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PROPERTIES OF VARIOUS SILICON OXIDE PHASES IN THIN FILMS

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16. Abstract

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PROPERTIES OF VARIOUS SILICON OXIDE PHASES IN THIN FILMS

E. Ritter*

Summary:

A survey is given on the properties of various silicon oxide phases in thin films. The properties of SiO- and Si_2O_3- film are more thoroughly discussed in relation to chemical and structural changes.

1. Historical Development /42**

SiO_2 is often used because of its exceptional dielectric properties and its strength in optics and in electrical technology. Therefore, it was natural to refer to this material in the development of thin film technology.

During the second World War, this was already possible using a chemical method at industrial levels (precipitation of colloidal acetic acid from solutions) [1]. For vacuum deposition however, a detour had to be used because silicon oxide was reduced to silicon monoxide [2-4] in the directly heated vaporization sources available to the beginning of the 40's [2-4]. Therefore, this deficiency was taken advantage of and silicon monoxide was directly vaporized. Either a mixture of Si and SiO_2 was heated or so-called "solid SiO" was used, which was obtained by sublimation from a mixture of

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Si and SiO_2 [2-4].

The layers obtained in this way are hard and durable and are well suited as protective layers and as replication layers [4]. They can be used as electrical insulation layers [5], as dielectric layers in the IR range [6] and as deposition media for so-called Cermet layers [7,8].

The strong absorption of above 550 nm [9] and a refraction value of 1.8-2.0 [9] means that it cannot be used in optical multilayer systems. Such a high loss factor compromises the usefulne as a condensation dielectric [5].

By means of subsequent tempering or by vaporization at an increased residual gas pressure, a certain degree of improvement was achieved [4,9] which however was not sufficient. At the beginning of the 50's, Auwärter discovered a method of reactive vaporization [10] which was a significant advance. A suboxide, silicon monoxide in our case, is vaporized in an oxygen atmosphere at about 10^{-4} Torr. By correctly selecting the parameters, both hard and strongly adhering layers are achieved in spite of the increased pressure, which are sufficiently oxidized. Using this method, the absorption in the visible ranges is for the most part eliminated and the refraction index is reduced to 1.55. In this way, it become possible to use these layers for more complicated multilayer systems. This represented a technical advance in the optical use of thin layers [11].

A detailed investigation of Cremer, Kraus and Ritter showed that this improvement is achieved already for the rough composition of the layers of $SiO_{1.5}$ [12]. Such layers are therefore often called Si_2O_3 layers since that time. Si_2O_3 layers are also used for electrical technical applications, and the loss factor can be reduced to 2-0.1 % [13].

At the beginning of the 60's, because of the development of high performance electron beam vaporization sources, it became possible to directly vaporize SiO_2 without reduction [14]. /43 At the same time, high performance methods and installations for reactive and high frequency vaporization were developed, with which high quality SiO_2 layers could be produced [15,16]. SiO and Si_2O_3 layers therefore are in part replaced today by pure SiO_2 layers.

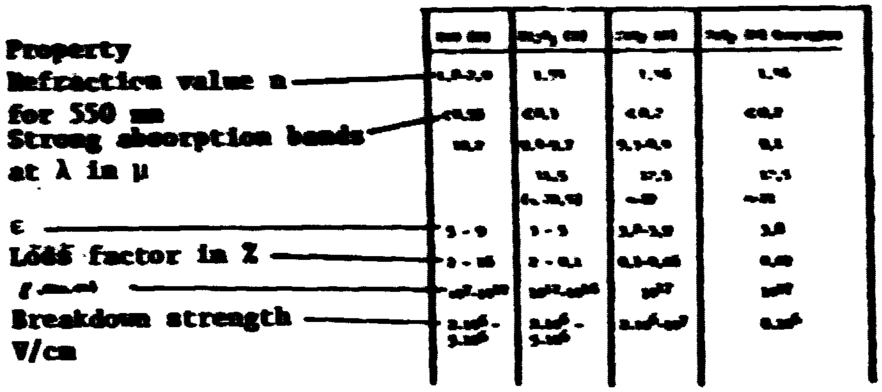
After this short summary, we will now describe the properties of individual silicon oxide phases in thin layers and will compare them.

2. The Properties of Various Silicon Oxide Phases

Figure 1 is a summary of the important properties. The values were taken from various publications and should be a representative cross-section of values. On the right side we show values of quartz glass for comparison.

It can be seen that the SiO_2 layers are quite close to the values for quartz glass. Smaller deviations depend primarily on the porosity of the layers. For electron beam vaporization, very thin layers are only obtained at increased substrate temperatures (T> 200°C). Measurements of Hacman in SiO_2 layers vaporized using an electron beam in the UHV, result in a packing density of 95% for substrate temperatures of about 50° C. They are 98.7% for substrate temperatures of 250° C [17]. Even for reactive vaporization, increased substrate temperatures are recommended in order to reduce the porosity of the layers [18]. Using high frequency atomization, very dense SiO_2 layers can be obtained [16].

Si_2O_3 and especially SiO layers deviate from the properties of quartz glass to an increasing degree. The dielectric properties become poorer, with the exception of the increased dielectric



Property	[illegible]	[illegible]	[illegible]	[illegible]
Refraction value n for 550 nm	[illegible]	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]	[illegible]
Strong absorption bands at λ in μ	[illegible]	[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]
		[illegible]	[illegible]	[illegible]
ε	3 - 9	3 - 5	[illegible]	[illegible]
Loss factor in %	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Breakdown strength V/cm	[illegible]	[illegible]	[illegible]	[illegible]

Figure 1.
Properties of various silicon oxide phases(S= layer, M= solid material)

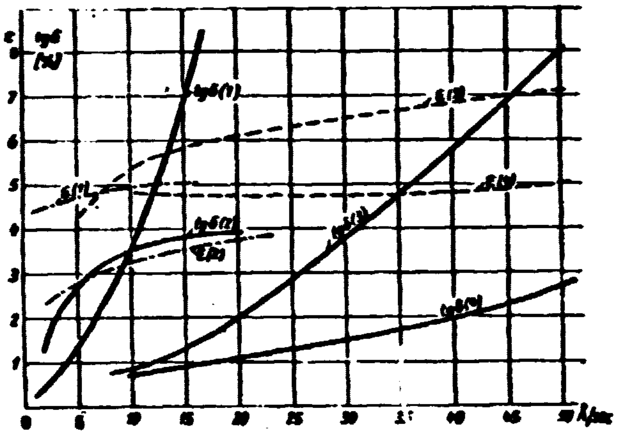


Figure 2.
Dielectric constant ε and loss factor tgδ of SiO-layers from various authors according to Zinsmeister [19].

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constant of the SiO, which has to be bought with a high loss factor. We will attempt to give an explanation of this later on using the structural model.

It is also remarkable that the data have a large scatter. Figure 2 shows an example of values for the dielectric constant and the loss factor of SiO layers as a function of the vaporization rate, taken from various papers [19]. The scatter of the values, especially for the SiO layers is related to two causes:

1. **Fluctuations in the composition of the layers**
2. **Structural changes in the layers**

Explanation to 1: SiO is easily oxidized during condensation if the corresponding partners are available, expecially oxygen and water vapor. Only a few papers refer to layers having the exact SiO composition with certainty. In many cases, we have a composition of the layers which varies between $SiO_{1.0}$ - $SiO_{1.3}$. For pure SiO layers, we can assume that the value deviates more from SiO_2 , for example $n = 2.0$, $\varepsilon = 9$, $\phi = 10^7$.

For intentional reactive vaporization, the degree of oxidation increases rapidly to about $SiO_{1.5} = Si_2O_3$. Since Si_2O_3 layers correspond much better to the SiO_2 layers, than would be expected from a linear decrease from SiO to SiO_2, most of the transition takes place from the SiO values to the quartz glass values in the range SiO - Si_2O_3. This makes it possible to more easily understand the large scatter in the reported values.

After the importance of the degree of oxidation was determined for the layer properties, numerous properties were investigated as a function of the degree of oxidation. Sometimes, the oxidation degree of the layers itself was not used as a parameter, but instead a collision number ratio O_2/SiO in the condensation surface

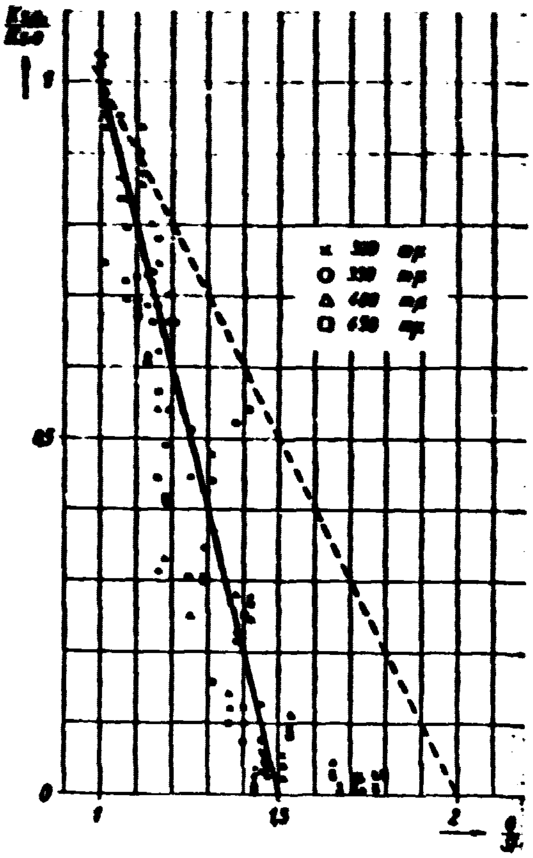

Figure 3.
Relative extinction constant of SiO$_x$ layers as a function of the quotient O/Si referred to the extinction constant of O/Si = 1 according to Cremer, Kraus and Ritter [12].

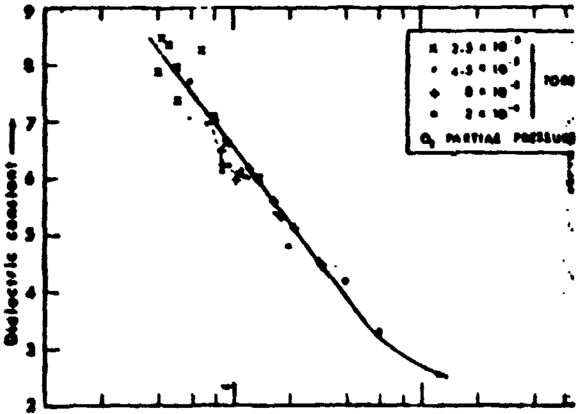

Figure 4.
Relationship between ε and collision number ratio p/r (p = illegible r = SiO) for vaporization according to Anastasio [20].

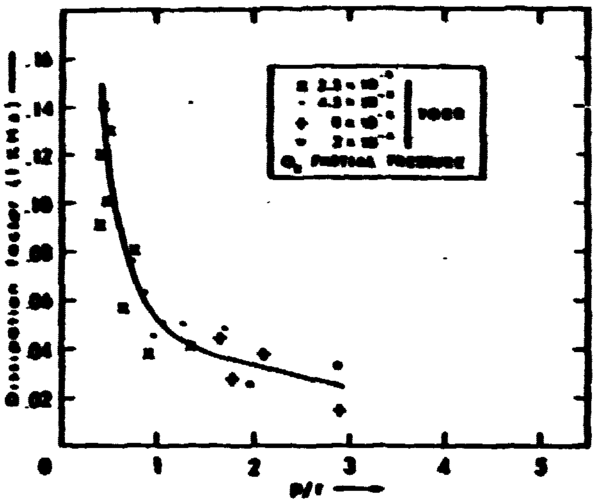

Figure 5.
Relationship between loss factor and collision number ratio p/r (p = O_2, r = SiO) for vaporization according to Anastasio [20].

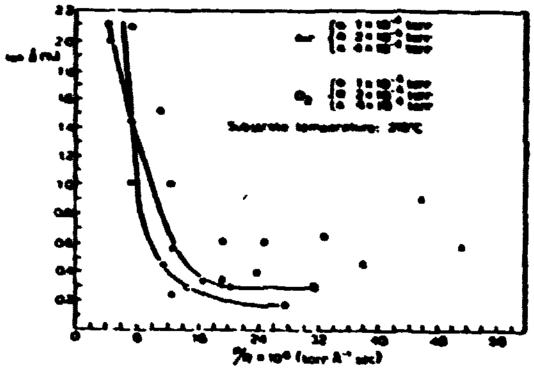

Figure 6.
Relationship between loss factor and collision number ratio P/R ($P=O_2$, pressure in Torr, R = SiO in Å/sec for vaporization according to Poat [21].

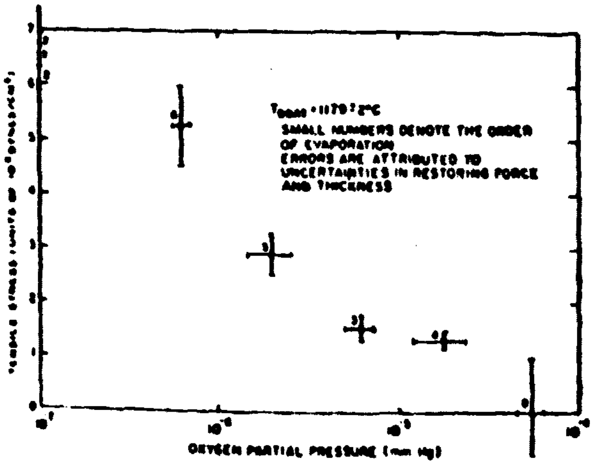

Figure 7.
Layer voltage as a function of O_2 partial pressure for vaporization according to Priest, Caswell and Budo [22].

which determines it.

Figure 3 shows the decrease of the normalized extinction /44 constant as a function of the layer composition according to Cremer, Kraus and Ritter [12]. The fact that the absorption vanishes already for a ratio $SiO_{1.5}$, leads to the assumption of Si_2O_3 phase.

Figure 4 gives a decrease in ε from 9 to 3 with increasing collision number ratio according to Anastasio [20]. The collision number ratios correspond to the range SiO-Si_2O_3. Figure 5 given by the same author shows the decrease in the loss factor from 16 to 2% in the range $SiO_{1.0}$-$SiO_{1.2}$. Figure 6 was taken from a paper of Poat [21] and gives the continuation for higher collision number ratios corresponding to about $SiO_{1.3}$ to $SiO_{1.7}$. (Decreased from 2.0 to 0.2%. The indicated secondary increase is caused by the installation of water vapor in the porous layers, a very high collision number ratio).

In Figure 7, according to measurements of Priest, Caswell and Budo [22], the stresses in the layers are plotted against the oxygen partial pressure. We can observe a decrease in the tensile stresses with increasing oxygen partial pressure, that is an increasing degree of oxidation.

These examples were intended to demonstrate the dependence of the layer properties on the degree of oxidation.

2. Changes in the properties of SiO and Si_2O_3 layers due to structural changes without changes in the chemical overall composition are not investigated as much and are not known as much. These structural changes usually occur when energy is supplied by tempering or by irradiation with UV.

Cremer and Pulker [23] reported about the decrease in the

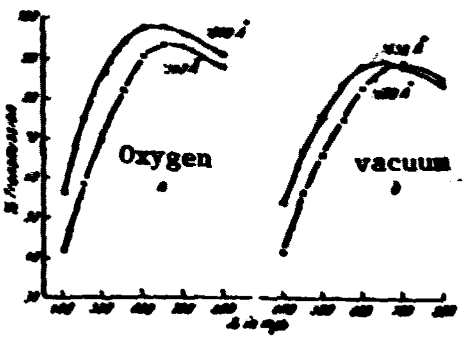

Figure 8.
Permeability of SiO layers before (x) and after (o) tempering at 300° C in oxygen and in a vacuum as a function of layering according to Cremer and Pulker [23].

a - tempering in the O_2 atmosphere

b - tempering in a vacuum

Layer thickness about the same in both experiments

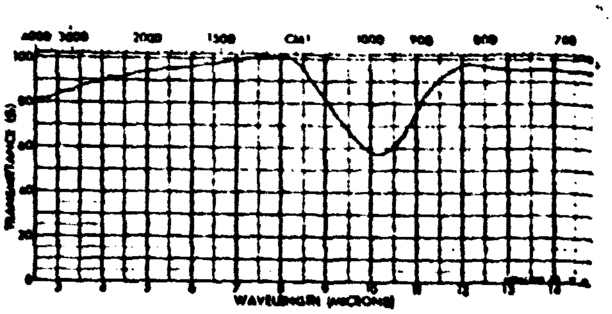

Figure 9.
Infrared transmission curve of a SiO layer 2200Å thick according to Ritter [42].

optical absorption of the SiO layers by tempering at 300°C in an inert atmosphere or in a vacuum without changes in the chemical composition of the layers. Up to that time, the decrease in the absorption was always observed during oxidation of the SiO layers.

Figure 8 shows the permeability curve before and after tempering treatment, for tempering in oxygen (oxidation) and for tempering in a vacuum (no oxidation). A similar effect as for vacuum tempering occurs during vaporization onto substrates at a high temperature.

Garski [24] investigated SiO_x layers ($x = 1.0$-1.2) in detail for changes in the IR spectrum, which resulted in no important changes in the composition after long time tempering at 350° and 600°C. Large changes were found and we will discuss these later on.

If tempering is carried out in an inert atmosphere at a very high temperature (700°-900°C), then there is a strong absorption increase in SiO layers and there is an increase in the refraction value, as described by Hass[4], Hass and Salzberg [9] and Nishimura et. al. [25].

Bradford and Hass [26], Bradford, Hass, McFarland and Ritter [27], as well as later on Mickelsen[28] and Hodgkins [29] observed the reduction of the UV absorption of Si_2O_3 layers for irradiation with ultraviolet radiation. A substantial part of the UV absorption can be removed without simultaneous oxidation of the layers.

Mickelsen also found that with UV irradiation there was a /45 reduction in the loss factor from 0.4 to 0.15%. These effects can only be understood after a closer analysis of the structure

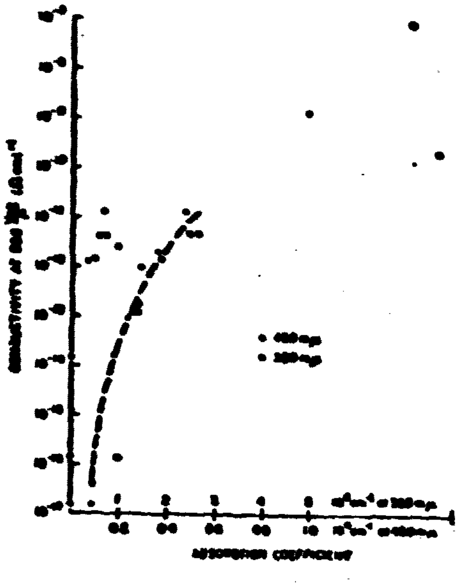

Figure 10.
Relationship between productivity and optical absorption coefficient according to Johansen [43].

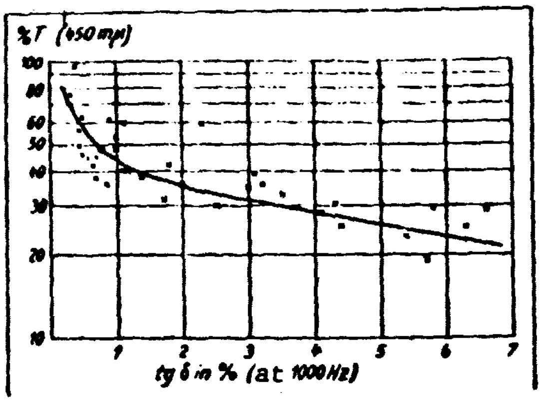

Figure 11.
Relationship between optical transmission and loss factor according to Ritter [44].

of the layers.

3. Discussion of the Structural Models for SiO and Si_2O_3

The existance of a SiO compound is demonstrated only in the gaseous state [30-32].

Solid SiO phases (massive or thin layers) are amorphous to x-rays. A diffuse refraction ring with d = 3.6Å is indicated to be characteristic [2-4]. For condensation temperatures over about 800° C or for subsequent heating above 700° C, amorphous silicon and amorphous SiO_2[2,4] appears in the refraction image. For higher tempering (> 900° C), the refraction diagram of crystalline Si and quartz glass [4] appear. Above 1100° C we find cristobalit [33]. This strong disproportionation explains the absorption increase and the refraction value increase found by Hass and other authors. It can be uniquely traced to the precipitation of silicon. The silicon crystals which precipitate at 950° C have diameters between 40 - 50Å [33]. Silicon precipitations of 1000Å up to 10μ are found in SiO condensors at points which were destroyed by breakdowns [34]. A secretion of the disperse phase at substantially lower temperatures can be observed in GeO layers. Here the Ge precipitation already starts at 200 - 300° C, or also in the case of UV irradiation and mechanical pressure. The at least partial disproportionation, as can be observed in technical SiO products, should be responsible for certain structural defect interpretations [35].

The question about the structural and binding conditions in the not disproportionated SiO remains open.

Several authors reached the conclusion based on Fourier analyses of the scattered intensities [36,37] or because of the SiK_x spectrum [38], that only a mixture of Si and SiO_2 is present, even though it is present in a very fine distribution. When Cermet layers are made Cr and SiO, Glang, Holmwood and Head found the formation of chromium silicide Cr_3Si by the reaction of Si and Cr [39]. This is an indication of the existence of silicon in the SiO which can react. Qualitatively most properties such as refraction index, absorption, ϵ, tg δ and ρ can be explained with a highly dispersed installation of Si in the SiO. One should remember however that in the SiO, the volume fraction of the silicon would still be 30%, but in Si_2O_3 it would be only 12%. For a uniform distribution, this would roughly give an increase in the Si-Si separation by a factor of 1.5 in the SiO, and a factor of 2 in the Si_2O_3. The characteristic properties of the solid silicon will be lost at least in part. A similar behavior is observed in cermet layers.

The installation layers of cermets are often used for electrical [7,8] and optical applications by [40]. For example, metallic SiO. Long ago Neugebauer showed that the electrical properties of metal silicon monoxide cermet are determined almost exclusively by the volume ratio of the installed metal to the installed medium [8]. The specific character of the metal is practically not involved at all.

On the other hand, if we assume a highly dispersed installation of Si in the SiO_2 , we can see that because of the high degree of dispersion and because of the close chemical relationship between the installed material and the installation medium, several kinds of bonds can be created.

Faessler and Krämer investigated the SiKα emission spectrum and found that SiO is not a uniform substance, but is probably made up of a mixture of Si and various Si-O compounds. A simple (rough) mixing of Si and SiO_2 is excluded [41].

The IR spectrum of SiO does not correspond to a simple mixture, but instead corresponds to a complicated superposition of several spectra (see Fig. 9) [9,42]. In the case of a rough mixing, only the spectrum of SiO_2 would be expected. This is also found for disproportionated products. The spectrum differs clearly from that of layers obtained by oxidation of Si (reactive vaporization) and which corresponds to the rough composition of SiO [23]. Garski comes to the conclusion based on IR investigations, that in SiO layers there are isolated SiO_4 tetrahedrons, between which the Si is statistically distributed. In addition, OSi_4 configurations can occur. Si can be present as cations for the SiO_4 tetrahedrons, or can be bound to other atoms. With a tempering at 350 (illegible) we find a linking up of the isolated tetrahedra. Part of the excess silicon is consumed.

This consumption of excess silicon in the (illegible) should explain the breakdown resistance increase found by Cremer and Pulker, because the absorption of (illegible) layers in the visible range without a doubt has to be distributed to some form of the installed silicon. Various authors established a direct relationship between the optical absorption and the conductivity [43] (Figure 10) and the loss factor [44,45] respectively (Figure illegible). It is understandable that the structural changes caused by tempering are also manifested in the improved electrical properties. This /47 was observed by numerous authors [13,21,28,43,44,46.47].

The Si_2O_3 phase is also amorphous to x-rays and only gives glass bands. A disproportionating with silicon precipitation was established for Si_2O_3 only at temperatures of 950° C, and quantitatively only above 1600° C [48].

Two papers are available on the question of the structural and bond conditions.

Investigations of the x-ray Kα emission of Si_2O_3 by Faessler and Krämer [41] also resulted in a defined Kα doublet with a clear

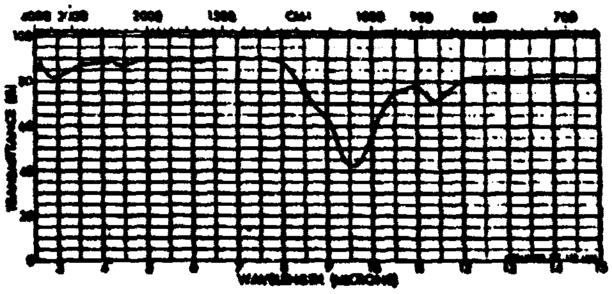

Figure 12.
Infrared transmission curve of a 2700 Å layer Si_2O_3 according to Ritter [42].

displacement with respect to SiO_2. This proves that only Si atoms bound in the same way are present.

Riechert and Weiner [48] suggested the following model for Si_2O_3 based on their x-ray analysis of the glass diagrams of Si_2O_3 with subsequent calculation of the electron density distribution: Si_2O_3 is made up of "SiO_4 just like SiO_2 glass in the form of tetrahedra. One-fourth of the oxygen atoms is replaced by defects on the average, that is, they do not exist."

Based on similar structural models, the effects mentioned above which occur during the UV irradiation Si_2O_3 layers were explained [28].

According to this the UV absorption is caused by electrons which are captured in the oxygen-ion defects. Because of the UV irradiation there is a photo triggering of the electrons and therefore a removal of the absorption.

The IR spectrum of Si_2O_3 is similar to that of SiO_2 (amorphous). However the side band does not occur at 12.5 μ but at 11.5 μ [42] (Fig. 12).

The 12.5 μ is interpreted as a ring band, because it only occurs when SiO_4 rings are present. The 11.5 μ band is interpreted as an indication of a different relationship. The occurrence of the 11.5 μ band is found in the description of certain manufacturing conditions for the manufacture of silicon oxide layers by oxidation of silicon hydrogen with N_2O in the presence of a glow discharge [50,51]. This could be the formation of a Si_2O_3 phase, because these processes have a very similar course as chemical methods for producing Si_2O_3[51,52].

The properties of Si_2O_3 layers can probably be explained as SiO_2 defects. Without knowing the binding and structural conditions, they could be explained qualitatively by the silicon installation model.

4. Summary

1. SiO_2 layers with reproducible properties can be manufactured relatively easily today. In the case of SiO and Si_2O_3 layers, it is necessary to carefully check all of the manufacturing parameters for producing layers with reproducible properties.
2. The properties of the layers in the case of SiO_2 do conform to expectations. In the case of Si_2O_3 and SiO, they can be understood at least qualitatively. Additional interesting models are available for a quantatative understanding.

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