

Metallization of Polymers Modified by Ion-Assisted Reaction (IAR)

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Abstract : Surfaces of PTFE and PVDF were modified by ion-assisted reaction (IAR) in which 1 keV Ar⁺ ions were irradiated on the surface of the polymer with varying ion dose in an oxygen gas environment, and Cu, Pt, Al and Ag thin films were deposited on the modified polymers. Wettability of the modified polymers was largely improved by the formation of hydrophilic groups due to chemical reaction between polymer surface and the oxygen gas during IAR. The change in wettability in the modified polymers was also related to the change in surface morphology and roughness. Adhesion between metal films and polymers modified by IAR was significantly improved, so that no detachment was possible in the Scotch™ tape test. The increase of adhesion strength between the metal film and the modified PVDF was mainly attributed to the formation of hydrophilic groups, which interacted with the metal film. In the case of the modified PTFE, the enhanced adhesion to metal film could be explained by the change in surface morphology together with the formation of hydrophilic groups. The electrical properties of the metal films on the modified polymers were also investigated.

Keywords: Ion-assisted reaction, PTFE, PVDF, hydrophilic group, adhesion, wettability

1. Introduction

Metallized polymers have been used in various technologies such as magnetic recording media, electroconductive films, computer technology, and flexible printed circuits¹⁻⁵. Different properties of metallized polymers are required depending on their applications. Particularly, the adhesion of a thin metal film to a polymeric substrate is the most basic property in any application. Of all polymers, fluoropolymers, e.g., poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF) have gained increased attention in the electronics industry. PTFE is a promising material for flexible printed circuits and capacitors due to good thermal and dielectric properties. PVDF is a very attractive polymer, exhibiting pyroelectric and piezoelectric characteristics that have been exploited in the development of electronic devices. Although PTFE and PVDF have superior properties, their practical application has been hampered because of their poor adhesion due to their

chemical inertness. In order to improve the adhesion between metals and polymers, many researchers have investigated various methods such as rf and ion beam sputtering, wet chemical etching, plasma treatment⁶⁻¹⁰. The approach to enhance the adhesion has been either creating a rougher surface or altering the surface chemistry. Recently, to improve wettability and adhesion to metals, we modified various polymers by Ion Assisted Reaction (IAR) in which 1 keV Ar⁺ ions were irradiated on the polymer surface in oxygen environment^{11,12}.

In this paper, we report on the investigations concerning surface modification of PTFE and PVDF by IAR, and metallization of the modified PTFE and PVDF. We have also examined the characteristics of thin metal films on the modified polymers.

2. Experimental

Commercial PTFE $(-\text{CF}_2-\text{CF}_2)_n$ and PVDF $(-\text{CH}_2-\text{CF}_2)_n$ were used and cut into 10×10×10 mm³ sample

sizes The samples were cleaned ultrasonically in acetone and methyl alcohol to remove organics, dried in an oven at 100°C for 1 hr, and loaded into the chamber for modification by IAR. For the surface modification, a 5-cm cold hollow cathode ion gun was used and the Ar⁺ ion dose was controlled from 5×10^{14} ions/cm² to 1×10^{17} ions/cm² by varying the exposure time at a fixed ion beam current. The flow rate of oxygen gas was fixed at 8 ml/min controlled by a mass flow meter and the oxygen partial pressure was kept constant at 2×10^{-4} Torr. Detailed experimental conditions were described in elsewhere¹¹⁻¹². The static water contact angles on the modified sample were measured by a contact angle meter (CAM-micro; Tantec Co., USA). The chemical bond environment of the modified samples was examined by X-ray photoelectron spectroscopy (XPS). The change in surface morphology of the modified samples was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Cu, Pt, Al, and Ag films with 5000 Å were deposited on the whole surfaces of PTFE and PVDF by ion beam sputtering using high purity targets (99.99%). The thickness of the metal films was measured by a quartz crystal monitor (Maxtec Inc., TM-103R) as well as a step (Tencor Co.). The pressure level during the metal deposition was in the range 9×10^{-5} – 1×10^{-4} Torr. Adhesion between the modified polymers and metals was examined qualitatively using the ScotchTM tape test as well as boiling water test, which was conducted by immersion in boiling water for 4 hours¹³. Electrical resistivity was measured by a four-point probe. Dielectric measurements were performed by depositing a top electrode on the modified polymers, thus creating a parallel plate capacitor structure. The dielectric constant and dissipation factor were measured using a Hewlett-Packard 4194 A impedance analyzer.

3. Results and Discussion

3.1. Surface modification of PTFE and PVDF

Figure 1 shows the change in water contact angles for the modified PTFE and PVDF as a function of ion dose which was varied from 5×10^{14} to 1×10^{17} ions/cm² with flowing 8 ml/min oxygen gas. As shown in Fig. 1(a), the contact angle decreases from 96° for the untreated

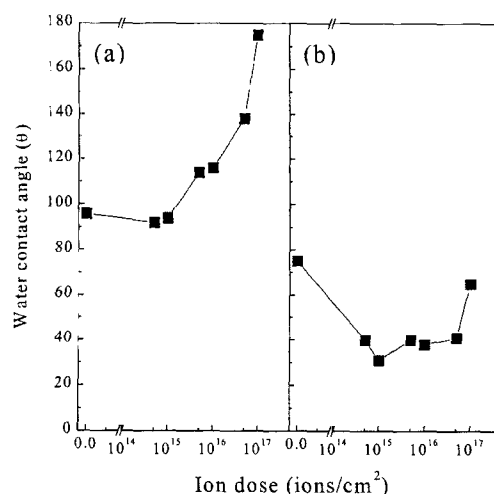


Fig. 1. Change in water contact angles on PTFE (a) and PVDF (b) modified by IAR as a function of ion dose.

PTFE to 92° for the PTFE modified at an ion dose of 1×10^{15} ions/cm² with flowing 8 ml/min oxygen gas. On increasing the Ar⁺ ion dose, however, the contact angle on the modified PTFE increases gradually and the surface of PTFE modified at an ion dose of 1×10^{17} ions/cm² becomes completely non-wettable. In the case of PVDF (Fig. 1(b)), the contact angle was reduced from 75° for the untreated PVDF to 31° for the PVDF modified at an ion dose of 1×10^{15} ions/cm² with flowing 8 ml/min oxygen gas. At higher ion dose of 1×10^{17} ions/cm², the contact angle on the modified PVDF increases to 67°.

In order to investigate the change in the surface morphology of the modified PTFE and PVDF by ion irradiation, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed. Figure 2 shows SEM photographs of the untreated and modified PTFE with varying ion dose. After a low ion bombardment (1×10^{15} ions/cm²), the small cones appear on the modified surface. The height of the cones increases with irradiating ion dose and the average density of the cones is about 30 cones/μm² at an ion dose of 1×10^{16} ions/cm² (Fig. 2(c)). At an ion dose of 1×10^{17} ions/cm² (Fig. 2(d)), the height of the cones reaches several μm. According to Michael and Stulik¹⁴ who reported the etch rate for fluoropolymers, and the resulting surface texture etched by the ion beam, the average density of the cones decreases with ion dose, and several cones

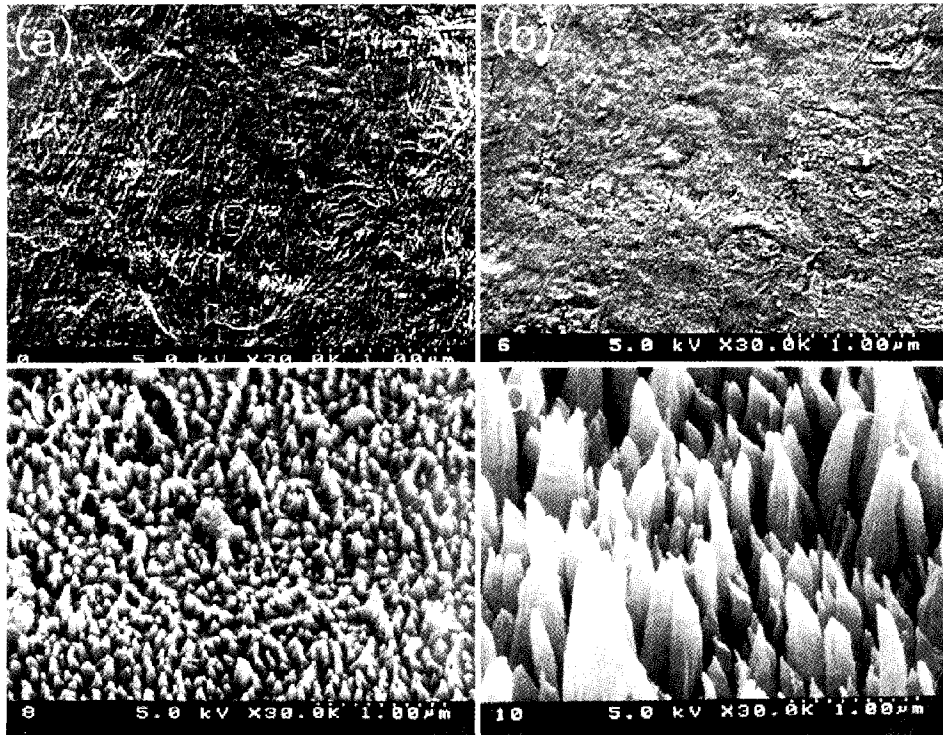


Fig. 2. SEM photographs of the untreated and modified PTFE with varying ion dose: (a) untreated, (b) 1×10^{15} ions/cm², (c) 1×10^{16} ions/cm², and (d) 1×10^{17} ions/cm².

transform into a single larger conical structure due to an emission-redeposition of the sputtered PTFE. Figure 3 shows AFM images and the root mean square (R_{ms}) surface roughness of the untreated and modified PVDF. As shown in Fig. 3, the R_{ms} decreases from 8.8 nm for the untreated PVDF to 5.6 nm for the modified PVDF at an ion dose of 5×10^{14} ions/cm². With increasing ion dose, the R_{ms} increases to 7.7, 9.0, and 10.6 nm at ion doses of 1×10^{15} ions/cm², 1×10^{16} ions/cm², and 1×10^{17} ions/cm², respectively. Compared to the modified PTFE, the surface morphology of the modified PVDF is not altered significantly.

XPS spectra were obtained to investigate the change in surface chemistry of the modified PTFE and PVDF during the IAR. The XPS C1s spectra of the untreated and modified PTFE are shown in Fig. 4(a). In the case of the unmodified PTFE, the CF_2 - peak is located at a binding energy of 292 eV and the hydrocarbon peak, contamination due to adsorbed hydrocarbon, is centered at 285 eV. The CF_2 - peaks become broader with increasing ion dose and this phenomenon originates

from chain scission, crosslinking, carbonization, and chemical reactions. A reduction in the CF_2 - peak intensity is caused by the preferential sputtering of fluorine atoms. If no bonds containing oxygen were formed on the modified PTFE surface, the intensities of C1s core level peak at 285 eV should increase. Therefore, it may be possible to infer that the reduction of C1s core level peak results from the formation of hydrophilic groups containing oxygen bonds. The peak intensity at 285 eV increases with ion dose to 1×10^{16} ions/cm², but saturates at an ion dose of 1×10^{17} ions/cm². The C-F chains such as $CH-CF_x$ -, $-CF$ -, and CF_3 - were formed newly at 286.9, 289.3, and 293.4 eV, respectively¹⁵. The small peaks between 285 eV and 291.6 eV may indicate the carbon-oxygen bond resulting from chemical reaction between oxygen gas and unstable chains, and the newly formed C-F chains. Figure 4(b) shows the XPS C 1s spectra of the untreated and modified PVDF. The C1s core level spectrum of the untreated PVDF includes CH_2 - (286.2 eV) and CF_2 - (290.8 eV), and shows a typical peak shape of PVDF. Compared to the untreated

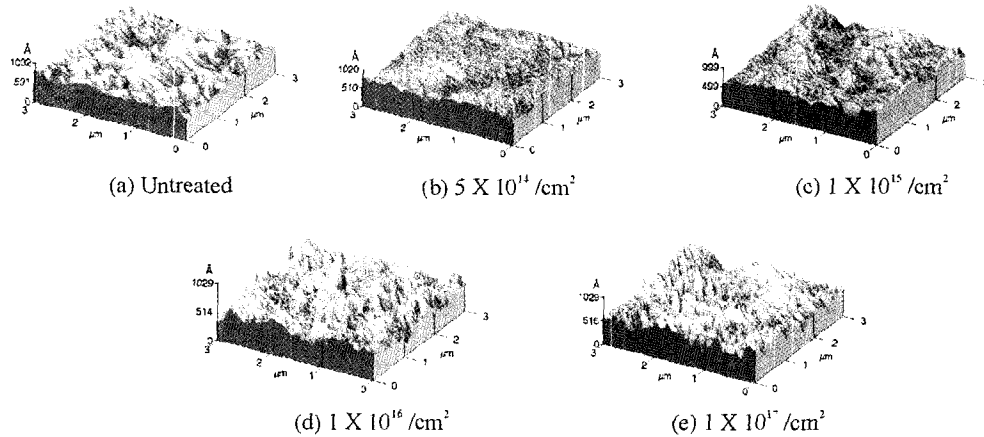


Fig. 3. AFM images of the untreated and modified PVDF with varying ion dose: (a) untreated, (b) 5×10^{14} ions/cm², (c) 1×10^{15} ions/cm², (d) 1×10^{16} ions/cm², and (e) 1×10^{17} ions/cm².

PVDF, the C1s core level spectra of PVDF modified at ion doses of 5×10^{14} ions/cm² and 1×10^{15} ions/cm², indicate that the peak intensity of CF₂- drastically decreases, and then new peaks related to oxygen and fluorine singly bonded carbon appear between CH₂- and CF₂- peak positions. The peak of CH₂- is shifted to a lower binding energy of about 285 eV, which means the vicinity of CH₂- was changed from the most electronegative fluorine atoms to some other atoms. The new bonds at binding energies >286 eV, which indicates that (C-O)-, (C=O)-, etc., are formed on the PVDF surface, and a remarkable reduction in CF₂- peak intensity also happens. The C1s spectra of PVDF modified by ion doses of 1×10^{16} ions/cm², and 1×10^{17} ions/cm² represent a sharp increase of doubly bonded carbon (=C=), and their shapes are skewed to lower binding energy. The carbonization of PVDF by high dose ion irradiation is similar to the results reported by many researchers who investigated high energetic ion and/or heavy ion irradiation^{16,17}.

It is well known that wettability of polymers towards water is closely related to the surface morphology and hydrophilic groups on the polymer surface. In the case of PTFE modified at low ion dose of 1×10^{15} ions/cm², the reduction in contact angle could be attributed to the oxygen-related bonds (hydrophilic groups) formed newly by chemical reaction between the unstable chains and oxygen gas. Although the hydrophilic groups are formed on the modified PTFE, the contact angle on PTFE modified at higher ion doses than 1×10^{16} ions/cm² in-

creases and finally the surface becomes non-wettable. This result is not due to the hydrophilic groups but due to the micro-sized, needle-type rough surface of the modified PTFE. The water droplets sit on the peaks of the cones, bridging over the cone peaks such that adsorption sites are reduced and the hydrophilic groups could not exert their influence on the water droplets. The contact angle on the modified PVDF has a minimum value at an ion dose of 1×10^{15} ions/cm². After further irradiation, surface wettability is degraded to 62°. The enhanced wettability of PVDF modified at ion doses less than 5×10^{15} ions/cm² results from the formation of the hydrophilic groups related to (C-O)- and (C=O)-. Degradation of PVDF surface wettability may be related to carbonization of the polymer chains because the surface morphology of the modified PVDF is not significantly altered. Therefore, the hydrophilic groups formed on the modified PVDF surfaces determine the wettability, while those of the modified PTFE are not a main factor.

3.2. Metallization of the modified PTFE and PVDF

Metals which are often used in making electronic circuits include Cr, Ni, and Cu. Due to its high electrical conductivity, Cu is the metal of choice for circuit lines. Cu films with a thickness of 500 nm were deposited on the untreated and modified PTFE, and the adhesion and electrical resistivity of Cu films were investigated by the ScotchTM tape test and the four-point probe method, respectively. In the case of the untreated PTFE, Cu film

is removed completely from the surface of PTFE. Partial detachment of Cu film is observed when the ion dose is 5×10^{14} ions/cm², and no detachment occurs when the ion dose is greater than 1×10^{15} ions/cm². Generally, the adhesion between a metal and a polymer can be enhanced by the mechanical interlocking due to the rough surface and chemical reaction due to the change in the surface chemistry. In the case of PTFE modified by Ar⁺ ion irradiation without flowing oxygen gas, the enhanced adhesion of Cu/PTFE is also observed. Therefore, the significant increase in adhesion of Cu/PTFE results from the mechanical interlocking due to the increased surface roughness, the chemical structural changes on the PTFE surface.

In the practical application of Cu film on the modified PTFE by IAR as a circuit board, the factor of surface roughness is important since it can affect the resistivity of Cu film significantly. Figure 5 represents the change in resistivity of Cu films on the untreated and modified PTFE with varying ion dose. The resistivity of Cu film on the unmodified PTFE is $2.7 \mu\Omega\text{-cm}$ which is relatively high compared to the bulk resistivity of $1.67 \mu\Omega\text{-cm}$. The resistivity of Cu film decreases from $2.7 \mu\Omega\text{-cm}$ for the unmodified PTFE to $2.4 \mu\Omega\text{-cm}$ for the PTFE modified at an ion dose of 1×10^{15} ions/cm². This reduction in resistivity can be explained in terms of the planar morphology observed on the deposited Cu film due to short sputtering of PTFE surface. As ion dose increases to 1×10^{16} ions/cm², the resistivity of Cu film increases continuously to $4.3 \mu\Omega\text{-cm}$. At the maximum ion dose of 1×10^{17} ions/cm², the resistivity of Cu film increases abruptly. The increase in resistivity with increase of ion dose to 1×10^{16} /cm² may be closely correlated with the surface scattering of electrons due to the partial decrease of film thickness. In the case of ion dose of 1×10^{17} ions/cm², the sudden change in resistivity may be due to disconnection in Cu film. Since the thickness of Cu film is about 500 nm, whereas the height of cones is over 1 μm , the Cu film can not cover all cones sufficiently. Considering the increase in the adhesion between Cu film and PTFE, and the increase in resistivity of Cu film by IAR, it can be concluded that the ion irradiation with a low ion dose of 1×10^{15} ions/cm² is more desirable than a higher ion dose.

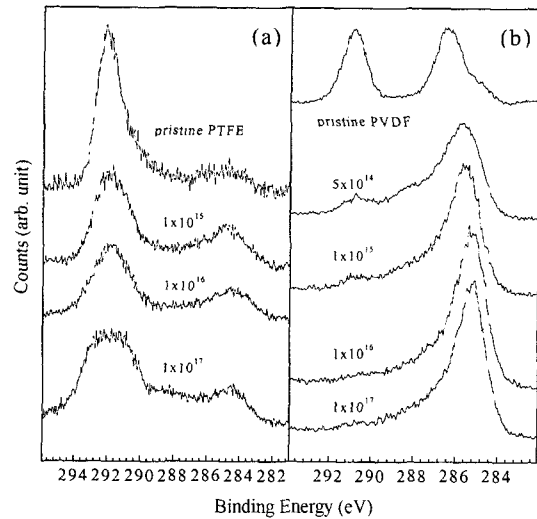


Fig. 4. XPS spectra of PTFE (a) and PVDF (b) as a function of ion dose.

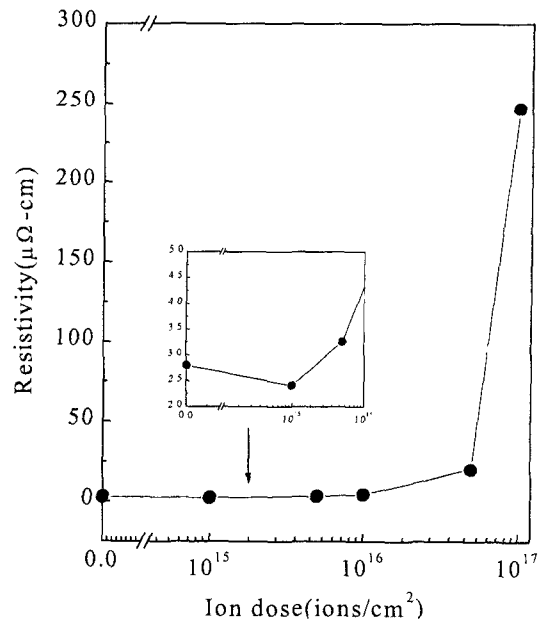


Fig. 5. Change in resistivity of Cu films on the untreated and modified PTFE with varying ion dose.

For a low dielectric loss of a metal/polymer/metal structure, an inert metal (such as platinum and gold) can be used. However, the adhesion strength between the inert metal and the polymer is not enough to justify the technological adoption of this approach. As PVDF is hydrophobic, surface modification will be required to

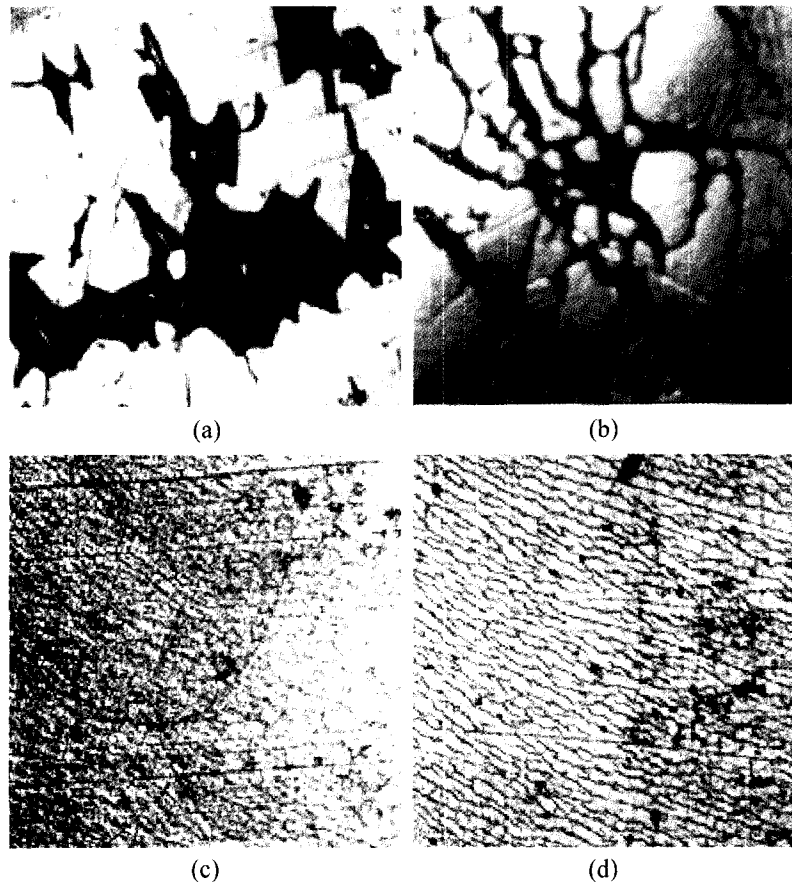


Fig. 6. Optical photographs of Pt thin films on PVDF modified by IAR immersed in boiling water for 4 hours; (a) untreated, (b) 5×10^{14} ions/cm², (c) 1×10^{15} ions/cm², (d) 1×10^{17} ions/cm².

render it hydrophilic. As shown in Fig. 4, the C1s core level spectra of the modified PVDF imply that the hydrophilic groups were formed on the PVDF surface by the reaction between free radicals and oxygen gas. In order to scrutinize the adhesion strength of Pt/modified PVDF, boiling water test was performed for 4 hours. The photographs of Pt thin films on the untreated and modified PVDF after boiling water test are shown in Fig. 6. As shown in Fig. 6(a), Pt thin film on the untreated PVDF has buckled due to difference in thermal expansion coefficient and penetration of boiling water. The buckled area of Pt thin film on the PVDF modified at an ion dose of 5×10^{14} ions/cm² is significantly reduced (Fig. 6(b)). However, the stress release mode for a Pt thin film on the PVDF modified at an ion dose of 1×10^{15} ions/cm² is changed to a crack prop-

agation. Instead of film buckling, the cracks have developed due to the enhanced adhesion. In Fig. 6(d), the crack density of Pt thin film on the PVDF modified at an ion dose of 1×10^{17} ions/cm² is decreased.

The enhanced adhesion between metals and PVDF suggests wide applications for electronic devices. Dielectric constant and dissipation factor of metal/modified PVDF/metal (MPM) structures were investigated with varying the electrode metals and the results are shown in Fig. 7. Al, Cu, Ag, and Pt were used for the electrode material. Workfunctions of Al, Cu, Ag, and Pt are 4.2, 4.7, 4.9 and 5.2 eV, respectively. Dielectric constant of MPM show a strong dependency on work function. Due to raising of the Schottky barrier, the motion of charge carrier at the interface of Pt-metallized PVDF is restricted. The large difference in workfunction can

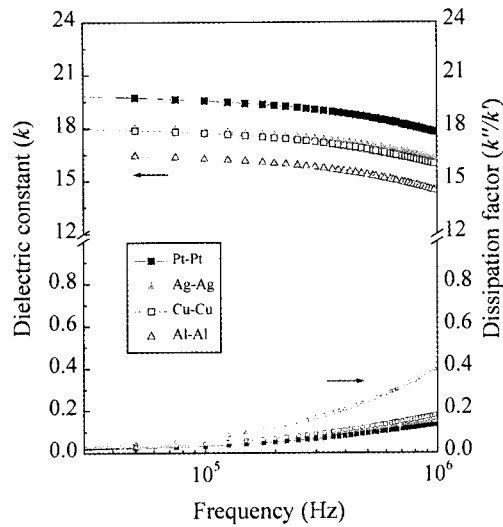


Fig. 7. Dielectric constant and dissipation factor of (a) Pt, (b) Ag, (c) Cu, and (d) Al double-side metallized PVDF modified by IAR.

result in a large Schottky barrier and can lower the charge-leakage component of an MPM structure. As shown in Fig. 6, dissipation factor increases with input frequency. However, the dissipation factor for Al/PVDF/Al structure is larger than that for other MPM structures because of the low workfunction of Al. Also, dissipation factors for MPM structures are in the inverse proportion to the metal workfunction.

4. Conclusions

Adhesion of metal thin films to PTFE and PVDF modified by IAR was enhanced significantly. The change in wettability and adhesion properties was closely related to the surface chemistry and surface roughness of the modified polymers. The enhanced adhesion of metal films to PTFE and PVDF was mainly dependent on the interlocking mechanism and interfacial chemical bonds due to hydrophilic groups, respectively. The successful usage of metallized PTFE and

PVDF modified by IAR can be expected in electronic devices such as flexible circuit boards and piezoelectric sensors.

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