

# Wetting of epitaxial silicium layer and pyrolytic SiO<sub>2</sub> layer

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The process of adhesion of water and organic liquids on the surface of Si and SiO<sub>2</sub> was studied. The values of dispersion  $\sigma_d(s)$  and polar  $\sigma_p(s)$  components of the density of the surface Gibbs energy  $\sigma(s)$  of epitaxial Si layer and pyrolytic SiO<sub>2</sub> layer were determined by the method based on measuring the angle of wetting  $\varphi$ . It has been found that the polar component of interaction regulates the density of the surface Gibbs energy of the above substrates.

Изучался процесс адгезии воды и органических жидкостей на поверхности Si и SiO<sub>2</sub>. Были определены величины дисперсных  $\sigma_d(s)$  и полярных  $\sigma_p(s)$  компонентов плотности поверхностной Гиббсовой энергии  $\sigma(s)$  эпитаксиального слоя Si и пиролитического слоя SiO<sub>2</sub> методом измерения угла смачивания  $\varphi$ . Было установлено, что о плотности поверхностной Гиббсовой энергии вышеприведенных субстратов решает полярный компонент взаимодействия.

An important problem in the surface chemistry is the valuation of quality of surfaces. For the determination of chemical purity, the methods of trace analysis are taken into consideration. However, a rougher criterion for valuating the degree of purity of the surface of solid substance is frequently sufficient in technology, e.g. photolithography. The basic problem in the production of microelectronic elements is the preparation of materials with perfect planar delimitation and maximum purity. In this sense, a convenient procedure is the evaluation of energetic relations in the interface Si and SiO<sub>2</sub> substrate—pure air.

The parameter characterizing the relations on the surface of solid substances is the density of the surface Gibbs energy  $\sigma(s)$ . The knowledge of this quantity significantly contributes to understanding the character and effects of interactions and structure of interfaces.

While the technique of determination of the density of the surface Gibbs energy of liquids  $\sigma(l)$  is sufficiently elaborated and its theory verified, this procedure is not feasible for solid substances because of viscosity hindrance. For this reason, we

must use indirect methods based e.g. on the adsorption of gases, measurement of the heats of wetting or angles of wetting.

The thermodynamic equilibrium of forces on a solid surface may be mathematically expressed by means of the Young equation [1]. Later, Dupré calculated the work of adhesion by using this equation, from which the Young—Dupré relation expressing the work of adhesion [2] resulted. The method of determining the density of the surface Gibbs energy  $\sigma(s)$  as additive quantity involving the dispersion  $\sigma_d(s)$  and polar forces  $\sigma_p(s)$  was put forward for the system solid—liquid by Kaelble [3].

Some authors modified this procedure (see later) in order to improve the reproducibility and quantification of the properties of surface layers of low- and high-energetic substrates.

At present, two fundamental methods are used for determining the angles of wetting, i.e. the method of inclined plate and the method of lying drop. Different variants of these methods are aimed at solving the problem of reproducibility and sensitivity of measurement as well as the easy attainment of results.

The method of inclined plate was described by Fowkes and Harkins [4]. The method of lying drop was used by Thompson [5]. The most widely used modification applied by many authors is the method of stable drop of a certain volume [6—10]. After establishment of the equilibrium of forces, the drop is usually photographed and the angle of wetting is determined by measuring on the positive or by projection of the negative. Other variant of this method is direct measurement with a revolving goniometer of microscope [9]. A more precise variant consists in measurement of the dimension of drop and calculation of the angle of wetting according to the pertinent relationship [9, 10]. Both methods have virtues and drawbacks. The method of stable drop requires much smaller volume of liquid and relatively smaller smooth surface of the sample. The advantage of inclined plate consists in the fact that the hysteresis of wetting is simultaneously measured [11—13].

The topic of this paper is the determination of the densities of the surface Gibbs energy  $\sigma(\text{Si})$  and  $\sigma(\text{SiO}_2)$  and their dispersion ( $\sigma_d(\text{Si})$  and  $\sigma_d(\text{SiO}_2)$ ) and polar ( $\sigma_p(\text{Si})$  and  $\sigma_p(\text{SiO}_2)$ ) contributions by direct measurement of the angle of wetting  $\varphi$ . The measured  $\sigma$  values may be used e.g. for qualitative and quantitative valuation of the degree of surface purification of the investigated surfaces of Si and  $\text{SiO}_2$ .

## Experimental

Preparation of samples: Samples of the width of 200  $\mu\text{m}$  and diameter of 37 mm were cut from a Si ingot of cylindrical form. These samples were chemically and mechanically cut on their surface where a Si layer (111) was formed by epitaxial growth. The samples were

protected in a desiccator over solid NaOH to prevent the sorption of H<sub>2</sub>O, which would alter the surface properties. Fresh Si samples prepared by adequate thermal treatment which ensured effective desorption of occlusion gases [4] were used. The SiO<sub>2</sub> samples were so prepared that a layer of pyrolytic SiO<sub>2</sub> of the width of 1 μm was formed on the surface of epitaxial Si with a mixture of SiH<sub>4</sub> + O<sub>2</sub> by thermooxidation process.

The angle of wetting  $\varphi$  was measured by the use of a reflex goniometer KERNCO [9] which was equipped with a scale for direct reading of the angle of wetting and a temperature chamber allowing the regulation of temperature accurate to  $\pm 1$  °C as well as a cell ensuring a standard medium with a constant vapour pressure. Water and liquids were put on by means of a micropipette (3 mm<sup>3</sup>). The values of the angles of wetting in equilibrium state were used for calculation. The resulting values are arithmetic mean of five measurements. The coefficient of variation for the angles of wetting  $\varphi < 90^\circ$  was 2.6 % for all liquids and the standard deviation was 2.1°.

Furthermore, the influence of temperature was measured at  $\theta/^\circ\text{C}$ : 20, 25, 35, and 40. A nonhomologous series of liquids (water, glycerol, ethylene glycol, solution of formaldehyde, triethylene glycol, n-octyl alcohol, and cyclohexanol) with the range of  $\gamma(l, 25^\circ\text{C})$  between 71.9 and 25.8 mJm<sup>-2</sup> was used for measuring the dependence of the angle of wetting  $\varphi$  on temperature. These liquids of anal. grade were two times distilled and held in nitrogen atmosphere. The liquids of different wetting properties and polarity make the angle of wetting  $\varphi > 0$  on the surface of the tested substrates.

The surface tension of liquids  $\gamma(l)$  was measured tensiometrically at 25 °C, 30 °C, 35 °C, and 40 °C by means of an instrument based on the principle of a two-arm lever which involved tearing of a Pt ring (or annular space) from the surface of the tested liquid after establishment of equilibrium. The resulting values are the mean of five measurements, while the constant of the Pt ring was calculated for each temperature. The Pt ring was purified by washing with HCl and CCl<sub>4</sub> before measurement and afterwards it was annealed. As the numerical values of the surface tension  $\gamma$  and the densities of the surface Gibbs energy  $\sigma$  are identical, we are going to use the quantities  $\sigma$ .

## Results and discussion

The values of  $\sigma(l)$  of the liquids selected for testing the surface of Si and SiO<sub>2</sub> (water, glycerol, ethylene glycol, triethylene glycol, n-octyl alcohol, cyclohexanol, formaldehyde) at temperatures of 25 °C, 30 °C, 35 °C, and 40 °C are given in Table 1. The reference liquids were so selected that their surface energies were in the whole range of real possible values, *i.e.* from 25 to 72 mJm<sup>-2</sup> (Table 1). From the view-point of the temperature dependence of  $\sigma(l)$ , it appears reasonable to compare triethylene glycol and glycerol because these substances manifest the smallest temperature change in the investigated temperature interval which is almost on the limits of the measurement precision.

We used the procedure put forward and improved by Newmann et al. [14–19] for determining the surface Gibbs energy  $\sigma(s)$ . The presumption for its application

Table 1

Densities of the surface Gibbs energy of liquids ( $\sigma(l)$ )

Liquid	$\sigma(25\text{ °C})/(\text{mJm}^{-2})$	$\sigma(30\text{ °C})/(\text{mJm}^{-2})$	$\sigma(35\text{ °C})/(\text{mJm}^{-2})$	$\sigma(40\text{ °C})/(\text{mJm}^{-2})$
Water	71.9	71.2	70.4	69.6
Glycerol	63.6	63.2	62.7	62.3
Ethylene glycol	49.8	49.2	47.9	47.7
Triethylene glycol	47.5	47.5	47.1	46.5
n-Octyl alcohol	27.2	27.2	26.6	25.9
Cyclohexanol	25.8	25.5	24.4	23.5

is the establishment of equilibrium state. It is described by the Young equation

$$\sigma(s,l) + \sigma(l,g) \cdot \cos \varphi = \sigma(s,g) = \sigma(s) - \pi \quad (1)$$

where  $\sigma(s,g)$  and  $\sigma(l,g)$  are the densities of the surface Gibbs energy of the solid phase or liquid in equilibrium with saturated vapour,  $\sigma(s)$  corresponds to the solid substance *in vacuo*, and  $\pi$  is the pressure of wetting.

By inserting eqn (1) into the Dupré<sup>2</sup> equation

$$W = \sigma(s) + \sigma(s,g) - \sigma(s,l) \quad (2)$$

we obtain the form of the known Young—Dupré equation valid for the work of adhesion

$$W = (\sigma(s) - \sigma(s,g)) + \sigma(l,g) \cdot (1 + \cos \varphi) \quad (3)$$

from which Fowkes [20] derived the relationship for the interfacial energy of two immiscible liquids  $\sigma(1,2)$

$$\sigma(1,2) = \sigma(1) + \sigma(2) - 2 \cdot [(\sigma_d(1) \cdot \sigma_d(2))^{1/2} + (\sigma_p(1) \cdot \sigma_p(2))^{1/2}] \quad (4)$$

where  $\sigma_d(1)$ ,  $\sigma_d(2)$ ,  $\sigma_p(1)$ , and  $\sigma_p(2)$  are geometrical means of the contributions of dispersion forces and polar forces of individual components (1 and 2). According to Kaelble [3], the density of the surface Gibbs energy of solid substance  $\sigma(s)$  is an additive quantity comprising the components of the dispersion forces  $\sigma_d(s)$  and the polar forces  $\sigma_p(s)$

$$\sigma(s) = \sigma_d(s) + \sigma_p(s) \quad (5)$$

If the condition  $\pi = \sigma(s) - \sigma(s,g) = 0$  is fulfilled, the Young—Dupré equation for the system solid—liquid assumes the form

$$\cos \varphi + 1 = \frac{2}{\sigma(l,g)} [(\sigma_d(l,g) \cdot \sigma_d(s,g))^{1/2} + (\sigma_p(l,g) \cdot \sigma_p(s,g))^{1/2}] \quad (6)$$

The influence of temperature on the angle of wetting may be described by the equation obtained by differentiating eqn (6) with respect to temperature  $\theta$

$$d \cos \varphi / d\theta = \frac{d}{d\theta} \left\{ \frac{2}{\sigma(l,g)} [(\sigma_a(l,g) \cdot \sigma_a(s,g))^{1/2} + (\sigma_p(l,g) \cdot \sigma_p(s,g))^{1/2}] \right\} = \frac{d}{d\theta} [W/\sigma(l,g)] \quad (7)$$

Provided the value of  $d[W/\sigma(l,g)]/d\theta$  is small, as it is for low-energetic surfaces, then  $d \cos \varphi / d\theta \approx 0$  and the angle of wetting is independent of temperature. It is valid for hydrophobic surfaces that  $\varphi > 90^\circ$  and the angle of wetting increases with temperature whereas the value of  $\varphi$  decreases with temperature in the case of hydrophilic surfaces.

The values of the angles of wetting of individual liquids on the surfaces of epitaxial Si layer and thin SiO<sub>2</sub> layer at temperatures  $\theta = 24^\circ\text{C} - 40^\circ\text{C}$  are presented in Tables 2 and 3.

The dependence of the angle of wetting on temperature  $\varphi = f(\theta)$  of liquids (water, glycerol, ethylene glycol, formaldehyde, triethylene glycol, methylsilicone oil, and benzaldehyde) for epitaxial Si surface is represented in Fig. 1.

The dependence  $\varphi = f(\theta)$  for a thin layer of pyrolytic SiO<sub>2</sub> surface and the investigated liquids (water, glycerol, ethylene glycol, n-octyl alcohol, formaldehyde, and cyclohexanol) is represented in Fig. 2.

As evident from Figs. 1 and 2, the angle of wetting decreases with increasing temperature for all investigated pairs, which is in good agreement with the theoretical assumption mentioned earlier.

Table 2

Angle of wetting  $\varphi$  for Si at temperatures  $25^\circ\text{C} - 40^\circ\text{C}$

Liquid	$\theta/^\circ\text{C}$			
	25	30	35	40
$\varphi/^\circ$				
Water	49.0	48.9	48.3	48.2
Ethylene glycol	32.8	31.8	30.5	30.3
Glycerol	41.4	41.2	40.1	37.7
Formaldehyde	36.8	34.7	31.7	28.1
Triethylene glycol	30.0	29.2	27.2	26.9
Methylsilicone oil	12.7	9.6	8.3	8.2
Benzaldehyde	8.8	7.7	7.4	7.2

Table 3

Angle of wetting  $\varphi$  for SiO<sub>2</sub> at temperatures 25 °C—40 °C

Liquid	$\theta/^\circ\text{C}$			
	25	30	35	40
Water	53.5	51.2	48.8	48.5
Ethylene glycol	30.6	29.4	28.8	27.1
Glycerol	37.9	37.2	36.6	36.2
Cyclohexanone	19.1	18.6	17.6	16.6
Formaldehyde	26.0	23.5	21.1	18.5
n-Octyl alcohol	29.4	28.4	25.3	22.2

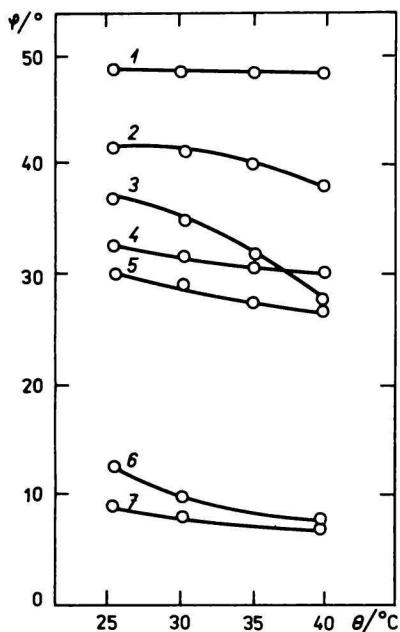
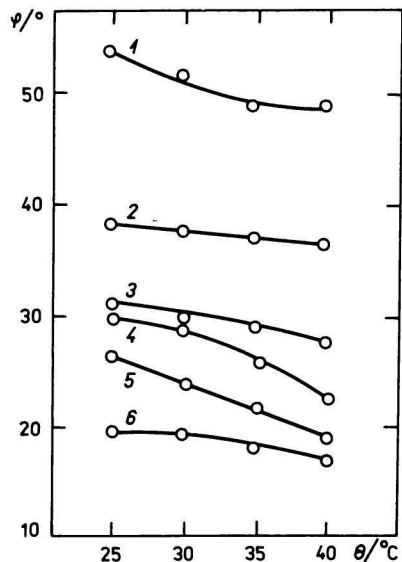


Fig. 1. Variation with temperature of the angle of wetting on the surface of epitaxial Si layer.

1. Water; 2. glycerol; 3. formaldehyde;  
4. ethylene glycol; 5. triethylene glycol;  
6. methylsilicone oil; 7. benzaldehyde.

Fig. 2. Variation with temperature of the angle of wetting on the surface of pyrolytic SiO<sub>2</sub>.

1. Water; 2. glycerol; 3. ethylene glycol;  
4. n-octyl alcohol; 5. formaldehyde; 6. cyclohexanone.

As for the graphical representations, the dependence of  $\varphi$  on temperature for formaldehyde has an interesting course which is evidently due to increasing depolymerization of formaldehyde according to common scheme



From the view-point of hydrophobization of the  $\text{SiO}_2$  surface, methylsilicone oil and benzaldehyde appear to be the most convenient among the above-mentioned solvents because their angles of wetting are in the range  $7.3 \leq \varphi \leq 12.7^\circ$

The density of the surface Gibbs energy  $\sigma(s)$  of the investigated Si and  $\text{SiO}_2$  surfaces was calculated as additive quantity comprising the arithmetic means of the dispersion contribution  $\sigma_d(s)$  and polar contribution  $\sigma_p(s)$  according to eqn (5).

The values of the dispersion contribution  $\sigma_d(l)$  at  $20^\circ\text{C}$  according to *Kaelble* [3] are given in Table 4.

Table 4

Values of dispersion component of the density of the surface Gibbs energy of liquids  $\sigma_d(l)$  at  $20^\circ\text{C}$

Liquid	$\sigma_d(l)/(\text{mJm}^{-2})$
Water	21.8
Glycerol	37.0
Ethylene glycol	26.3
Triethylene glycol	26.5
Cyclohexanol	25.5
n-Octyl alcohol	18.1

The dispersion and polar components  $\sigma_d(s)$  and  $\sigma_p(s)$  of the Si and  $\text{SiO}_2$  surfaces were determined from the plot of eqn (8) by the method of least squares

$$\frac{1 + \cos \varphi}{2} \frac{\sigma(l)}{\sqrt{\sigma_d(l)}} = \sqrt{\sigma_d(s)} + \sqrt{\sigma_p(s)} \sqrt{\frac{\sigma(l) - \sigma_d(l)}{\sigma_d(l)}} \quad (8)$$

The values of the density of the surface Gibbs energy  $\sigma(s)$ , the values of polar component  $\sigma_p(s)$  and dispersion component  $\sigma_d(s)$  of epitaxial Si surface and pyrolytic  $\text{SiO}_2$  surface for  $\theta/^\circ\text{C} = 25, 30, 35,$  and  $40$  are summarized in Table 5.

The values of  $\sigma(s)$  and its dispersion  $\sigma_d(s)$  and polar components  $\sigma_p(s)$  given in Table 5 are in agreement with the views of *Matijević et al.* [17]. It results from this table that the value of  $\sigma(s)$  for Si and  $\text{SiO}_2$  varies with temperature and the polar component has essential influence on the magnitude of  $\sigma(s)$ . This piece of knowledge means that the effectual component of contaminants must have polar

Table 5

Density of the surface Gibbs energy  $\sigma(s)$  and its dispersion and polar components ( $\sigma_d(s)$ ,  $\sigma_p(s)$ ) of epitaxial Si layer or pyrolytic SiO<sub>2</sub> layer at temperatures 25 °C—40 °C

Layer		$\theta/^\circ\text{C}$			
		25	30	35	40
Si	$\sigma(s)/(\text{mJm}^{-2})$	49.9	51.5	51.5	49.9
	$\sigma_d(s)/(\text{mJm}^{-2})$	13.7	12.7	12.4	14.7
	$\sigma_p(s)/(\text{mJm}^{-2})$	36.2	38.8	39.1	34.6
SiO <sub>2</sub>	$\sigma(s)/(\text{mJm}^{-2})$	48.0	50.7	53.2	51.9
	$\sigma_d(s)/(\text{mJm}^{-2})$	5.8	5.3	4.2	5.8
	$\sigma_p(s)/(\text{mJm}^{-2})$	42.2	45.4	49.0	45.1

character. This requirement is fulfilled best by water. The essence of defects in adhesion of nonpolar light-sensitive layers on SiO<sub>2</sub> surfaces in photolithographic operations of planar technology results from the above fact.

## References

1. Young, T., *Phys. Trans. Roy. Soc.* 95, 65 (1805).
2. Dupré, A., *Théorie Mécanique de la Chaleur*. Gauthier-Villars, Paris, 1869.
3. Kaelble, D. H., *Physical Chemistry of Adhesion*. Wiley—Interscience, New York, 1971.
4. Fowkes, F. M. and Harkins, W. D., *J. Amer. Chem. Soc.* 62, 209 (1940).
5. Aveyard, R. and Haydon, D. A., *An Introduction to the Principles of Surface Chemistry*. University Press, Cambridge, 1973.
6. Brewis, D. M., *Polym. Eng. Sci.* 7, 17 (1967).
7. Gabriel, S., *J. Oil Colour Chem. Ass.* 58, 52 (1975).
8. Lörinc, A. and Stryopoulos, K., *Proc. Int. Conf. Colloid Surface Sci.*, p. 169. Budapest, 1975.
9. *Tech. Rep. 15. Contact Angle Meters by Kernco Reflective Goniometers*. Kernco Instruments Co. Inc. Horizon City Ind. Park, El Paso, Texas.
10. Janczuk, B., Waksmundski, A., and Wójcik, W., *Ann. Soc. Chim. Polonorum* 51, 985 (1977).
11. Osipov, L. I., *Surface Chemistry. Theory and Industrial Applications*. Krieger, R. E., Huntington, 1977.
12. Grindskaff, T. H., *Text. Res. J.* 39, 959 (1969).
13. Bikerman, J. J., *Physical Surfaces*. Academic Press, New York, 1970.
14. Harkins, W. O., *Physical Chemistry of Surface Films*. Reinhold, New York, 1952.
15. Adamson, A. W., *Physical Chemistry of Surfaces*. Wiley—Interscience, New York, 1976.
16. Schwartz, A. M. and Perry, J. W., *Surface Active Agents*. Wiley—Interscience, New York, 1948.
17. Matijević, E. and Eirich, F., *Surface and Colloid Science*. J. Wiley, New York, 1969.
18. Good, R. J., *J. Colloid Interface Sci.* 44, 63 (1973).
19. Good, R. J. and Elbing, E., *Ind. Eng. Chem.* 62, 54 (1970).
20. Fowkes, F. M., *Advances in Chemistry*. Amer. Chem. Soc., Washington, D.C., 1964.

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