Study on Metal-Organic Interface Modified by Ion-Assisted Reaction

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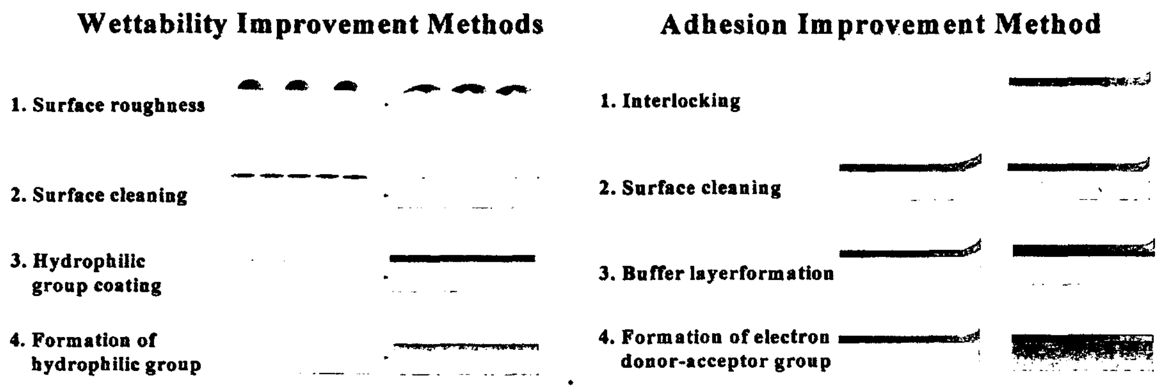
1. Introduction

The modification of chemical inertness to improve the adhesion between metals and polymers has been focusing on either creating rougher surface or altering the surface chemistry by sputtering, wet etching, plasma treatment.



Ion Assisted Reaction with 1 keV Ar^+ irradiation and oxygen flux investigated to modify surface of PTFE and PVDF.
* PTFE (polytetrafluoroethylene), PVDF (polyvinylidenefluoride)

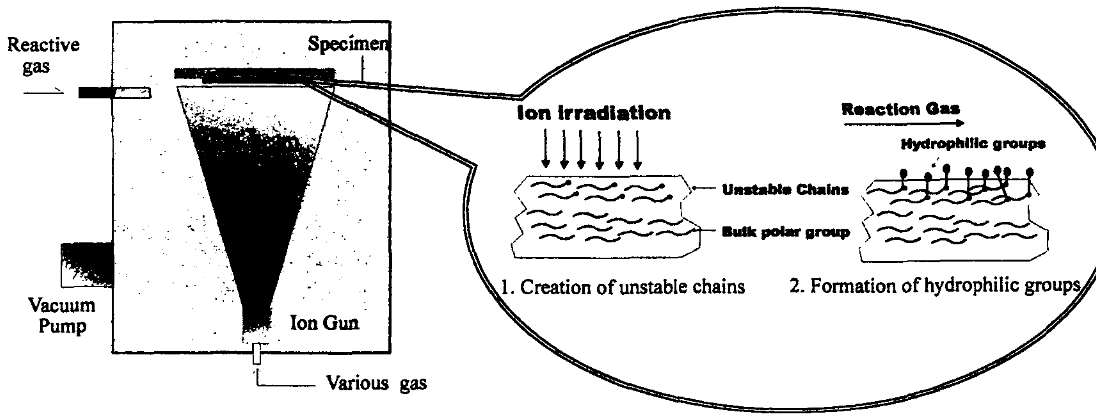
2. Experimental details

Sample size of commercial PTFE($-CF_2-CF_2-)_n$ and PVDF($-CH_2-CF_2-)_n$: 10x10x10mm^3
Ar^+ ion dose with time at fixed beam current : $5\times10^{14} \sim 1\times10^{17}$ ions/cm^2 (5-cm cold hollow cathode ion gun)
Oxygen flux and partial pressure : 8 *ml/min* at 2×10^{-4} Torr
Static water contact angles (Cam-micro), chemical bonding (XPS), surface morphology (SEM, AFM)
Metal film (Cu, Pt, Al, and Ag) deposition : ion beam sputtering using 99.99 % targets in the range of 9×10^{-5}~1×10^{-4} Torr
Film thickness (measured by quartz crystal monitor and α-step) : 500nm
Qualitative measurement of adhesion strength : peel-off test and boiling water test (immersed for 4 hrs)
Electrical resistivity (4-point probe), dielectric constants and dissipation factors (HP 4194A impedance analyzer)

Ion Assisted Reaction (IAR)

1. Creation of unstable chains : surface is activated by energetic ion irradiation
2. Modification of hydrophobic into hydrophilic : reactive gases flow around ion-irradiated surface

Schematic diagram of IAR apparatus (2-step model)



3. Results and Discussion

The wettability of water is closely related to morphology and hydrophilic groups on polymer surface.

3.1 Surface modification of PTFE and PVDF

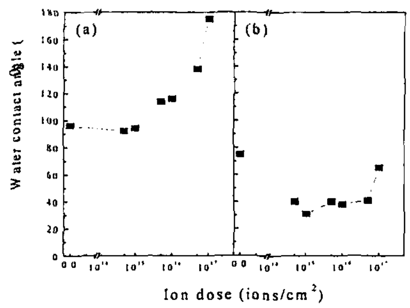


Fig.1 Water contact angle changes with ion doses at fixed oxygen flow.

a) PTFE : 96° (untreated), 92° (1×10^{15} ions/cm^2), non-wettable (1×10^{17} ions/cm^2)

The angle reduction is related to the oxygen-related bonds (hydrophilic groups) newly formed by chemical reaction between unstable chains and oxygen gas
The non-wettable result is from the micro-needle-type rough surface making the water droplet bridge over the cone peaks, as shown in Fig.2.

b) PVDF : 75° (untreated), 31° (1×10^{15} ions/cm^2), 67° (1×10^{17} ions/cm^2)

The enhanced wettability at ion doses less than 5×10^{15} ions/cm^2 results from the formation of the hydrophilic groups related to -(C-O)- and -(C=O)-.
The degradation of surface wettability to 67°, even though the surface morphology is not significantly altered, is related to carbonization of the polymer chains.

Therefore, the hydrophilic groups formed on the modified PVDF surfaces determine the wettability, while those are not a main factor for the modified PTFE

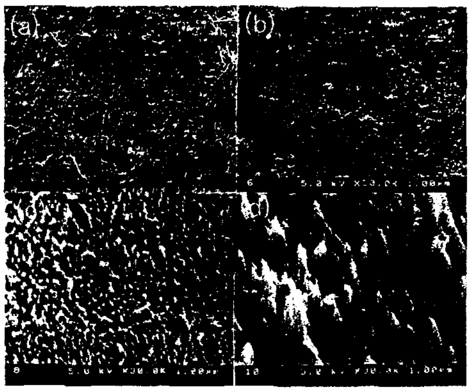


Fig.2 SEM of PTFE surface with varying ion dose (ions/cm^2)

a) untreated
b) 1×10^{15} : no cones
c) 1×10^{16} : average cone density of about 30/μm^2
d) 1×10^{17} : conical structure of several μm high via redeposition of the sputtered PTFE

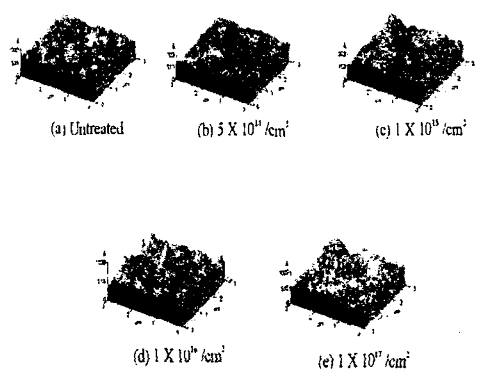


Fig.3 AFM of PVDF with varying ion dose (ions/cm^2)

a) untreated : R_{ms}=8.8 nm
b) 5×10^{14} : R_{ms}=5.6 nm
c) 1×10^{15} : R_{ms}=7.7 nm
d) 1×10^{16} : R_{ms}=9.0 nm
e) 1×10^{17} : R_{ms}=10.6 nm

The surface morphology is not altered significantly. (compared with PTFE)

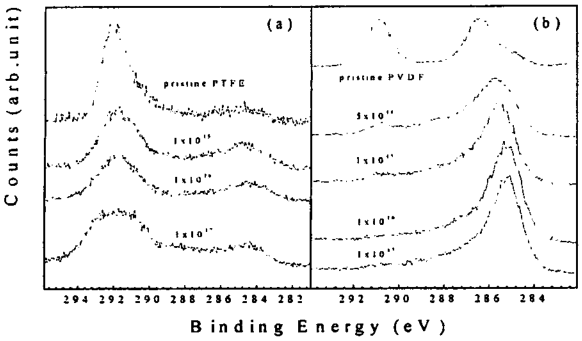


Fig.4 XPS (C1s) changes as a function of ion dose.

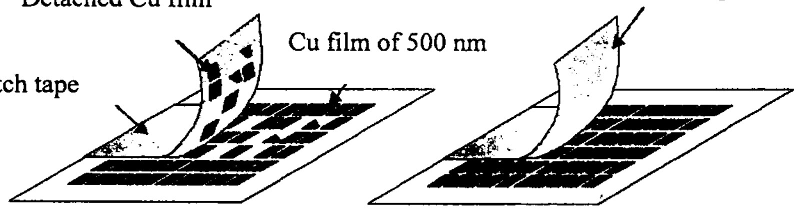
(a) PTFE
Unmodified : $-CF_2-$ peak at 292eV, adsorbed hydrocarbon peak at 285eV
The $-CF_2-$ peak broadening with dose : chain scission, cross-linking, carbonization, and chemical reactions
The $-CF_2-$ intensity reduction at 285eV : preferential sputtering of F-atoms, hydrophilic groups containing oxygen bonds
The peak intensity at 285eV increases with dose, but saturates at 1×10^{17} ions/cm^2.
The small peaks at 285~ 291.6eV : C-O bond, new C-F chains ($-CH-CF_x-$ at 286.9, -CF- at 289.3, and $-CF_3-$ at 293.4eV)

(b) PVDF
Uumodified : a typical peak shape including $-CH_2-$ at 286.2 and $-CF_2-$ at 290.8eV.
At 5×10^{14} and 1×10^{15} ions/cm^2 : $-CF_2-$ peak intensity decreases drastically
and new peaks of oxygen and fluorine singly bonded carbon between $-CH_2-$ and $-CF_2-$ peaks.
$-CH_2-$ peak shift to ~285eV : the most electronegative F-atoms were changed with others in the vicinity of $-CH_2-$
New -(C-O)- and -(C=O)- bonds at >286eV, and a remarkable intensity reduction of $-CF_2-$ peak
At 1×10^{16} and 1×10^{17} ions/cm^2 : sharp increase of =C=, skewed shape to lower binding energy

The carbonization of PVDF at high dose ion irradiation is similar results to high energetic ion and/or heavy ion irradiation

3.2 *Metallization of the modified PTFE and PVDF*

In general, the metal-polymer adhesion can be enhanced by
- the mechanical interlocking due to rough surface
- chemical reaction due to surface chemistry change



Modified at 5×10^{14} ions/cm^2 Modified at 1×10^{15} ions/cm^2

The Scotch™ tape test removes completely Cu film of 500nm thick from the untreated PTFE surface.

PTFE modified by Ar^+ ion irradiation without oxygen gas flow ➔ Cu-PTFE adhesion is also enhanced

Therefore, the significant increase in adhesion of Cu/PTFE results from
- the mechanical interlocking due to the increased surface roughness
- the chemical structural changes at the PTFE surface.

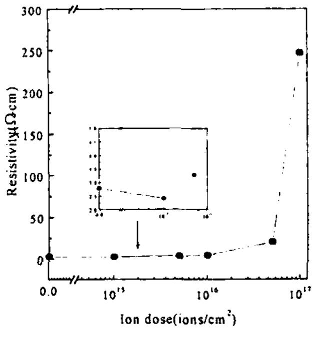


Fig.5 Resistivity changes of Cu films on PTFE with varying ion dose

The surface roughness of PTFE film is important to the Cu film resistivity.
unmodified : 2.7μΩ-cm
1×10^{15} ions/cm^2 : 2.4μΩ-cm, film planarity obtained by sputtering at short time
1×10^{16} ions/cm^2 : 4.3μΩ-cm, surface electron scattering due to local thinning
1×10^{17} ions/cm^2 : local discontinuity in Cu film of 500nm thick
cannot cover all cones of over 1μm high sufficiently

Taking both adhesion and resistivity into account, 1×10^{15} ions/cm^2 is more desirable.

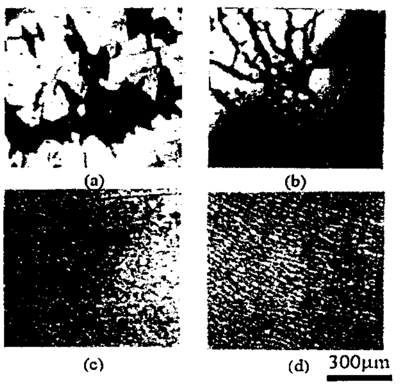


Fig.6 Photographs of Pt films on PVDF immersed in boiling water for 4 hrs

(a) untreated : Pt film was buckled due to CTE difference and water penetration.
(b) 5×10^{14} ions/cm^2 : the buckled area is significantly reduced.
(c) 1×10^{15} ions/cm^2 : enhanced adhesion, the stress release mode to cracking
(d) 1×10^{17} ions/cm^2 : the crack density is decreased.

For low dielectric loss, Pt and Au can be used for electrodes, since energy state of PVDF is changed to hydrophilic by IAR as shown in Fig.4(b).

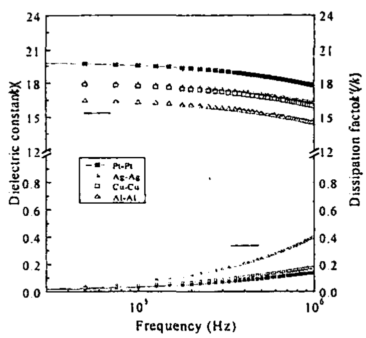


Fig. 7 Dielectric constants and dissipation factors of PVDF modified by IAR

Dielectric constant : strongly dependent on metal work functions (ϕeV)

Pt (5.2), Ag (4.9), Cu (4.7), Al (4.2)

Big Schottky barrier in Pt : limit charge to the interface to lower leakage current.

Dissipation factors increase with f (frequency) and 1/ϕ.

4. Conclusions

The wettability and adhesion was closely related to surface chemistry and roughness of modified polymers.
Adhesion of thin metal films to PTFE and PVDF modified by IAR was enhanced significantly.
Metal-PTFE (polytetrafluoroethylene) adhesion is enhanced by surface roughness and hydrophilic groups.
Metal-PVDF (polyvinylidenefluoride) adhesion is increased mainly by hydropholoc groups.
The metallized PTFE and PVDF modified by IAR can be used in flexible circuits and piezoelectric sensors.