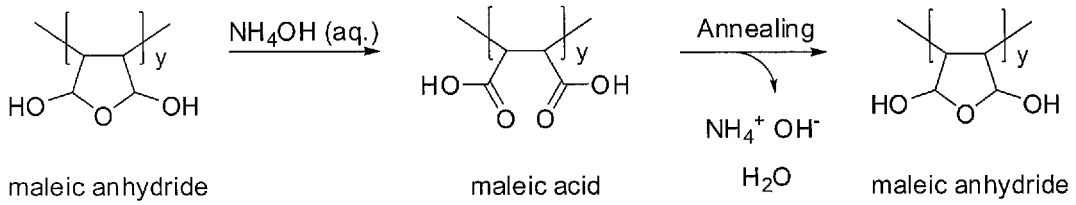
FIGURE 1



maleic anhydride maleic acid maleic anhydride

FIGURE 2

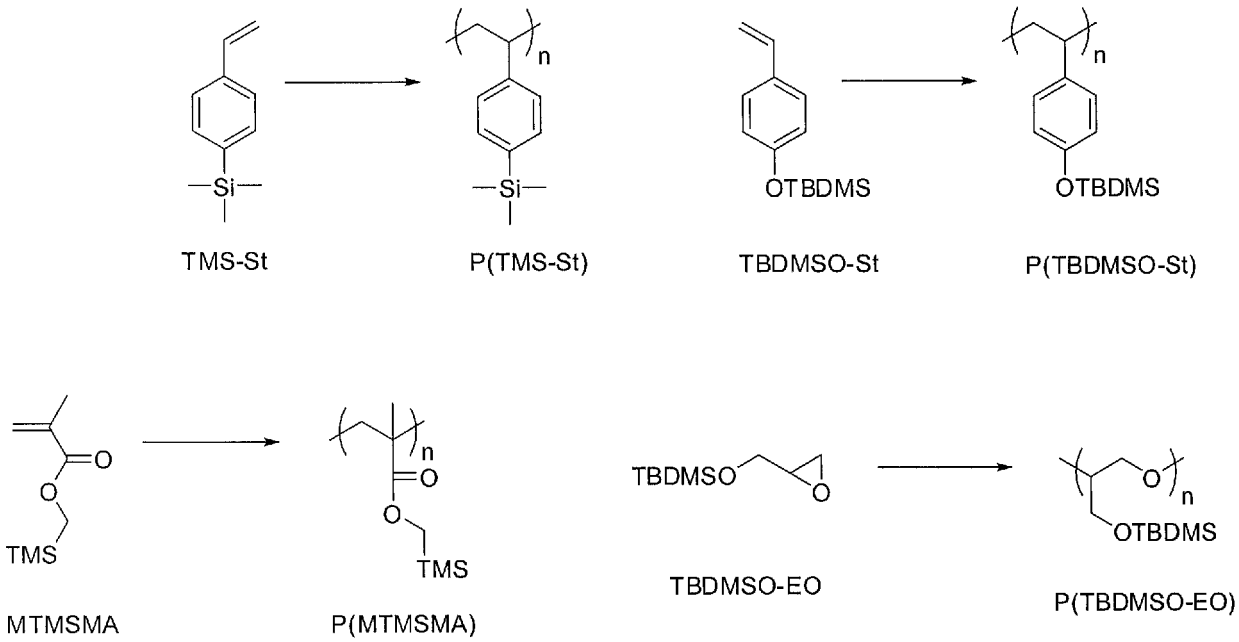

Si
n
Si
OTBDMS
n
OTBDMS
TMS-St
P(TMS-St)
TBDMSO-St
P(TBDMSO-St)
O
O
TMS
n
O
O
TMS
TBDMSO
O
O
n
OTBDMS
MTMSMA
P(MTMSMA)
TBDMSO-EO
P(TBDMSO-EO)

FIGURE 3

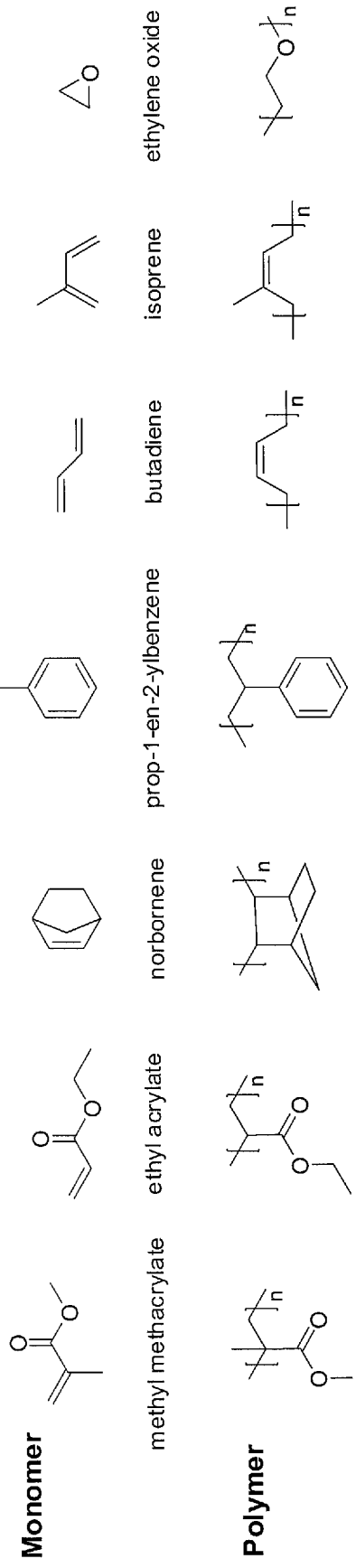
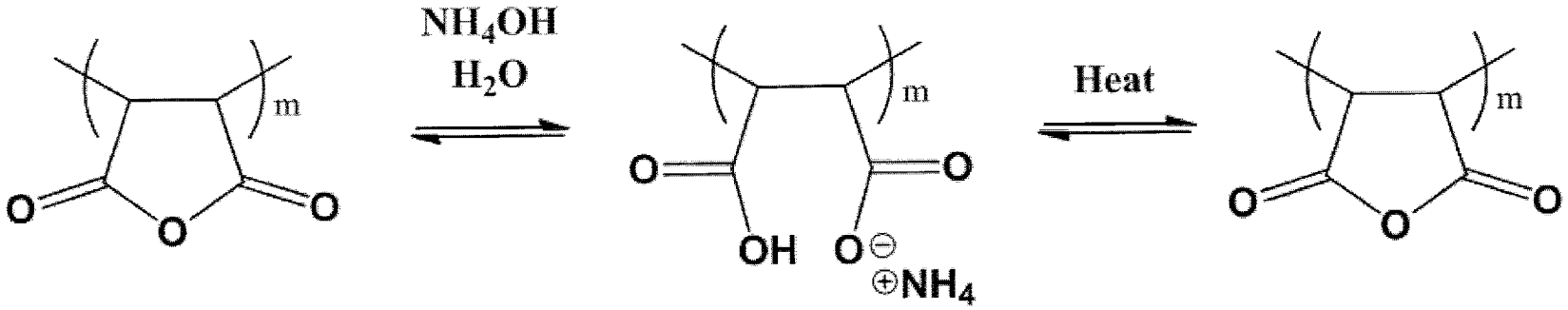
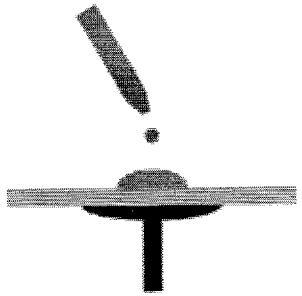

Monomer
Polymer
methyl methacrylate
ethyl acrylate
norbornene
prop-1-en-2-ylbenzene
butadiene
isoprene
ethylene oxide

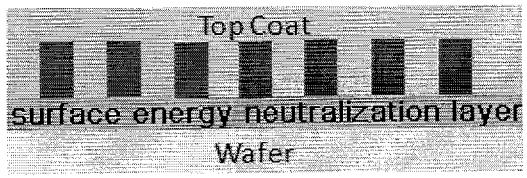
FIGURE 4

Top Coats – The idea







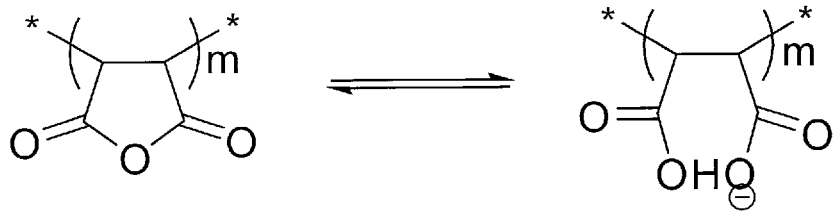


Not soluble in H_2O
Cannot spin-coat onto block copolymer

Spin-coatable out of H_2O
BUT, now it has a high surface energy because it is very polar

Lower surface energy!
Allows self- assembly of BCP

FIGURE 5

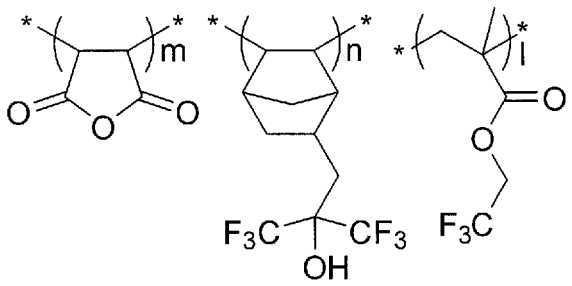


Water contact angle and surface energy change as a function of annealing a thin film, because ring opens and closes.

Longer annealing times correspond to the ring closed form (higher contact angle because it's less polar, dislikes water)

Ring opened anionic form is aqueous weak base soluble, ring closes to lower the surface energy once it is applied to the thin film and annealed.

FIGURE 6



m:n:l = 43 : 32 : 25 mol%

FIGURE 7

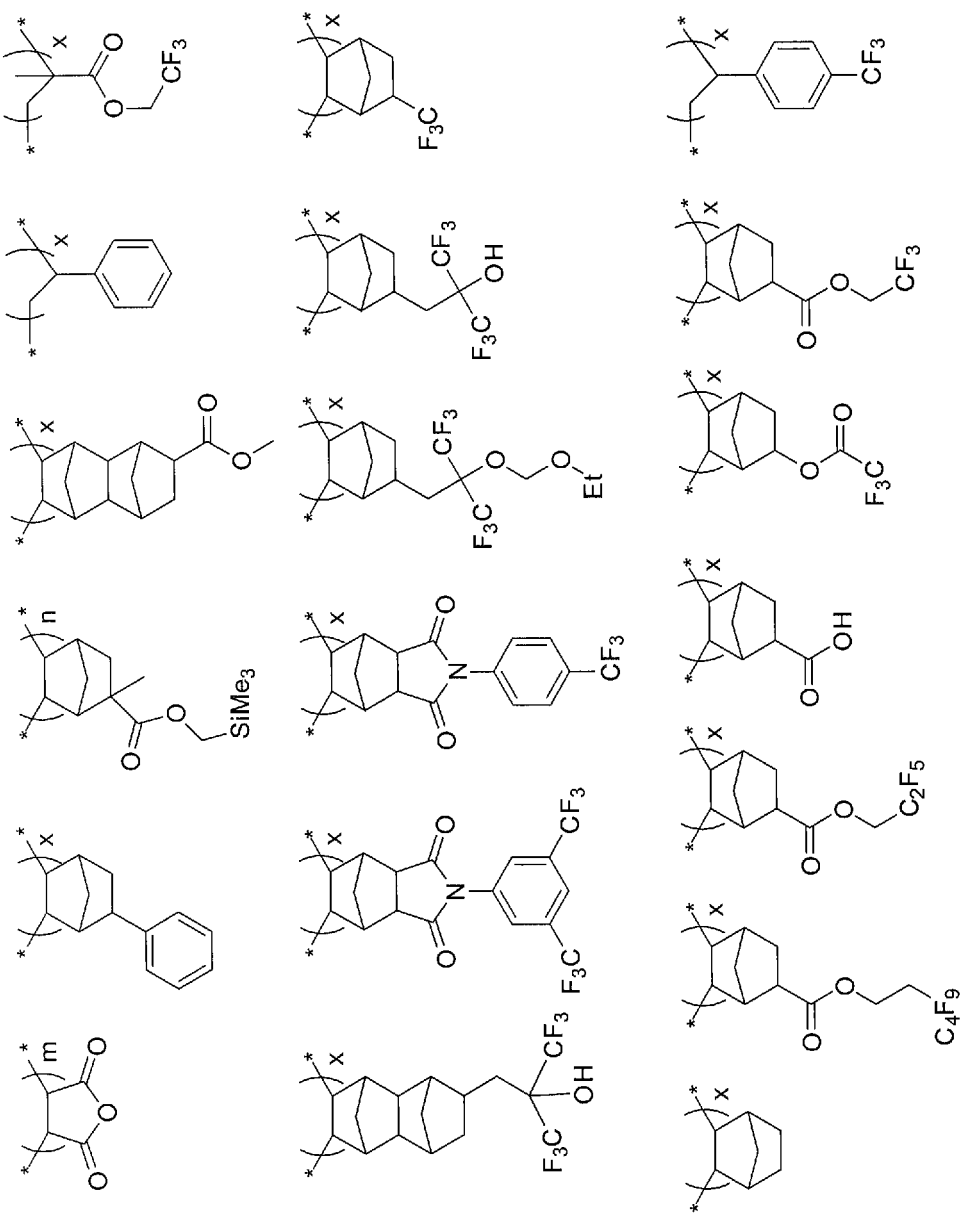


FIGURE 8

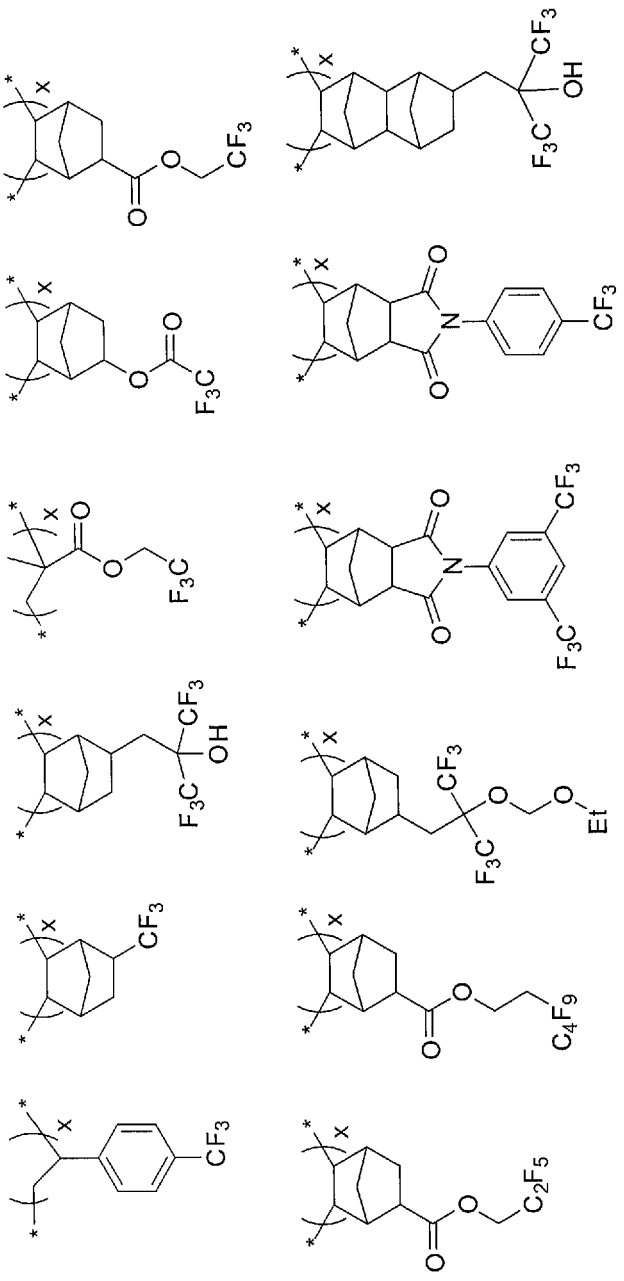


FIGURE 9

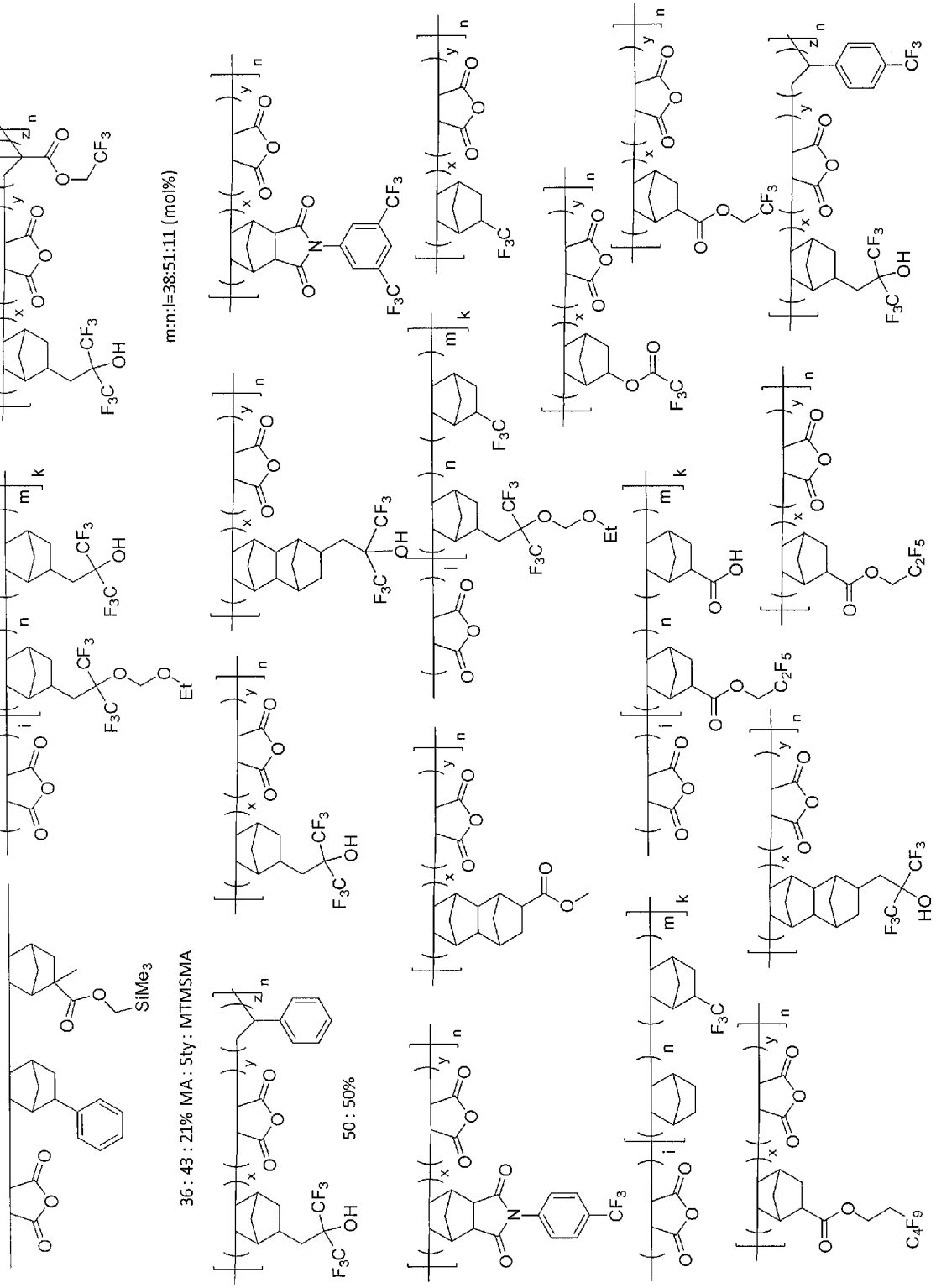


FIGURE 10

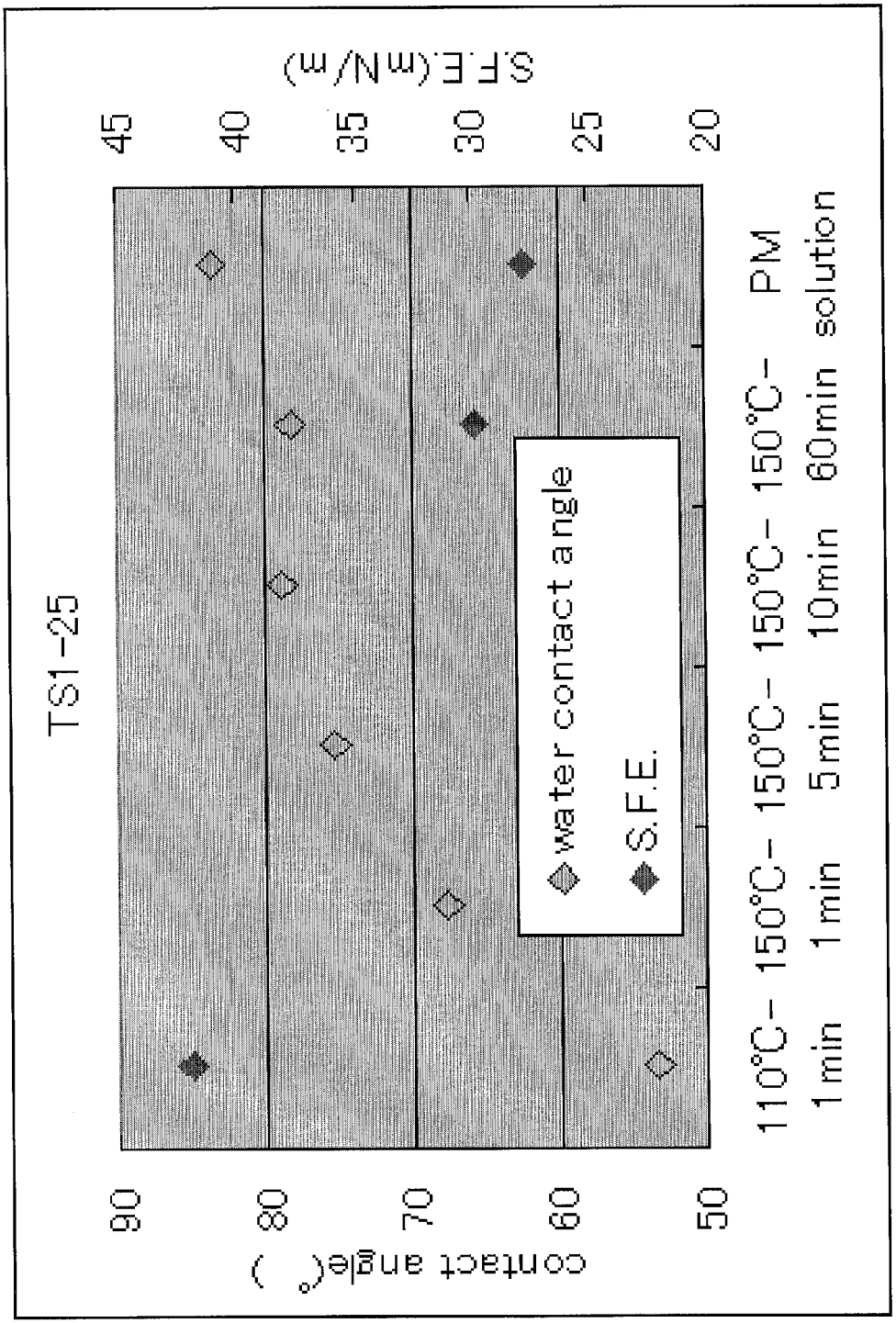
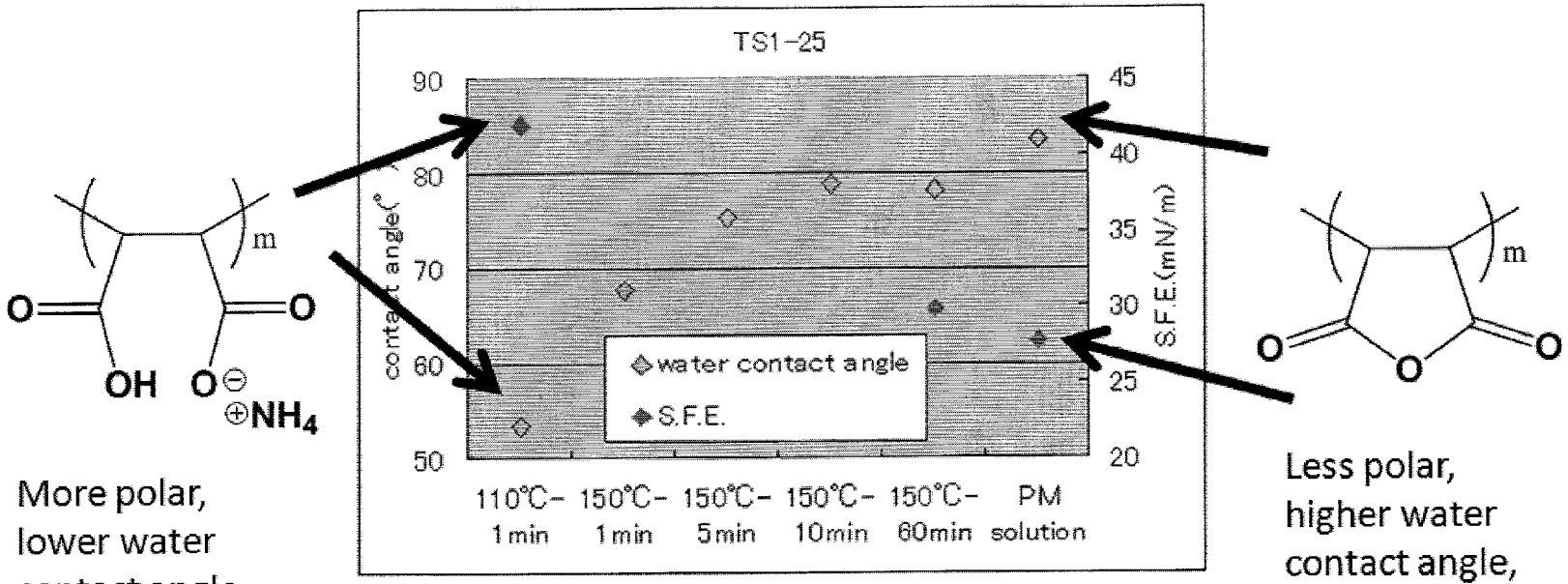

TS1-25
contact angle(°)
S.F.E.(mN/m)
90
80
70
60
50
45
40
35
30
25
20
water contact angle
S.F.E.
110°C- 150°C- 150°C- 150°C- 150°C- PM
1min 1min 5min 10min 60min solution

FIGURE 11

How do we know maleic anhydride opens and closes??



More polar, lower water contact angle, higher surface energy

Less polar, higher water contact angle, lower surface energy

Water contact angle and surface energy change as a function of annealing a thin film

Longer annealing times correspond to the ring closed form

FIGURE 12

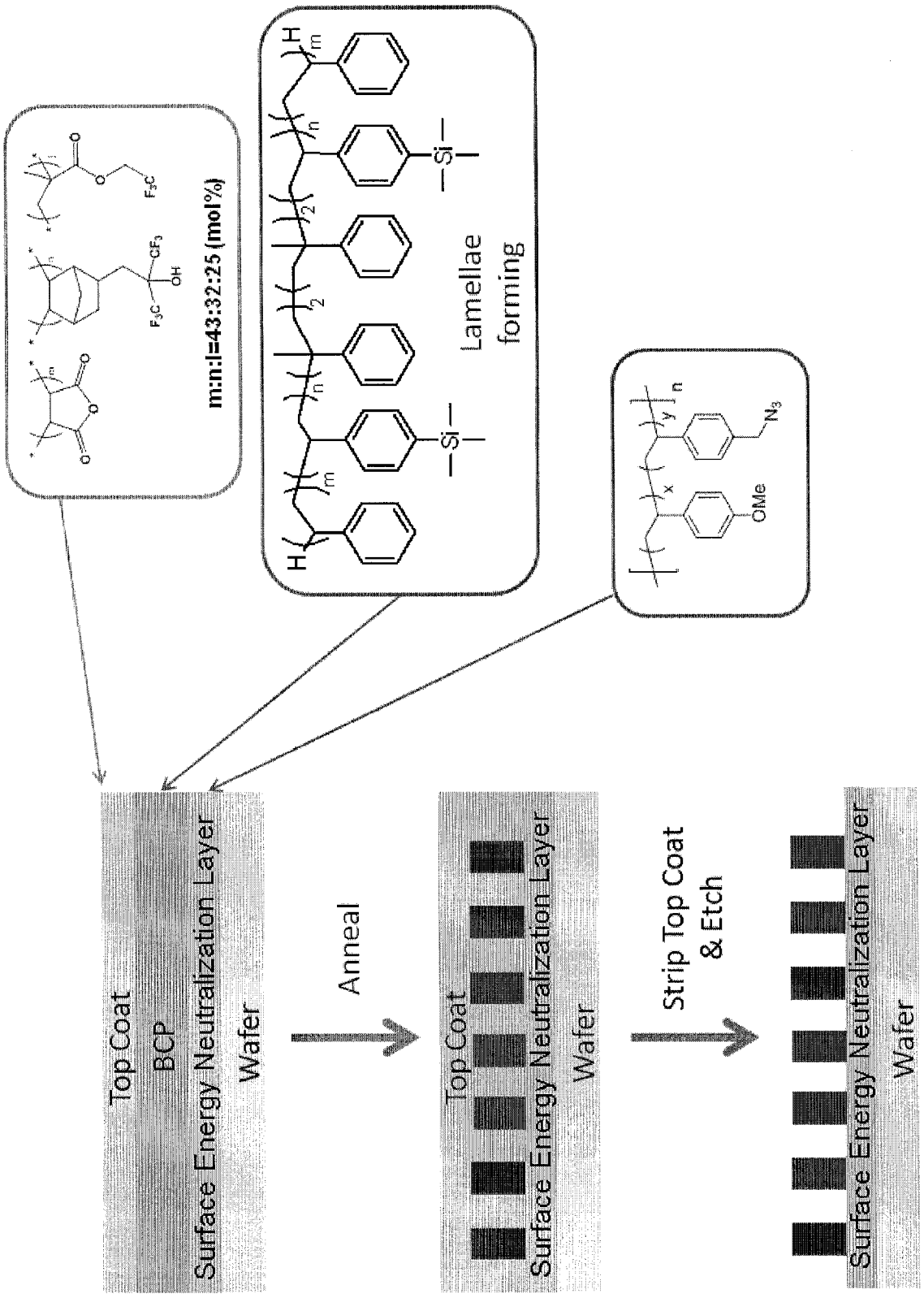
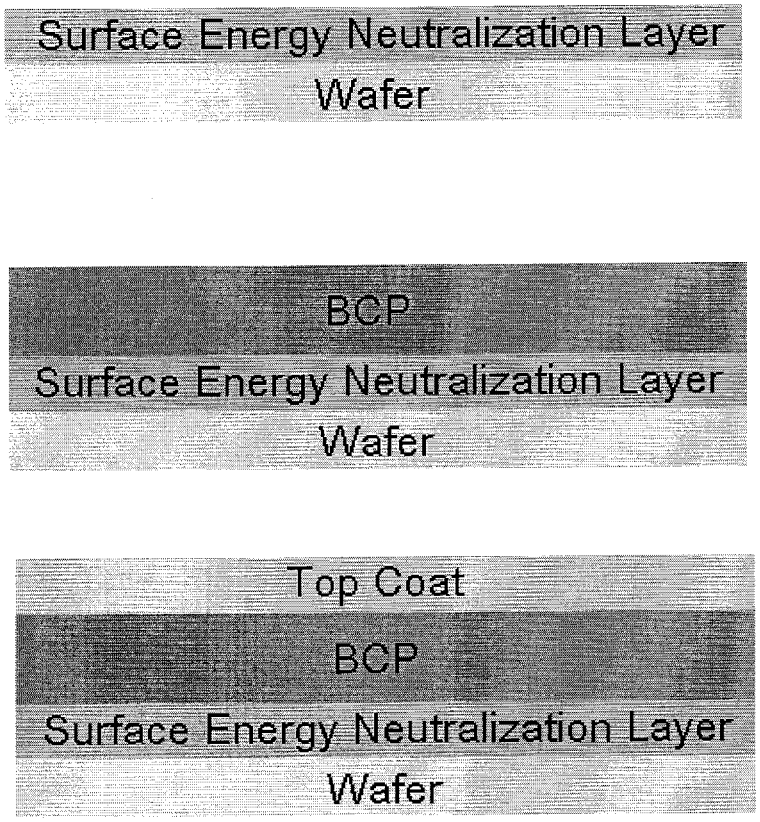

m:n:l=43:32:25 (mol%)
Lamellae forming
Top Coat
BCP
Surface Energy Neutralization Layer
Wafer
Anneal
Top Coat
Surface Energy Neutralization Layer
Wafer
Strip Top Coat & Etch
Surface Energy Neutralization Layer
Wafer

FIGURE 13

Experimental Procedure

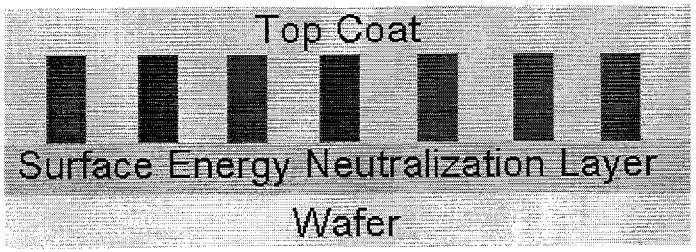


1) Surface energy neutralization layer polymer is dissolved in toluene and spin coated
2) Cross-linked at 250 °C for 5 min
3) Washed with toluene 2 times

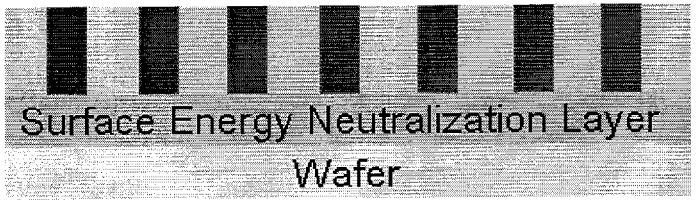
4) Block copolymer is dissolved in toluene and spin coated
5) Post apply bake at 110 °C for 1 minute

6) Top coat is dissolved in 30 wt% NH_4OH and spin coated
7) Post apply bake at 150 °C for 5 minutes

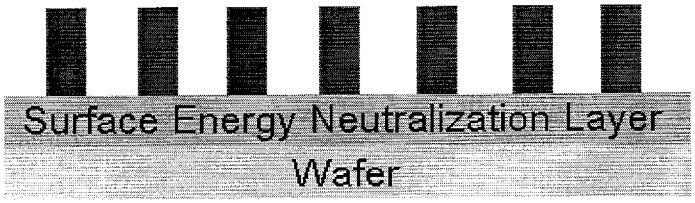
Experimental Procedure (Cont)



8) Anneal the thin films at 170 °C for 18 hours.



9) Strip the top coat by spinning the wafer at 3000 rpm and applying 10 drops of 30 wt% NH_4OH aqueous solution dropwise.

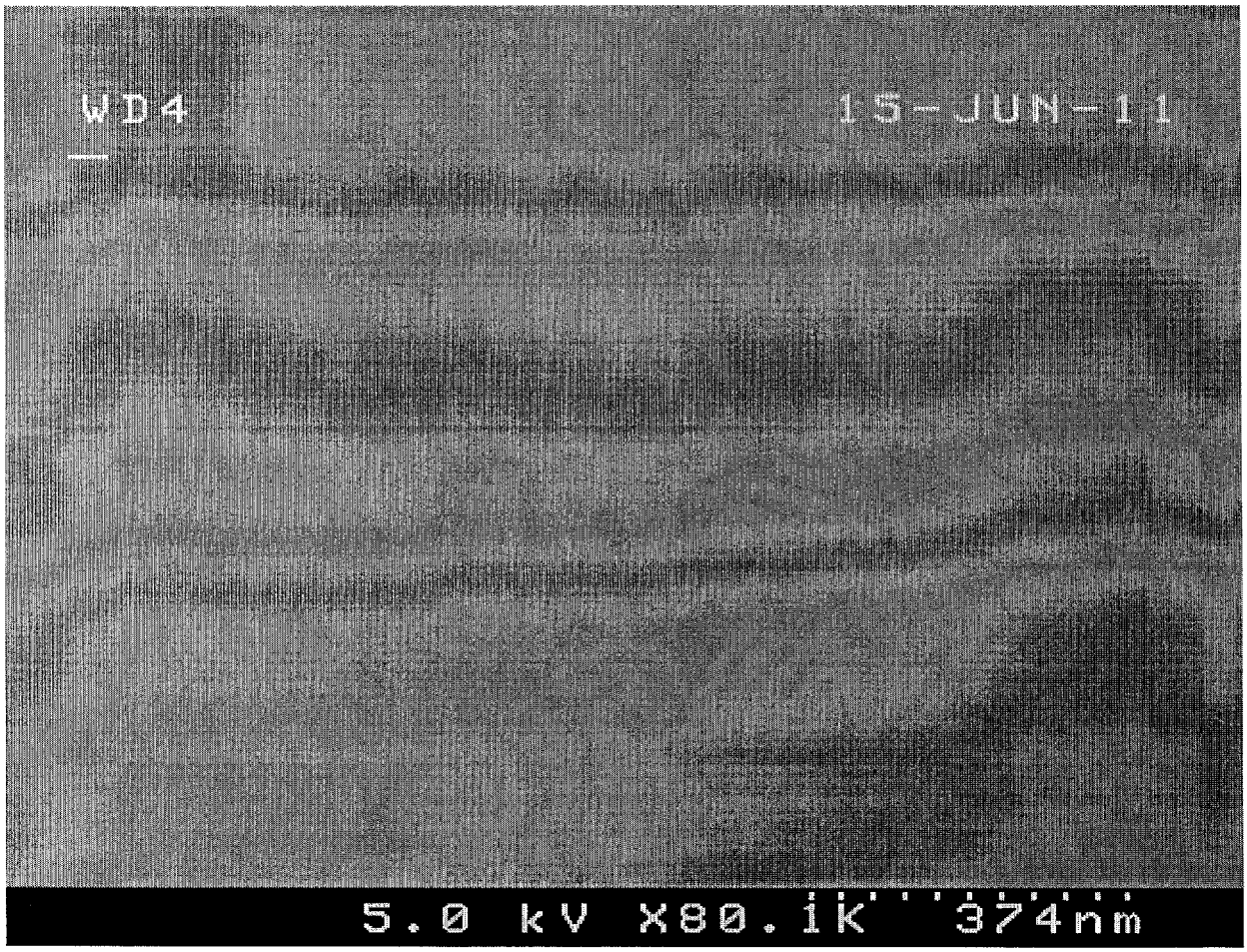


10) Oxygen plasma etch the block copolymer with the following conditions:
Pressure=20 mTorr, RF Power=10 W, ICP Power=50 W, O_2 flow rate=75 sccm, Argon flowrate=75 sccm, temperature=15 °C, time=45 sec.

WO 2013/119832
PCT/US2013/025174

FIGURE 15

SCANNING ELECTRON MICROSCOPE



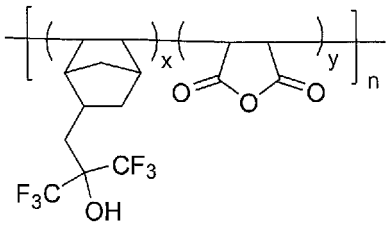
BCP Thickness before anneal: 65.6 nm

After stripping the top coat: 66.9 nm

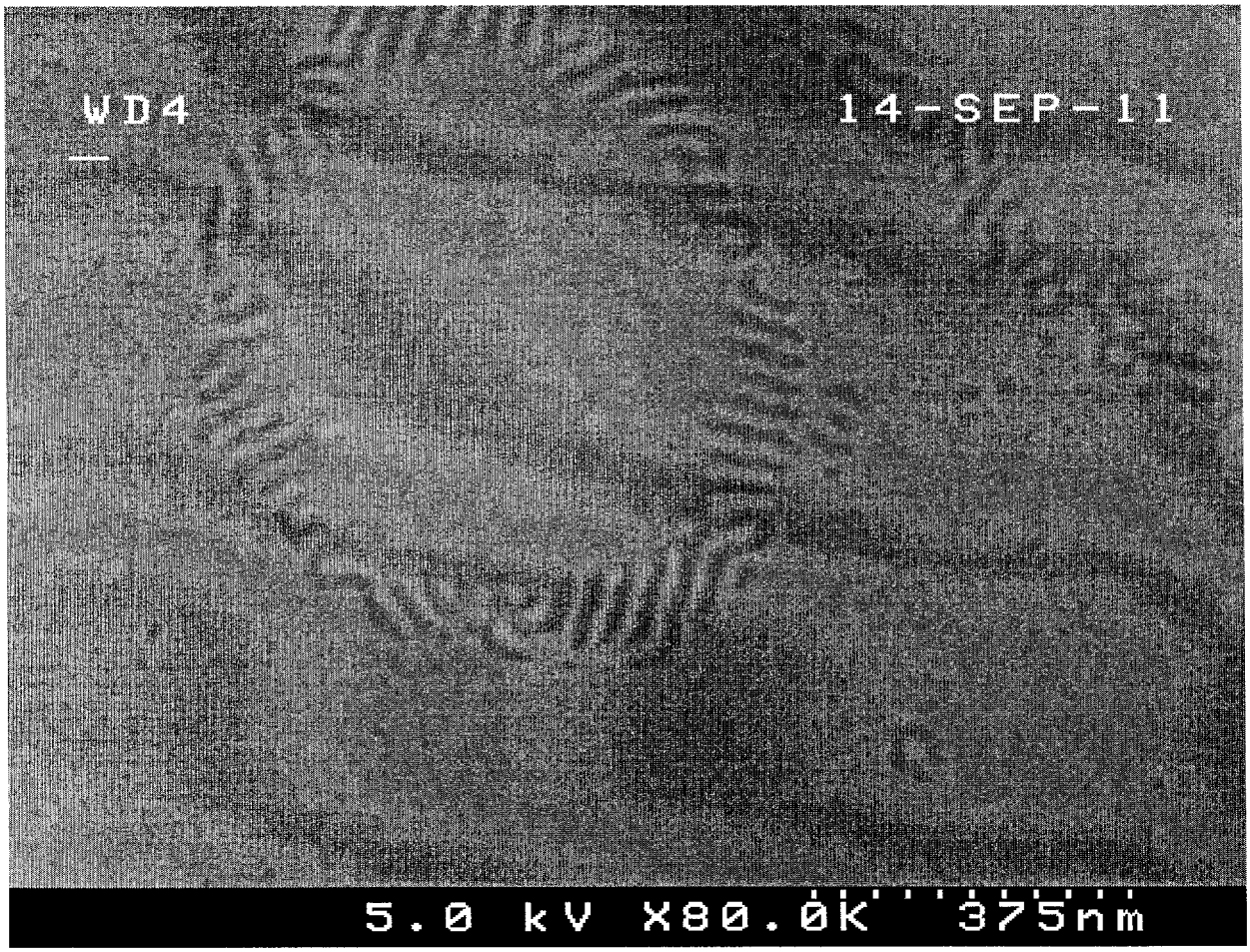
Film has been etched with O_2 plasma

Demonstrates perpendicular lamellar features

FIGURE 16



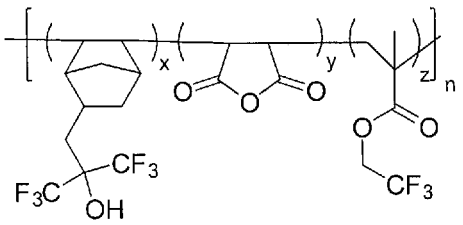
TS 1-15



170 °C
TS 1-15 Top Coat
TMSSty – 34 nm (~ $1L_0$)

CB 2-154-170C-3a-2

FIGURE 17



27:35:38

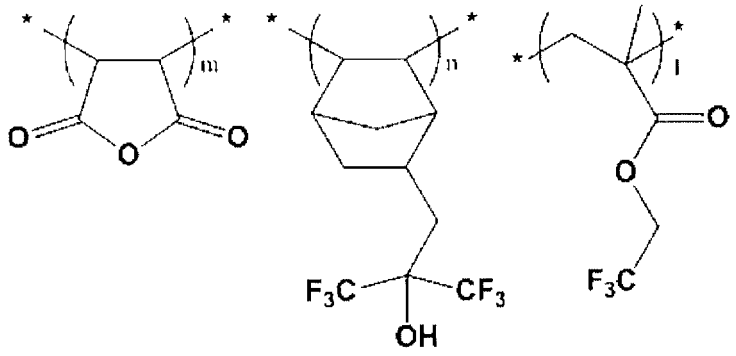


170 °C

Block thickness = 29.4 nm (1 L_0)

LD 1-74-4
Etched 1-2

FIGURE 18



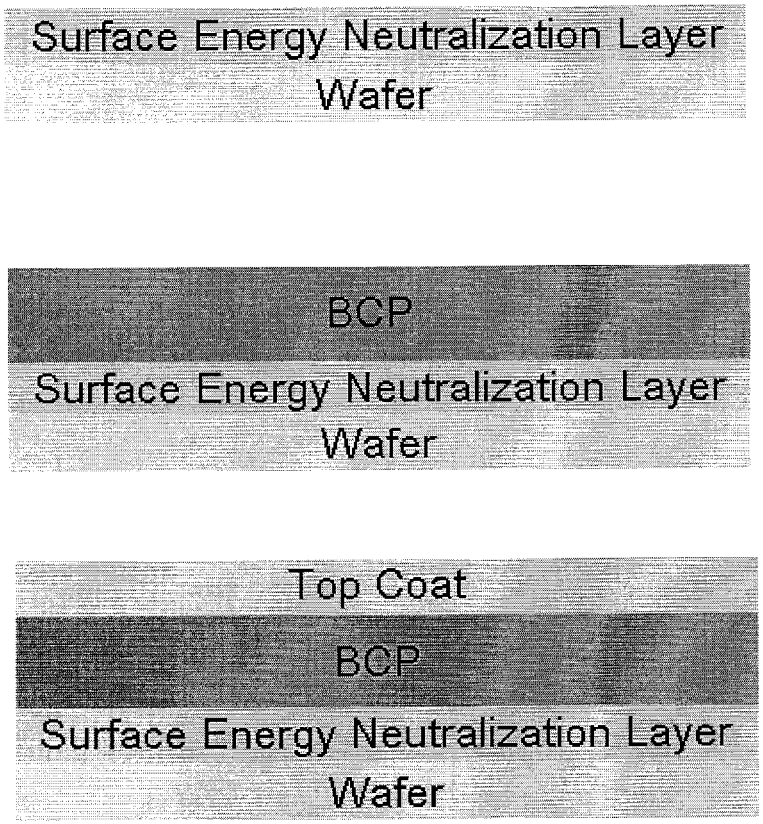
m:n:l=35:27:38 (mol%)
Tg = 161 °C



⊥ Lamellae!

FIGURE 19

Alternative Procedure



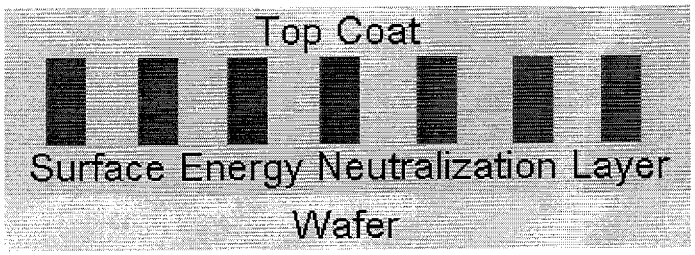
1) Surface energy neutralization layer polymer is dissolved in 30 wt% NH_4OH and spin coated
2) Post apply bake at 150 °C for 5 minutes

3) Block copolymer is dissolved in toluene and spin coated
4) Post apply bake at 110 °C for 1 minute

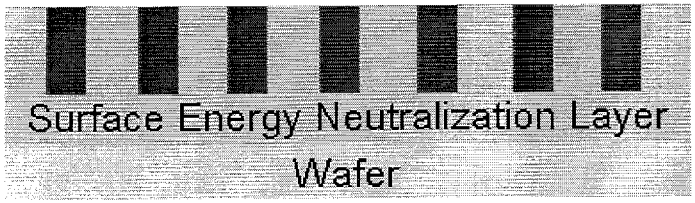
5) Top coat is dissolved in 30 wt% NH_4OH and spin coated
6) Post apply bake at 150 °C for 5 minutes

FIGURE 20

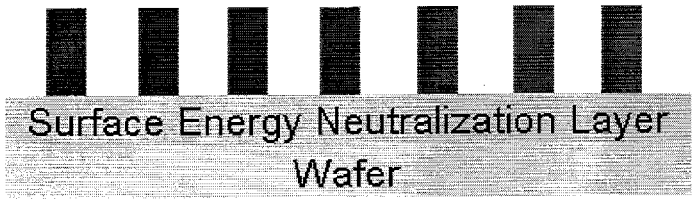
Alternative Procedure (Cont)



7) Anneal the thin films at 170 °C for 18 hours.



8) Strip the top coat by spinning the wafer at 3000 rpm and applying 10 drops of 30 wt% NH_4OH aqueous solution dropwise.



9) Oxygen plasma etch the block copolymer with the following conditions:
Pressure=20 mTorr, RF Power=10 W, ICP Power=50 W, O_2 flow rate=75 sccm, Argon flowrate=75 sccm, temperature=15 °C, time=45 sec.