PROPERTIES OF IR SPECTRA OF PHOSPHORUS DOPED SiO$_2$ FILMS

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1. Introduction

The phosphorus doped SiO$_2$ films deposited by pyrolysis are succesfully used as diffusion sources in the semiconductor technology. The characteristics (surface concentration of the dopant, p-n junction depth) of the diffusion layer in the Si substrate obtained with the help of the doped SiO$_2$ film can be calculated knowing the P-concentration of the film and some parameters of the diffusion.

The phosphorus concentration of the SiO$_2$ film can be determined with the help of infrared (IR) absorption [1, 2]. This procedure is based on the fact that the P-concentration of the SiO$_2$ film is directly proportional to the area below the absorption-wave number curve corresponding to the P=O bond. Since the absorption band of the P=O bond is found in the 1200 to 1500 cm^{-1} wave number interval — according to Nakamoto [3] — therefore the absorption spectra of the SiO$_2$ films were determined primarily in the 1200 to 1600 cm^{-1} interval. Several absorption peaks were observed to appear in this wave number interval.

Two interdependent problems arise in connection with the foregoing peaks:
1. Which absorption bands are related to the P=O bond?
2. Which atomic groups correspond to the remaining absorption peaks?

Considering the use of the P-doped SiO$_2$ films as diffusion sources, it is important to answer the above mentioned questions.

2. Experimental

For the purpose of IR transmission measurements, phosphorus doped SiO$_2$ films were deposited onto two-side polished Si slices. For deposition the pyrolytical decomposition of tetraethoxysilane (TEOS; Si(OC$_2$H$_5$)$_4$) and dopant

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material was used. The dopant materials were: triethylphosphate (TEF, $C_6H_{15}O_4P$) and phosphoroxychlorid (POCl$_3$).

The mixture of TEOS and dopants (POCl$_3$, TEF) was introduced through bubbling system with N_2 gas into the reaction space, where oxidation occurred at 520 °C.

Table 1

Data of samples used in IR transmission and diffusion measurements

Sample	Substrate [Ohm · cm]	SiO$_2$ film		C_f [atom/cm^3]
		d [nm]	dopant	
AT	6.3	135	TEF	$\times 10^{18}$
BT	6.3	139	TEF	—
CT	6.3	153	TEF	9.2
DT	6.3	158	TEF	—
ET	6.3	167	TEF	—
FT	7.85	651	TEF	3.0
GT	7.85	633	TEF	—
HT	7.85	632	TEF	—
IT	7.85	597	TEF	—
JT	7.85	610	TEF	1.0
KT	7.85	602	TEF	—
LT	7.85	537	TEF	—
MT	7.85	889	TEF	—
NT	7.85	910	TEF	—
OT	7.85	926	TEF	—
PT	7.85	868	TEF	—
AP	6.3	338	POCl$_3$	—
BP	6.3	334	POCl$_3$	—
CP	6.3	306	POCl$_3$	47.5
DP	6.3	301	POCl$_3$	—
EP	6.3	304	POCl$_3$	—
FP	4.5	382	POCl$_3$	80
GP	4.5	386	POCl$_3$	300
HP	4.5	391	POCl$_3$	—
IP	8.0	336	POCl$_3$	—
JP	8.0	344	POCl$_3$	—
KP	8.0	367	POCl$_3$	—
LP	8.0	398	POCl$_3$	—
MP	8.0	426	POCl$_3$	—
NP	8.0	503	POCl$_3$	400

In order to find the limits of the spectrum relating to the P=O group in the 1200 to 1600 cm^{-1} interval, diffused layers of different surface dopant concentrations were prepared making use of SiO$_2$ films of different initial P-concentrations. The diffusion processes were carried out at 1100 °C in N$_2$-atmosphere. The surface concentrations were determined by the method of IRVIN [13], making use of the surface resistivity of the diffused layer and the p-n junction depth. The data of the SiO$_2$ films and Si substrates are summarized in Table 1.

The IR transmission and attenuated total reflection (ATR) spectra of the SiO$_2$ films were measured using a Zeiss UR 10 double beam recording spectrophotometer. The absorption coefficients as a function of wave number were calculated by the method described in [2].

The ATR measurements were performed making use of the ATR attachment produced in the Institute for Technical Physics [4]. Samples of parallelepiped shape, prepared from high purity Si were applied in the ATR measurements. The sample surfaces were coated by the SiO$_2$ films to be examined. The data of the ATR samples and the SiO$_2$ films are contained in Table 2.

Table 2

Data of samples used in ATR measurements

Sample	SiO₂ film			Si substrate		
	d* [um]	dopant	preparation	Ohm · cm	type	N
TA 2	321	TEF	pyr.	195	n	38
H3 Si	821	---	therm.	300	n	10

pyr:. pyrolytically deposited
therm.: thermally grown
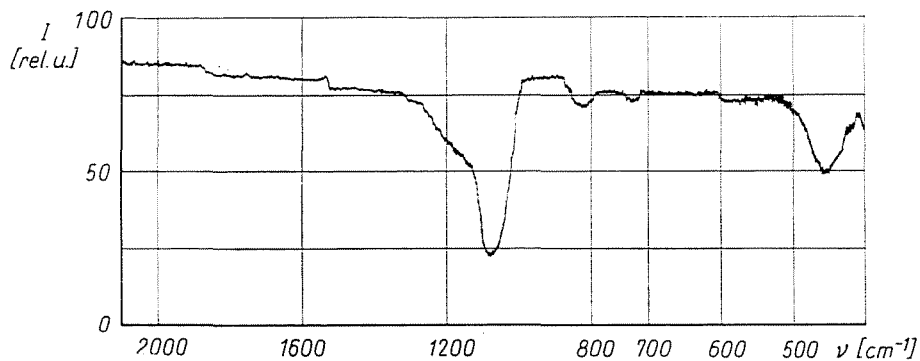* The total thickness of the SiO₂ films being on both sides of the ATR sample

Fig. 1. The transmission spectrum of the TEF doped pyrolytically deposited SiO₂ film in the 400 to 2100 cm^{-1} interval

The transmission spectrum of TEF doped SiO₂ film is shown in Fig. 1, while the ATR spectrum of the same film is shown in Fig. 2. For the purpose of comparison, the transmission (Fig. 3) and the ATR spectra (Fig. 4) of the pure SiO₂ film were recorded.

Comparing Figs 1 and 2, the difference between the spectra of doped SiO₂ and pure film is seen to be small; under these conditions considerable errors can occur in the calculated absorption coefficients. The mean values of wave numbers $\bar{\nu}$ corresponding to the absorption peaks, their standard deviations and probability frequencies of the peak appearance p are contained in Table 3.
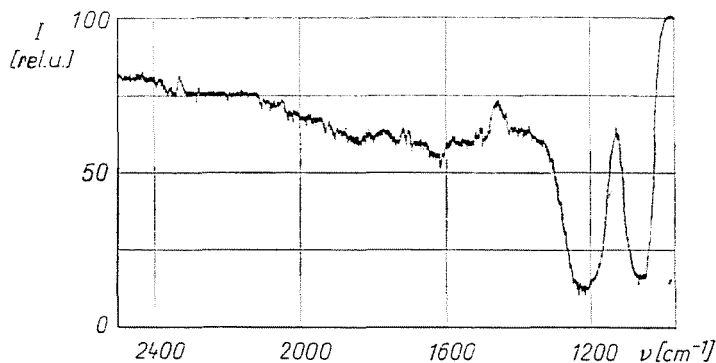

Fig. 2. The ATR spectrum of the TEF doped pyrolytically deposited SiO₂ film in the 1000 to 2500 cm⁻¹ interval

Table 3

The mean values of the wave numbers $\bar{\nu}$ relating to the absorption peaks, their standard deviations $\delta\nu$ and probability frequency p

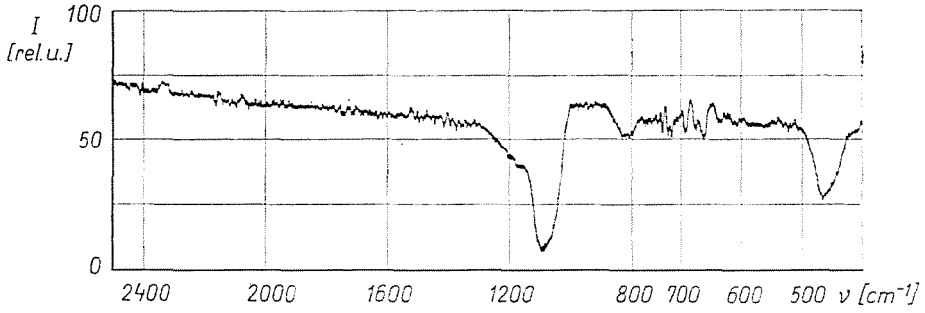| Serial number of the peaks	Dopant: TEF			Dopant: POCl₃		
	$\bar{\nu}$ [cm⁻¹]	$\delta\nu$ [cm⁻¹]	p	$\bar{\nu}$ [cm⁻¹]	$\delta\nu$ [cm⁻¹]	p
1.	1305	9	1	1303	8	1
2.	1340	8	1	1332	10	1
3.	1363	6	1	1361	6	1
4.	1395	7	1	1403	9	0.9
5.	1423	5	0.25	1419	2	0.47
6.	1461	9	1	1456	10	1
7.	1501	6	0.94	1498	7	0.76
8.	1536	5	0.75	1534	5	0.53
9.	1469	5	0.90	1564	9	0.88
10.	1598	9	0.34	1588	3	0.20

Fig. 3. The transmission spectrum of the pure thermally grown SiO₂ film in the 400 to 2500 cm⁻¹ interval
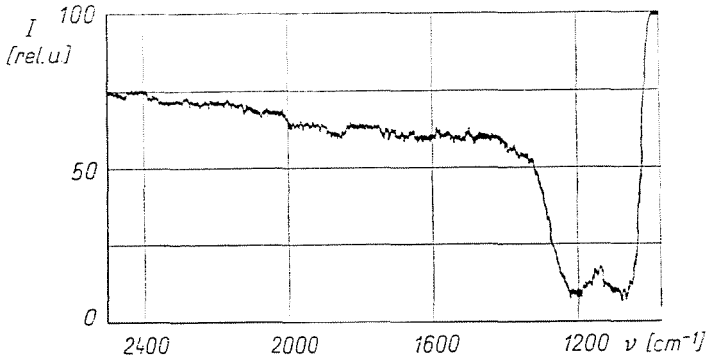
Fig. 4. The ATR spectrum of the pure thermally grown SiO₂ film in the 1000—2500 cm⁻¹ interval
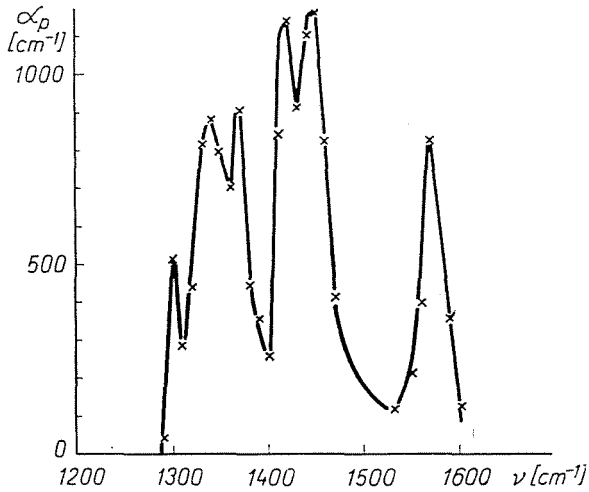
Fig. 5. The difference between the absorption coefficients of TEP doped and pure SiO₂ films as a function of wave number
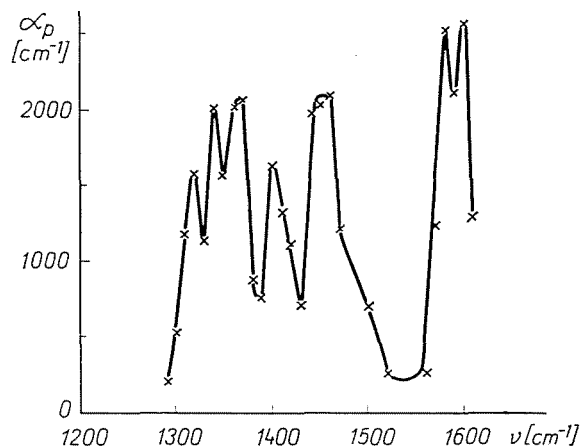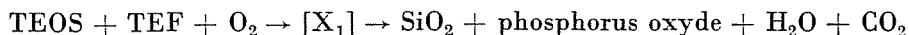
Fig. 6. The difference between the absorption coefficients of POCl$_3$ doped and pure SiO$_2$ films as a function of wave number

The difference between the absorption coefficients relating to the doped and pure SiO$_2$ films as a function of wave number is shown in Fig. 5 for TEF dopant (sample CT); and this function for POCl$_3$ dopant is shown in Fig. 6 (sample HP). The absorption coefficients were calculated from the recorded curve, using the method described in [2].
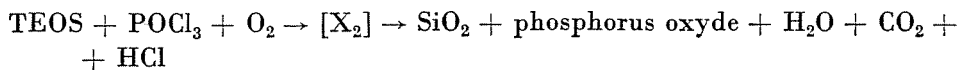
3. Discussion

The course of reaction during the deposition of the doped SiO$_2$ film can be considered as the pyrolytic decomposition of alcoxysilanes [5]. Namely, the decomposition of the alcoxysilanes is realized through formation of complex radicals. The radicals of type R$_3\overset{\bullet}{\text{Si}}$; R$_2\overset{\bullet}{\text{Si}}$—O, O=$\overset{\bullet}{\text{P}}$(OR), O=$\overset{\bullet}{\text{P}}$(OR$_2$) and O=P—$\overset{\bullet}{\text{O}}$ formed in the reaction space are chemisorbed on the surface of the Si substrate, where their further decomposition occurs [6]. Finally a SiO$_2$ film containing phosphorus is formed.

Considering the above mentioned conception and the conditions of the pyrolysis, the reaction equations of principle can be written as follows:
for TEF dopant:

$$\text{TEOS} + \text{TEF} + \text{O}_2 \rightarrow [\text{X}_1] \rightarrow \text{SiO}_2 + \text{phosphorus oxyde} + \text{H}_2\text{O} + \text{CO}_2$$

for POCl$_3$ dopant:

$$\text{TEOS} + \text{POCl}_3 + \text{O}_2 \rightarrow [\text{X}_2] \rightarrow \text{SiO}_2 + \text{phosphorus oxyde} + \text{H}_2\text{O} + \text{CO}_2 + \\ + \text{HCl}$$

where $[X_1] = A_1 \rightarrow B_1 \rightarrow \ldots \rightarrow Z_1$
$[X_2] = A_2 \rightarrow B_2 \rightarrow \ldots \rightarrow Z_2$
are consecutive reactions.

In principle several oxides and acids can form with phosphorus (e.g. P_4O_6, P_4O_7, P_4O_8, P_4O_9, P_4O_{10} and H_3PO_2, HPO_2, $H_4P_2O_5$, H_3PO_3, $H_4P_2O_6$, HPO_3, $H_4P_2O_7$, H_3PO_4) [7].

Since the oxidation value of both TEF and $POCl_3$ is 5, and as the pyrolysis is basically an oxidizing process, therefore it is probable that the oxide formed consists mostly of P_4O_{10}. It is to be noted that differences between the IR spectra of the different phosphorus oxides are too small to be distinguished even in the case of pure phosphorus oxides.

It can be concluded from the foregoing train of thought that the thin film deposited by pyrolysis is composed primarily of SiO_2 and phosphorus oxide (probably P_4O_{10}). The film would contain H_2O, OH groups, C, CO_2, hydrocarbon groups and in the case of $POCl_3$ dopant HCl as contaminations. Therefore, besides peaks relating to the P=O, P—O and P—O—P groups, peaks corresponding to the impurities may appear in the IR absorption spectrum.

Examining the absorption peaks contained in Table 3 it can be stated that peaks 1 to 5 relate to the P=O bond. This can be proved in the following way:

For the absorption coefficient corresponding to the P=O group the relation

$$\alpha = \sigma(\nu) \, C_0 \tag{1}$$

holds, where
σ is the absorption cross section of the P=O group,
ν the wave number,
C_0 the P concentration of the SiO_2 film. On the other hand, according to [2]:

$$C_0 = f \cdot C_s \tag{2}$$

where C_s is the surface P-concentration of the diffused layer, and f is a function of the segregation coefficient, and of diffusion coefficients of P in SiO_2 and Si, resp. The coefficient f is constant at invariant temperatures, therefore, according to formulas (1) and (2), α is in direct proportion to C_s. Consequently the rate of absorption coefficients equals the rate of surface concentrations. The ratio of surface concentrations (C_{s1}/C_{s2}) for different diffused layers and the mean values of $\alpha(1)/\alpha(2)$ rates for peaks 1—2, 1—3, ... 1—10 (see Table 3) are summarized in Table 4. C_{s1}/C_{s2} is seen to closely approximate $\alpha(1)/\alpha(2)$ if the peaks 1—5, 1—6 are involved into the mean value. The deviation between C_{s1}/C_{s2} and $\alpha(1)/\alpha(2)$ is greater in the case of peaks 1—7...1—10. Moreover, SIMS (secondary ion mass spectroscopy) measurements on pyrolytically depos-

ited SiO_2 films have revealed the presence of CH_2 and CH_3 groups in the film [12]. The peak 6 can be assigned to these hydrocarbon groups [8]. This means that the peaks 1—5 follow the variations of the P-concentration, therefore the spectrum between 1284 ± 12 cm^{-1} and 1433 ± 6 cm^{-1} relate to the P=O groups.

Table 4

The ratio of surface concentrations (C_{S1}/C_{S2}) for different diffused layers prepared with P-doped SiO_2 films and the mean values of peak absorption coefficient rates ($\alpha(1)/\alpha(2)$) for the oxide films in the 1300 to 1600 cm^{-1} interval

Sample	Dopant	C_{S1}/C_{S2}	$\alpha(1)/\alpha(2)$								
			1—2	1—3	1—4	1—5	1—6	1—7	1—8	1—9	1—10
CT: 1, FT: 2	TEF	3.1	5.1	4.0	3.3	3.0	2.8	2.5	2.3	2.3	2.3
NO: 1, CP: 2	$POCl_3$	1.3	1.6	1.5	1.6	1.5	1.5	2.1	2.0	2.0	1.9
CP: 1, FP: 2	$POCl_3$	0.6	1.4	1.3	1.1	0.9	0.8	1.0	1.0	1.2	1.4

A further evidence of the foregoing statement is provided by the ATR spectrum of the P-doped SiO_2 film (Fig. 2). In this spectrum, absorption peaks have been found at 1305 cm^{-1}, 1330 cm^{-1}, 1354 cm^{-1}, 1372 cm^{-1}, 1404 cm^{-1}, 1416 cm^{-1} and 1424 cm^{-1} wave numbers; the end of this band is at 1442 cm^{-1}. Remark that the peaks 1—10 are hardly visible in the transmission recorded curve, they are revealed by the calculated absorption coefficient — wave number function.

Another evidence of the above mentioned statement is that probability frequencies of the peaks 1—4 are equal to about 1, that is in general they appear together in the spectra. Therefore they are caused by intentionally introduced dopant rather than by the contaminants.

The absorption band of the P—O bond is in the 900 to 1200 cm^{-1} interval [3, 8]. Though in the transmission recorded curve (Fig. 1) "steps" are found in this interval (at 1130 cm^{-1}, 1160 cm^{-1}, 1200 cm^{-1}), however, at most the peak at 1130 cm^{-1} can be assigned to P—O bond. That is, the steps at 1160 cm^{-1} and 1200 cm^{-1} are also found in the spectrum of the pure SiO_2 film (Fig. 3).

The recognition of the absorption peak relating to the P—O bond in the SiO_2 film is still made more difficult by the overlapping absorption bands. An intensive absorption band appears at 1215 cm^{-1} in the ATR spectrum (Fig. 2) of the P-doped SiO_2 film. Beside this band another intensive band (νSiO_2) is seen at 1048 cm^{-1}. In the transmission curve only a small step is seen at 1215 cm^{-1} (Fig. 1).

We are of the opinion that the absorption peak at 1215 cm^{-1} does not relate neither to P=O nor to P—O bonds. Namely, a similar absorption

peak is seen at 1200 cm^{-1} in the ATR spectrum of the pure SiO$_2$ film (Fig. 4). (The ν(SiO$_2$) band is at 1062 cm^{-1} in this spectrum.)

In a previous paper [9] an ATR absorption peak at 1189 $\pm$ 9 cm^{-1} has been described, and assigned to a SiO$_2$ modification of denser (perhaps crystalline) structure with higher oscillator force than the average of the amorphous SiO$_2$ film.

Comparing the spectra in Figs 2 and 4, the conclusion can be drawn that the above mentioned SiO$_2$ modification is present both in pure and in P doped SiO$_2$ films. However, there are differences between the ATR spectra of the two kinds of SiO$_2$ films, namely:

a) The wave number of the peak in the case of a P-doped film is higher (1215 cm^{-1}) than for a pure thermally grown SiO$_2$ film (1200 cm^{-1}).

b) In the spectrum of the P-doped film the absorption band (at 1215 cm^{-1}, Fig. 2) is more separated from the ν(SiO$_2$) band than the corresponding band (at 1200 cm^{-1}) in the spectrum of the pure film (Fig. 4). The difference between the peak's wave numbers of the ν(SiO$_2$) and the other bands in question are:

for P-doped SiO$_2$: $\Delta\nu = 147$ cm^{-1} and

for pure SiO$_2$: $\Delta\nu = 138$ cm^{-1}.

From the results described above it can be concluded that the oscillator force is higher in the mentioned SiO$_2$ modification of P-doped SiO$_2$ and it is more separated from the amorphous SiO$_2$ than in the thermally grown SiO$_2$ films. Thus the formation of this denser SiO$_2$ phase may be enhanced by the P-dopants. In the case of boron-doped SiO$_2$ films, V. G. Litovchenko came to the same conclusion [10].

The absorption band relating to the δ(O—P—O) vibration is in the 300 to 650 cm^{-1} interval [3]. In the transmission spectrum (Fig. 1) only the peak (at 453 cm^{-1}) corresponding to δ(SiO) vibration has appeared in the 400 to 650 cm^{-1} interval.

The spectra revealed the presence of some contaminants in the SiO$_2$ films. Primarily peaks of OH groups and H$_2$O appeared in the spectra, they are shown in Table 4 (peak number 10), Fig. 2 (peak at 1610 cm^{-1}) and the ATR absorption band obtained in the 2700 to 3660 cm^{-1} interval.

Accordingly, P=O and OH groups were detected in the doped SiO$_2$ film, therefore presence of O=P—OH groups in the film is realizable. This seems to be proved by the band in the 1580 to 1700 cm^{-1} interval (Fig. 2) containing a step at 1670 cm^{-1} [8].

According to [11], CO$_2$ can also be built into the SiO$_2$ film. The small peak in the ATR spectrum at 2340 cm^{-1} indicates the presence of CO$_2$ in the oxide film.

Acknowledgements

Summary

Information has been obtained on the composition of P-doped pyrolytically deposited SiO_2 films from their IR transmission and ATR spectra. The absorption band (calculated by substracting the pure SiO_2 absorption from the total absorption) in the interval 1284 and 1433 cm^{-1} related to the $P=O$ group. This conclusion can be drawn from comparing results of IR transmission, ATR, diffusion and SIMS measurements.

The intensive absorption band at 1215 cm^{-1} in the ATR spectrum of P doped SiO_2 films have been assigned to inhomogeneities in the film of denser structure, having higher oscillator force than the average amorphous SiO_2. These inhomogeneities are similar to those previously revealed by the ATR spectra of thermally grown SiO_2 films [9].

The presence of some contaminants can be inferred from the IR transmission and ATR spectra of pyrolytically deposited SiO_2 films. Primarily the absorption bands of OH groups and H_2O appear in the spectra, but a minor quantity of hydrocarbon groups, CO_2 and $O=P--OH$ groups are also contained by the films.

References

1. TENNEY, A. S.—GHEZZO, M.: J. Electrochem. Soc. **120**, 1276 (1973)
2. HOFFMANN, G.—NAGY, A.—PUSKÁS, L.: J. Phys. D: Appl. Phys. **8**, 1044 (1975)
3. NAKAMOTO, K.: Infrared Spectra of Inorganic and Coordination Compounds. J. Wiley, New York (1963)
4. SCHANDA, J.—SASS, G.: MÜFI Közl. **03**, 33 (1971)
5. KHLERER, J.: J. Electrochem. Soc. **112**, 503 (1965)
6. VESZPRÉMI, T.: HIKI Közl. **11**, 55 (1972)
7. NAGY, J.: Theoretical and Inorganic Chemistry. III. Tankönyvkiadó, Budapest, 1976 (in Hungarian)
8. HOLLY, S.—SOHÁR, P.: Infrared Spectroscopy. Műszaki Könyvkiadó, Budapest, 1968 (in Hungarian)
9. HOFFMANN, G.—NÉMETH-SALLAY, M.—SCHANDA, J.: Acta Phys. Acad. Sci. Hungaricae **36**, 349 (1974)
10. LITOVCHENKO, V. G.: (Semiconductor Research Institute, Kiev) (private communication)
11. PLISKIN, W. A.—SIMMONS, R. C.—ESCH, R. P.: Infrared Spectra of CO_2 and CO in RF-Sputtered SiO_2 Films. Thin Film Dielectrics Ed. by F. Vratny The Electrochem. Soc. Inc., New York)1969)
12. ROMANOVA, G. F.: (Semiconductor Research Institute, Kiev) (private communication)
13. IRVIN, J. C.: Bell Syst. Tech. J. **41**, 387 (1962)

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