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Quantitative estimation of the reactivity of the surface of solids on the basis of inductive constants

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Abstract. Attempts at using correlation analysis and the inductive constants for quantitative estimation of the reactivity of the solid surface and for predicting the character of surface reactions are discussed on the basis of the macromolecular concept of the structure of solids. The results of experimental studies of the reactivity of some solid oxides and single-crystal matrices, which confirm the good prospects of this approach, are presented. The bibliography includes 33 references.

I. Introduction

The active development of the chemistry and technology of a solid surface is associated with the prospects for using small-size surface structures in various fields of engineering, first of all, in micro- and nanoelectronics, heterogeneous catalysis and sorption techniques. Progress in the development of chemical methods for the synthesis of nanostructures is largely related to the possibility of predicting the pattern of surface reactions on the basis of a quantitative theory. An approach to quantitative estimation of the reactivity of the surface of solids is the use of correlation analysis, which underlies the quantitative theory of organic reactions [1, 2] based on the linear free energy (LFE) principle proposed by I Brønsted and M Polanyi. According to this principle, the reactivity of the members of a series of isostructural compounds having a reaction centre of the same type can be predicted using either empirical or experimentally determined constants. The numerical values of the constants can be used to compare and predict the equilibrium and kinetics of chemical processes involving these compounds. For example, compounds incorporating functional groups Y of the same type are combined into the reaction series

$$X_1-Y,\ X_2-Y,\ \ldots,\ X_n-Y;$$

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for any member of this series, the rate constant of the reaction

$$X_i-Y + Z \longrightarrow X_i-Z + Y$$

depends unambiguously on the nature of X_i. The influence of X_i can be described by a set of dimensionless constants. This allows one to predict the behaviour of various compounds in chemical processes.

Qualitatively, the reactivity of X_i-Y molecules can be described by revealing the mechanism of interaction between the substituent X_i and the reaction centre Y. The major contributions to this interaction are made by inductive, steric, resonance, and some other effects. When a particular chemical reaction is considered, various types of interaction are postulated to be independent of each other and additive.[1, 2] The ability of a substituent to be involved in a particular type of interaction is described quantitatively by a constant which is expressed as a relative value, *i.e.*, describes the effect of a given substituent with respect to a reference one. For example, the effective electronegativity of the substituent is usually characterised by the constant σ_I, which reflects the inductive effect of this substituent. The qualitative views on the inductive interaction represent an integral part of the classical electronic theory of organic reactions. However, this does not mean that the nature of the inductive effect is now completely clear. The most widely used concept is intramolecular polarisation transmitted along the chain of bonds. This polarisation, induced by some charged or electronegative group, decreases with distance.

Quantitatively, the inductive effect of substituents as a formal type of interaction has been considered by Hammett and Taft.[2, 3] They proposed one-parameter correlation equations for various reaction series

$$\log K_i = \log K_0 + \rho\sigma_I, \qquad (1)$$

where K_i and K_0 are the equilibrium (or rate) constants for the reactions for substituted and unsubstituted members of the series, respectively; ρ is the proportionality coefficient reflecting the sensitivity of the reaction centre to the effect of the substituent in this reaction. The first term represents the part of the reaction free energy that does not depend on the nature of the substituent X.

In Taft's opinion, strict correlations between the inductive constants and the electronegativities can be established only for

monoatomic substituents. However, while developing a quantitative theory of organic reactions, Palm[1] made the inductive constants universal and assumed that any influence of the inductive effect can be described by the equation

$$A = A_{XY} + \rho_Y \sigma_X, \quad (2)$$

where A is any correlated value (for example, log$K$). According to Palm, this equation is valid for a variable substituent X_i of any complexity.

The experience of using structure–property relationships accumulated in organic and organoelement chemistry,[3–5] can be successfully applied to surface processes. This was promoted by the appearance of the core model of the structure of solids and development of the chemistry of supramolecular compounds.[6–8] An approach based on the use of the LFE principle and correlation analysis in the chemistry of the surface of solids can provide the basis for the development of a quantitative theory of surface reactions.

This review considers some results that demonstrate good prospects of using correlation analysis in the chemical investigations of solid surfaces, in particular, for quantitative estimation of the reactivity of functional groups on the surfaces of dispersed and single-crystal matrices on the basis of their inductive constants. This approach was verified in relation to dispersed silica, beryllia, titania and alumina and single-crystal silicon.

II. Macromolecular concept of surface chemical reactions and quantitative estimation of the reactivity of the solid surface from the inductive constants

In conformity with the main concept of the structure of solids,[6] any solid can be represented as a combination of a chemically inert core and reactive functional groups located on the surface (*e.g.*, OH groups). All surface reactions involving these groups and not affecting the core structure are considered as polymer analogous transformations.[7] Within the framework of a formal approach, this allows one to apply the LFE principle to solids containing similar functional groups and to use linear correlations of type (1) and (2). Usually, experimental results are represented as more or less complicated correlation equations. When the results deviate from dependences of types (1) and (2), the factors responsible for these deviations (steric, resonance, π-conjugation or hyperconjugation, *etc.*) should be taken into account using the stage-by-stage 'from simple to complex' procedures.

In a quantitative description of the inductive effect, a reaction series of solid matrices is not necessarily considered resorting to the X–Y system. If X is any substituent, in the X–Y series, one can distinguish the X–G–Y subseries where G is any divalent structural unit. If the inductive interaction has at least limited universality within a particular set of substituents X, the values for the considered characteristic A, present in Eqn (2), for the X–Y and X–G–Y series with the same range of substituents X should follow a linear correlation with each other. This means that the correlation equation (2) for the X–G–Y series can be written in two ways

$$A_{X-G-Y} = A_{X_0-G-Y} + \rho_{GY}\sigma_X$$

and

$$A_{X-G-Y} = A_{X_0-G-Y} + \rho_Y\sigma_{GX},$$

which implies inclusion of the fragment G in the reaction centre and in the substituent, respectively. For solids with hydroxylated surfaces that present a separate reaction series (for example, metal oxides), the electrophilic and nucleophilic substitution reactions can be presented in the following way:

$$X-OH + B \longrightarrow X-OB,$$

$$X-OH + B \longrightarrow X-B.$$

The type and the rate of the reaction are dictated by the effective electronegativity of the surface group (X or X–O). The reactivity of the hydroxyl groups is affected by all atoms that form the core; however, the effect of the nearest atoms that form the surface group is the most significant. The effective electronegativity of this group as a substituent in a surface compound can be evaluated from the inductive effect using one-parameter correlations. The value for the inductive effect (inductive constant) can be derived from any physicochemical process or phenomenon in which it is manifested to a sufficient extent. High sensitivity to electronic effects is typical of nuclear magnetic resonance; this is one of the best methods for determining the inductive constants.[1] However, strict requirements to investigation objects restrict the scope of its applicability. The bond force constants (and, hence, the stretching frequencies) depend on the electronic state of the system; therefore, with allowance for the LFE principle, one can use the relationships between the parameters σ_I and the spectral characteristics of the compounds of interest (for example, data of IR spectroscopy). These relationships have been used, for example, in a study of organosilicon compounds.[4,5]

Study of the influence of substituents on the spectroscopic characteristics of the Si–Cl, Si–F, Si–O–Si, and Si–H bonds in organosilicon compounds has shown that the shifts of the stretching frequencies of these bonds depend on the electronic state of the substituents present in the surroundings of the functional group and obey an equation of the form

$$\nu_i = \nu_0 + \alpha\sum \sigma^*, \quad (3)$$

where ν_i, ν_0 are the stretching frequencies of the bonds in this compound and in the methyl-substituted silane (or siloxane), respectively, α is a coefficient, $\sum\sigma^*$ is the sum of the Taft inductive constants of all substituents in this compound.

Relation (3) reflects a general feature of these compounds — the dependence of spectral characteristics on the electronic effects of substituents. The steric factors are insignificant in this case, and the inductive effect predominates.[4] This allows one to separate quantitatively the effects of different substituents by juxtaposing the data on chemical transformations of particular compounds with their spectral characteristics.

The linear dependence (3) was first established by Thompson,[4] who analysed the spectral characteristics of a small series of silanes R_3SiH with different substituents R. For compounds $R_{3-n}X_nSiH$, where X is halogen, a deviation from linear dependence (3) was observed and suggested [5] to be due to conjugation. The deviation can be quantitatively described by the difference between the calculated (ν_{cal}) and experimental (ν_{exp}) vibration frequencies of the Si–H group

$$\Delta\nu = \nu_{calc} - \nu_{exp}.$$

The ν_{calc} value was found using Eqn (3) taking into account the inductive constants for the corresponding substituents X [σ^*(X)] and R [σ^*(R)] and the relation

$$\sum\sigma^* = n\sigma^*(X) + (3-n)\sigma^*(R).$$

However, for a particular substituent X, the $\Delta\nu$ value was constant and did not change upon the variation of R. This allowed the researchers to separate quantitatively the effects of substituents.[5]

An IR-spectroscopic study of the ≡Si–Cl, ≡Si–F and ≡Si–H groups on the silica surface showed a shift of the characteristic absorption bands of these groups.[9] The authors interpreted these shifts as being due only to the effect of the surface. Meanwhile, the quantitative analysis of the changes in the spectral characteristics of chemisorbed (and, hence, substituted) silanes provides information on the electronic structure and the influence of all substituents that belong to the environment of silicon, including the surface group. To study the surface proper-

ties, it is most convenient to follow the characteristic absorption frequencies of the silicon hydride bond. First of all, this is due to the values of the Si—H stretching frequencies, which occur in the range of 2100–2300 cm^{-1}. Here, the absorption of the IR emission by the core of most solids is insignificant and the observed changes in $\Delta\nu$(Si—H) for various substituted silanes are fairly great, being equal to 100 to 150 cm^{-1} (see Refs 5, 9). This increases the accuracy and reliability of the results.

The surface compounds containing Si—H bonds are formed on hydroxylated surfaces of solid oxides when they are treated with chloro- or alkoxysilane vapours. By analysis of the changes in the chemical reactivity and spectroscopic characteristics, one can estimate quantitatively the influence of the surface groups or the whole core of the solid on the reaction centre.

The real surfaces of most metals and semiconductors contain oxide layers; therefore, the reactivity of such surfaces will be dictated, first of all, by the oxide microstructure and the type of hydroxyl groups. Studies of the hydroxyl cover of silicas and other oxides (for example, Al_2O_3, $xAl_2O_3 \cdot ySiO_2$, TiO_2, ZnO) which exhibit catalytic properties have shown [10] that, in terms of the number of coordination bonds formed by oxygen, three types of OH bonds can be distinguished, those attached to the metal of the oxide core by one (I), two (II) and three (III) bonds (all the M—O bonds are considered to be equivalent). The ratio of the concentrations of hydroxyl groups of each type to their total concentration is determined by both the oxide composition and the surface temperature. The formation of an additional coordination bond results in a lower stretching frequency of the OH groups. This underlies the identification of the type of hydroxy group based on its spectral characteristics.[10–12] For a particular oxide, the relation

$$\Delta\nu(\text{OH})\ (\text{III}) > \Delta\nu(\text{OH})\ (\text{II}) > \Delta\nu(\text{OH})\ (\text{I})$$

usually holds, which is due to a decrease in the electron density on the O—H bond and an increase in the positive charge on the hydrogen atom following an increase in the coordination number of oxygen in the corresponding OH groups. The involvement in surface reactions is determined by both the proton-donor capacity and the steric arrangement (steric factor) of the hydroxyl group. Also, for quantitative estimation of the reactivity of the surface hydroxyl groups, one can use the inductive effect of the matrix and calculate its inductive constant σ_s from the shift of the adsorption maximum for the Si—H stretching vibrations of the surface compounds formed upon the chemisorption of silanes.[12–15] As noted above, this bond is highly sensitive to the electronic effects of substituents. In this case, relation (3) has the form

$$\nu_I = \nu_0 + \alpha(\sum\sigma_I + \sigma_s). \quad (4)$$

When the Taft constants are used as σ_I, the σ_s value can be determined from the scale of these constants.

The fact that the spectral characteristics [ν(Si—H)] of chemisorbed silanes depend only on the electronic effects of substituents allows one to distinguish the influence of each of them; therefore, this method should be considered as legitimate. Evidently, the substituent effect of the core of a solid follows a complex pattern; therefore, experimental results can either obey or depart from Eqn (4), which will provide additional information on the object in question. The availability of Taft inductive constants for a large number of low-molecular-mass substituents [16] markedly simplifies the computational part of the procedure and makes this approach versatile.

III. Inductive effect of a silica matrix and regularities of its variation during dehydration

We tested the above approach in relation to silica samples (Aerosil A-175). The coefficients present in correlation equation (4) were determined for a reaction series of oxides. The concentration of the hydroxyl groups was determined by a reported procedure [17] and compared with the data of IR spectroscopy [18] obtained in the experiments described below.

The characteristic stretching frequencies of the Si—H bond of chemisorbed silanes were determined from the IR spectra recorded on UR-20 and Bruker spectrometers. The deviations of individual measurements from the statistical average values in the region of 2100–3800 cm^{-1} were smaller than 2 cm^{-1}.

For calculation of the coefficients for correlation equation (4), experimental ν_i values for a series of chemisorbed silanes are needed. The frequencies of the maxima of the stretching bands of the Si—H bonds incorporated in different functional groups of compounds synthesised on the Aerosil surface pretreated at 673 K *in vacuo* are listed in Table 1. On chemisorption of methyldichlorosilane and phenyldichlorosilane, surface compounds with different compositions can be obtained. This is due to the fact that these silanes mainly react with the Aerosil surface as monofunctional reagents (compound No. 3 or No. 8), which was confirmed by Tertykh *et al.*[19] During the subsequent treatment of these samples with water or alcohol vapour, the Si—Cl groups remaining intact were hydrolysed or alkoxylated. These processes were accompanied by the corresponding changes in the IR spectra (Fig. 1), namely, partial restoration of the absorption band due to the Si—OH groups (ν = 3750 cm^{-1}, spectrum *2*) in the case of hydrolysis or the change in the shape and intensity of the C—H bands (spectrum *5*) upon alkoxylation. In both cases, the introduction of a new substituent (OH, OCH_3 or OC_2H_5) in the environment of the silicon hydride bond was accompanied by displacement of the ν(Si—H) mode (see Table 1, compounds Nos. 3, 5, 6, 7 and 8, 10, 11, 12; Fig. 1). The subsequent maintenance of these samples at T = 673 K for 1 h resulted in some decrease in the intensity of the ν(Si—H) absorption bands and the appearance of new bands (2260 and 2270 cm^{-1}). This was accompanied by the

Table 1. Influence of the nature of the substituent on the stretching frequency of the silicon hydride bond.[14]

No.	Chemisorbed chlorosilane	Surface compound	ν(Si—H) /cm^{-1}	$\sum\sigma^*$ (see [14])	$\sigma^* + \sum\sigma_s^*$
1	$ClMe_2SiH$	≡Si—O—$SiMe_2H$	2161	0	5.05
2	$ClPh_2SiH$	≡Si—O—$SiPh_2H$	2182	1.104	6.14
3	Cl_2MeSiH	≡Si—O—SiMeClH	2215	2.880	7.91
4	Cl_2MeSiH	$(\equiv Si-O)_2SiMeH$	2260	0	10.15
5	$Cl_2MeSiH + H_2O$	≡Si—O—SiMe(OH)H	2190	1.550	6.61
6	Cl_2MeSiH + MeOH	≡Si—O—SiMe(OMe)H	2189	1.450	6.50
7	Cl_2MeSiH + EtOH	≡Si—O—SiMe(OEt)H	2187	1.366	6.40
8	Cl_2PhSiH	≡Si—O—SiPhClH	2225	3.480	8.49
9	Cl_2PhSiH	$(\equiv Si-O-)_2SiPhH$	2270	0.552	10.67
10	$Cl_2PhSiH + H_2O$	≡Si—O—SiPh(OH)H	2203	2.147	7.23
11	Cl_2PhSiH + MeOH	≡Si—O—SiPh(OMe)H	2200	2.050	7.07
12	Cl_2PhSiH + EtOH	≡Si—O—SiPh(OEt)H	2199	1.966	7.03
13	Cl_3SiH	≡Si—O—$SiCl_2H$	2272	5.760	10.77

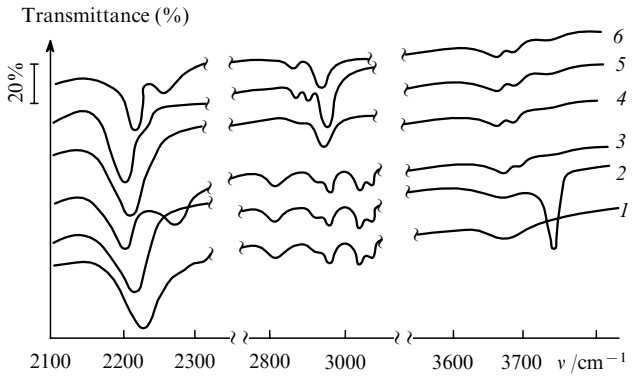
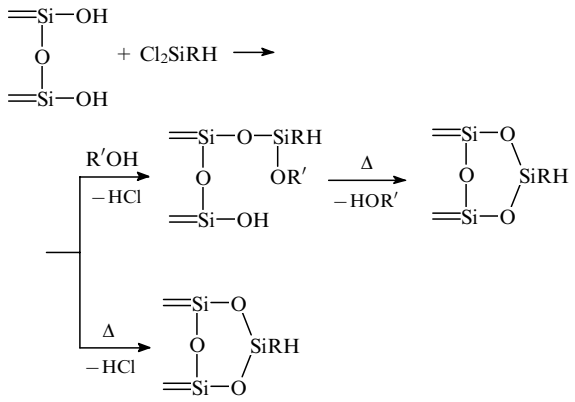


Figure 1. IR spectra of Aerosil treated with phenyldichlorosilane vapour at 473 K (*1*) with subsequent rehydration (*2*) and maintenance at 673 K for 60 min (*3*); and Aerosil treated with methyldichlorosilane vapour at 473 K (*4*) and then with ethanol vapour (*5*) and maintained at 673 K for 60 min (*6*).

disappearance of the absorption bands due to the OH groups (3750 cm^{-1}) and the C–H bonds of the alkoxy groups (2850, 3070 cm^{-1}, Fig. 1, spectra *3* and *6*).

On the basis of these results, it was concluded that the reactions



R = Me, Ph; R′ = H, Me, Et

yield silicon hydride groups linked to the surface by two siloxane bonds. It is noteworthy that the characteristic vibration frequencies of the Si–H bonds of the $(\equiv Si-O)_2-SiRH$ groups do not depend on the way they were prepared and are determined only by the structure of the groups.

By mathematical processing of the experimental data given in Table 1 using the Taft inductive constants ($\sum\sigma^*$) for known substituents,[16] the coefficients of relation (4) were determined and the following expression was derived:

$$\nu_i = 2064 + 19.21(\sum\sigma^* + \sigma_s^*). \quad (5)$$

The value $\sigma_s^* = 5.05$, which was also obtained using these experimental data, serves as a measure of the inductive effect of the silicon–oxygen group on the reaction centre.

It can be seen from Table 1 that the surface functional groups can contain various substituents (for example, Cl, Ph); however, this does not cause a significant departure of the ν_i values from linear dependence (5). The presence of a linear correlation between ν_i and σ^* shows that the electronic effects are transmitted through the silicon atom by the inductive mechanism, while the conjugation effects do not play a significant role. The value $\sigma_s^* = 5.05$ serves as a quantitative measure of the electronic state of the silica surface under the experimental conditions.

Table 2. Influence of thermal treatment on the concentration of hydroxyl groups and the inductive constant of silica.[18]

Parameter	Temperature of the thermal treatment /K						
	473	573	673	773	873	973	1073
Concentration of the OH groups /μmol m^{-2}	7.8	5.6	3.4	3.0	2.6	2.3	1.5
ν (Si–H) /cm^{-1}	2152	2155	2161	2163	2165	2168	2170
σ_s^*	4.57	4.73	5.05	5.15	5.25	5.41	5.52

The data of spectroscopic investigations [20, 21] and quantum-chemical data [22, 23] showed that the reactivity of the surface silanol groups depends on their concentration, which, in turn, is a function of the temperature of dehydroxylation of the silica surface. This is due to an increase in the electronegativity of some surface silicon atoms caused by the removal of hydroxyl groups and/or water molecules from their coordination sphere and to electron density redistribution in the Si–O bonds. Thus, for samples with different degrees of hydration, the numerical σ_s^* values should be different. This was confirmed by experimental results. The experimental ν(Si–H) values for a series of Aerosil A-175 samples pre-evacuated at 473–1073 K were used to calculate, from Eqn (5), the σ_s^* values (Table 2) for samples with different concentrations of hydroxyl groups. Analysis of these results taking into account the high sensitivity of the Si–H bond to electronic effects of substituents showed that the relative shift of ν(Si–H) upon dehydration is rather small, namely, it does not exceed 20 cm^{-1} ($\sim$10% of the absolute value). This is due to the fact that the surface silicon atoms responsible for the change in the electronegativity of the [SiO_4] substituent are linked to the Si–H centre by a siloxane bond, which can suppress the inductive effect. The suppression coefficient (the transmission factor of the bond) Z can be derived from the ratio of the inductive constants for compounds with a chain of bonds

$$\sigma_{\equiv Si-(OSi\equiv)n} = \sigma_{(\equiv Si-)}Z^n. \quad (6)$$

The numerical value of Z was found from the values of σ_s^* for the following surface groups: (*1*) $\equiv$Si–H ($n = 0$); (*2*) $\equiv Si-O-Si(CH_3)_2H$ ($n = 1$) (see Table 2); and (*3*) $\equiv Si-O-Si(CH_3)_2-O-Si(CH_3)_2H$ ($n = 2$).

Compounds with type *1* and *3* fragments were synthesised by the reactions

$$\equiv Si-OH + CH_3OH \xrightarrow[-H_2O]{} \equiv Si-OCH_3 \xrightarrow{1023\ K}$$
$$\longrightarrow \equiv Si-H + CH_2O,$$
$$\equiv Si-OH + Cl_2Si(CH_3)_2 \xrightarrow[-HCl]{} \equiv Si-O-SiCl(CH_3)_2 \xrightarrow[-HCl]{H_2O}$$
$$\longrightarrow \equiv Si-O-Si(CH_3)_2-OH \xrightarrow[-HCl]{ClSi(CH_3)_2H}$$
$$\longrightarrow \equiv Si-O-Si(CH_3)_2-O-Si(CH_3)_2H.$$

These reactions were monitored by IR spectroscopy directly in the IR cell serving as the reaction vessel, by following the disappearance of the absorption band for isolated Si–OH groups (3750 cm^{-1}) and the appearance of bands for the methoxy group [ν(C–H) = 2930 and 2970 cm^{-1}]. During high-temperature treatment, the methoxy groups were detached as formaldehyde to give silica hydride [24] with ν(Si–H) = 2280 cm^{-1}. The last reaction was accompanied by the appearance of absorption bands for the methyl groups with ν(C–H) = 2920 cm^{-1}. Using the ν(Si–H) values for the $\equiv Si-O-$, $\equiv Si-O-Si(CH_3)-O-$ and $\equiv Si-O-Si(CH_3)_2-O-Si(CH_3)_2-$ substituents, which were 2280, 2161 and 2120 cm^{-1}, respectively, the inductive

constants σ_s^* were calculated from Eqn (5) ($\sigma_{0s}^* = 11.24$ for $n = 0$; $\sigma_{1s}^* = 5.05$ for $n = 1$; $\sigma_{2s}^* = 2.91$ for $n = 2$). The Z value was determined as the average of the three values obtained by substitution of pairs of values into Eqn (6):

$$Z_1 = \frac{\sigma_{1s}^*}{\sigma_{0s}^*} = 0.449,$$

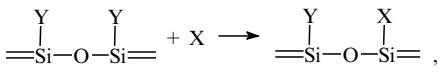
$$Z_2 = \frac{\sigma_{2s}^*}{\sigma_{1s}^*} = 0.576,$$

$$Z_3 = \left(\frac{\sigma_{2s}^*}{\sigma_{0s}^*}\right)^{0.5} = 0.509.$$

The resulting value, $Z = 0.51 \pm 0.04$, implies that the transmission ability of the siloxane bond in the synthesised surface compounds is rather great and does not differ much from that for linear siloxanes ($Z = 0.48$).[25] It can serve as a quantitative measure of the long-range effect of the silicon–oxygen core in the cases outlined below.

1. Variation of the reactivity of the functional group Y separated from the core by a chain of siloxane bonds, for example, $\equiv Si-(O-SiR_2-O)_n-Y$.

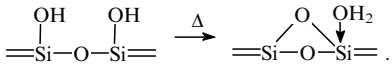
2. Variation of the reactivity of the functional group Y or X toward the reaction



for example, in the synthesis of silicas with functional groups of different types.

The parameters of the $\equiv Si-O-Si\equiv$ bond for silicas (the Si–O distance is 0.160–0.167 nm, the SiOSi angle is 150–170°) vary in the same range as those for linear or cyclic siloxanes.[25] This suggests that the transmission ability of siloxane bonds located on the silica surface should not differ much from that for silanes synthesised on the silica surface; this was confirmed by experimental data.

The relatively small shifts of ν(Si–H) during dehydration can also be attributed to the fact that dehydroxylation of the surface is usually accompanied by the formation of new aqua complexes



Therefore, the decrease in the coordination number of surface silicon atoms is partially compensated. The high sensitivity of the Si–H bond to the nature of the substituent allowed the researchers to detect the deviation of the dependence $\sigma_s^* = f(T)$ from the general linear dependence at $T < 600$ K ($c_{OH} > 5$ μmol m^{-2}) (Fig. 2). A substantial increase in the concentration of aqua complexes under these conditions and an increase in the coordination number of surface silicon atoms resulted in a decrease in their effective electronegativity, which told on the dependence $\sigma_s^* = f(T)$. The activation energy for dehydroxylation estimated based on the temperature dependence of the total concentration of the hydroxyl groups was ~160 kJ mol^{-1}; this value falls within the range reported by Gorlov *et al.*[26]

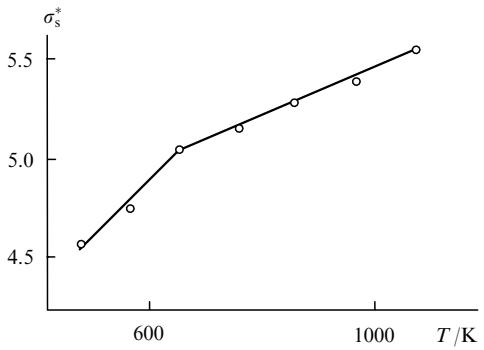


Figure 2. Influence of thermal treatment on the Taft inductive constant of silica.

IV. Estimation of the inductive effect of the core of some dispersed oxides

The good prospects of using correlation analysis for establishing the pattern of the electronic influence of a solid core were demonstrated for zinc, magnesium, beryllium, titanium and aluminium oxides, whose acidity constants vary over a rather broad range. Pelleted samples of these oxides were hydroxylated by water vapour and then treated with dimethylchlorosilane (DMCS) vapour at temperatures recommended for each oxide.[11,12]

For surface groups of the $MO-SiR_2H$ type, the ν(Si–H) values should depend not only on the metal of the surface but also on the type of OH groups involved in the formation of the silicon hydride group. In other words, the ν(Si–H) values should reflect the electron-withdrawing properties of the metal oxide surface fragment and, hence, the reactivity of the hydroxyl groups attached to it.

The IR spectra of these oxides treated with a DMCS vapour showed a number of specific features.[15] Figure 3 presents the IR spectra of the initial and DMCS-vapour treated samples of beryllia, titania and alumina. As a result of chemisorption, thermally stable compounds $MOSi(CH_3)_2H$ were formed on the

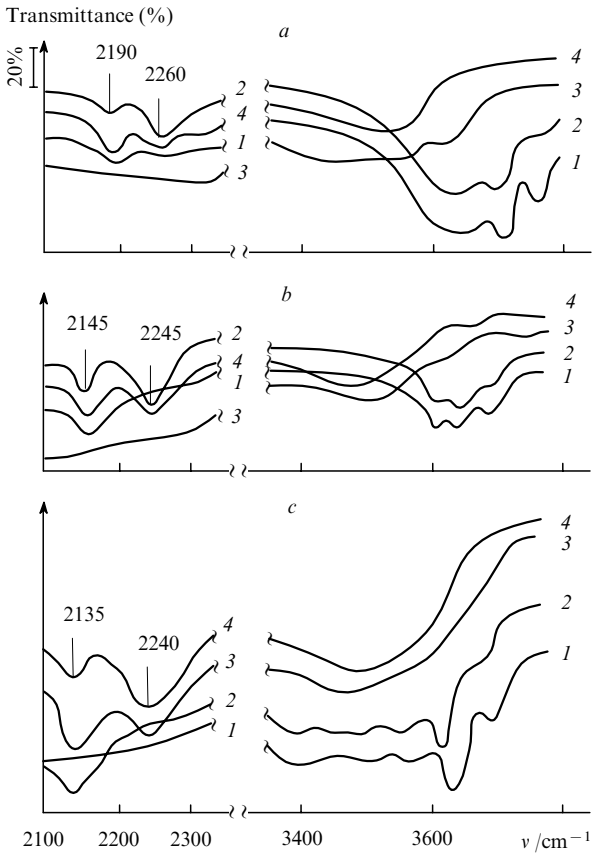


Figure 3. IR spectra of alumina (*a*), titania (*b*) and beryllia (*c*).[15] Samples: (*1*) initial; (*2*) treated with traces of DMCS at 473 K, $P = 1$ Pa, $\tau = 30$ min; (*3*) treated with traces of DMCS at 473 K, $P = 50$ Pa, $\tau = 30$ min; (*4*) evacuated while maintained at a constant temperature (523 K), $\tau = 60$ min.

oxide surface. For low pressures of DMCS vapour (~ 1 Pa), the spectrum of beryllia showed a decreased intensity of the band for the OH groups of type I (3720 cm^{-1}) and a new absorption band for the Si–H bond (2135 cm^{-1}, see Fig. 3 *c*; curves *1*, *2*). When the DMCS vapour pressure was increased to 50 Pa, the OH groups of type II (3630 cm^{-1}) entered into the reaction to give new silicon hydride groups [ν(Si–H) = 2240 cm^{-1}, see Fig. 3 *c*; curve *3*]. Similar changes were noted for TiO_2 (anatase) (see Fig. 3 *b*) and γ-Al_2O_3 samples (see Fig. 3 *a*).

It was found that the hydroxyl groups of type I were the first to react on the surfaces of all of the oxides. However, judging by the intensity of the Si–H absorption band and the thermal stability of the groups formed, type I hydroxyl groups are expected to be least reactive in electrophilic substitution. This contradiction can be explained by the influence of steric factors in heterogeneous chemical processes. The low concentration and the spatial positions of the 'sunk' OH groups of types II or III are unfavourable for surface reactions.

Treatment of the surfaces of zinc and magnesium oxides with DMCS vapour did not give thermally stable surface compounds of the $MOSiR_2H$ type. In this case, the absorption bands for type I and II hydroxyl groups were found to shift due to the presence of chlorosilane on the surface. The subsequent thermal treatment resulted in complete desorption, indicating the absence of chemical bonds with the surface. A possible reason is low electrophilicity of DMCS in surface reactions with the relatively inert hydroxyl groups of these matrices.

By comparison of the σ_s^* values calculated using the experimental ν(Si–H) frequencies for the $\equiv$SiH groups synthesised on reaction centres of the same type (Table 3), the oxides studied can be arranged in the following sequence according to increasing effective electronegativity of the core:

$$MgO \approx ZnO \ll BeO < TiO_2 < SiO_2 < \gamma\text{-}Al_2O_3.$$

No hydroxyl groups of type III were revealed in these experiments, probably, because they are present in a very low concentration if at all.

Table 3. Vibration frequencies of the OH and SiH groups and the Taft inductive constants of the oxide core ($T = 473$ K).[15]

Oxide	Type of OH groups	ν(OH) /cm^{-1}	ν(Si–H) /cm^{-1}	σ^*
BeO	I	3720	2135	3.70
	II	3630	2240	8.93
TiO_2	I	3700	2145	4.21
	II	3640	2245	9.42
γ-Al_2O_3	I	3780	2190	6.55
	II	3720	2260	10.20
SiO_2	I	3750	2152	4.57

The inductive effect is polarisation of σ bonds transferred along the chain of atoms; therefore, the inductive effect of the core would affect the electron density distribution in a hydroxyl group connected to this core. The above sequence reflects not only the effective electronegativity of the solid core; the particular value of σ_s^* of each member of the sequence can be used to estimate the reactivity of the surface hydroxyl groups. The data obtained using this approach are in good agreement with the results obtained by other procedures, for example, based on acidity constants.[10–12]

V. Quantitative estimation of the reactivity of hydroxylated surfaces of single-crystal matrices

The possibility of using the inductive effect to describe the surface phenomena demonstrated for dispersed oxide matrices opens up prospects for quantitative estimation of the reactivity of the surface hydroxyl groups on single-crystal, in particular semiconductor, matrices. Solution of this problem would allow one to predict the processes of template synthesis of nanostructures and promote the chemical nanotechnology for elaboration of the submicrometer component base for electronic engineering. As an example, one can consider the results obtained for silicon samples with (111) and (100) orientations by multiple attenuated total internal reflection (ATIR) IR spectroscopy.[27,28] In experiments, the angle of incidence of the beam θ was 45° and the number of reflections n was 28. The ATIR spectra were recorded directly in the cell-reaction vessel, which ensured treatment of the sample surfaces either in a vacuum (down to 10^{-3} Pa) or in a controlled medium in the temperature range of 20–600 °C.

Study of the hydroxylation of freshly etched silicon and the subsequent sorption of DMCS has shown[27,28] that the spectral pattern in the frequency region 3700–3750 cm^{-1} is similar to that observed for a dehydrated surface of narrow-pore silica gels.[29] The adsorption of DMCS resulted in the formation of tetramethyldisiloxane as a result of hydrolysis of the sorbed compound by the water molecules present on the surface as thermally stable aqua complexes. The tetramethyldisiloxane formed was not chemically bonded to the silicon surface and was completely desorbed upon temperature rise.[27,28]

On the basis of these data, it was concluded that silanol groups present on the silicon surface, like the hydroxyl groups of zinc and magnesium oxides, do not react with DMCS, whereas the OH groups on the silica surface are chemically reactive under similar conditions and form thermally stable surface compounds, $\equiv Si-O-Si(CH_3)_2H$ [ν(Si–H) = 2152 cm^{-1}]. This fact can be attributed either to low electrophilicity of DMCS or to different electronic structures of silicon and silica surface atoms. A surface of even freshly etched silicon contains an ultrafine (1.0–1.5 nm) oxide film;[30] therefore, on treatment with water vapour, in addition to silanol groups, one can also expect the formation of a hydration cover linked by coordination bonds. Presumably, the energy of the coordination bonds of aqua complexes is somewhat higher in this case, because the ultrafine oxide film on the surface of a single crystal is depleted in oxygen. In the depleted surface film, the probability of electron density displacement from silanol groups is much lower; therefore, they do not exhibit sufficient proton-donor capacity and do not react with DMCS.

The activation energy for the electrophilic replacement of the proton of silanol groups is known[31] to depend on the proton-acceptor properties of the attacking reagent; therefore, one can choose a substituted silane capable of reacting with relatively inert hydroxyl groups on the silicon surface. Triethoxysilane (TES) was chosen for this purpose. Its reaction with the silicon surface was studied at different temperatures ranging from room temperature

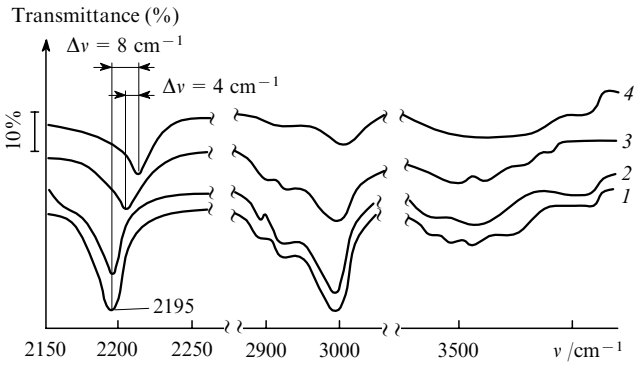


Figure 4. ATIR infrared spectra of a silicon surface;[28] (*1*) after hydration at 473 K and subsequent treatment with TES vapour at 300 K; (*2*, *3*) after evacuation at constant temperatures of 373 K and 473 K, respectively, for 30 min; (*4*) after rehydration in water vapour at 473 K.

to 673 K. Figure 4 shows the ATIR spectra of samples subjected to different types of thermochemical pretreatment. Stable surface compounds containing Si—H bonds were synthesised, and not only the inductive effect of the matrix but also the stoichiometry of the surface reaction was determined.

When samples evacuated for 1 h at 473 K are treated with water vapour at the same temperature, then cooled and treated with TES vapour at room temperature, the spectrum (see Fig. 4, spectrum *1*) exhibits an absorption band for the Si—H bond and a characteristic set of bands for the C—H bonds of the ethoxy groups. The ν(Si—H) frequency in this spectrum coincides with the Si—H stretching frequency for triethoxysilane (2195 cm^{-1}). This points to the absence of any chemical reactions in the system. After maintaining the sample for 30 min at 373 K, the spectrum (spectrum *2*) shows deformation of the low-frequency region of the Si—H band caused by the appearance on the silicon surface of adsorbed alkoxy-substituted disiloxane having formed in a reaction similar to the reaction with DMCS. Only after maintenance at 473 K for 1 h do the intensities of the Si—H and C—H absorption bands decrease. As this takes place, the band of the Si—H vibrations becomes symmetrical and its maximum shifts by 8 cm^{-1} to shorter wavelengths relative to the position of this band in the spectrum of sample *1* not kept at a constant temperature. The decrease in the intensity of the Si—H and C—H absorption bands is due to the thermal desorption of excess reagent and the disiloxane formed, while the observed shift of the ν(Si—H) absorption maximum is caused by the replacement of one or several alkoxy groups by more electronegative substituents. The above-listed changes in the spectral characteristics and the thermal stability of the product obtained at 473 K attest to its chemical bonding to the surface, which could result only from the reaction between the silanol groups and the ethoxy groups of the sorbed silane,

$$(\equiv Si-OH)_m + (C_2H_5O)_3SiH \longrightarrow$$
$$\longrightarrow (\equiv Si-O-)_mSi(OC_2H_5)_{3-m}H + m\,C_2H_5OH.$$

The alkoxy groups not involved in the reaction can be replaced by hydroxyl groups by treating the sample surface with water vapour. Indeed, when comparing spectra *2* and *3* (see Fig. 4), one can see that hydration entails an increase in the intensity of the C—H absorption band and substantial enhancement of the absorption in the OH stretching region (3600–3700 cm^{-1}). The ν(Si—H) mode shifts by 4 cm^{-1} to shorter wavelengths. The changes observed in spectra *3* and *4* are due to the reaction

$$(\equiv Si-O)_mSi(OC_2H_5)_{3-m}H + (3-m)\,H_2O \longrightarrow$$
$$\longrightarrow (\equiv Si-O)_mSi(OH)_{3-m}H + (3-m)\,C_2H_5OH.$$

The stoichiometry of the surface reactions, *i.e.*, the numerical value of the coefficient m, can be determined using correlation equation (5). By transforming this relation and replacing $(3-m)$ alkoxy groups with $\sigma^*(OC_2H_5) = 1.366$ (see Ref. 16) by an equivalent number of OH groups with $\sigma^*(OH) = 1.550$ (see Ref. 16), one can determine the shift of the stretching frequency of the Si—H bond

$$\Delta\nu(Si-H) = a(3-m)[\sigma^*(OH) - \sigma^*(OC_2H_5)];$$

hence,

$$m = 3 - \frac{\Delta\nu(SiH)}{a[\sigma^*(OH) - \sigma^*(OC_2H_5)]} =$$
$$= 3 - \frac{4}{19.21(1.550 - 1.366)} = 1.86 \approx 2.$$

Thus, the structure of the surface compounds formed in the reaction with TES can be represented as $(\equiv Si-O)_2Si(OC_2H_5)H$. By using Eqn (5) and substituting the value ν(Si—H) = 2203 cm^{-1} (see Fig. 4, spectrum *4*) for this compound into the equation, one can estimate the inductive effect of the silicon–oxygen groups present on the surface of single-crystal silicon against the scale of the Taft inductive constants

$$\sigma_s^* = \left[\frac{\nu_i - \nu_0}{a - \sigma^*(OC_2H_5)}\right]m^{-1} =$$
$$= \frac{(2203 - 2064)/19.21 - 1.366}{2} = 2.90.$$

For silica, this parameter is much higher. Thus for Aerosil dehydrated at the same temperature, $\sigma_s^* = 4.57$ (see Table 2). Comparison of the numerical values of these parameters showed that the silanol groups on the silicon surface are much weaker proton donors than the same groups on the silica surface. Most probably, this is due to the inhibitory inductive effect of the silicon core.

In addition, the hydration cover formed upon heating of the silicon surface in water vapour, was found to contain, apart from silanol groups, the OH groups of water molecules attached to the surface silicon atoms by coordination bonds. The results shown in Fig. 2 may suggest that quantitative dehydration of the surface of the oxidised single crystal would take place during evacuation only at $T > 600$ K. It is noteworthy that the observed changes in the spectral characteristics of silicon cells did not depend on the crystallographic orientation of the samples to within the sensitivity of the method. The lack of this dependence is due to the fact that the influence of the surface oxide layer is more significant than that of the single-crystal silicon core.

The inductive effect of the core of the GaAs binary semiconductor with orientation (100) was estimated for ATIR cells having $\theta = 30^\circ$ and $n = 28$. At temperatures of 423–523 K, active chemisorption of DMCS was observed on the GaAs surface containing a natural oxide layer [ν(Si—H) = 2165 cm^{-1}]; the calculated value is $\sigma^* = 5.25$. After etching of the surface of this semiconductor with a $CH_3OH : Br_2$ (100 : 1) mixture with subsequent washing with methanol and double-distilled water, the σ^* value decreased to 5.1 [ν(Si—H) = 2162 cm^{-1}], which is due to a decrease in the oxide layer thickness. However, in any case, the σ^* value is greater for the GaAs surface than for silicon or silica surfaces. The higher inductive effect of this matrix is caused by the fact that it incorporates a more electronegative component (arsenic) and its oxides. Therefore, there are grounds for believing that the hydroxyl groups on a real GaAs surface should exhibit rather high proton-donor capacity and hence, they can be used in surface chemical reactions with relatively weak electrophilic reagents. This fact is of certain interest for the production of surface nanostructures on this matrix.

VI. Effect of the thickness of the oxide layer on the activity of silanol groups on the silicon surface

On the basis of analysis of the experimental data concerning the inductive effect of silica, silicon and gallium arsenide cores, one can suggest that the reactivity of the hydroxyl groups occurring on the real surface of a semiconductor crystal would be determined by sample prehistory, namely, the thickness of the oxide layer formed during the pretreatment. From the inductive effect, this influence can be derived and the pattern of variation of the reactivity of the silanol groups present on the silicon surface with different degrees of oxidation can be elucidated. To this end, one merely has to analyse the spectral characteristics of chemisorbed silanes on matrices with different known thicknesses of the oxide. These experiments were carried out for silicon samples (ATIR cells) on which a specified oxide layer was synthesised by molecular layering,[27, 28, 31] *i.e.*, by alternating treatment of the surface with silicon tetrachloride and water vapours. The layer thickness was determined by ellipsometric measurements and calculated in the Drude–Tronston one-layer model approximation.[32] The measurements were carried out using an ellipsometer with a

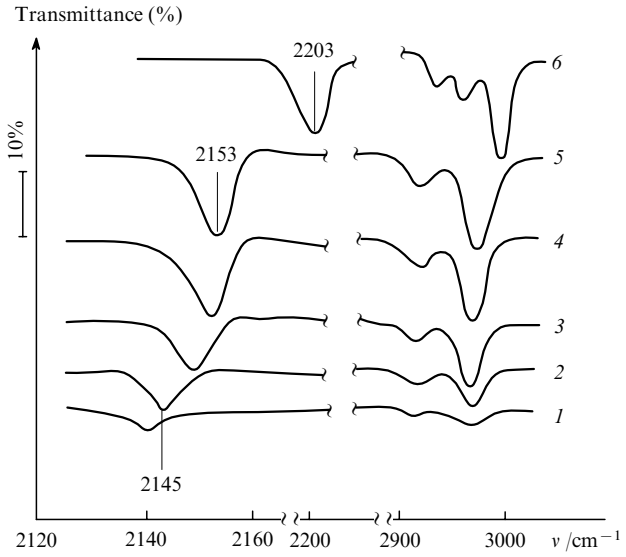


Figure 5. ATIR infrared spectra of the (111) silicon surface subjected to cyclic treatment with silicon tetrachloride and water vapours at 473 K with subsequent treatment with DMCS at the same temperature.[27,31]
The number of cycles is 4 (*1*), 10 (*2*), 20 (*3*), 30 (*4*), 40 (*5*); spectrum of the sample after etching and treatment with triethoxysilane (*6*).

fixed compensator and magnetic modulation of the light beam. The error of determination of these parameters did not exceed $\pm 0.01'$.

Figure 5 shows the IR spectra of ATIR silicon samples with a synthesised SiO_2 layer pretreated with DMCS vapour at 473 K, and Fig. 6 shows the dependence of the thickness of this layer (d) and the relative Si—H absorption intensity on the number of molecular layering cycles (N). Comparison of spectra *1–4* (see Fig. 5) showed that an increase in the thickness of the synthesised oxide layer entails a substantial increase in the absorption intensity in the region of the Si—H (2135–2150 cm^{-1}) and C—H (2900–3000 cm^{-1}) stretching frequencies and a noticeable shift of the ν(Si—H) bond to shorter wavelengths. This pointed unambiguously to an increase in the concentration of silanol groups capable of reacting with DMCS; moreover, up to $N \approx 15$ ($d \approx 3$ nm), the number of reactive centres increased in proportion to N and subsequently it changed only slightly (see Fig. 6).

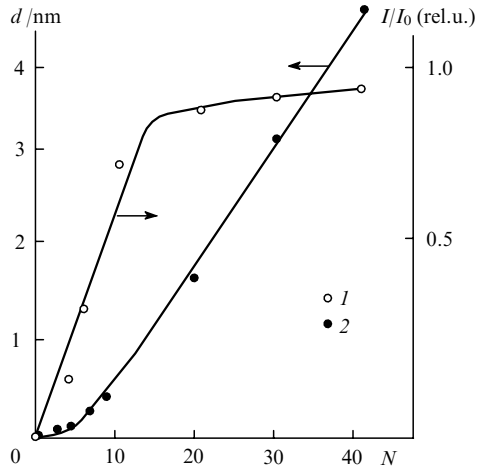


Figure 6. Relative intensity of the absorption bands for the Si—H bond (*1*) and thickness of the oxide layer (*2*) *vs.* the number of molecular layering cycles (N).[31]

As shown above, the silanol groups on a freshly etched silicon surface did not react with DMCS at all, but they did react with more active TES to give surface compounds. For comparison, Fig. 5 shows a fragment of the spectrum (curve *6*) of a freshly etched ATIR silicon cell pretreated with TES vapour. With an increase in the oxide thickness, the influence of the silicon core becomes less pronounced, while the role of the oxide with a large σ_s^* value is enhanced and, hence, the reactivity of the silanol groups increases. This appears to be also the reason for the retardation of the formation of the oxide layer upon chemisorption of $SiCl_4$, which is observed in the initial stages of the synthesis ($N < 10$) (see Fig. 6).

These results allowed the researchers to establish the quantitative relationship between the thickness of the oxide layer on the silicon matrix and its inductive effect and, hence, the activity of the hydroxyl groups (Fig. 7). As noted above, the most pronounced changes in σ_s^* were observed up to an oxide layer thickness of $\sim$3 nm. The inductive effect of the silicon core with thick oxide layers was almost the same as the effect of silica. In this case, as expected, active chemisorption of DMCS took place. It should be borne in mind that even a silicon surface freshly etched in aqueous solutions has a thin oxide layer ($\sim$1 nm, according to our estimates) and the σ_s^* value calculated from experimental ν(Si—H) to be 2.9, refers to such a surface.

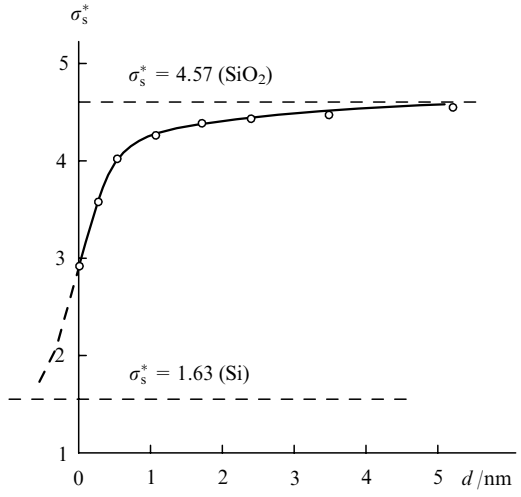


Figure 7. Influence of the thickness of the synthesised oxide layer on the inductive constant of silicon.[28]

The inductive constant estimated from the stretching frequency of the Si—H groups formed during etching of silicon with hydrofluoric acid [ν(Si—H) = 2096 cm^{-1}] amounts to 1.63. This value refers to a silicon surface almost deprived of the oxide layer and is indicative of a low reactivity of the silanol groups linked directly to the silicon core. If the surface contains a SiF group, the σ_s^* value can only increase; however extrapolation of the $\sigma_s^* = f(d)$ curve to $\sigma_s^* = 1.63$ (see Fig. 7) gives a real thickness of the residual oxide that coincides with ellipsometric estimates.

Thus, all real silicon matrices can be represented as a number of chemical compounds with the general formula $Si_m(SiO)_x.(SiO_2)_yOH$ where each particular composition (x and y values) is matched by a particular σ_s^*; at great y, this corresponds to the final member of the series, silica $(SiO_2)_yOH$.

The σ_s^* values obtained were indicative of relatively weak proton-donor properties of silanol groups both for a pure silicon surface and for a surface coated by a thin (< 3.0 nm) oxide layer. This means that for complete involvement of these groups in surface reactions, conditions should be provided for additional protonisation of hydroxyl groups. These conditions can be attained by raising the temperature (or by another activating

treatment) or by using proton-acceptor chemical reagents. For example, the use of triethylamine [27] as an exchange catalyst eliminates the latent period in the formation of silicon oxide layers (see Fig. 6) and allows the synthesis of silicon oxide nanostructures on hydroxylated surfaces of metals [33] in which the inductive effect of the core is relatively low for the same reasons as for silicon.

It should be noted that, judging by the transmission effect of the silicon–oxygen bond ($Z_{Si-O-Si} = 0.51$), the changes in $\Delta\sigma_s^*$ and, hence, the shift of ν(Si—H) should be much smaller for $N < 10$. If one oxide monolayer is synthesised per cycle of molecular layering, for N cycles, this should be

$$\Delta\sigma_s^* \sim Z^N = 0.51^N.$$

However, this relationship was not observed. Probably, in the initial stages of the molecular layering synthesis ($N < 10$), surface reactions involve only a part of hydroxyl groups and give rise to two-dimensional islet structures whose area increases upon further treatment. This is also indicated by the increase in the intensity of the bands for both Si—H and C—H bonds caused by the increase in the area occupied by the oxide.

An attempt to establish the general relationship between the inductive constants and the energetic characteristics of the studied matrices has revealed a linear correlation with the energy of the crystal core. For a gallium arsenide surface whose composition can be represented as a mixture of gallium and arsenic oxides, the experimental σ_s^* values fit well into the general linear dependence. The estimation of the presumptive σ_s^* values for MgO and ZnO using this dependence gave 2.8 and 2.2, respectively. These values could not be determined experimentally due to the low electrophilicity of DMCS.

VII. Conclusion

The material considered in this review shows good prospects for the use of the inductive effects and correlation analysis to study chemical transformations on the surface of solids. By comparison of inductive constants, it becomes possible not only to estimate quantitatively the influence of the core and the state of the surface for various solids on the processes taking place during thermal treatment but also to predict the pattern of surface reactions with various reagents. For this purpose, one should compare the σ_s^* and σ^* values for a substituent in a low-molecular-weight reagent. The reaction would proceed toward the replacement of the given substituent by a substituent with a greater inductive constant.

In a study of surface reactions on objects with small surface areas, for example, on single crystals, an important feature is the possibility of determining their stoichiometry when the use of direct chemical or analytical methods is difficult. The cited example of solving this problem for the silicon matrix convincingly demonstrates the utility of the parametric constants of the correlation equations.

Further development of the quantitative approach based on the use of inductive constants would involve selection of a standard surface reaction and determination of its characteristics (rate and equilibrium constants). This would enable quantitative prediction of the pathways and yields of surface reactions merely based on one-parameter correlation equations taking into account only the inductive effect. As a standard reaction, one can use the rearrangement [33] between chemisorbed chloro- and alkoxysilanes whose equilibrium constant can be found experimentally without much difficulty.

At the current stage of research, the inductive effect of substituents (including the core of a solid) can be estimated only as a certain approximation. Therefore, any task of exact determination of the inductive component in nonuniform surface phenomena is arbitrary and the result will depend on the choice of the standard process which underlies the scale of inductive constants used. However, this approach, which provides a quantitative description of surface processes, may prove useful for development of the routes of deliberate synthesis of surface nanostructures and development of chemical nanotechnology.

* * *

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