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Infrared study of oxygen precipitate composition in silicon

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High spatial resolution Fourier transform absorption measurements were performed with polarized light on oxygen precipitates grown in silicon samples briefly annealed. We demonstrate that the wave-number position and intensity of the 1230-cm^{-1} absorption band, directly related to the precipitates, give information regarding stoichiometry of the oxide constituting such precipitates and their density. In particular, the precipitates in our samples are made of amorphous suboxides, mainly $SiO_{1.8}$, with 5 ppm local concentration. Moreover, our conclusions give evidence that disk-shaped precipitates in silicon have the same optical properties of thermal oxide films with comparable thickness grown on silicon.

I. INTRODUCTION

It is well known that oxygen is the most important impurity that is incorporated at interstitial sites in the crystal lattice of Czochralski (CZ) -grown silicon. During heat treatments oxygen atoms diffuse through the lattice, forming small microdefects (precipitates), which have been identified as constituted by some form of SiO_2. The study of the behavior of such silicon dioxide particles is of interest in both technological and fundamental research. In fact, the presence of precipitates causes lattice defects that have detrimental effects if they occur in the active regions of devices. Away from such regions, however, precipitates have the advantageous effect of acting as getters for unwanted metallic impurities. Moreover, silicon with oxygen precipitates is an interesting composite medium since (i) new optical effects, related to the small dimensions and to the shape of the inclusions, become evident, and (ii) very particular Si/SiO_2 interfaces, grown without any atmosphere contamination, are present in this system.

A lot of papers have been published concerning both fundamental aspects and applications in the subject, but reported results are often in contrast, leaving many questions wide open. For example, the connection between sample thermal history and the particular SiO_2 form constituting oxygen precipitates is not at all clear. A stoichiometry different from SiO_2 was suggested, but never well supported nor studied in detail, due to experimental difficulties in detecting and clearly resolving the precipitate contribution from the average sample optical response. Density determination of SiO_2 particles in silicon as a function of different heat treatments is usually performed measuring the interstitial oxygen (O_i) content, but this method does not give reliable results.

Several techniques have been used to characterize and analyze oxygen precipitate behavior in silicon. Among these, infrared (IR) absorption is one of the most powerful, because it permits detection of precipitated oxygen both indirectly from the decrease of O_i content (related to an absorption band at 1107 cm^{-1}) and directly from a band near 1230 cm^{-1}, related to the SiO_2 particles. This latter absorption band, which is not present in SiO_2 bulk or film spectra, has been attributed by Hu[1] to the longitudinal optical mode that is IR active in disk-shaped precipitates. He applied an effective-medium theory (EMT) to calculate the absorption coefficient of a system consisting of differently shaped SiO_2 particles in silicon. In the case of disks, he found a precipitate-related peak at 1215 cm^{-1}, to be compared with the experimental one at 1230 cm^{-1}. In our opinion, this disagreement makes any quantitative conclusion unreliable.

Recently, the authors demonstrated that high-spatial-resolution Fourier-transform IR (HSRFTIR) spectroscopy is able to detect regions containing very high concentrations of precipitates, also in samples annealed for a very short time.[2] The absorption spectra collected from these regions have a strong band at 1230 cm^{-1}, not substantially influenced by the 1107-cm^{-1} O_i band. Moreover, they showed that it is possible to avoid any average effects by using polarized light in order to study homogeneous aggregations of disk-shaped precipitates all lying in particular planes. The high intensity of the 1230-cm^{-1} peak allows a detailed study of line-shape, amplitude, and wave-number position.

In our paper we perform a careful analysis of the 1230-cm^{-1} band using HSRFTIR with polarized light. As a result we show for the first time that it is possible to obtain information about the chemical nature and stoichiometry of the precipitates.

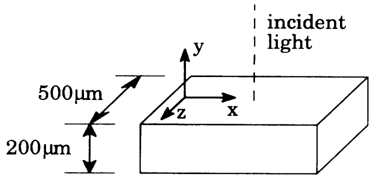

FIG. 1. Silicon sample as cut from the wafer. (100) wafer surface was along the xy plane; optical measurements were performed at normal incidence on the xz sample plane.

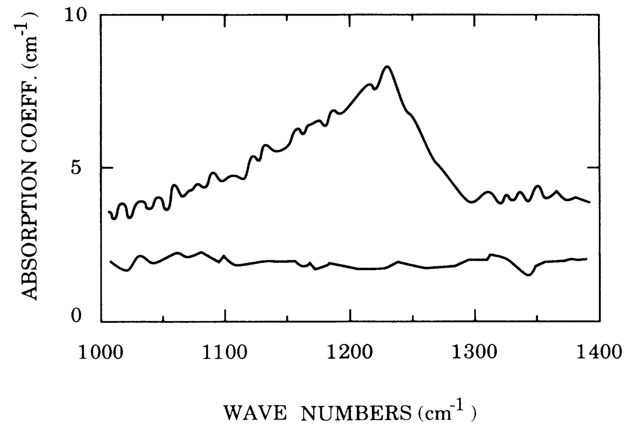

FIG. 2. Absorption coefficient of oxygen precipitates in silicon, as obtained by the transmission of a sample 200 μm thick. The upper and the lower curves were taken with the electric field polarized along the z and the x axes, respectively.

II. EXPERIMENT

The samples used in our experiment were n-type (P-doped, resistivity about 4 Ω cm) wafers, grown with the CZ method in the $\langle 100 \rangle$ direction, with a diameter of 100 mm and average thickness of about 512 μm. The nominal oxygen concentration was 8×10^{17} atoms/cm^3, while the carbon concentration was lower than 10^{16} atoms/cm^3. A thermal treatment was performed during the growth of an intrinsic epitaxial layer by chemical vapor deposition from trichlorosilane in a pancake-type rf heated reactor at 1100 °C. Before deposition the wafers received a basic cleaning, leaving hydrophilic surfaces, and were etched at 1180 °C in HCl atmosphere for 2 min. The etch temperature was reached at a rate of 70 °C/min as well as the room temperature after the deposition.

Stripes with parallel sides about 200 μm wide and 1–2 cm long were cut from the wafers (see Fig. 1) and optically polished. We performed several IR absorption measurements at normal incidence in different positions on the xz surface of the stripes. All the spectra were taken in the wave-number range from 5000 to 500 cm^{-1} with a Fourier-transform IR spectrometer Bruker IFS 113v equipped with an A 590 IR microscope and a KRS-5 polarizer. The instrumental resolution was 4 cm^{-1} and 2048 spectra were accumulated to improve the signal-to-noise ratio. The measurements were performed with a nominal spot diameter of 20 μm, using an Ealing $\times$36 objective with 0.5 numerical aperture. All measurements were performed using incident light linearly polarized, with the electric field either along x or along z.

III. RESULTS AND DISCUSSION

Some of the spectra collected with the light electric field along z show a strong absorption band at 1230 cm^{-1}, like the one reported in Fig. 2 in the wave-number range from 1000 to 1400 cm^{-1}. The same figure also presents a spectrum collected at the same sample position, but with the electric field of the radiation along x: no absorption band appears. The strong effect of light polarization on the 1230-cm^{-1} absorption, as discussed in Ref. 3, is due to the fact that oxygen precipitate platelets lie in the (100) plane parallel to the wafer surface (xy plane).

A similar peak has already been found in IR spectra of thermally treated CZ silicon, and attributed to the presence of SiO_2 precipitates.[1,4–6] Since the 1230-cm^{-1} band is not present in the IR spectra of any SiO_2 film or bulk, a novel approach is necessary to interpret it. As already proposed by Hu,[1] its appearance can be explained by an effective-medium theory, considering the system as the homogeneous dispersion of disk-shaped SiO_2 particles in a silicon matrix. Regarding the precipitate shape, this conclusion is well supported both by thermodynamic and kinetic considerations[7] and by transmission electron microscopy (TEM) studies.[7–9] Nevertheless, the agreement between the simulated and the experimental spectra reported by Hu is not very good as far as the peak position is concerned (1215 cm^{-1} with respect to the experimental value 1230 cm^{-1}). We believe that the wave-number position of the peak holds fundamental information about the chemical nature of the precipitates.

Looking for the best simulation of the experimental curves, such as the one reported in Fig. 2, we considered silicon samples with precipitates made of different SiO_2 polymorphs, choosing those previously proposed by different authors. In particular, precipitates of α-quartz, cristobalite, amorphous SiO_2, thermally grown SiO_2, and B-doped SiO_2 were examined. Our samples were modeled by an effective-medium approach, i.e., the optical response of the composite medium (Si matrix plus precipitates) was quantitatively described by defining an average dielectric function $\tilde{\epsilon}_{\rm av}$. Following Genzel and Martin,[10] the average electric field inside the composite medium was assumed to be a volume average of the uniform fields inside the particles, $\mathbf{E}_p$, and outside the particles, $\mathbf{E}_m$. The effective dielectric function, in the case of disk-shaped precipitates and with light polarized along z, is given by[3]

$$\tilde{\epsilon}_{\rm av} = \frac{\tilde{\epsilon}_m}{(1-f)\tilde{\epsilon}_m + f\tilde{\epsilon}_p}, \qquad (1)$$

where f is the volume fraction of the particles in the matrix, and subscripts m and p refer to silicon matrix and precipitates, respectively. Starting from Eq. (1), the absorption coefficient α_{av} can be calculated as a function of the wave number $\bar{\nu}$ by

$$\alpha_{\mathrm{av}} = \frac{\mathrm{Im}\{\tilde{\epsilon}_{\mathrm{av}}\}}{\mathrm{Re}\{\sqrt{\tilde{\epsilon}_{\mathrm{av}}}\}} 2\pi\bar{\nu}. \tag{2}$$

Equation (1) refers to disk-shaped particles in a matrix, i.e., to particles with depolarization factors $L_x{=}L_y{=}0$ and $L_z{=}1$. The choice of oblate ellipsoid particles [$L_x = L_y > 0$ and $L_z < 1$ (Ref. 11)], instead of the disk limit case, leads to a redshift of the EMT absorption band. Nevertheless, the TEM measurements clearly indicate that in CZ silicon samples treated at 1100 °C the precipitates are discoidal particles with a substantially constant thickness. Therefore, the assumption of an ellipsoidal shape does not represent the real system. Moreover, precipitates grown upon different heat treatments show a variety of ratios between length and thickness.[6,9,12] Considering oblate ellipsoids with a ratio between the minor and the major axes similar to experimental ones, a variety of EMT absorption peak positions will result from Eq. (2), within a 150-cm^{-1}-wide range, passing from the disk to the sphere. On the contrary, all experimental IR data indicate positions near 1230 cm^{-1}. All these arguments clearly suggest that the disk shape is the best one modeling our precipitates.

The α_{av} calculated from Eq. (2) for different $\mathrm{SiO_2}$ polymorphs are shown in Fig. 3. The values of the corresponding $\tilde{\epsilon}_p$ were taken from the literature.[13–17] The precipitate's volume fraction was taken as 5 ppm. Some conclusions can be drawn about our precipitate composition. (i) We can exclude the fact that cristobalite and quartz are the $\mathrm{SiO_2}$ forms constituting oxygen precipitates. In fact, the corresponding IR spectra show the absorption maximum at 1264 and 1241 cm^{-1}, respectively. (ii) Regarding the case of B-doped $\mathrm{SiO_2}$ inclusions, the related absorption peak lies at 1210 cm^{-1}. The calculation was performed on the basis of the optical functions of Ref. 17. It is worth noting that they refer to a boron concentration of about 10^{21} atoms/cm^3. This value seems to be almost two orders of magnitude higher than the possible B concentration in our precipitates, such as that roughly estimated from the dopant content in the CZ wafer, the B diffusivity at 1100 °C, and the annealing time; therefore the physical conditions are quite different from the case under consideration. (iii) On the basis of the peak positions in Fig. 3, amorphous and thermal $\mathrm{SiO_2}$ must also be excluded.

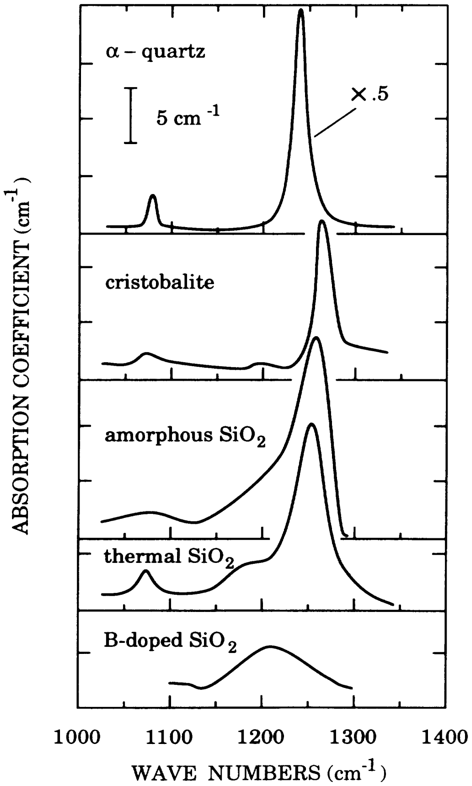

FIG. 3. Absorption coefficient of precipitates made of different $\mathrm{SiO_2}$ forms, as calculated by EMT. The optical functions of α-quartz, cristobalite, amorphous $\mathrm{SiO_2}$, thermal $\mathrm{SiO_2}$, and B-doped $\mathrm{SiO_2}$ were taken from Refs. 13, 14, 15, 16, and 17, respectively.

However, we note that stable amorphous oxide forms can exist with a stoichiometry richer in silicon, i.e., as SiO_x, $1 < x < 2$. We believe that disagreement in the band position can be related to precipitates made of such substoichiometric compounds.

To check this hypothesis we calculated the absorption coefficient by EMT, considering the sample as homogeneous dispersion of disk-shaped SiO_x particles in silicon. To our knowledge, no dielectric function data in the spectral range of interest are available in the literature for SiO_x. A possible attempt to calculate $\tilde{\epsilon}$ for such compounds is based on the use of a Maxwell-Garnett approach,[18] starting from SiO and $\mathrm{SiO_2}$ optical functions. As discussed by Aspnes and Theeten,[19] this would lead to unsatisfactory results because SiO_x have well-defined structural properties, so that their dielectric function is not merely a linear superposition of those of SiO and $\mathrm{SiO_2}$. Therefore, we considered the experimental IR transmission spectra of Si-rich oxides[20,21] and we obtained the corresponding dielectric functions by an oscillator based model. The oscillator parameters were optimized starting from those given in Ref.16 for thermally oxidized $\mathrm{SiO_2}$. In this case, among the four vibration modes, those at 445, 800, and 1075 cm^{-1} are related to the well-known transversal optical resonances and give rise to strong peaks in the IR transmission spectra, while the oscillator at 1190 cm^{-1} leads only to a weak shoulder. As far as the Si-rich oxides are concerned, the redshift of the stretching mode driven by the decrease of x values (1075 cm^{-1} for $x{=}2$ and 1032 cm^{-1} for $x{=}1.5$) is the most striking feature of the IR spectra.

Figure 4 reports the calculated absorption coefficients of disk-shaped SiO_x precipitates in silicon, with different x values and with $f{=}5$ ppm. As a limit case, the spectrum of Si with SiO precipitates is also shown. The agreement with the experimental peak position is found considering $\mathrm{SiO_{1.8}}$ precipitates. The line shapes of the experimental and calculated absorption curves are quite different. The large asymmetry of the experimental peak shown in Fig. 2 can be explained in terms of the presence of a wide distribution of substoichiometric oxides

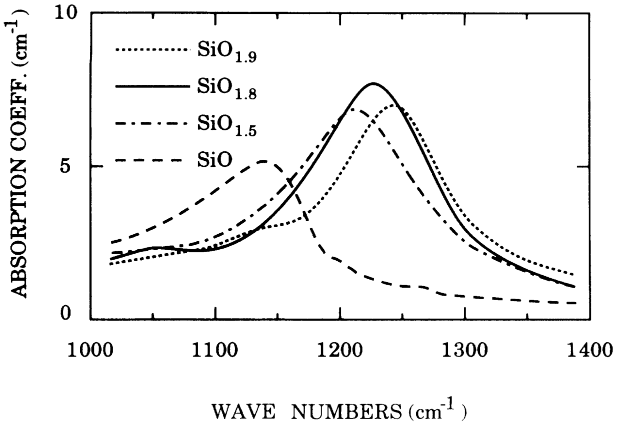

FIG. 4. Absorption coefficient of precipitates made of Si-rich oxides, as calculated by EMT. The optical functions of SiO were taken from Ref. 30.

with $x < 1.8$, whose density is much less than 5 ppm and that decreases by decreasing x. In the same way, the slightly shifted experimental wave-number peak position found in the literature for precipitates grown in different conditions has to be related to a predominant composition slightly different from $SiO_{1.8}$.

Comparing the intensity of experimental and calculated peaks, reported in Figs. 2 and 4, respectively, we can deduce that the volume fraction f occupied by precipitates in our samples is about 5 ppm. It has to be noted that such density evaluation is valid only locally for the particular region investigated during the measurement. This concentration value, therefore, cannot be considered as the average value over the whole sample, where only a few regions reveal precipitate presence by the IR band.

We stress that the $SiO_{1.8}$ dielectric function was obtained considering the stretching band at 1050 cm^{-1}. The position of such a band has been studied as a function of the thickness in silicon dioxide films grown on silicon.[22–24] A shift from 1072 to 1050 cm^{-1} was seen for thicknesses decreasing from 300 to 28 Å. This behavior was attributed to a significant transition region of Si-rich oxide, extending up to ~150 Å from the SiO_2/Si interface. Since our precipitates are expected to be about 50 Å thick and completely embedded in Si, it is reasonable to imagine that they are constituted by an oxide different from stoichiometric SiO_2. The interpretation of the 1230-cm^{-1} band on the basis of the $SiO_{1.8}$ precipitates agrees very well with these experimental findings as well.

An important factor affecting the optical response of thin SiO_2 films on silicon is the interface strain,[25] as it is also well known that a shift of the 1075-cm^{-1} band appears in compressed SiO_2 glasses.[26–29] We then considered the possibility that one of the spectra in Fig. 3 could shift and peak at 1230 cm^{-1} due to a strain effect. As discussed by Tempelhoff *et al.*,[4] the strain related to the formation of precipitates in silicon induces dislocations, leaving a possible residual strain lower than 0.5 kbar. Pressure values lower than 30 kbar cause a blueshift of the SiO_2 stretching band,[27] while, as we demonstrated, only a redshift of the stretching band toward 1050 cm^{-1} leads to the absorption band at 1230 cm^{-1}. In conclusion, we exclude any stress-related effect on the experimental peak position.

IV. CONCLUSIONS

HSRFTIR measurements performed on briefly annealed silicon samples with polarized light and wave-number resolution of 4 cm^{-1} allow selection of regions with high precipitate density. The related absorption band at 1230 cm^{-1}, clearly resolved from the O_i band, presents high intensity and well-defined line shape and position. The analysis of the experimental spectra by EMT permits exclusion of a detectable presence of quartz, cristobalite, B-doped SiO_2 or amorphous SiO_2 particles, because they would give rise to IR bands at 1241, 1264, 1210, and 1256 cm^{-1}, respectively. The 1230-cm^{-1} band is well reproduced only if precipitates made of amorphous $SiO_{1.8}$ are considered.

This result is in good agreement with optical properties of thin thermal oxide films grown on silicon. In fact, the spectral position of Si-O stretching band in $SiO_{1.8}$ is 1050 cm^{-1}, which is the one relative to films of thickness comparable with that of our precipitate. The redshift of the stretching band with respect to the stoichiometric case (1075 cm^{-1}) must be related to the Si-rich composition of the thin films.

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