Surface Tension and Adhesion of Photo and Electron-Beam Resists

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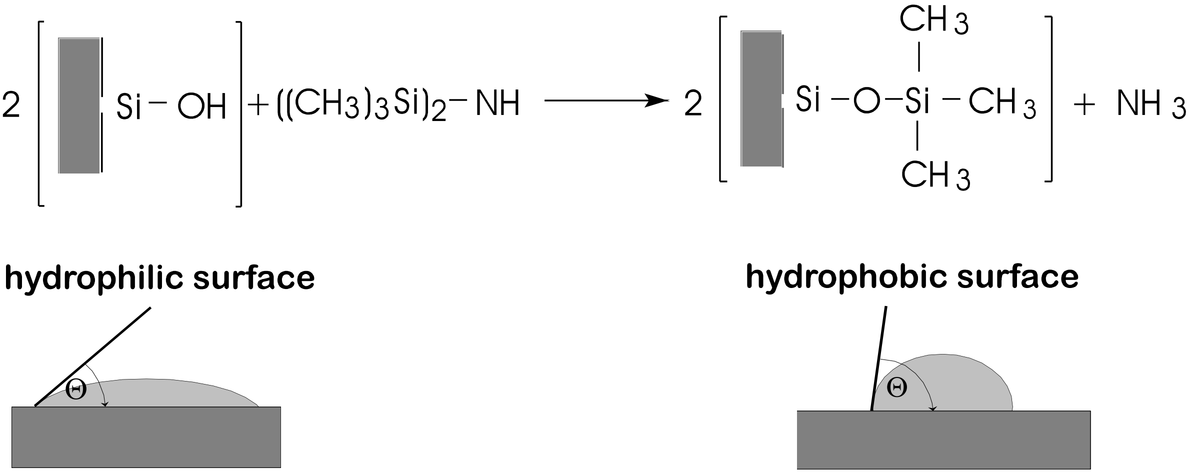
In order to reduce the defect density of resist structures, a general optimization of surface tension was developed and successfully applied, using Si, SiO_2, Si_3N_4, AlCu, WTi and Cr as substrates, modified by priming. We demonstrate that the contact angle water Θ_w can be used to reach the optimal conditions for adhesion of resists. We use models based on the **Young** and **Dupre`** equations and the model of interaction of molecules by **Wu** to determine the surface tension and work of adhesion.

Good resist adhesion results if the work of adhesion is greater than 5dyn/cm [1]. We outline preferred process windows for the contact angle for certain combinations of different types of resist and developer.

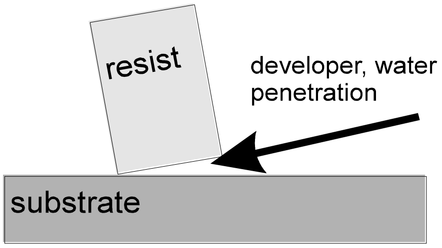
1. Introduction

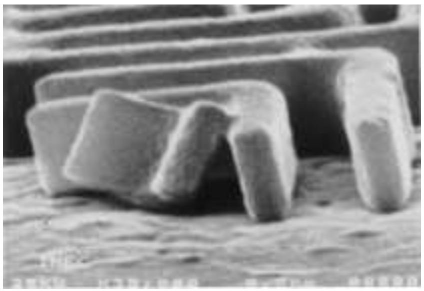
Surface tension of lithographic materials like resists and developers plays an important role. For instance, homogeneity of spin coatings, planarization and adhesion depend directly on surface tension of the involved materials. Generally the lithographic process requires a modification of the substrate surfaces before resist coating in order to prevent small features from ablation during development, rinsing and wet etch processes. Good resist adhesion results if the work of adhesion is greater than 5dyn/cm [1]. Primers like HMDS (hexamethyldisilazane), TMSDEA (trimethylsilyldiethylamine) and others reduce strongly surface tension of materials used in semiconductor technology like Si, SiO_2, Si_3N_4, AlCu, WTi, and Cr. The primer reacts chemically with water deposition or bounded OH-groups held by high-energy substrate surfaces (Fig. 1). Thus surface tension is reduced and the penetration of developer, water or etchants between resist and the modified substrate surface is suppressed [2]. Examples for the importance of adhesion are demonstrate in Fig. 2.



$$2\left[\,Si-OH\,\right]+((CH_3)_3Si)_2-NH \longrightarrow 2\left[\,Si-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3\,\right]+NH_3$$

Fig. 1 Modification of high-energy hydrophilic surfaces by applying HMDS to improve resist adhesion.



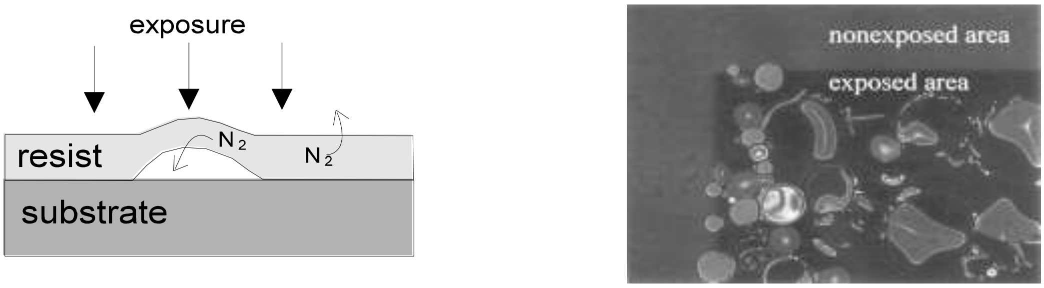


A: Resist separation during developing or rinsing

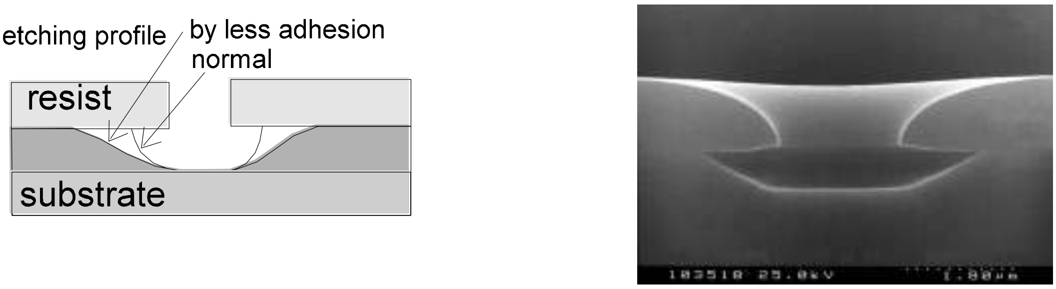
SEM: M. Op de Beeck et al, Proc. SPIE 1262, 139 (1990)

a) b) a) nonpolar developer b) polar developer

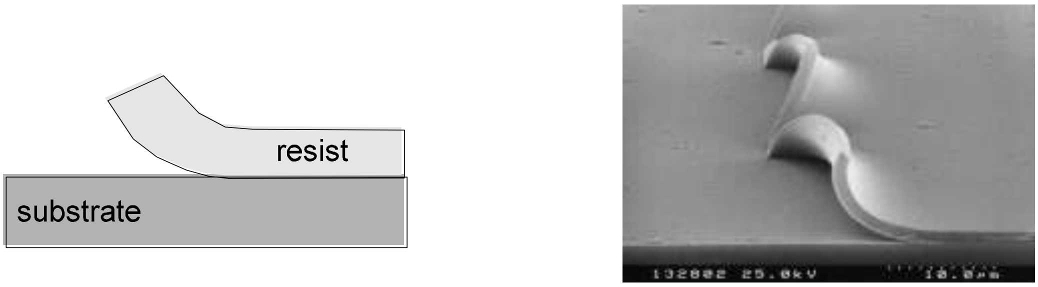
B: Profile defects by adhesion failure (b): developer penetration along the interface



C: Popping of resist caused by small adhesion and high exposure doses



D: Undercut during wet etch process by adhesion problems



E: Resist ablation by stress in the resist film (for example: high-dose implantation)

Fig. 2. Examples for adhesion problems.

2. Theoretical basics

2.1. Surface tension

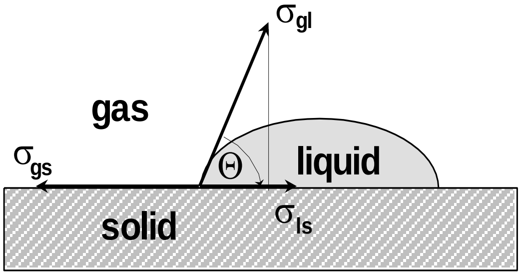


Fig. 3. Scheme of the contact angle method

We use models based on the Young

$$\sigma_{gs} = \sigma_{ls} + \sigma_{gl} \cos\Theta \qquad (1)$$

and Dupre` equations

$$W_{asl} = \sigma_{gl} + \sigma_{gs} - \sigma_{ls} \qquad (2)$$

and the model of interaction of molecules by Wu [3]

$$W_{asl} = 4 \left[\frac{\sigma_{gl}^{d}\, \sigma_{gs}^{d}}{\sigma_{gl}^{d} + \sigma_{gs}^{d}} + \frac{\sigma_{gl}^{p}\, \sigma_{gs}^{p}}{\sigma_{gl}^{p} + \sigma_{gs}^{p}} \right] \qquad (3)$$

for the determination of the surface tension by contact angles Θ measurements (Fig. 3) of test liquids (measurement device: SURFTENS from OEG GmbH). Work of adhesion W_{asl} is defined as reversible work necessary to create an interface area of 1 cm^2 between two different materials. σ_{gl} is the surface tension gas/liquid, σ_{gs} is the surface tension gas/solid, and σ_{ls} is the interfacial tension liquid/solid, where the surface tension is an additive approach ($\sigma=\sigma^p+\sigma^d$) of the polar part of surface tension σ^p (caused by dipole interaction, induced dipole moments and hydrogen bonds) and the non polar part of surface tension σ^d (caused by dispersion energy between molecules).

Using two testing liquids of different polarity it is possible to determine σ^p and σ^d of the substrate by an analytical solution of equation (1-3). In our experiments water (16-17MΩcm): σ_{gl}^p=50.7dyn/cm, σ_{gl}^d=22.1dyn/cm and methylene iodide (CH_2I_2): σ_{gl}^p=6.7dyn/cm, σ_{gl}^d=44.1dyn/cm were used.

In contrast to this, if the surface tension of the substrates is known, the surface tension of liquids can be determined by solving equation (1-3) numerically [1].

2.2. Work of adhesion of resist

The work of adhesion W_{a12} of resist in air environment is according to equation (2) given by:

$$W_{a12} = \sigma_1 + \sigma_2 - \sigma_{12} \qquad (4)$$

where σ_1 is the surface tension of the resist, σ_2 the surface tension of the substrate and σ_{12} the interfacial tension between resist and substrate; and work of adhesion W_{l12} in environment of a liquid (developer or water)

$$W_{l12} = \sigma_{13} + \sigma_{23} - \sigma_{12} \qquad (5)$$

where σ_{13} is the interfacial tension between resist and liquid, and σ_{23} the interfacial tension between substrate and liquid. The calculation of interfacial tensions may be carried out according to equation (2 and 3) as follows

$$\sigma_{ij} = \sigma_i + \sigma_j - 4 \left[\frac{\sigma_i^{d}\, \sigma_j^{d}}{\sigma_i^{d} + \sigma_j^{d}} + \frac{\sigma_i^{p}\, \sigma_j^{p}}{\sigma_i^{p} + \sigma_j^{p}} \right] \qquad (6)$$

where i,j=1,2,3 and σ_3 is the surface tension of developer.

3. Results

3.1. Surface tension

The results of the measurement of contact angle and calculated surface tension of modified substrate materials (e.g. Si, SiO_2, phosphor doped SiO_2 (PSG), AlCu(0.5%Cu), WTi(10%Ti), and Cr) are shown in Fig. 3 and 4 and Tabl.1-3. Modification of surface properties were done with primer (HMDS / 5% TMSDEA) in a gaseous atmosphere at a hotplate temperature of T_p=120°C to reduce surface tension of high hydrophile materials. This was done with Si, SiO_2, PSG and Si_3N_4 successfully. For metals, it is necessary to use a different primer or to change the process of applying the primer caused by the high surface tension (σ_2=60dyn/cm). The pretreatment of the substrates (cleaning, dehydration and exposure to humidity) will greatly influence their surface tension (see Table 1-3). Contamination with water (dependent on relative ambient humidity) and organic materials on high-energy surfaces will occur during the time of exposure to air, which strongly reduces the surface tension of those substrates. Ambient oxygen and cleaning processes with oxidizing effect lead to thin oxide layers on substrate surfaces like on Si and Cr, Al [1] and thus to high-energy surfaces. For example Cr coated mask are typically treated with oven bake (200°C, t=20min) before resist coating. This process reduces strongly the surface tension of Cr and results in good adhesion of resist. For this case, we suppose organic contamination’s, while the hotplate bake with the same cleaning procedure shows a greater surface tension. In our opinion variations of surface tension force specific surface modification to provide stable surface conditions for reproducible and defect free lithography process steps.

The results of the measured surface tension and the polarity $x^p=\sigma^p/\sigma$ of lithographic materials are shown in Tabl. 4 and 5. Resists and developers from Hoechst, Shipley, Allresist and Microchrome were investigated. The resists and developers can be divided into a polar type (x^p>0,3) and nonpolar type (x^p<0,3). The polarity of the developer could be modified by adding special wetting agents (Table 5, for instance, developer E6).

3.2. Work of adhesion of resist

We have demonstrated, that the development is the most critical process relating to adhesion [1]. The Work of adhesion in air W_{a12} obviously reduces by increasing the process time of HMDS coating (Fig.6(a)). The real effect of improved adhesion can be estimated by means of the behavior of thr resist layer during developing and rinsing(Fig.6(b) and 6(c)). Fig. 7 and 8 show the calculated work of adhesion (equation 5) for resist on modified surfaces of Si and AlCu in developer environment. Coming out by the investigation the resist/developer combination can be divided into two groups: (i) the polar type of developer and (ii) the nonpolar type.

The work of adhesion in polar developer environment at contact angles of water about Θ_w<50° is negative and spontaneous separation occurs. The experimental verification we have monitored in [1]. For such combination the surface condition have to be about Θ_w≥60° by primer treatment. To apply nonpolar developer, the work of adhesion is uncritical by small Θ_w. In this case, the Θ_w should not exceed 85° for good adhesion. In addition, there are three processes to take into account, the rinsing (water), the wetting (developer, resist) and the popping (N_2 blistering by exposure reaction, Fig. 2C). Thereafter, a Θ_w≤10° causes ablation of resist during rinsing [1]. Secondary, in the case of Θ_w>75° problems with wetting and popping can be obtained [4]. Fig. 9 depicts the influence on the work of adhesion by changing the surface tension of resist and developer. An improvement of adhesion was obtained using increased polarity and decreased surface tension of resist while surface tension of developer is comparative high.

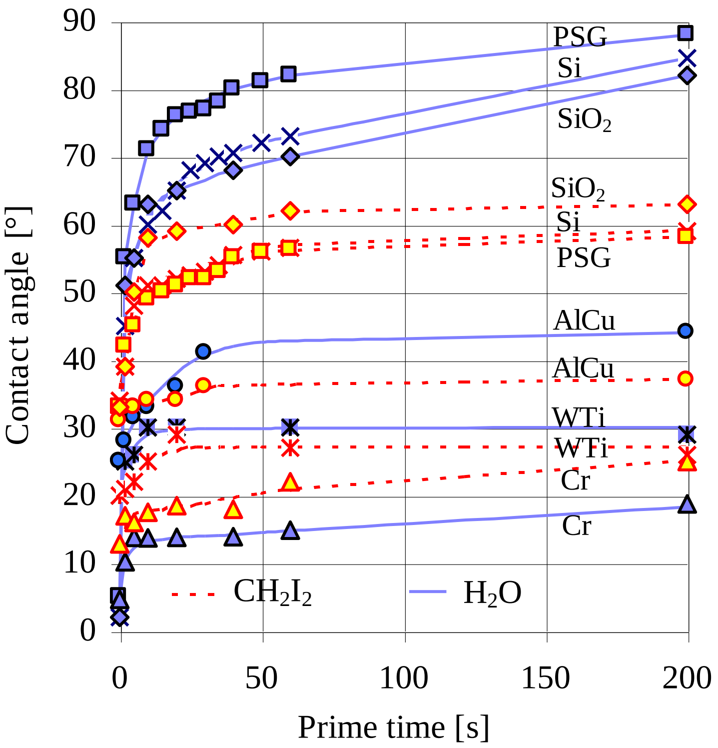


Fig. 4. Contact angle for methylene iodide and water obtained with HMDS and 5%TMSDEA for different priming times (hotplate 120°C).

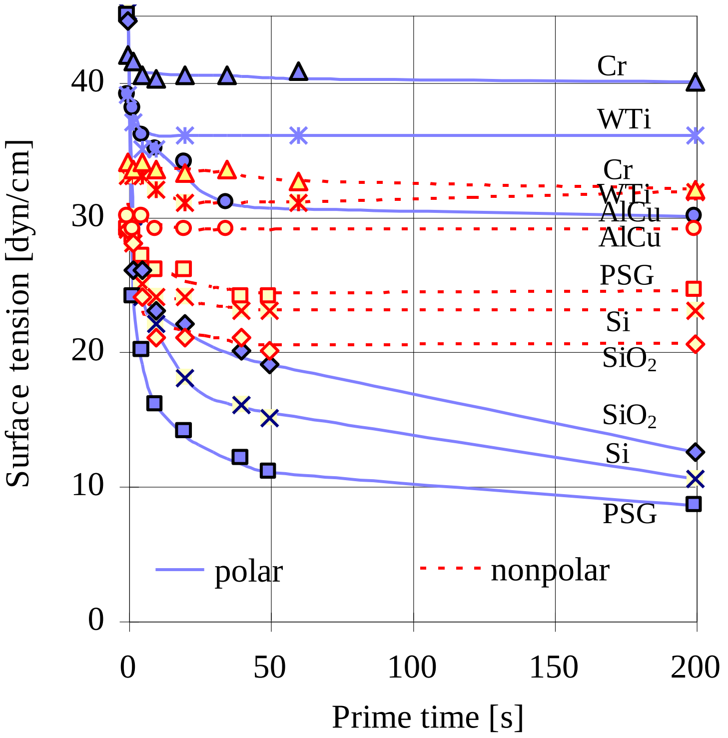


Fig. 5. Surface tension σ_2 of modified surfaces determined from the measurement of the contact angle.

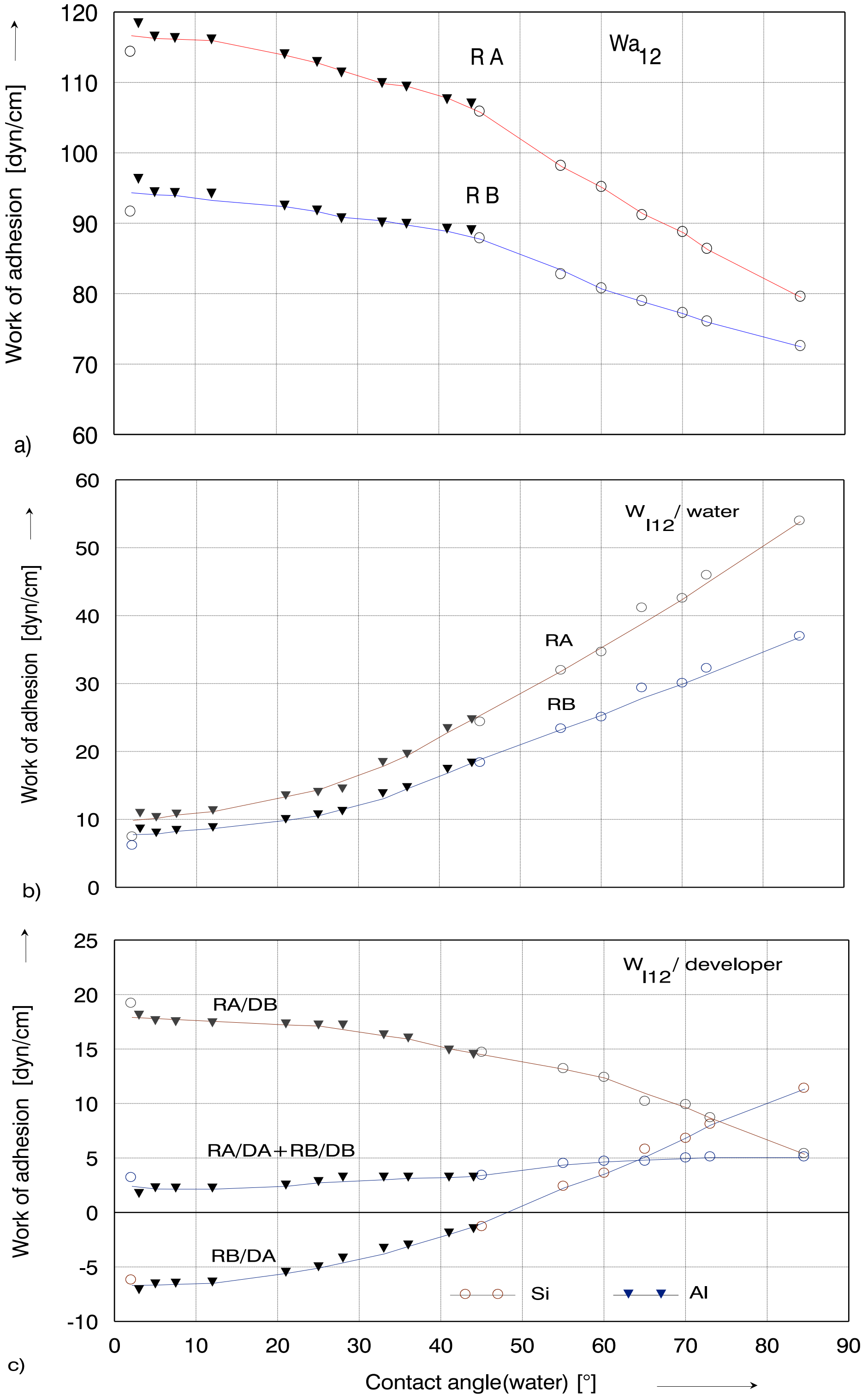


Fig. 6. Work of adhesion for resist as function of contact angle of modified Si(○), AlCu(▼) substrates (a) under air, (b) under water, and (c) under developer environment.

RA - polar type of resist (σ_1^p=20dyn/cm, σ_1^d=30dyn/cm), RB - non polar type of resist (σ_1^p=10dyn/cm, σ_1^d=30dyn/cm), DA - polar type of developer (σ_3^p=20dyn/cm, σ_3^d=40dyn/cm), DB - non polar type of developer (σ_3^p=10dyn/cm, σ_3^d=40dyn/cm)

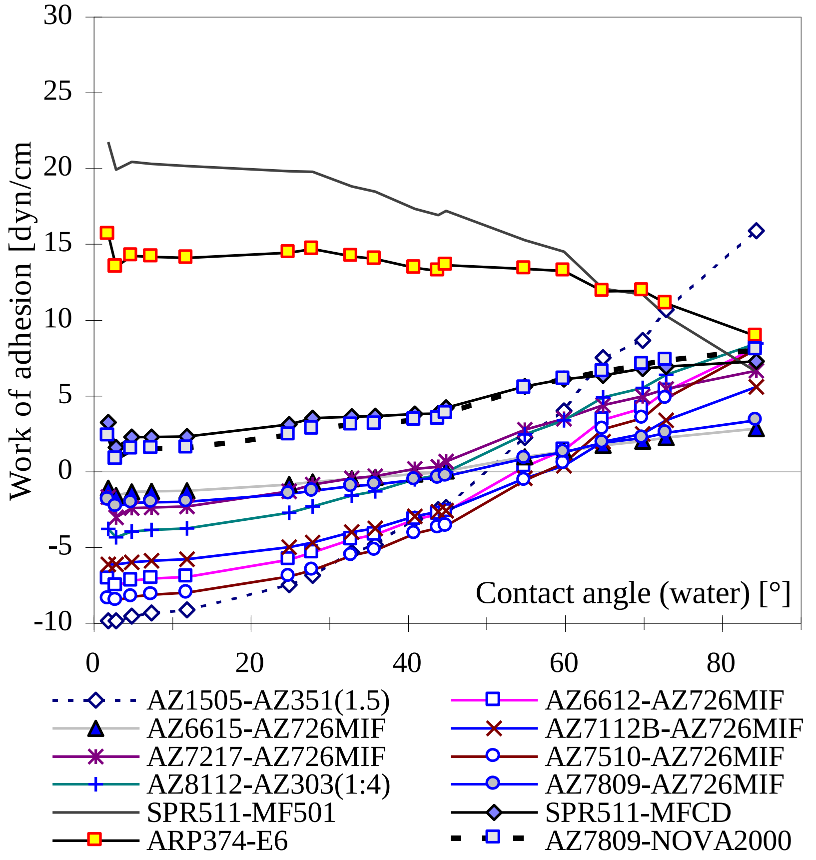


Fig. 7.

Work of adhesion W_{l12} for photo resist in developer environment as function of the contact angle water for modified substrates (Si, AlCu).

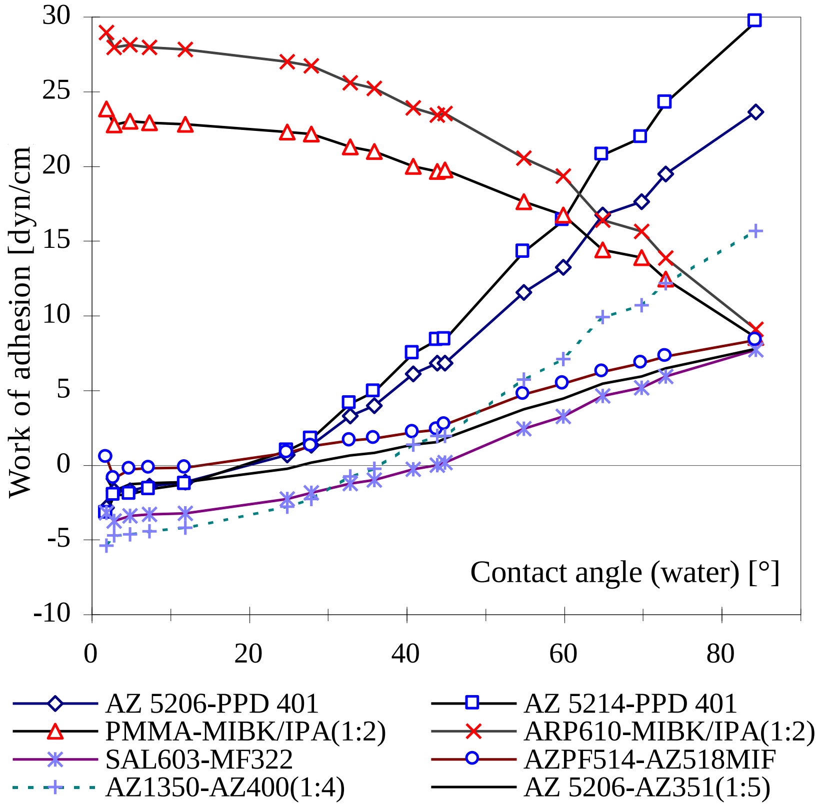


Fig. 8.

Work of adhesion W_{l12} for electron-beam resist in developer environment as function of the contact angle water for modified substrates (Si, AlCu).

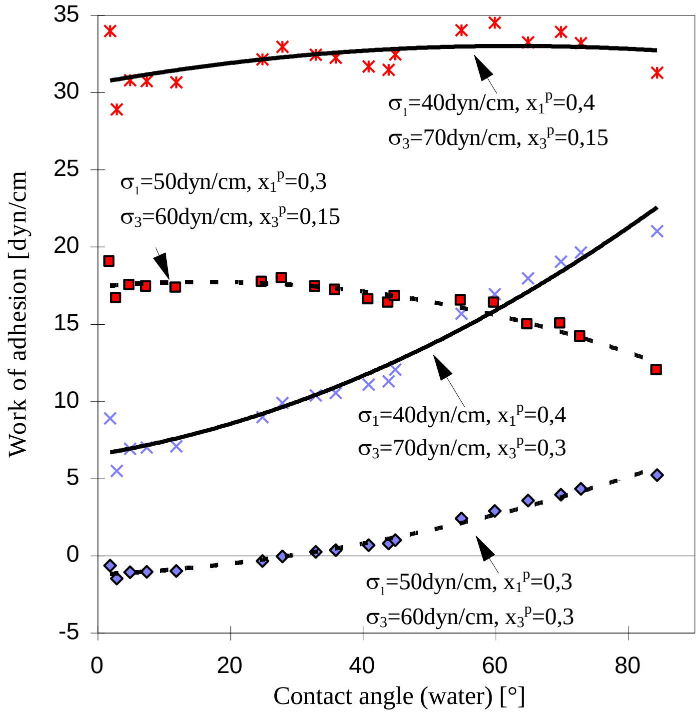


Fig. 9. Improvement of adhesion by increase of resist polarity x1p and the surface tension of developer σ3 and decrease of surface tension of resist σ1 relative to the average surface tension (◆, ■, Tabl 4, 5) of the resist by using of polar developer (◆, x) and nonpolar developer (■, ∗).

4. Conclusion

We have demonstrated that the contact angle water Θ_w can be used to adjust optimal conditions for adhesion of resist on different substrate materials. We showed pretreatment caused variations of surface tension can be compensated by specific surface modification to provide stable surface conditions for a reproducible and defect free lithography process steps. Good adhesion >5dyn/cm was obtained when a low-polarity developer ($x_3^P<0{,}3$) is used, corresponding to a process window $10° \leq \Theta_w \leq 75°$. In contrast, when a high-polarity developer ($x_3^P>0{,}3$) is applied, the priming process has to be modified, so that the surface tension of the substrates can be reduced. The process window for this case is $60° \leq \Theta_w \leq 75°$. We show that a resist with a relatively small surface tension (σ_1=40dyn/cm) and high polarity (x_1^P=0,4), combined with a developer with high surface tension is a good prerequisite for adhesion.

References

1. J. Bauer, G. Drescher and M. Illig, J. Vac. Sci. Technol. B Vol. 14, No. 4 (1996).
2. H. Yanazawa, Colloids and Surfaces, 9 (1984) 133-145
3. S. Wu, Polymer Interface and Adhesion, Marcel Dekker, New York, 1982.
4. M.C.B.A. Michielsen, V.B. Marriott, J.J. Ponjée, H. van der Wel, F.J. Touwslager and J.A.H.M. Moonen, Microelectronic Engineering 11 (1990) 475-480.

Acknowledgments

The authors wish to thank Mr. Th. Steglich (Präzisions-Optik Gera GmbH) for preparation of the Cr layers and Mrs. U. Hoffmann (Technical University of Chemnitz-Zwickau) for providing of several chemicals.

Table 5. Surface tension σ_3 of developers

developer	surface tension polarity			
	σ_3^p dyn/cm	σ_3^d dyn/cm	σ_3 dyn/cm	x_3^p
MF 501 (Shipley) [1]	8	39	47	0.17
MFCD (Shipley) [1]	20	42	62	0.32
MF 322 (Shipley) [2]	23	40	63	0.36
AZ 303 (1:4) (Hoechst) [1]	23	40	63	0.36
AZ 351 (1:5) (Hoechst) [1]	23	43	66	0.35
AZ 400 (1:4) (Hoechst) [1]	33	37	70	0.47
AZ 518 MIF (Hoechst) [3]	20	42	62	0.32
AZ 726 MIF (Hoechst) [1]	20	36	56	0.36
AZ 326 MIF (Hoechst) [1]	13	41	54	0.24
NOVA 2000 (Hoechst) [1]	20	44	68	0.29
E 6 (Allresist) [1]	9	40	49	0.18
E6, without wetting agent (Allresist) [1]	16	42	58	0.28
PPD 401 (Microchrome) [4]	40	35	75	0.53
MIBK/IPA (1:2) [5]	5	39	44	0.11
MIBK/IPA (1:3) [5]	4	39	43	0.09
MEK/IPA (1: 3) [5]	5	37	41	0.12

[1] developer for photo resist, [2] developer for SAL resist, [3] developer for AZ PF 514 e-beam resist,
[4] developer for AZ 5206, AZ 5214 resist (e-beam exposure), [5] developer for PMMA and P(MMA/MA)

Table 4. Surface tension σ_1 of photo and electron-beam resist

photo resist	softbake T_s	surface tension polarity σ_1^p dyn/cm	σ_1^d dyn/cm	σ_1 dyn/cm	x_1^p
SPR 511 (Shipley)	hotplate: 90°C ,60s	19	30	49	0.38
AZ 1505 (Hoechst)	hotplate: 100°C, 60s	7	37	44	0.16
AZ 6612 (Hoechst)	hotplate: 90°C, 60s	11	30	41	0.27
AZ 6615 (Hoechst)	hotplate: 120°C, 60s	18	32	50	0.36
AZ 7112B (Hoechst)	hotplate: 90°C, 60s	13	33	46	0.28
AZ 7217 (Hoechst)	hotplate: 110°C, 60s	16	26	42	0.38
AZ 7510 (Hoechst)	hotplate: 90°C, 60s	10	32	42	0.24
AZ 8112 (Hoechst)	hotplate: 100°C, 60s	15	34	49	0.31
AZ 7809 (Hoechst)	hotplate: 90°C, 60s	17	32	49	0.35
AR-P374 (Allresist)	hotplate: 90°C, 60s	13	29	42	0.31
AR-P515 (Allresist) [1]	hotplate: 110°C, 60s	20	30	50	0.40
AR-P525 (Allresist) [2]	hotplate: 110°C, 60s	9	34	43	0.21
electron-beam resist					
PMMA (Allresist)	convection oven: 150°C, 30min	15	35	50	0.30
AR-P610 (Allresist) [3]	convection oven: 200°C, 60min	18	36	54	0.33
SAL 603 (Shipley)	convection oven: 90°C, 30min	16	34	50	0.32
AZ PF514 (Hoechst)	hotplate:100°C, 60s	16	31	47	0.34
AZ 5206 (Hoechst) [4]	convection oven: 90°C, 30min	18	35	53	0.34
AZ 5214 (Hoechst) [4]	convection oven: 90°C, 30min	14	34	48	0.29
AZ 1350 (Hoechst) [4]	convection oven: 90°C, 30min	17	36	53	0.32

[1] precoating resist, [2] planarisation resist, [3] P(MMA/MA), [4] photo and electron-beam resist

Table 1. Contact angle and surface tension of Si for different treatments

pretreatment	contact angle		surface tension		
	H_2O	CH_2I_2	σ^p dyn/cm	σ^d dyn/cm	σ dyn/cm
no pretreatement, delivery quality	31°	41°	38	26,5	64,5
SC1-cleaning	2°	32°	45	30	75
SC1,2-cleaning	2°	33°	45	29	74
SC1,2-cleaning, exposure time=5days	16°	38°	44	27	71
SC1,2-cleaning, O_2-plasma treatment	6°	35°	45	28	73

SC1-cleaning: ammoniumhydroxide hydrogenperoxide mixture
SC2-cleaning: hydrocloricacid hydrogenperoxide mixture

Table 2. Contact angle and surface tension of Al/Cu for different treatments

pretreatment	contact angle		surface tension		
	H_2O	CH_2I_2	σ^p dyn/cm	σ^d dyn/cm	σ dyn/cm
no pretreatement, exposure time<10min	29°	31°	37	30	67
1day	32°	40°	31	30	61
5days	73°	51°	15	25	40
HNO_3-cleaning, DI- water	4°	20°	42	34	76
HNO_3-cleaning, DI-water, temp.200°C, 30min	8°	24°	43	32	75
HNO_3-cleaning, DI-water, exposure time=5days	28°	30°	37	30	68
HNO_3-cleaning, DI- water, O_2-plasma treatment	2.5°	34°	45	29	74

Table 3. Contact angle and surface tension of Cr, Cr-Oxid for different treatments

pretreatment		contact angle		surface tension		
		H_2O	CH_2I_2	σ^p dyn/cm	σ^d dyn/cm	σ dyn/cm
$H_2O_2/H_2SO_4/H_2O$-cleaning	Cr	5°	13°	42	34	76
	Cr-Oxid	6,5°	22°	43	32	75
$H_2O_2/H_2SO_4/H_2O$-cleaning	Cr	50°	40°	27	28	55
exposure time>10days	Cr-Oxid	50°	43°	27	27	54
$H_2O_2/H_2SO_4/H_2O$-cleaning	Cr	13°	18°	41	33	74
HMDS/5%TMSDEA, 120°C hotplate	Cr-Oxid	13°	22°	41	32	73
$H_2O_2/H_2SO_4/H_2O$-cleaning	Cr	50°	25°	25	33	58
oven bake 200°C, 20min	Cr-Oxid	50°	30°	25	32	57
$H_2O_2/H_2SO_4/H_2O$-cleaning	Cr	6°	15°	42	34	76
hotplate bake 200°C, 20min	Cr-Oxid	7°	20°	42	33	75