

Influence of relative humidity on the wettability of silicon wafer surfaces*

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Investigation of wetting properties of the original silicon wafers and modified by oxidation was carried out by contact angles measurements of water at varying relative humidity (RH) of the atmosphere present in the measuring chamber. At three selected humidities (10, 30 and 50%) contact angles of diiodomethane and formamide were also determined for the original silicon wafer only. The topography of the tested surfaces was determined with the help of atomic force microscopy (AFM). Using the measured contact angles the total apparent surface free energy and its components of studied silicon wafers were determined using two models: the contact angle hysteresis (CAH) and Lifshitz-van der Waals acid-base (LWAB) approaches. In the former approach the advancing and receding contact angles are employed, and in the latter only the advancing angles. It was found that in the case of original silicon wafer the contact angles and surface free energy depend on the humidity only in the RH range from 10 to 40% with a minimum at 30% RH, and then they fluctuate around a mean value. For the oxidized silicon wafer the changes in the contact angles and the surface free energy depend on the relative humidity and change periodically with increasing RH. These changes can result from water adsorption on the hydrophilic silicon surface.

1. INTRODUCTION

In recent years interest in silicon wafers has increased significantly due to their application as the semiconductor material used in the fabrication of

* Dedicated to Professor Emil Chibowski on the occasion of his 65th birthday.

integrated circuit and other microdevices, the substrate for deposition of various materials and photolithographic patterning. Knowledge of the physicochemical properties of silicon wafers is important because the freshly created solid surface undergoes various transformations such as oxidizing, reduction, hydrolysis and adsorption from the gas phase. In the presence of oxygen on the surface a passive thin layer of SiO_x and crystallographic defects form. Moreover, technological process of semiconductor devices consists of certain amount of thermal processes which modify surface layer of silicon wafer. These processes lead to changes of electronic parameters of various semiconductor integrated circuits.

A bare solid surface can be maintained only in conditions of high vacuum of $133 \cdot 10^{-10}$ Pa or even higher [1]. At vacuum of $133 \cdot 10^{-6}$ Pa still a lot of water molecules collide with surface that the formation of a monolayer is possible in one second. Hydration of surface influences the changes of its physicochemical properties, e.g. intermolecular interactions at the interfaces, which also play a crucial role in natural environment and technological processes. The surface free energy, which is a consequence of these interactions, is a fundamental quantity used for characterization of surface and interfacial phenomena. The knowledge of the energy and its components allows calculation of the work of spreading, immersion and adhesion. Thus the surface wettability by the liquid, the adhesion strength, the system stability and other properties can be predicted. Determination of acid-base: electron-donor and electron-acceptor parameters of the energy makes possible to conclude about the functional groups which can form hydrogen bonding.

In wetting processes contact angle is an important experimental parameter, which allows evaluation of surface free energy. The fundamental equation which relates the energetic balance in the solid–liquid drop–air system is given by the well-known Young's equation [2]. In this equation contact angle and liquid surface tension are measurable quantities, but the solid surface free energy and the solid/liquid interfacial free energy are unknown and, therefore, this equation cannot be solved. However, a useful expression, derived by combining Young's equation with Dupré equation, allows calculation of the work of adhesion W_A of the solid/liquid [2]:

$$W_A = \gamma_L (1 + \cos \theta) \quad (1)$$

According to the approach of van Oss, Chaudhury and Good (called Lifshitz-van/der Waals acid-base approach – LWAB), the Young– Dupré equation for polar solids W_A becomes [3–5]:

$$W_A = \gamma_L (1 + \cos \theta) = 2(\gamma_s^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_s^+ \gamma_L^-)^{1/2} + 2(\gamma_s^- \gamma_L^+)^{1/2} \quad (2)$$

where: γ^{LW} is the Lifshitz-van der Waals component, γ^+ and γ^- are electron-acceptor and electron-donor parameters of the acid-base component, respectively, and subscripts L and S stand for liquid and solid, respectively.

Hence, measurement of the advancing contact angles of three liquids (among which two have to be polar, like water and formamide) which surface tension are known and solving simultaneously three equation (2) the solid surface free energy and its components can be calculated. There is a hidden assumption that the strength of the interactions originating from the solid surface is the same irrespective of the probe liquid used, which is debatable.

Recently, Chibowski [6–9] has proposed a new approach (called contact angles hysteresis approach – CAH) to determine the solid total surface free energy (γ_s) from the surface tension of the probe liquid (γ_L) and hysteresis of the contact angles of this liquid (H), which is defined as the difference between the advancing (θ_a) and receding (θ_r) contact angles. The phenomenon of hysteresis has been known for a couple of decades and it was explained by roughness of real surfaces and/or their chemical heterogeneity, surface swelling, penetration of liquid into the solid surface, and surface functional groups reorientation [10–19]. On the other hand, on molecularly smooth surface the advancing and receding contact angles differs for example of cyclohexane on mica by 0.5° [20]. On other smooth surfaces like Teflon [21,22], self-assembled hexadecyltrimethylchlorosilane monolayers deposited on glass slides or silicon [23] or damaged self-assembled monolayer of cetyltrimethylammonium bromide [24], polystyrene with fluorocarbon substituents [25] and polymer-grafted silicon wafers [26], the hysteresis of water and other liquids were also observed.

Chibowski and co-workers [6–9,27,28] considered that contact angle hysteresis might also result from the liquid film left behind the droplet upon retreat its three-phase contact line, which causes the receding contact angle to be lower than the advancing one. The equation describing the total surface free energy of a solid is expressed as:

$$\gamma_s = \frac{\gamma_L(1 + \cos \theta_a)^2}{(2 + \cos \theta_r + \cos \theta_a)} \quad (2)$$

However, thus determined values of γ_s are apparent ones, because to some extent they depend on the kind and magnitude of the interactions taking place across the interface [8,9,28,29]. In other words, surface free energy thus determined depends on the kind of probe liquid used. The difference in the values of the surface free energy of solid as determined via the hysteresis model of different probe liquids are due to change of the solid/liquid interfacial

interactions, which reflect in the measured contact angles. If diiodomethane is used to determine this energy, the interactions are practically of dispersive nature only, but those with water and formamide are polar acid-base too.

It may be expected that both on low surface energy polymers and polar solid surfaces an adsorbed film of contact-angle liquids is present, which influences the contact angles and the surface free energy. Our previous study indicates that even on molecularly flat surface PMMA surface contact angle hysteresis appears and the advancing and receding contact angles vary depending on the relative humidity of the environment, but the changes are not monotonic [29]. The changes in measured water contact angles reflect in the surface free energy determined from the CAH model. The observed apparent surface free energy changes of the PMMA surface may result from coalescence of the adsorbed water nano- and/or micro- droplets that occurs with changing the humidity.

The purpose of this study was to determine the effect of increasing humidity of the ambient atmosphere on the advancing and receding contact angles and thus on the surface free energy of original and modified silicon wafers. At three selected humidities contact angles of diiodomethane and formamide were also determined. Two approaches for determination of total surface free energy and its components were used: the contact angle hysteresis (CAH) approach and Lifshitz-van der Waals acid-base (LWAB) approach.

2. EXPERIMENTAL

Materials. Silicon wafers of 100 mm in diameter and 0.5 mm in thickness were obtained from the ON Semiconductor Company in the Czech Republic. The advancing and receding contact angles were measured on silicon slides (5 cm²), which were cut from the wafers. The three probe liquids used for contact angle measurements were water (from Milli-Q 185 and then distilled using Destamat Bi18E system), formamide (Fluka, >99%) and diiodomethane (POCH S.A., Poland, p.a.).

Sample preparation. In the first series original silicon wafers were cleaned in an ultrasonic acetone bath for 15 min, followed by a thorough rinse with Milli-Q water, and placed into an ultrasonic bath in Milli-Q water two times for 15 min. Next the slides were dried in a desiccator at 100°C for 20 min. In the second series the silicon wafers were immersed in a 1:1 volume ratio mixture of 30% H₂O₂ and concentrated H₂SO₄ for 30 min. After that, the wafers were extensively rinsed with Milli-Q water until the water conductivity was reached the value of about 5 μS cm⁻¹. Next the slides were placed again into an ultrasonic bath in water two times for 15 min, and then dried in a desiccator at 100°C for 20 min.

Finally, all the slides were stored in a desiccator with a molecular sieve at room temperature until their use.

Contact angle measurements. Digidrop GBX Contact Angle Meter (France) equipped with video-camera system and computer software was used for the contact angle measurements by the sessile drop method. The advancing contact angles of water and two other probe liquids (diiodomethane and formamide) were measured after settling 6 μL droplets on the surface (Figure 1a and b). Then after sucking of 2 μL from the droplet into the syringe the receding contact angle was measured (Figure 1c and d).

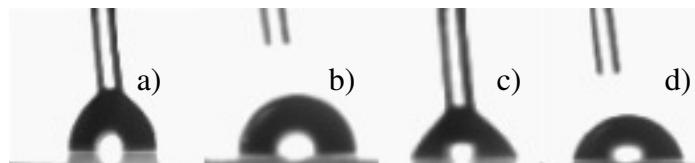


Fig. 1. Photographs of water droplets at advancing and receding contact angles measurements.

The contact angles of water were measured at $20\pm 1^\circ\text{C}$ in a closed chamber at relative humidity ranging from 10 to 95% taking readings on the left and right sides of 20 droplets. The humidity of the atmosphere was controlled and maintained constant within $\pm 0.1\%$ by digital hygrometer from Elmetron (Poland). Before contact angle measurements the silicon plates were placed in the measuring chamber of the apparatus with controlled humidity and were conditioned for 5 min in a given humidity. At selected humidities (10, 30 and 50%) contact angles of diiodomethane and formamide were also determined.

AFM investigations. The silicon surface topology was investigated using atomic force microscopy (AFM instrument Nanoscope III, Veeco, USA) with a standard silicon tip, in which contact mode can be applied. All 3-D images of the wafer surfaces were obtained from $1\times 1\ \mu\text{m}$. The roughness of the surface and distribution of heights were determined by means of WSxM4.0, Develop 8.0 scanning probe microscope software [30].

3. RESULTS AND DISCUSSION

To learn about the surface topography of silicon wafers prepared in two different ways the AFM were taken in contact mode with silicon tip. In Figures 2 and 3 are shown 3D and 2D images of $1 \times 1 \mu\text{m}^2$ original silicon wafer (Figure 1a) and silicon wafer oxidized in 30% H_2O_2 and concentrated H_2SO_4 (Figure 2b) together with the roughness distribution and the roughness profiles taken along the marked line on the images (from top right to left bottom) of these surfaces.

The rms values and other topography parameters of two investigated silicon wafers are presented in Table 1. These data were obtained using WS x M 5.0 Develop 8.0 Scanning Probe Microscope software [30].

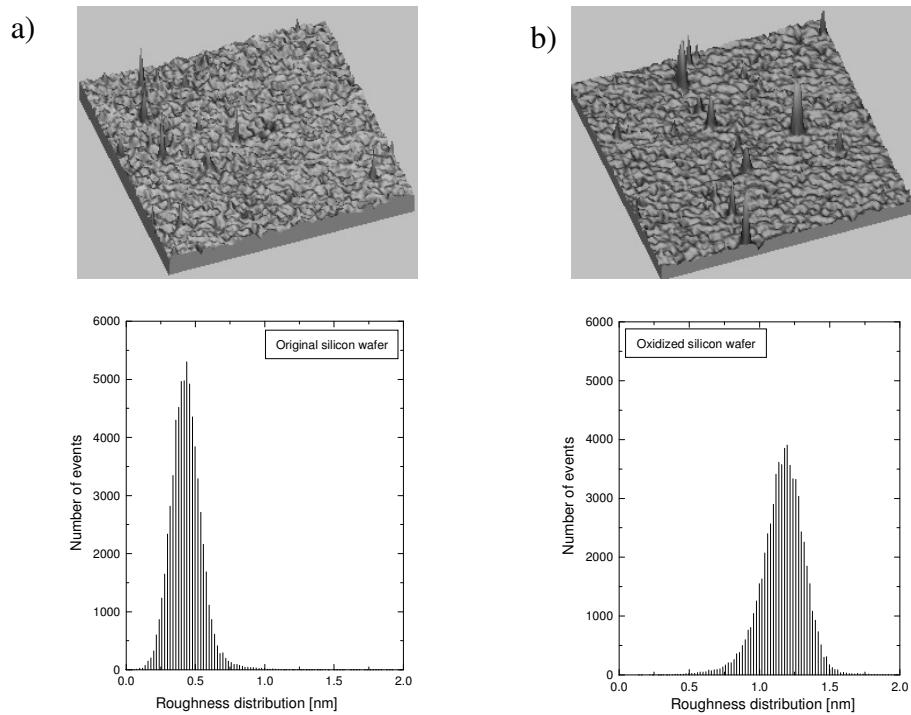


Fig. 2. 3D AFM images of $1 \mu\text{m}^2$ of original (A) and oxidized (B) silicon wafers and roughness distribution of these surfaces.

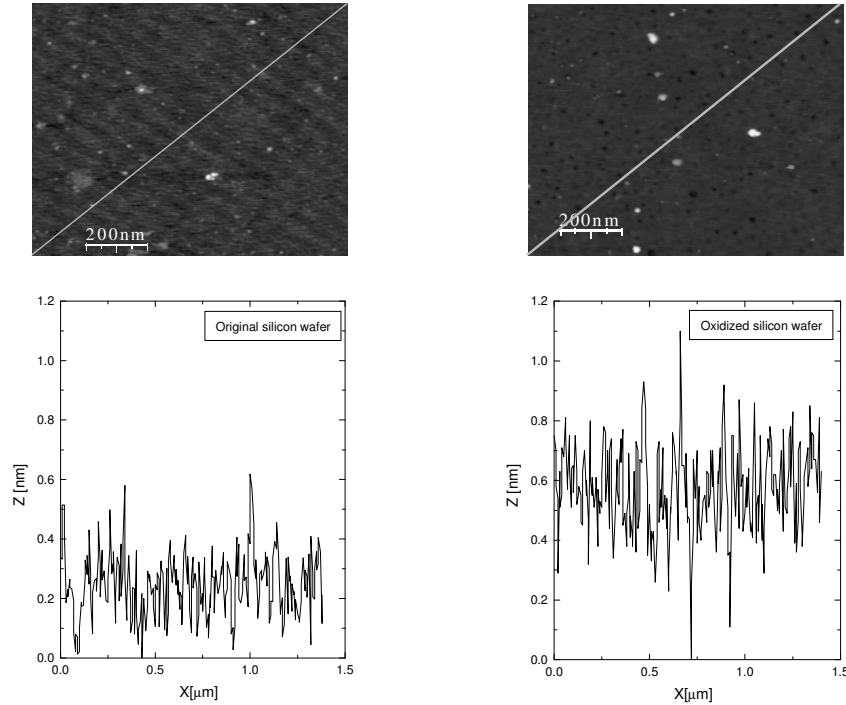


Fig. 3. 2D AFM images of $1 \mu\text{m}^2$ of original (A) and oxidized (B) silicon wafers and its roughness along the marked line (from top right to left bottom).

Tab. 1. Parameters characterizing the topography of the tested $1 \mu\text{m}^2$ silicon wafers; number of the scanned 'events' 65529 and 65067 for original and oxidized silicon wafers, respectively

Silicon wafer	rms, nm	av height, nm	Height (h), nm		
			$0 \geq h \leq 0.14$ 0.25%	$0.16 \geq h \leq 0.76$ 98.6%	$0.78 \geq h \leq 1.98$ 1.15%
Original	0.12	0.44			
Oxidized	0.27	1.19	$0 \geq h \leq 0.7$ 1.1%	$0.72 \geq h \leq 1.52$ 98.1%	$0.78 \geq h \leq 1.98$ 0.8%

Analyzing the AFM data placed in Table 1 and presented in the Figures 2 and 3, it can be found, as could be expected, that much more rough is the oxidized silicon wafer surface, because rms roughness of this surface is over 2 times higher than the original one. The average heights of the roughness for these

surfaces are 0.44 and 1.19 nm, respectively. On the original silicon wafer 98.6% of the surface ($1 \mu\text{m}^2$) possesses a broad range of the protrusions between 0.16 and 0.76 nm, and 1.15% of this surface is covered by 0.78–1.98 nm high roughness (Table 1). As can be seen the original silicon wafer has very smooth surface and therefore polished silicon wafers are used in optical photolithography. In the case of oxidized silicon wafer surface the roughness distributions are similar, but their height is about twice higher and 98.1% of the protrusions are 0.72–1.52 nm high (Table 1).

Our previous study shows that the apparent PMMA surface free energy determined from water contact angle hysteresis decreases with increasing humidity of the environment [29]. To get more data about the free energy dependence on the relative humidity the advancing and receding contact angles of water on original and oxidized silicon wafers were measured at 20°C at various relative humidities, from 10 to 95%, and they are shown in Figure 4.

As can be seen, in the case of original wafer with the increasing RH the advancing contact angles change from 29.8° (at 30% RH) to 54.5° (at 80%RH). However, the biggest changes in contact angles occur below 50% RH. At ca. 30% of humidity water contact angles show significant minimum. In the interval from 40 to 95% of relative humidity the values of advancing contact angles do not depend on RH and they are fluctuating around $51.5 \pm 2.1^\circ$. The standard deviations of the contact angles of 20 water drops ranges from 1.7 to 2.9° . The trend of the receding contact angles of water vs. relative humidity is similar to the advancing one, but their values are smaller.

In the next series similar measurements of water contact angles have been conducted on oxidized silicon wafer. Results of the advancing and receding contact angles as a function of relative humidity of the environment are shown in Figure 4. Here both the advancing and receding contact angles fluctuate periodically between 28.2 and 49.5° . The changes result in three significant maxima at ca. 20, 60 and 95% RH and distinct minima at 30–50% and 80–90 % RH.

The observed changes in the advancing and receding contact angles are evidently due to water vapor adsorption on silicon surface. The used silicon wafers contain large amount of oxygen interstitial atoms. In the case of oxidized silicon surface the oxide layer has a substantially uniform thickness somewhere between 1 to 20 Å and consists essentially of silicon dioxide [31], therefore its surface possesses as high affinity to water as quartz or silica. Jańczuk and Zdziennicka [32] found that long time contact of quartz with water vapour caused a decrease in the advancing contact angles from 52 to 24° , but an increase in the contact angle as a function of relative humidity was observed.

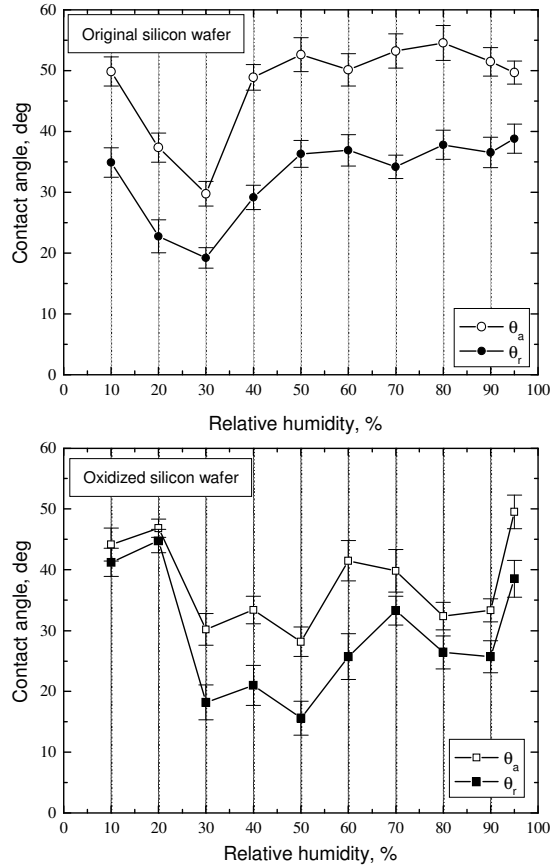


Fig. 4. Advancing and receding contact angles of water droplets on original and oxidized silicon wafers vs. relative humidity.

On the polar, hydrophilic surface, strong adsorption of water molecules occurs and as a result water film is formed in which up to 10–15 statistical monolayers the water molecules possess somewhat different properties compared with those in the bulk phase. The structure of such film depends on its thickness [33].

Feng and co-workers [34] studied the rate of adsorption and desorption of water on silica surface by gravimetric, FTIR and X-ray photoelectron spectroscopy. They heated silica powder in vacuum from 200–1000°C and analyzed IR spectra of silica and found that the silica surface becomes hydrophobic on thermal treatment but then becomes hydrophilic immediately on contact with water at low temperature.

In Figure 5 are presented the resulting water contact angle hysteresis on both studied surfaces versus relative humidity.

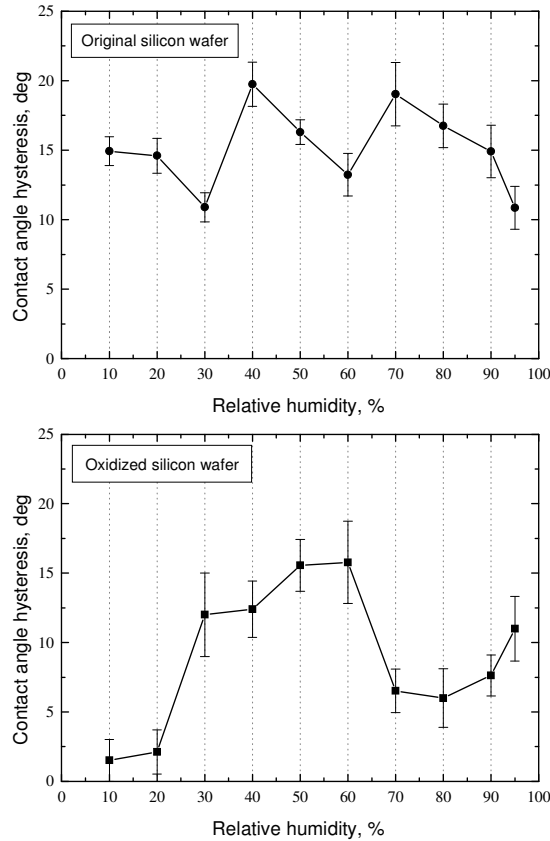


Fig. 5. Contact angles hysteresis of water droplets on original and oxidized silicon wafer vs. relative humidity.

The values of hysteresis on original wafer oscillate periodically between 10.9 and 19° and three distinctive areas are observed. The lowest contact angle hysteresis appears in the RH range from 10 to 30% and in the RH ranges 10–30, 40–60 and 70–95% it decreases roughly linearly. In the case of oxidized surface the maximum values of hysteresis appears at 30 to 60% RH.

However, besides characterization of the surface by contact angles, more information can be obtained by calculation of the apparent surface free energy from the contact angle hysteresis from equation (2). Thus obtained values of γ_s as a function of relative humidity are shown in Figure 6.

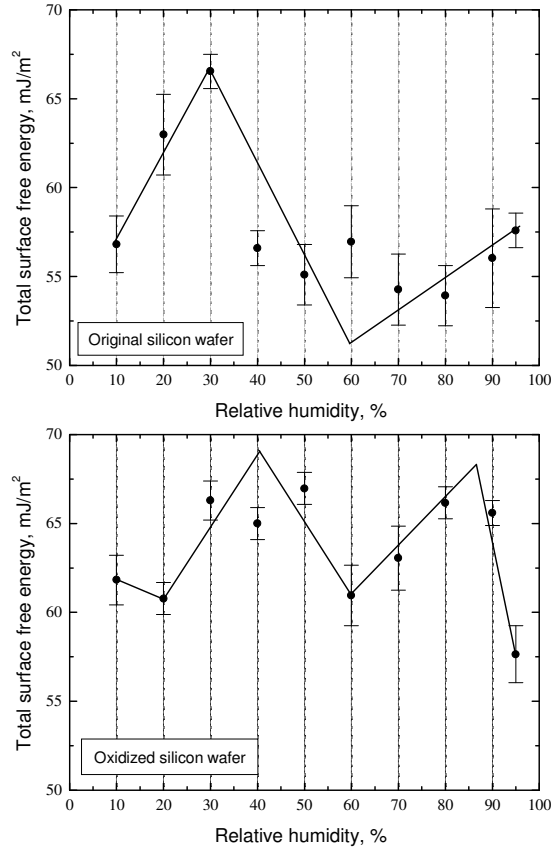


Fig. 6. The apparent surface free energy of original and oxidized silicon wafer depending on the relative humidity.

From our studies it is clearly seen that the changes of total surface free energy of both silicon wafers depend on the relative humidity of environment. The greatest changes of apparent γ_s of original silicon wafer appear between 10 and 30% RH, from 56.8 to 66.5 mJ/m² and in the range of 30–60% RH, from 66.5 to again ca. 55 mJ/m². In the second system the total surface free energy of the oxidized wafer fluctuates with increasing relative humidity. The minima appear at 20, 60 and 95% RH, and the maxima are seen at 40 and 85% RH. The greatest γ_s occurs at 50% RH (Figure 6) and the largest decrease in γ_s occurs between 80 and 95% of RH, from 66.2 to 57.6 mJ/m². Mean value of the total surface free energy in the whole interval of humidity equals 63.4 ± 3.1 mJ/m².

At least in the case of strongly polar solid, e.g. silicon wafers covered by thin layer of silica, the presence of adsorbed and oriented water molecules cannot be

ignored because they essentially affect the surface free energy. Hence, the obtained values of surface free energy should be considered in terms of water molecules adsorbed on the surface.

Jańczuk and Zdziennicka [32] found that the changes in wettability of quartz by water as a function of the air humidity and the time of quartz contact with water, resulted from the changes in the surface free energy components due to adsorption of water molecules on the solid surface and the structure of the formed film.

Siliceous surfaces, like those of other oxides, are naturally hydrophilic. Their properties depend among others on the chemical composition of the surface. Silica surface may consist of different functional groups. The hydroxyl functional groups present on the silica surface play a major role in the hydrophobicity of the surfaces because they can interact with water molecules by hydrogen bonds and are considered as the adsorption sites [35]. According to Kisielew and co-workers [36,37] amount of hydroxyls on the completely hydroxylated silica surface is constant and equals 4.6 groups on one square nanometer, which is in agreement with the average amount of Si atoms on the octahedral face of β -cristobalite (c.a. 4.55 atoms per nm^2) [38,39]. The surface concentration of the silanol groups influences the surface free energy of silica due to magnitude of the intermolecular interactions. Hołysz [40] examined surface free energy of thermally pretreated silica gel using the wicking method and found linear decrease of the electro-donor component γ_s^- from 58.4 to 23.8 mJ/m^2 with decrease number of $-\text{OH}$ groups present on the surface between 200 and 800°C.

Because of the presence of hydroxyls on the surface, which are the adsorption sites for water, silica is “covered” by water multilayer [35]. It was found by thermogravimetric and IR analysis that the first water layer has different character than the subsequent layers. Basing on the measured intensity of near-IR diffuse-reflectance spectra, Klier and co-workers [41] confirm in the BET monolayer the presence of SiOH-OH_2 complexes with about one half of the silanols on a Hisil 233 silica. Moreover, additional water molecules adsorb rather to the adsorbed water molecules than to free hydroxyls, which are energetically less favorable. Also Yamauchi and Hondo [42] examining water adsorption to silica gel found that water would adsorb only to a part of the hydroxyl groups, as SiOH-OH_2 complex and the additional water would ‘settle’ on the previous ‘silanol water’. The adsorption of water on a fully hydroxylated surface of $\beta(\alpha)$ -cristobalite covered by the geminal hydroxyl groups was also studied by Yang and co-workers [43] using density-functional total-energy and molecular dynamics calculations. They suggested a new, well-defined and stable up to room temperature ice phase, well described by the quadrangular and

octagonal patterns of hydrogen bond networks. In this new phase, called ice tessellation, all OH groups in water and surface hydroxyls are fully saturated by hydrogen bonds.

Surface free energy of quartz, as well as its changes caused by adsorption of water vapor on its surface was also investigated by Staszczuk and co-workers [33]. Based on Fowke's model they found that 94.3% of the changes in the dispersion component of the free energy of a quartz surface occurred in first two statistical monolayers of the adsorbed water, while 98.3% in first four. This may result from the ordered structure of water film up to 4 statistical monolayers. Above four statistical monolayers coverage the field of the forces originating from the quartz surface is so weak that the energy of the adsorbed water molecules is almost equal energy in its bulk phase. They also suggested that changes in quartz-water free energy can be different depending on water adsorption process, which would result in different thickness of the water film [33].

As mentioned earlier, the surface free energy of original silicon wafer at three relative humidities of the atmosphere, i.e. 10, 30 and 50%, was determined from the advancing contact angles of diiodomethane, water and formamide using LWAB approach and from the advancing and receding contact angles of these probe liquid using CAH approach. The results are presented in Figure 7 and in Table 2.

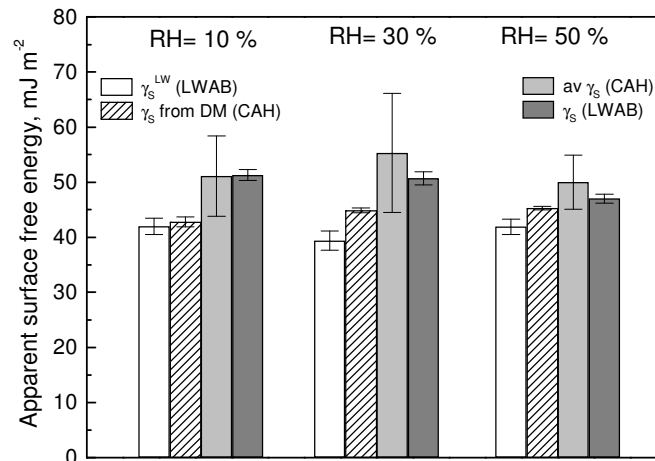


Fig. 7. Apparent total surface free energy of original silicon wafer determined from the contact angle hysteresis of diiodomethane (DM), water (W) and formamide (F) and apolar component of the surface free energy determined from DM at various relative humidity.

In the figure are also shown the values of apolar component of surface free energy, and the electron-donor γ_s^- and electron-acceptor γ_s^+ parameters of the surface free energy calculated from the advancing contact angles of diiodomethane (DM), water (W) and formamide (F) using LWAB approach (Table 2). From our studies it appears that the surface free energy of silicon wafer determined from CAH approach is consistent with the values obtained via surface free energy components. However, thus calculated silicon surface free energy depends on liquid tension and the kind and strengths of liquid–solid interfacial interactions (Table 2), which is reflected in the measured contact angles of the probe liquids.

Tab. 2. The values of surface free energy and its components of original silicon wafer at three relative humidities determined from LWAB and CAH approaches.

RH, %	LWAB approach				CAH approach			
	γ_s^{LW}	γ_s^-	γ_s^+	γ_s	γ_s (DM)	γ_s (W)	γ_s (F)	γ_s^{mean}
	mJ/m ²							
10	42.0	24.9	0.86	51.3	42.8	56.8	53.6	51.1
30	39.4	46.7	0.69	50.7	44.9	66.5	54.4	55.3
50	41.9	26.0	0.25	47.0	45.3	55.1	49.6	50.0

From the results presented it appears that total γ_s and γ_s^{LW} values of silicon wafer obtained from diiodomethane contact angles by the two approaches are similar, but γ_s is slightly larger than γ_s^{LW} , although at 10% RH the difference is much less. The differences can result from closer interacting distances, which appear in the receding contact angles used in the calculation from CAH approach [44].

At all three RH the mean total surface free energy determined from CAH agrees with the value calculated from van Oss and co-workers [3–5] approach. The greatest difference appears at 30% RH.

Because from CAH approach the apparent values of total surface free energy depend on the probe liquid used, therefore it was considered that the differences are due to polar interaction with water and formamide. Basing on this the acid–base interactions γ_s^{AB} were calculated from the difference $\gamma_s(W) - \gamma_s(DM)$ and $\gamma_s(F) - \gamma_s(DM)$ (Table 3).

Tab. 3. The values of acid-base components of surface free energy of original silicon wafer at three relative humidities determined from LWAB and CAH approaches.

RH, %	γ_s^{AB}	$\gamma_s^{AB} = \gamma_s(W) - \gamma_s(DM)$	$\gamma_s^{AB} = \gamma_s(F) - \gamma_s(DM)$
	LWAB	CAH	
10	9.3	14.0	10.8
30	11.4	21.6	9.5
50	5.1	9.8	4.3

The calculated acid-base component values show, that polarity of the original silicon wafer depends on RH. It is worth to notice that γ_s^{AB} values calculated from LWAB and CAH approaches are similar if formamide and diiodomethane were taken into account in the contact angle hysteresis approach. The results seem to confirm hypothesis of water pre-adsorption on the silicon surface. However, to suggest full mechanism of humidity influence on the surface free energy of solid surfaces more investigations are needed.

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