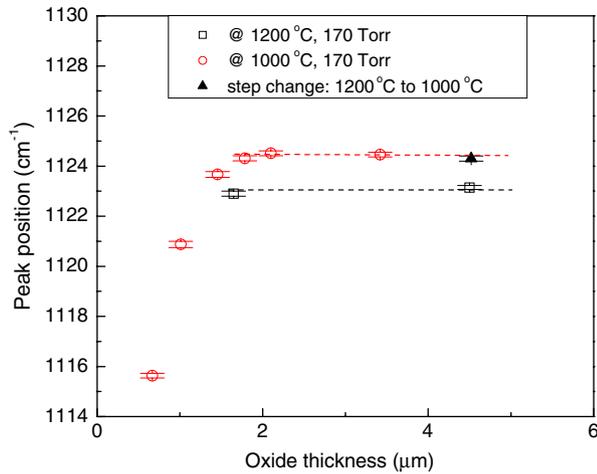


Fig. 5. IR reflection peak wavenumber of silica asymmetric stretching band of amorphous silica film grown on silicon in wet atmosphere. ○ and □: heat-treated samples at 1000 °C and 1200 °C, respectively. ▲: samples subject to temperature step change from 1200 °C to 1000 °C. The error bars represent \pm one standard deviation. Dotted lines are drawn horizontally through the data points for thicker films.

$$\nu(\text{cm}^{-1}) = 1103.915 - 0.0065 T_f(^{\circ}\text{C}),$$

with the error range : $\pm 0.32 \text{ cm}^{-1}$ (1)

The corresponding error range of the fictive temperature is $\pm 50 \text{ }^{\circ}\text{C}$.

The oxide film thickness dependence of the IR reflection peak wavenumber is shown in Fig. 5. In this case, the IR peak wavenumber became constant for a film thickness greater than 2 μm . The obtained constant IR peak wavenumber appears unique to the heat-treatment temperature. When a $\sim 4.5 \mu\text{m}$ thick film grown at 1200 °C was given an additional heat-treatment at 1000 °C, the IR reflection peak wavenumber changed from the value corresponding

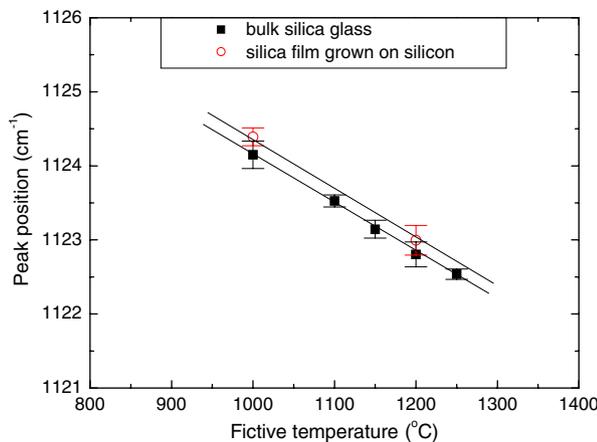


Fig. 6. The IR reflection peak wavenumber at equilibrium of silica asymmetric stretching band as function of heat-treatment (or fictive) temperature. ○: measured reflection peak wavenumber of amorphous silica films grown on silicon. ■: measured reflection peak wavenumber of bulk silica glass (2 mm thick). The error bars represent \pm one standard deviation. The slope for bulk silica glass was obtained by the least square fitting to the data while that for silica films grown on silicon was chosen to be same as that for bulk silica glass [22].

to 1200 °C to that corresponding to 1000 °C as shown as the filled triangle in Fig. 5, indicating that the fictive temperature of the films reached the heat-treatment temperature. These constant IR reflection peak wavenumbers were compared with those for silica glasses [22] in Fig. 6. In this case also, the peak wavenumbers for amorphous silica film on silicon were slightly larger than those of silica glasses. The obtained IR reflection peak wavenumber and the heat-treatment temperature, which is considered the fictive temperature, can be represented by

$$\nu(\text{cm}^{-1}) = 1130.876 - 0.0065 T_f(^{\circ}\text{C}),$$

with the error range : $\pm 0.16 \text{ cm}^{-1}$ (2)

again using the same slope as those of the IR reflection peak wavenumber vs. fictive temperature of bulk silica glass. The corresponding error range of the fictive temperature is $\pm 25 \text{ }^{\circ}\text{C}$.

4. Discussion

The IR difference absorbance spectrum of successive heat-treatments is due to a thin layer grown during that time period. The new layer grows at the Si/SiO₂ interface by reaction of the oxidant (water molecule in the present experiment) and silicon wafer. However, at a longer heat-treatment time, it is expected that a steady state is reached such that film structural variation with thickness near the interface remains unchanged during the successive heat-treatment time. Then the difference spectrum of IR absorbance is expected to represent the structure of the thin surface layer corresponding to the additional thickness grown between successive heat-treatment times. The constant IR peak wavenumber obtained for difference spectra at longer heat-treatment times shows that the thin surface layer of the film has reached the metastable equilibrium state corresponding to the heat-treatment temperature. In other words, the IR peak wavenumber of the absorption difference spectra corresponds to the fictive temperature, which is equal to the heat-treatment temperature. The steady increase of the IR absorption peak wavenumber for the entire film with the total film thickness comes from the gradual increase of the contribution of the surface layer with a larger, constant peak wavenumber and the corresponding gradual decrease of the contribution of the part close to the interface with the lower peak wavenumber.

Some researchers [23,24] attributed the IR absorption peak wavenumber increase during oxide growth to an optical geometry effect. In this model, the IR peak wavenumber should monotonically increase with increasing film thickness. In Fig. 7, the change of the IR absorption peak wavenumber with the thickness of the silica films obtained under constant heat-treatment temperature at 1000 °C and 1200 °C, are shown. Also shown is the change of IR peak wavenumber caused by a step change of heat-treatment temperature from 1000 °C to 1200 °C. Here, first, amorphous silica film was grown at 1000 °C until the thickness of the

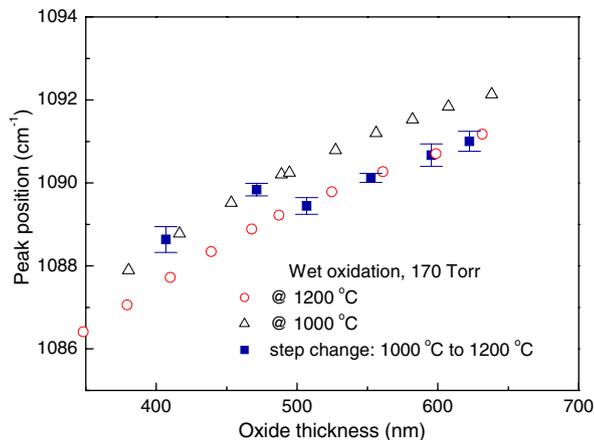


Fig. 7. The IR absorption peak wavenumber of amorphous silica film grown on silicon as a function of the film thickness. Δ and \circ : continuously heat-treated samples at 1000 °C and 1200 °C, respectively. \blacksquare : samples subjected to temperature step change from 1000 °C to 1200 °C at the film thickness \sim 470 nm. The error bars represent \pm one standard deviation. The error ranges for open symbols are approximately same as the size of the symbols.

film reached approximately 470 nm and then the heat-treatment temperature was changed from 1000 °C to 1200 °C. From the Fig. 7, it is clear that the IR peak wavenumber responded quickly to the change of heat-treatment temperature and the peak wavenumber decreased while the film thickness increased. Therefore, the wavenumber variation of amorphous silica with thickness appears to represent the structural state of the film rather than the optical geometric effect. A similar view was expressed by Queeney et al. [13] for thin amorphous films on silicon. The constant IR wavenumber obtained from the difference signal at each heat-treatment temperature, shown in Fig. 4, therefore, reflects the fictive temperature of the sample. The lower IR peak wavenumber of the difference spectra at lower thickness than \sim 0.5 μ m probably reflects a different structure of the film.

The finite difference between the two sets of data in Fig. 4, i.e., IR peak wavenumber for amorphous silica film on silicon wafers and for thin silica glass film made from bulk silica glass, is probably due to the compressive stress which is generated in the former due to the thermal expansion mismatch between the film and the substrate. Amorphous silica is known to have a much lower thermal expansion coefficient than silicon substrate and during cooling to room temperature from the heat-treatment temperature, amorphous silica would contract much less than silicon putting the amorphous silica under a compressive stress. It has been observed that the IR peak wavenumber of the silica asymmetric stretching band moves to a higher wavenumber under compressive stress [18] and a lower wavenumber under tensile stress. The consistent trend was observed with the Raman study by Michalske et al. [25].

IR peak reflection wavenumbers for two types of materials shown in Fig. 6 also exhibit a similar trend, with the peak wavenumber obtained for amorphous films on silicon being

slightly larger than that of silica glasses, the difference again being attributable to the compressive stress in the film. The minimum thickness of the film which gives a constant IR reflection peak wavenumber, \sim 2 μ m, is greater than the minimum thickness for a constant IR peak wavenumber for absorption difference spectra, \sim 0.5 μ m. The IR reflection probes the surface layer, the thickness of which is determined by the absorption coefficient [26]. The effective thickness of the IR reflection probe is estimated by taking the surface depth at which the light intensity is reduced to $1/e$ of the incident intensity. This gives approximately 0.22 μ m for the asymmetric stretching band used in the present study for the normal incidence. With the reflection angle of 28° employed here a slightly smaller effective thickness can be expected. Apparently, the IR reflection peak wavenumber reflects the structure of a much deeper part of the film than the effective thickness, also.

Using the obtained relationship between the IR absorption peak wavenumber and fictive temperature shown in Fig. 4, it is possible to determine the fictive temperature of amorphous silica on silicon with an unknown thermal history and to estimate various properties. One method is to obtain IR absorption spectra before and after HF etching of the surface layer of 20–30 nm. The IR peak wavenumber of the difference spectra of these spectra can be converted to the fictive temperature using the Eq. (1). This method assumes that the difference IR absorption spectra between successive heat-treatments give the same IR peak wavenumber as the difference spectra between successive etchings. In Fig. 8, the IR peak wavenumber obtained from the difference absorption spectra between successive heat-treatment times during the film growth is compared with that obtained from the difference absorption spectra between successive etchings. The agreement appears satisfactory.

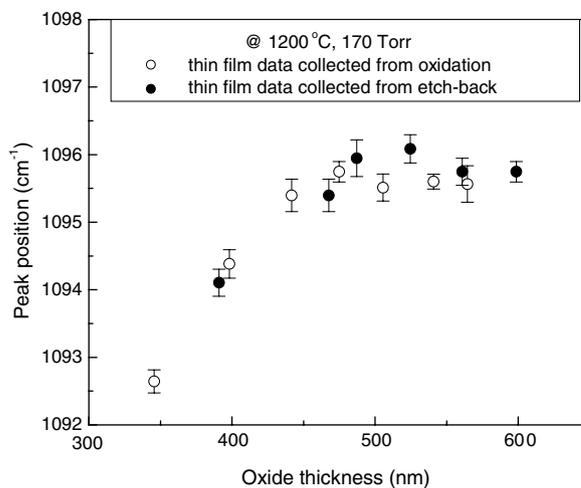


Fig. 8. IR absorption peak wavenumber of amorphous silica films obtained by silicon oxidation at 1200 °C in water vapor with 22.7 kPa (170 Torr) pressure. \circ : evaluated from the difference absorption spectra of successive heat-treatment times (with increasing film thickness). \bullet : evaluated from difference absorption spectra of successive etching (with decreasing film thickness). The error bars represent \pm one standard deviation of multiple measurements.

For IR reflection, as long as the film thickness is greater than $\sim 2 \mu\text{m}$, the measured IR peak wavenumber can be converted directly to the fictive temperature of the surface layer using Eq. (2).

The error range of the fictive temperature of amorphous silica films on silicon, estimated by the present IR method, is $\pm 50^\circ\text{C}$ for absorbance method and $\pm 25^\circ\text{C}$ for reflection method. The larger error range for the absorbance method comes from the need of taking the difference signal before and after etching of thin surface layer.

5. Conclusions

A simple IR method to determine the fictive temperature of silica glass was extended to amorphous silica films grown on silicon. A reasonable correlation was found between the IR peak wavenumber of the silica structural band, both in difference absorption spectra and reflection spectra, and the fictive temperature of amorphous silica film on silicon. Fictive temperature of amorphous silica film can be determined, as long as the film thickness is greater than $\sim 0.5 \mu\text{m}$, by obtaining the IR absorption peak wavenumber of the silica structural band from the difference spectra before and after a light etching of the surface layer of 20–30 nm and comparing the peak wavenumber to the calibration relation, Eq. (1). The error range of the fictive temperature determined by this method would be $\pm 50^\circ\text{C}$. When the film thickness is greater than $\sim 2 \mu\text{m}$, the IR reflection peak wavenumber of the silica structural band can be measured and directly converted to the fictive temperature using Eq. (2). The error range of the fictive temperature determined by the reflection would be $\pm 25^\circ\text{C}$.

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