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SILICON WAFER TECHNIQUE FOR INFRARED SPECTRA OF SILICA AND SOLID SAMPLES (I)

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Abstract— By using silicon wafer, penetrable to the infrared beam, the i.r. spectra of silica and solid samples were measured, and this method was proved to be advantageous than the conventional methods.

The silicon wafer was thermally stable below 800°C, and not significantly oxidized below the temperature. The silicon wafer technique for the gas adsorption studies had advantages on getting sharper absorptions of the brittle mineral samples and the efflorescent samples which were unable to be self-supported. Besides, this technique was effectively applicable to the samples such as cupric sulfate which easily react with KBr.

INTRODUCTION

In order to obtain the infrared spectra of solid samples like silica, several techniques such as KBr pellet method, self-supported film method [1], I.R.S. method [2-3] were known. These methods, however had many difficulties for the brittle and less penetrable samples. The silicon wafer made of silicon crystals [4] has a particular property to be penetrable to the infrared beam. But few applications of silicon wafer for the infrared spectroscopy was attempted so far.

Benesi and Jones [5] studied that the Si-O stretching bands appeared at 1090, 810cm^{-1}. Spitzer and Ligenza [6] observed the silica absorption at 1090-1040cm^{-1}. And Pliskin [7] noticed that the Si-O absorption bands on the i.r. spectra shifted to higher frequency according to the increase of oxygen ratio in the silica. Morrow and Cody [8] studied on an active site on the silica to prove the absorption at 888cm^{-1}. Boccuzzi [9] observed that the Si-OH absorption bands appeared at 908cm^{-1}. On the other hand, Shikha [10] investigated the mineralogical composition of soils by the characteristic bands on the i.r. spectra. We found that the silicon wafer technique for the i.r. spectroscopy was one of the most useful method for the minerals, particularly, the reactive samples to the KBr as well as brittle mineral which were unable to be self-supported.

EXPERIMENT

1. Materials

The silicon wafer used in this work was produced by the Monsanto company. The silicas, Cabosil EH-5 and Zeosil, had the BET surface area of 200m^{2}g^{-1}. And, zeolites were the Linde molecular sieve, SK-40, 13X and 5A. In order to remove the oxidation layer from the silicon wafer surface, the wafer was immersed in the etching solution of 30% HF for 2 minutes.

2. Preparation and Instrument

To obtain cation saturated zeolites, Na-zeolites were introduced to the 1N aqueous solutions of metal chlorides in a thermostated bath at 100°C ± 1°C for 3 hours, and were dried in air after washing with the distilled water 4-5 times. All samples were grinded finely and sieved to yield 200mesh size. The sample specimens were prepared by drying a few drop of 1M-sample suspensions on the wafer. After drying, the sample wafers were cut to fit in a sample holder. The i.r. spectra were taken on the JASCO model A-202 spectrophotometer and the accuracy and resolution power were promoted by using extention method. All absorption intensities were calibrated by means of polystyrene reference intensity at 1602cm^{-1}. The i.r. gas cell [5] for the adsorption study was made of pyrex with KBr windows as shown in Fig. 1.

RESULT & DISCUSSION

1. Infrared spectra of the silicon wafer

The spectroscopic properties of silicon wafers were studied by comparing the i.r. spectra of heat-treated wafers obtained at various temperatures as shown in Fig. 2.

Only two absorption bands at 1110cm^{-1}, 610cm^{-1}

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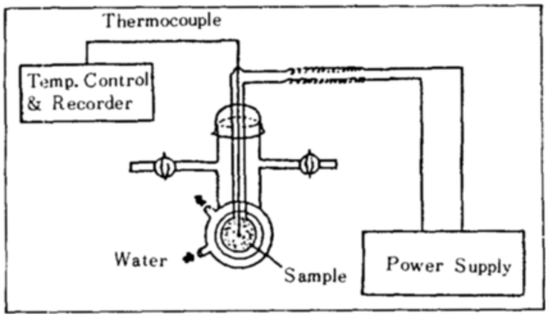

Fig. 1. Heatable i. r. gas cell.

were observed on the spectra of silicon wafer pretreated up to 800°C, and no other bands appeared. The absorbance of those two bands remained unchanged up to 800°C and increased suddenly at temperatures higher than 800°C. The 1110cm^{-1} band also shifted to 1090 cm^{-1}, and new bands appeared at 810cm^{-1}, 460cm^{-1} at the temperatures. These facts proved at least that the silicon wafer was relatively stable below 800°C. The 1090cm^{-1} and 810cm^{-1} bands were temperature dependent and assigned to the Si-O stretching vibration [11]. The 460cm^{-1} band was assigned to the Si-O bending vibration [11] likewise. The 610cm^{-1} band was independent of the temperature variation, which was assigned to the Si-Si stretching vibration. The bond force constants of Si-O were calculated as in table 1 from the Bjerrum's equations (1), (2), (3) [12].

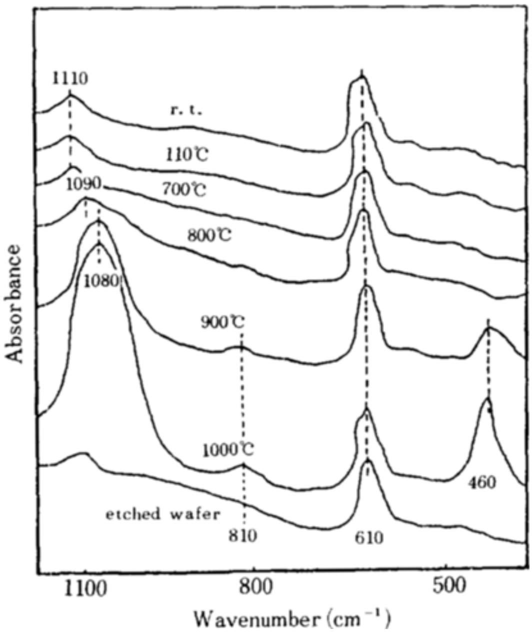

Fig. 2. I. R. spectra of Si wafer treated at various temperature for 3hrs in air.

Table 1. Bond force constants of various samples.

sample	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	k_1 ($\times 10^5$ dyne/cm)	k_σ ($\times 10^{-11}$ dyne·cm)
wafer (r. t.)	–	–	1110	–	–
wafer (800℃)	810	460	1090	3. 13	2. 22
wafer (1000℃)	810	460	1080	3. 07	2. 56
SiO	625	330	960	2. 43	1. 21
$SiO_{1.5}$	790	340	1020	2. 74	1. 67
SiO_2	805	470	1090	3. 17	2. 25

$$4\pi^2\nu_3^2 = \left(1+\frac{2My}{Mx}\sin^2\alpha\right)\frac{K_1}{My} \tag{1}$$

$$4\pi^2(\nu_1^2+\nu_2^2) = \left(1+\frac{2My}{Mx}\cos^2\alpha\right)\frac{K_1}{My} + \frac{2}{My}\left(1+\frac{2My}{Mx}\sin^2\alpha\right)\frac{K\delta}{l^2} \tag{2}$$

$$16\pi^2\nu_1^2\nu_2^2 = 2\left(1+\frac{2My}{Mx}\right)\frac{K_1}{My}\cdot\frac{K\delta}{l^2} \tag{3}$$

Both of K_1, K_σ values increased proportionally with the oxygen ratio. Comparing the bond force constants of

Table 2. Oxide depths on the silicon wafer surfaces.

sample	peak area (cm^2)	sample wt.* (g$\times 10^{-5}$)	depth** (A)
0. 05% SiO_2	3. 35	2. 5	1330
0. 10% SiO_2	6. 50	5. 0	2654
0. 20% SiO_2	11. 05	10. 0	5308
0. 40% SiO_2	23. 71	20. 0	10616
silicon wafer (r. t.)	0. 44	0. 13	69
silicon wafer (700℃)	0. 45	0. 14	74
silicon wafer (800℃)	0. 87	0. 50	265
silicon wafer (900℃)	3. 33	2. 62	1391
silicon wafer (1000℃)	8. 65	7. 21	3827

* sample wt. = wt. % of SiO_2 × coating amount of soln. /100

**depth = (sample wt. /sp. gr.) /coating area of SiO_2 soln. coating amount of SiO_2 soln. : 0. 05ml, sp. gr. of SiO_2 : 2. 4, coating area of SiO_2 soln. : 0. 785 cm^2, wafer heating : 3hrs

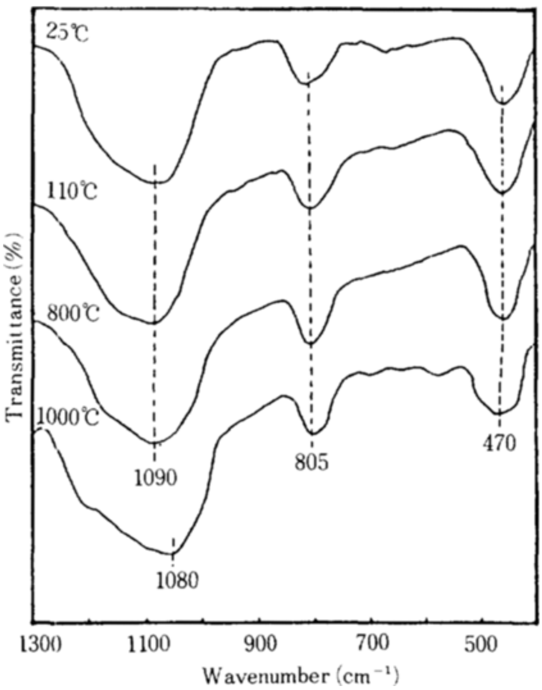

Fig. 3. I. R. spectra of cabosil M-5 treated at various temperature for 3hrs in air.

silica and oxidized wafer, the composition of oxidation layer of silicon wafer was deducible since their values were nearly same. The depth of oxidation layer could be determined by measuring the peak area of 1090cm^{-1} obtained for different amounts of silica. The results are shown in Table 2.

The depth of oxidation layer of the silicon wafers did not appreciably change until 800°C, and increased abruptly above the temperature.

This proved that the surface property of silicon wafer was relatively stable below 800°C. It's seemingly clear that the wafer has a protective layer of about 70A on the surface, which prevents further oxidation of the wafer until vigorous thermal agitation takes place at 800°C. And, partial fluidization stimulated by the thermal agitation at higher temperatures than 800°C induced the destruction of the protective layer. Furthermore, the cancellation technique using blank wafer in the path of reference beam is regarded as an additional advantage.

Applicability of silicon wafer as sample supporter to the i.r. spectroscopy below 800°C is definate by its stability in the temperature range.

2. Infrared spectra of silica

The i.r. spectra of silica were obtained at 25, 110, 800 and 1000°C using the silicon wafer as supporter, and the results are shown in Fig. 3.

The frequencies, areas, intensities of absorption bands on the spectra are illustrated in Table 3.

The bands at 1090cm^{-1} and 805cm^{-1} have been attributed to the Si-O asymmetric and symmetric stretching vibration, and the 470cm^{-1} band was assigned to the Si-O bending vibration[11].

Thus, the silicon wafer method is useful even for silica which has similar absorption bands as the surface-oxidized silicon in the i.r. spectrum.

3. Adsorption studies

For the gas adsorption study, the silicon wafer was coated with silicate and was activated at 300°C for 2 hours. The i.r. spectra of CO_2 [13] allowed to contact the silicate are shown in Fig. 4, and shift of the C-O stretching band to lower frequency, from 2304cm^{-1} to 2276 cm^{-1}, is an account for weakening of the C-O bond [14] due to the gas adsorption.

In Fig. 5, the Si-O band was shifted from 1080cm^{-1} to 1060cm^{-1} similarly. Additional interactions between the

Table 3. I. R. bands of cabosil M-5 and Si wafer.

Temp.	Cabosil M-5			Si Wafer				Iw/Ic
25 ℃	1090 (38)	805 (2.6)	470 (6.0)	1110 (0.4)	610 (1.4)			0.01
110 ℃	1090 (44)	805 (2.7)	470 (6.0)	1110 (0.4)	610 (1.5)			0.01
200 ℃	1090 (46)	805 (2.7)	470 (6.0)	1110 (0.5)	610 (1.4)			0.01
400 ℃	1090 (44)	805 (3.1)	470 (6.5)	1110 (0.6)	610 (1.4)			0.01
600 ℃	1090 (42)	805 (2.8)	470 (6.9)	1110 (0.5)	610 (1.3)			0.01
700 ℃	1090 (41)	805 (2.7)	470 (6.0)	1110 (0.5)	610 (1.5)			0.01
800 ℃	1090 (44)	805 (3.0)	470 (6.5)	1102 (0.9)	610 (1.7)			0.02
900 ℃	1085 (49)	805 (3.6)	470 (7.3)	1080 (3.3)	610 (1.7)	810 (0.1)	460 (1.1)	0.07
1000 ℃	1080 (43)	803 (2.8)	470 (6.7)	1080 (8.7)	610 (1.6)	810 (0.3)	460 (2.1)	0.20

unit: cm^{-1}, ( ): peak area, cm^2, Iw: Intensity of Si wafer at 1110cm^{-1}
Ic: Intensity of Cabosil at 1090cm^{-1} conc. of Cabosil M-5 soln. : 1 wt. %

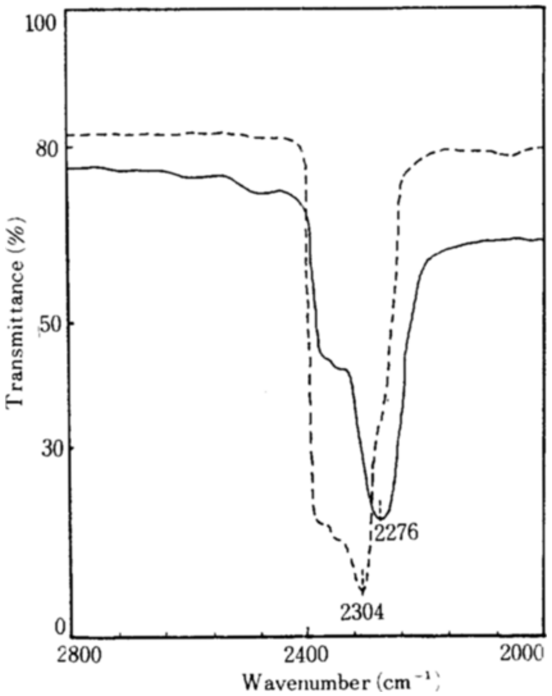

Fig. 4. I. R. spectra of CO_2 gas.

--- pure CO_2 gas
— CO_2 adsorbed on Silica pretreated at 300℃ under vacuum for 2hrs

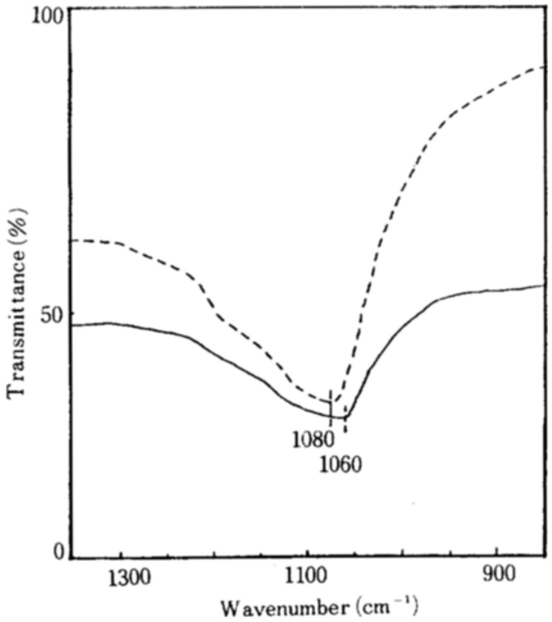

Fig. 5. I. R. spectra of silica adsorbed by CO_2.

--- silica without CO_2
— adsorbed CO_2 for 10min. and evacuated for 30 sec

silicon wafer and the adsorbate were not noticed below 800°C. Accordingly, validity of this technique for adsorption studies is assured below 800°C.

4. For mineral samples

As silicas of different crystal structures were generally classified by X-ray diffraction method, the i.r. spectra obtained by this technique were also useful to differentiate one from the other as shown in Fig. 6.

Zeolites consisted of many different types of composition and structures, differed by Si/Al ratio or by different cations, were distinguished by a difference in i.r. absorption spectra.[15]. The spectra of zeolites obtained by silicon wafer technique are shown in Fig. 7, and Fig. 8.

In Fig. 7, the significant absorption at 3600-3000cm^{-1} indicated that all the samples were adsorbed by H_2O in common. Similar bands appearing at 3600-3100cm^{-1} had been reported by Scherzer[16].

And, the Si-O band on the spectra shifted to higher frequencies according to increase in the Si/Al ratio of the zeolites.

As a similar work, Blackwell[17, 18] calculated frequencies of Si-O absorption bands on the i.r. spectra using different bond force constants for different Si/Al ratios of zeolites.

The substitution of various divalent cations of zeolites manifested each characteristic absorption band as shown in Fig. 8, which is distinct enough to differen-

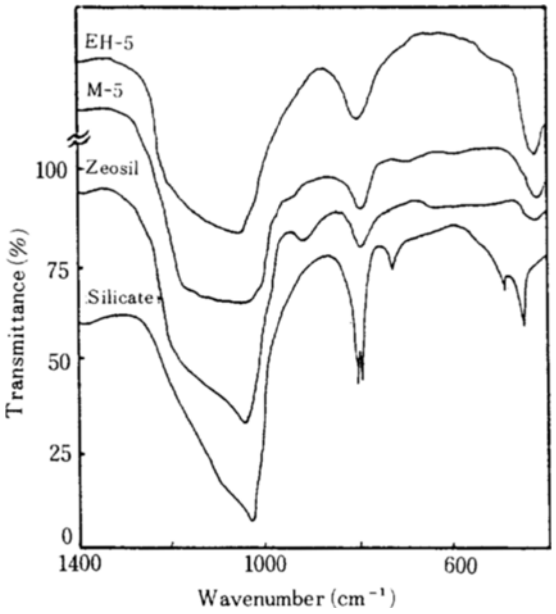

Fig. 6. Characteristic bands of various silicas and silicates on Si wafer.

The transmittance scale applies to the spectrum of silicate

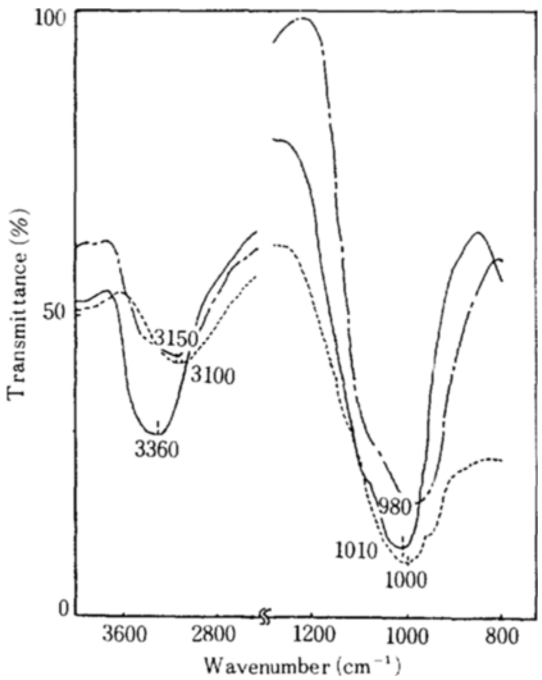

Fig. 7. I. R. spectra of various zeolites on Si wafer at 25℃.

------ A type zeolite
— · — X type zeolite
——— Y type zeolite

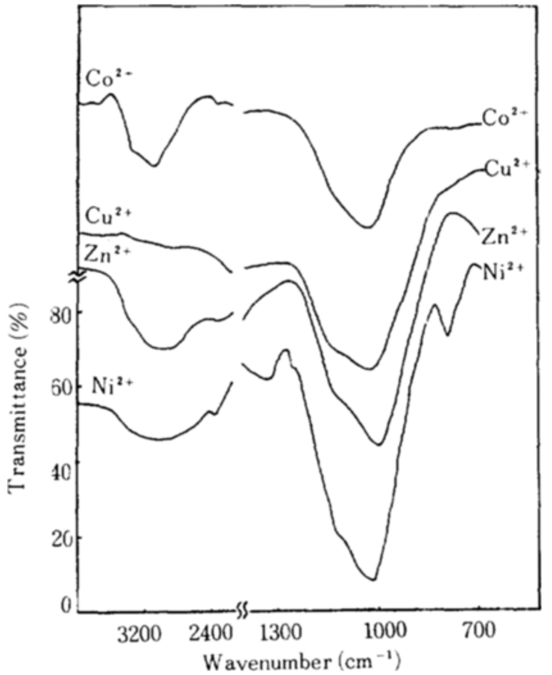

Fig. 8. I. R. spectra of natural zeolites substituted by various cations at 25°C.

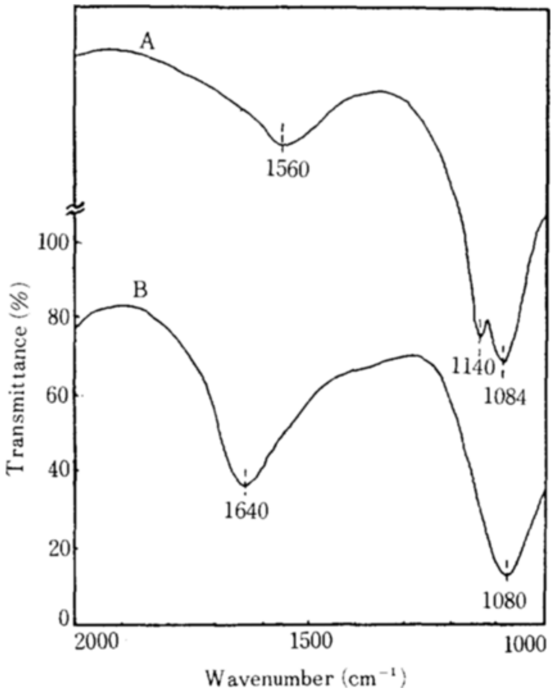

Fig. 9. I. R. spectra of cupric sulfate.

A : KBr pellet method
B : Si wafer method

tiate one from another.

5. For KBr-reactive samples

There have been considerable doubt to the cursory study of the i.r. spectra taken for solid samples which are reactive with KBr. For example, an efflorescent sample, cupric sulfate, was investigated, and the i.r. spectra are shown in Fig. 9.

The 1640cm^{-1} hand obtained by KBr method was assigned to the O-H bending vibration, and the 1080cm^{-1} band to the S-O stretching vibration[19]. On the other hand, in the i.r. absorption obtained by the silicon wafer method, the band at 1560cm^{-1} was assigned to the O-H bending vibration and those at 1140cm^{-1} and 1084cm^{-1} were assigned to the S-O stretching vibration. Difference in the observed spectra may be attributed to specific chemical reactivity of the cupric sulfate with KBr. However, surface of silicon wafer was stable and no interactions with the sample at the experimental temperature were observed. Conclusively, the silicon wafer method is recommended for reactive samples to obtain more accurate absorption bands.

6. For unstable samples

The magnesium oxide, an example of brittle samples, is unable to pelletize or becomes less self-supporting after severe heat treatment. However, the spectrum of magnesium oxide coated and on silicon

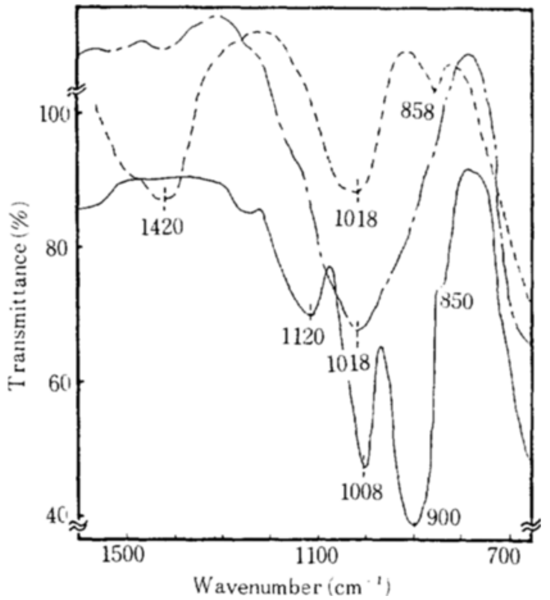

Fig. 10. I. R. spectra of MgO on Si wafer.
----- room temperature
—·— calcined at 600℃ for 3hrs.
—— calcined at 900℃ for 3hrs.
The transmittance scale applies to the spectrum at 900℃.

wafer at room temperature are illustrated in Fig. 10.

The 1420cm^{-1} band assigned to the C-O band in CO_3 gradually diminished with rising temperature and disappeared completely at 600°C. Similarly, Aika and Lunsford[20] observed the C-O band in CO_3 at 1462-1454cm^{-1} on the i.r. spectrum. The carbonate was caused by CO_2 adsorption on MgO in air.

Although the previous report[21] for the adsorption of CO_2 on MgO gave a somewhat different spectrum, it coincided in that the C-O band disappeared at 600°C with our result in Fig. 10.

Magnesium oxide which was calcined at 900°C on the silicon wafer had i.r. absorption at 1120cm^{-1}, 1008cm^{-1}, 900cm^{-1} and 850cm^{-1} those were assigned to the various Mg-O stretching vibration [22]. The sample heated at 900°C had complicated absorption bands, possibly due to its interaction with silicon wafer. This is attributed to the destruction of the protective layer to have oxidized surfaces to react significantly with MgO.

CONCLUSION

The silicon wafer exhibited its characteristic thermal stability remaining stable against significant oxidization below 800°C, and transparent to the i.r. beam. The i.r. absorption bands of silica were observed at 1090cm^{-1}, 805cm^{-1}, 470cm^{-1} at elevated temperatures. They were assigned to the asymmetric and symmetric stretching vibrations, and to the bending vibration of SiO_2, respectively. The Si-O bands shifted to higher frequencies with increasing oxygen contents in silica.

As a result of applying this techique to the studies of gas adsorption on the brittle mineral samples and on the efflorescent samples those unable to be self-supported, we concluded that this method were obviously useful for obtaining sharper spectra with high resolutions. Besides, this technique was more effectively applicable to the samples such as cupric sulfate which were chemically reactive with KBr than any other mothods.

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