Surface Modification of Polytetrafluoroethylene by Ar^+ Irradiation for Improved Adhesion to Other Materials

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ABSTRACT: A surface of thin square polytetrafluoroethylene (PTFE) samples ($1 \times 1 \times 0.2$ cm^3) was irradiated with Ar^+ at 1 keV with varying ion dose from 5×10^{14} to 1×10^{17} ions/cm^2 with and without an oxygen environment. The irradiated surface of the samples was examined by scanning electron microscopy (SEM) for surface textural changes and x-ray photoelectron spectrometry (XPS) for changes in chemical structure. A wettability test was conducted on the irradiated surface of PTFE samples by water droplets. A Scotch™ tape adhesion test, after a thin film of Cu or Al was evaporated on the irradiated surface, and a tensile test after irradiated samples were glued to sample holders by an adhesive glue (Crystal Bond) was also run. The SEM micrographs showed increasing roughness with fiber forest-like texture with increasing ion dose. The Ar^+ with an O_2 environment produced finer and denser fiber forest-like texture than that without O_2. The high-resolution XPS spectra showed decreased intensity of the F1s peak and formation of the O1s peak when irradiated with the O_2 environment. The increase of the O1s peak may be attributed to the reaction of oxygen atoms and the free radicals created by Ar^+ bombardment. The wettability of water droplets on the irradiated surfaces was found to be inversely proportional to the surface roughness. Adhesion tests were conducted on 2000 Å thick Al or Cu film. Full detachment of the metal films was observed when PTFE samples were not modified. Partial detachment of the Al film occurred when PTFE was irradiated without the O_2 environment, regardless of ion dose. No detachment of the film occurred when PTFE was irradiated with the O_2 environment with the ion dose exceeding 1×10^{16} ions/cm^2. Partial detachment of Cu film was observed with or without the O_2 environment when the ion dose was 5×10^{14} ions/cm^2. No detachment occurred with or without the O_2 environment when the ion dose was 1×10^{15} ions/cm^2 or greater. The tensile test showed that adhesion of an adhesive cement (Crystal Bond) to the irradiated PTFE samples increased significantly with increasing ion dose up to 1×10^{16} ions/cm^2. Possible mechanisms for the improved adhesion are given. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1913–1921, 1997

INTRODUCTION

An increasing number of researchers have been working on the ion irradiation of polymers in recent years because it could be used to tailor chemical, physical, mechanical, and electrical properties of polymers. Such property tailoring or enhancements have been observed by Pae et al.[1] and Forest et al.[2] on crystallinity; Puglisi et al.[3] on wettability; Rao et al.[4] on wear resistance; Basheer et al.[5] on conductivity; Calcagno et al.[6] on

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density; and Koh et al.,[7] and Chang et al. and Baglin et al. on adhesion.[8,9] Various mechanisms for the enhancement of the polymer properties have been attributed to chain scission, cross-linking,[10] carbonization,[11] chemical reactions,[8–10] and surface roughness[8,9] depending on the experimental conditions. Solubility of polymers has been varied with changes in molecular weight that were caused by scission of main chain. Crystallinity has been increased by chain scission and loosening entangled chains. Wettability has been improved by changing the surface chemistry and increasing surface roughness.

Polytetrafluoroethylene (PTFE) is widely used because of its low frictional coefficient, high stability against heat, high resistance to chemical reagents, and/or high electric resistance. However, its poor adhesion property with other materials limits its application in microelectronic devices, coatings, etc. Many attempts have been made to improve its adhesion property of PTFE by using rf plasma,[12] glow discharge,[13] electron beam,[14] and ion irradiation.[8,9] Nevertheless, no significant adhesion enhancement has been achieved with plasma, glow discharge, and electron beam methods. Rather, the treatment caused damage to the surface.

Recently, we reported that ion irradiation with 1 keV energy under a reactive gas environment improved significantly the wettability of PMMA and PC[15] to water and adhesion of the polymers to Al and Cu films. In this article, we present the results of Ar^+ irradiation on PTFE that led to dramatic improvement of adhesion of PTFE to Al and Cu films and an adhesive cement (Crystal Bond) and also to worsening of wettability of PTFE with water. Possible mechanisms for the improved adhesion property of PTFE are given.

EXPERIMENTAL

Ar^+-irradiated Sample Preparation

A sheet of commercial PTFE was cut into small samples of $1 \times 1 \times 0.2$ cm^3. The samples were polished by a polishing compound (Al_2O_3 particle size ~ 0.1 μm), rinsed with soapy water, cleaned in an ultrasonic cleaner with acetone, and dried in an oven at 100°C for one hour to remove any residual solvent. The 1×1 cm^2 surface of the samples was irradiated with Ar^+ with varying ion dose from 1×10^{14} to 1×10^{17} ions/cm^2. The irradiation was conducted with a cold hollow cathode-type ion source. The ion dose was measured by a Faraday cup. Ar^+ gas (99.99%) was injected into the ion gun at a flow rate of 4 mL/min to produce ionized Ar^+ beams. Oxygen gas (99.99%) was blown onto the sample surface at a flow rate of 2, 4, and 6 mL/min, respectively, during the irradiation. The working vacuum pressure of the apparatus was maintained at $1 - 4 \times 10^{-4}$ torr. A schematic diagram of the ion irradiation apparatus is shown in Figure 1.

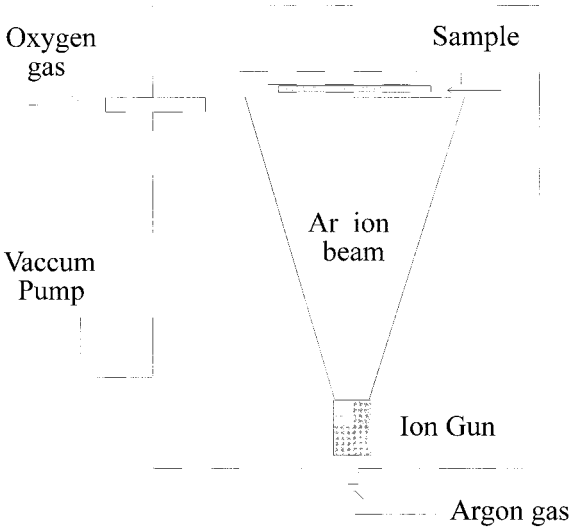

Figure 1 Ion irradiation apparatus.

Wettability Tests

The wettability of the virgin samples and the modified PTFE samples with and without an O_2 environment was determined by measuring the contact angle between water droplets and the PTFE surface using a contact anglemeter (ERMA, goniometer type, Model G-1) at room temperature and 60% humidity. The water droplets made of 0.025 mL of distilled water were dropped at four different sites on each sample, and the measured values of the contact angle were averaged.

X-ray Photoelectron Spectrometry

Chemical structural changes on the irradiated surface of the PTFE samples were examined by x-ray photoelectron spectrometry (XPS) (Surface Science Instrument, Model 2803-S). The high-resolution XPS spectra were obtained on the samples irradiated with and without an O_2 environment. The F1s, C1s, and O1s spectra were obtained and analyzed.

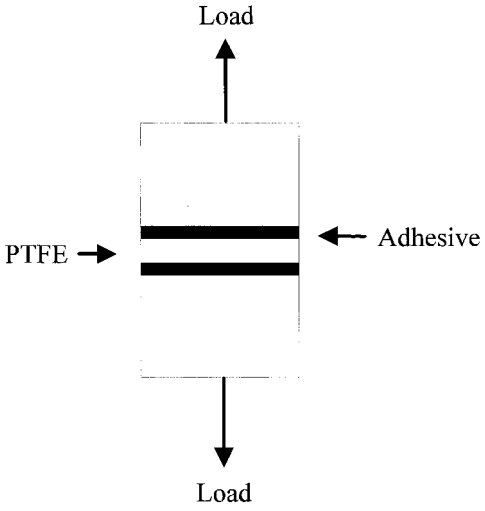

Figure 2 Tensile test configuration of Crystal Bond/PTFE system.

Adhesion Tests

The adhesion tests were conducted by means of Scotch™ tape test on Al/PTFE and Cu/PTFE samples. The Al/PTFE samples were made by depositing a 2000 Å thick film of Al (99.99%, Aldrich Co.) by a vacuum thermal evaporation technique onto the unirradiated and irradiated surfaces of the PTFE samples. The Cu/PTFE samples were made by ion sputtering of Cu (99.99%, Aldrich Co.) at the rate of 0.3 Å/s at 1 keV ion beam energy to the same thickness. The thickness of the evaporated film was confirmed by step profiler measurements. The adhesion between an adhesive cement (Crystal Bond, Buehler, Thermoplastic Cement No. 40-8100) and the irradiated PTFE samples was determined by tensile tests. For these tests, two flat surfaces of the PTFE samples were irradiated. The irradiated PTFE samples were sandwiched between the sample holders with the adhesive glue on both the top and the bottom surfaces. The sample arrangement was cured at 60°C in an oven for one day and then tested in an Instron Testing Machine, as shown in Figure 2.

RESULTS AND DISCUSSION

Scanning Electron Microscopy

A scanning electron microscopy (SEM) micrograph of an unirradiated virgin sample showed a smooth surface with unidirectional and irregular lines, as shown in Figure 3(a). These lines were produced during polishing of the PTFE samples. The Ar^+ irradiated surface with the ion dose of 10^{14} ions/cm^2 revealed numerous small grains that were uniformly distributed, as shown in Figure 3(b). The surface morphology may be described as the beginning of the formation of fiberous texture. The fiberous texture was formed probably by the pitting action of high-speed ions on the PTFE surface. When the ion dose was increased to 10^{15} ions/cm^2, the surface became rougher with the uneven but taller fibers, as shown in Figure 3(c). When the Ar^+ dose was further increased to 10^{16} ions/cm^2, the irradiated surface revealed a dense fiber forest-like texture. The fibers, however, have blunted ends. Some fibers are bundled together, as shown in Figure 3(d). When Ar^+ dose was increased to 10^{17} ions/cm^2, the fibers were taller yet, and the blunted ends became sharper, as shown in Figure 3(e).

When the Ar^+ irradiation was conducted with an O_2 environment (O_2 flow rate was fixed at 4 mL/min), the surface texture underwent further modifications. At Ar^+ dose of 10^{15} ions/cm^2, the length of the fibers became shorter than those without O_2 at the same ion dose, as shown in Figure 3(c). It appeared that the fibers were cut off, leaving only the rounded ends, as shown in Figure 4(a). With the ion dose of 10^{16} ions/cm^2 in the O_2 environment, the fibers were longer, yet blunted [Fig. 4(b)], but much shorter than those without an O_2 environment at the same ion dose. The fiber density per unit area appears to be greater than that without O_2 environment. When the ion dose was increased to 10^{17} ions/cm^2 in the O_2 environment, the surface exhibited numerous fibers with pointed ends, as shown in Figure 4(c). Once again, the fiber density per unit area is even larger compared with that at the ion dose of 10^{16} ions/cm^2 and that without the O_2 environment at the same ion dose.

Wettability Tests

Figure 5 shows the changes of the contact angle (θ) between water droplets and the unirradiated and irradiated surfaces of PTFE samples as a function of Ar^+ dose with and without an O_2 environment. The O_2 flow rates used were 2, 4, and 6 mL/min. It can be seen in Figure 5 that the θ decreases from $\sim$ 100 degrees for the unirradiated surface to $\sim$ 92 degrees for the irradiated with 5×10^{14} ions/cm^2 without an O_2 environment. The

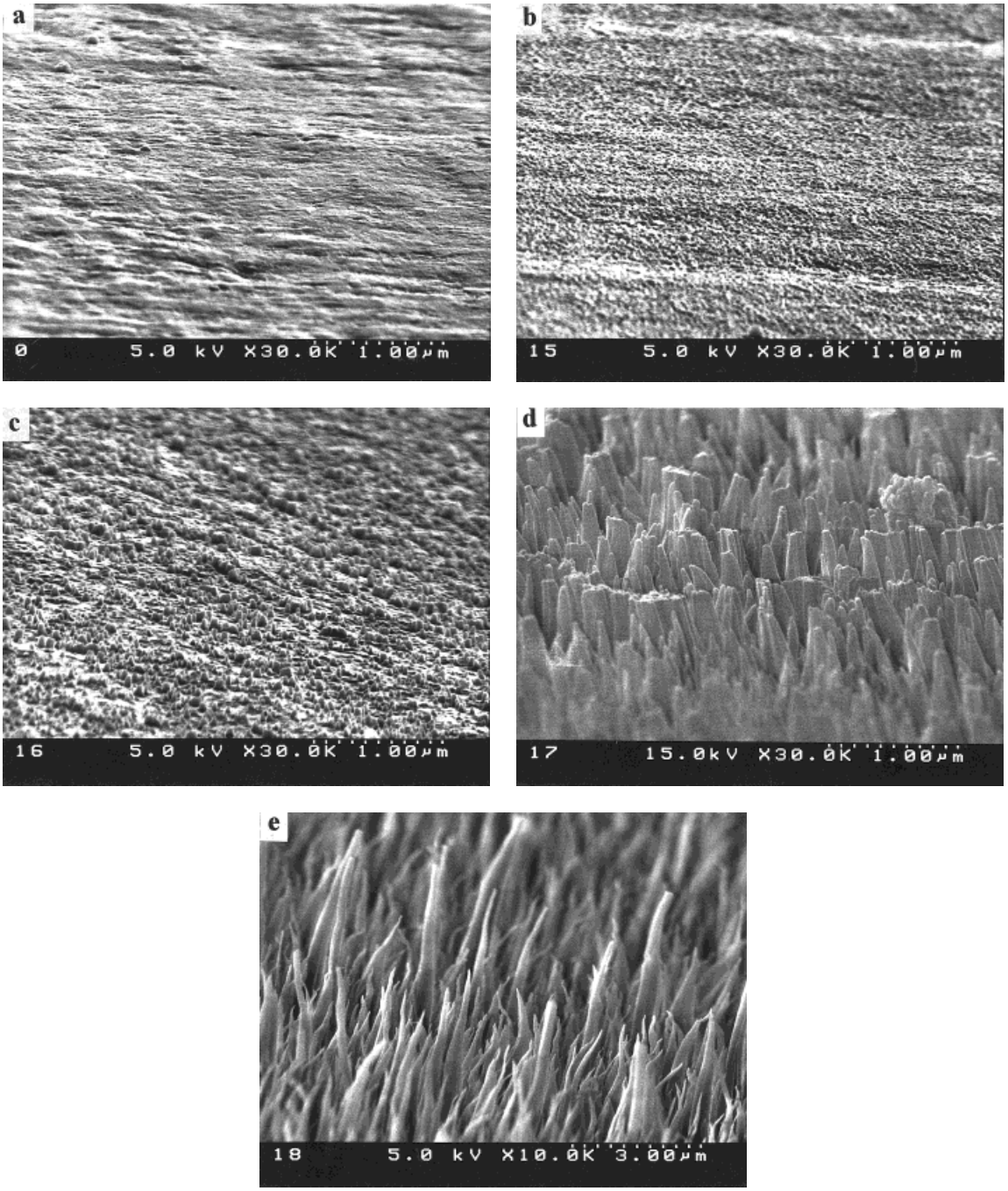

Figure 3 SEM micrograph of (a) a surface of the virgin PTFE sample, (b) an irradiated PTFE sample with 1 keV and 10^{14} ions/cm^2, (c) an irradiated PTFE sample with 1 keV and 10^{15} ions/cm^2, (d) an irradiated PTFE sample with 1 keV and 10^{16} ions/cm^2, and (e) an irradiated PTFE sample with 1 keV and 10^{17} ions/cm^2.

θ then increases with increasing ion dose. It can also be seen in Figure 5 that the θ is higher for the irradiated surface with O_2 environment than that without it when the ion dose is greater than 5×10^{14} ions/cm^2. The amount of O_2 flow rates has little bearing on the contact angle at all ion doses. It was not possible to determine the contact angle beyond the ion dose greater than 5×10^{16} ions/cm^2 because the water droplets would not stay on the surface of PTFE samples. When Figures 3 and 4 are compared with Figure 5, it becomes apparent that the increase of the θ is re-

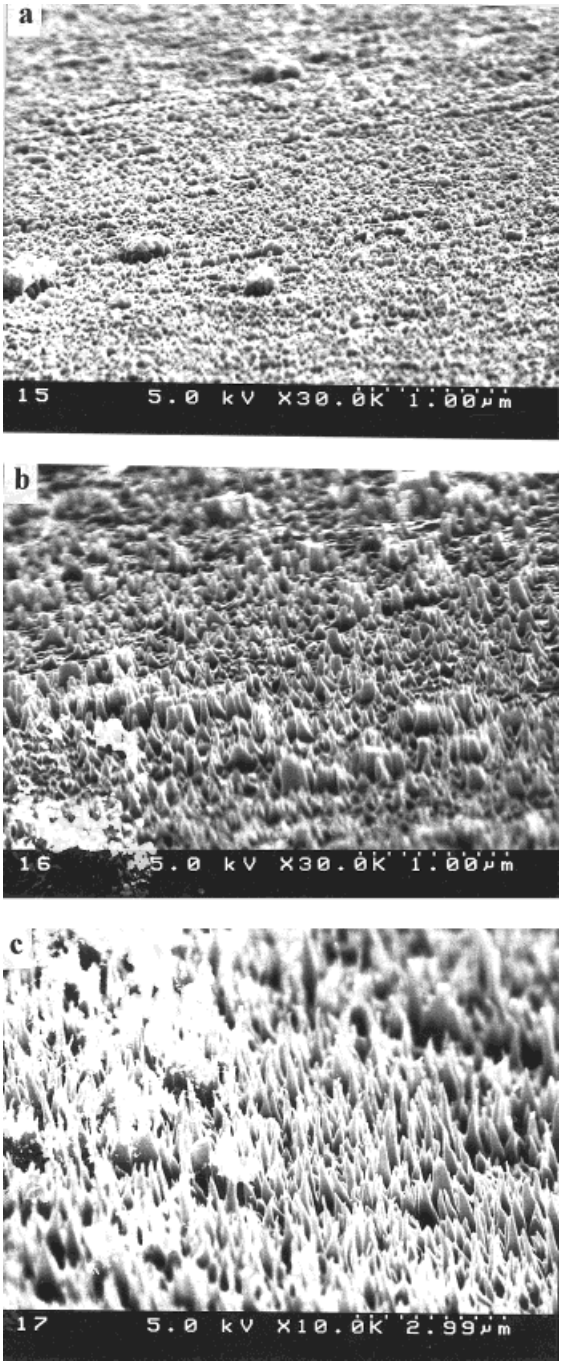

Figure 4 SEM micrograph of an irradiated PTFE sample in O_2 with (a) 1 keV and 10^{15} ions/cm^2, (b) 1 keV and 10^{16} ions/cm^2, and with (c) 1 keV and 10^{17} ions/cm^2.

lated to the surface roughness of the irradiated surface of PTFE.

X-ray Photoelectron Spectrometry

The high-resolution XPS spectra of the irradiated PTFE samples without O_2 environment are shown in Figure 6(a). The XPS spectrum of an unirradiated surface of PTFE exhibits the strong C1s peak at 292 eV binding energy corresponding to the C—F bonding and a small peak at around 285 eV due probably to impurities. When the ion dose is increased, the intensity of C1s peak is reduced and broadened. The reduction and the broadening of the C1s peak may be the result of the changes in the C1s environment caused by the Ar^+ irradiation since the incident energetic Ar^+ on the PTFE chains can lead to chain scission, cross-linking, carbonization, and chemical reactions. The peak at 285 eV would be assigned to the C1s peak for the C—C bond because its binding energy is about 6.5–7.0 eV lower than that of the C—F. This assignment of the binding energy of the C—C bond is in good agreement with the result of Ginnard and Riggs.[16]

The peak intensity situated at 285 eV increases with Ar^+ dose up to 1×10^{16} ions/cm^2 but decreases at an ion dose of 1×10^{17} ions/cm^2. Other surface modification methods,[13,17,18] however, produced a significant decrease of the C1s peak for the C—F bond and a significant increase of the C1s peak for the C—C bond with treatment time. However, in our study, it appears that a small ridge was formed at the energy levels between 285 and 292 eV. The appearance of the ridge may be attributed to the formation of various types of C—F bonds having different environments.

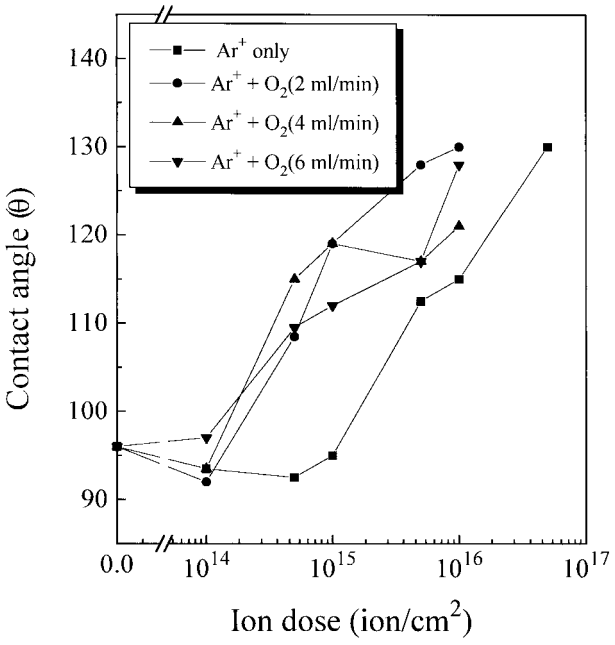

Figure 5 Variation of contact angle with ion dose with O_2 flow rate of 0, 2, 4, and 6 mL/min.

Therefore, it may be possible to infer that Ar^+ irradiation without O_2 environment rearranged the chemical structure of PTFE.

When PTFE samples were irradiated with an O_2 environment, broadening of the peak for the C—F bond was greater than that without an O_2 environment, as can be seen in Figure 6(b). Also, a large O1s peak appears at the binding energy of 532 eV with the ion dose of 1×10^{15} ions/cm^2. The binding energy of carbon (C1s) bonded to oxygen would also rise in the energy range between 285 and 292 eV. The intensity level of the ridge between 285 and 292 eV is high compared with that without O_2 environment, as can be seen in Figure 6(b). It would thus seem that the irradiation severed the C—C and C—F bonds randomly and produced free radicals. These radicals then reacted with the other carbon atoms to form cross-links and oxygen atoms to form hydrophilic groups.

The hydrophilic groups may be responsible for initial decrease of the contact angle θ up to the ion dose of 5×10^{14} ions/cm^2. The θ, however, increases rapidly with an increase of the ion dose.

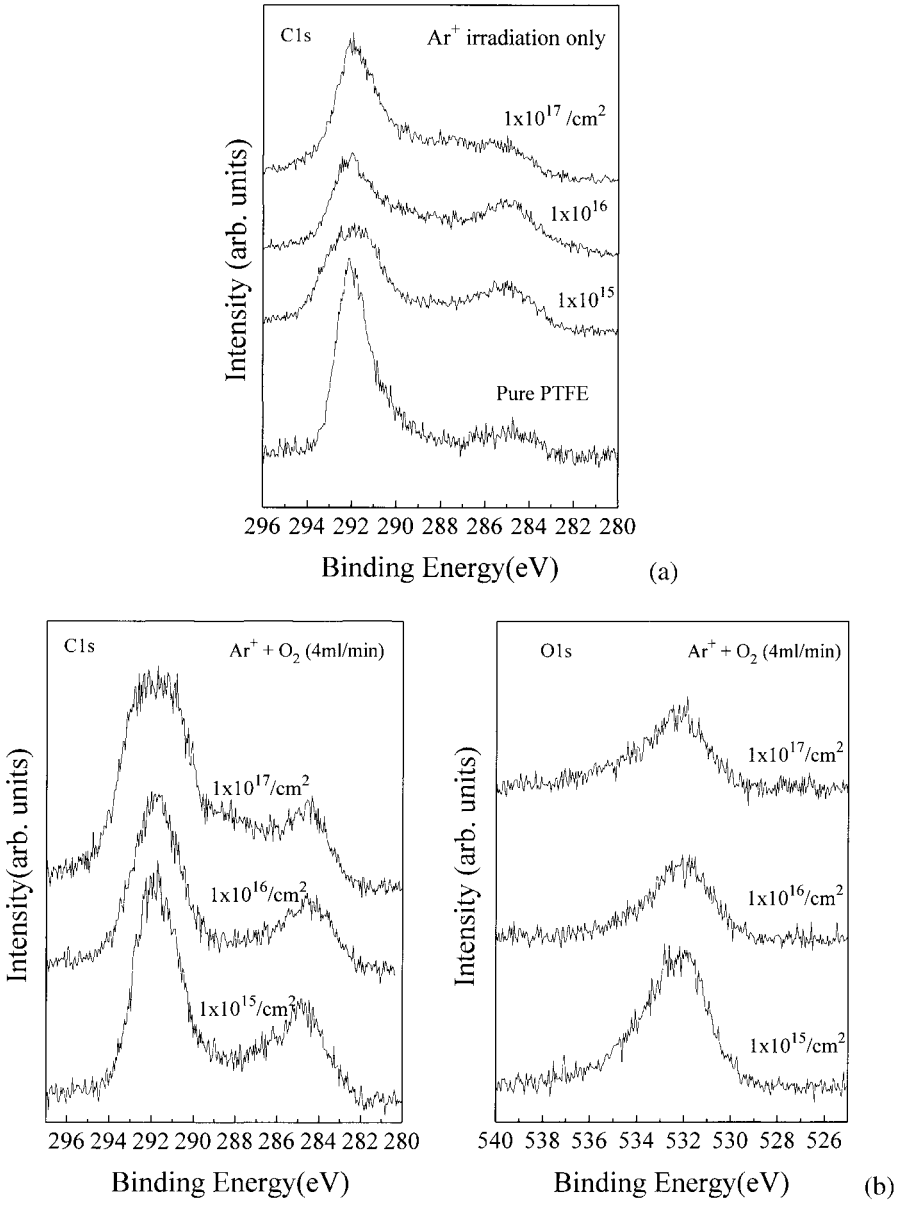

Figure 6 XPS spectra of PTFE irradiated (a) without and (b) with an O_2 environment with varying ion dose.

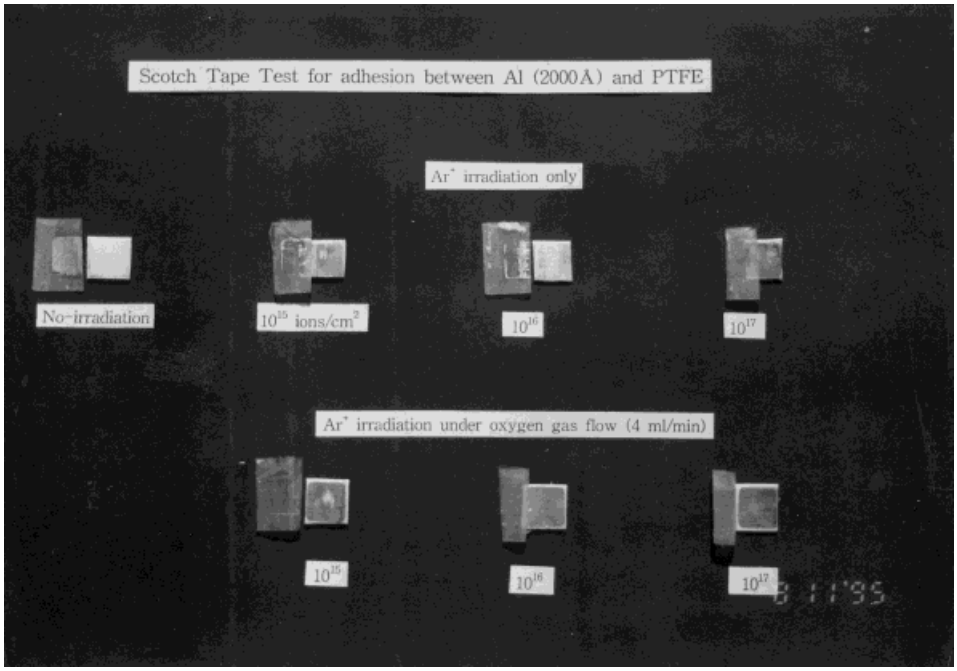

Figure 7 Photograph of partially detached (at an ion dose = 10^{15} ions/cm^2) and undetached (at an ion dose = 10^{15} ions/cm^2) Al film from irradiated PTFE samples without O_2.

It is believed that the increase of the θ, although the hydrophilic groups exist on the surface, is due to roughness of the surface, as described SEM, Results and Discussion Section. That is, the water droplets sit on the peaks of the fibers, bridging over the fiber peaks such that the hydrophilic groups could not exert their influence on the water droplets. When the ion dose reached 1×10^{17} ions/cm^2, the water droplets did not stay on the surface because they rolled over the sharp peaks of fibers [Fig. 4(d)].

Adhesion Tests on Al/PTFE and Cu/PTFE Samples

The adhesion tests using the Scotch™ tape method were conducted on Al/PTFE and Cu/PTFE samples. With regard to Al/PTFE samples, Al film was partially detached from the PTFE sample that was irradiated without an O_2 environment, regardless of the ion dose. When PTFE was irradiated with an O_2 environment, however, the Al/PTFE adhesion depended on ion dose. For instance, when the ion dose was 1×10^{15} ions/cm^2, only a partial detachment was observed, while no detachment occurred when the ion dose was 1×10^{16} ions/cm^2 or higher. Figure 7 shows a partially detached Al film from PTFE samples at the ion dose of 1×10^{15} ions/cm^2 and undetached Al film at the ion dose of 1×10^{16} ions/cm^2.

The Cu/PTFE adhesion appeared to be better than that of Al/PTFE. The adhesion did not depend on the O_2 environment, but on ion dose. Partial detachment of Cu film was observed when the ion dose was 5×10^{14} ions/cm^2, and no detachment occurred when the ion dose was 1×10^{15} ions/cm^2 or greater. Figure 8 shows a partially detached Cu film at the ion dose of 5×10^{14} ions/cm^2 and undetached Cu film at the ion dose of 1×10^{15} ions/cm^2.

It appears that three separate mechanisms are at work in improving the adhesion in Cu/PTFE and Al/PTFE systems. The first mechanism is the chemical environmental change of PTFE surface by Ar^+ irradiation as observed in the XPS study. The second is due to chemical bonding at the metals/PTFE interface. The third is the surface roughness of PTFE created by Ar^+ irradiation (see Fig. 9).

The Ar^+ irradiation severs C—C and C—F bonds, creating free radicals. Some are consumed in cross-linking and some in forming C—O bonds. Severed F atoms may be available for bonding with the metals. Moreover, the surface may no longer be a PTFE-like slippery surface due to de-

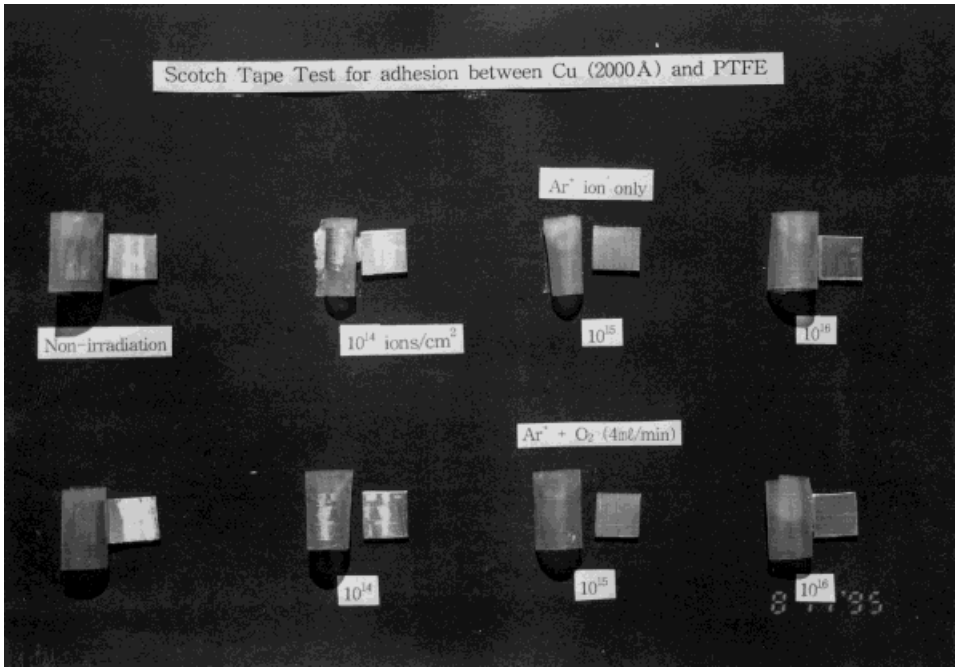

Figure 8 Photograph of partially detached (at an ion dose = 10^{14} ions/cm^2) and undetached (at an ion dose = 10^{15} ions/cm^2) Cu film from irradited PTFE samples with O_2.

fluorinization of the surface layers. When the metals are evaporated on the irradiated PTFE surface, Cu—O, Al—O, Al—F, and Cu—F bonds would be readily formed.[8] These new bonds could be a source for the increased adhesion. According to Chang et al.[8] and Kim et al.[9], the surface of irradiated PTFE becomes rough. The PTFE surface of our samples also exhibited extremely rough surface texture. This roughness plays an important role in improving the adhesion by increasing the metal/PTFE contact area and mechanical interlocking. The difference in adhesion of Al and Cu to PTFE, as described above, appears to come from the deposition methods used.

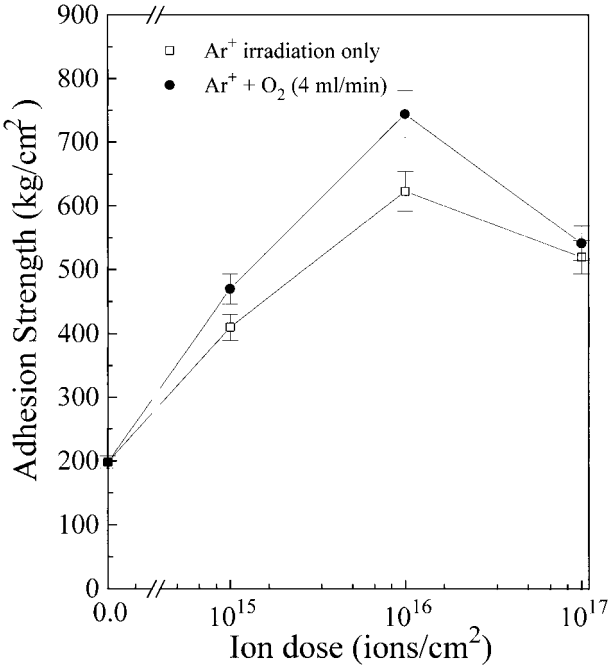

Figure 9 Variation of adhesion strength of Crystal Bond/PTFE with varying ion dose.

Adhesion Tests on Crystal Bond/PTFE Samples

The adhesion strength of Crystal Bond to the PTFE surfaces with and without Ar^+ irradiation was determined by means of tensile tests, as shown in Figure 2. The sandwiched PTFE samples between the sample holders with Crystal Bond on both the top and bottom surfaces were pulled under the tensile load, and the maximum fracture strength was determined. A low adhesion strength of 200 kg/cm^2 was obtained when the unmodified PTFE samples were used (see Fig. 9). With Ar^+ irradiation, the adhesion strength increased as an increasing function of ion doses up to 1×10^{16} ions/cm^2. The maximum value obtained was 750 kg/cm^2 at the ion dose of 1×10^{16}

ions/cm^2 with an O_2 environment, which is 3.75 times the value obtained with unmodified PTFE. The mechanism responsible for the increased adhesion of Crystal Bond/PTFE appears to be the surface roughness that increases the contact area and mechanical interlocking.

CONCLUSION

Many methods have been employed to improve the adhesion properties of polymers by increasing surface roughness, forming an interface layers,[19] and introducing electron donor and acceptor groups at the interface,[20] etc. In this study, PTFE samples were irradiated with Ar^+ with and without an O_2 environment with varying ion dose from the ion doses of 5×10^{14} to 1×10^{17} ions/cm^2.

The wettability of the irradiated surface of PTFE with and without an O_2 environment, which was determined by the contact angle between water droplets and the PTFE surface, decreased first at the lower ion doses up to 5×10^{15} ions/cm^2 and then increased with higher ion dose, but was not measurable at an ion dose greater than 5×10^{16} ions/cm^2 because the water droplets would not stay on the surface. The wettability is lower with an O_2 environment than that without an O_2 environment, although hydrophilic groups were formed on the surface with an O_2 environment. The increase of the contact angle can be attributed to the extreme surface roughness of PTFE caused by Ar^+ irradiation, as observed in the SEM study.

The adhesion of Al on the irradiated PTFE surface with an O_2 environment increased significantly such that no detachment was possible in Scotch™ tape tests when the ion dose was 1×10^{16} ions/cm^2 or greater. No detachment of Cu film was observed on the irradiated PTFE samples, with or without an O_2 environment when the ion dose is 1×10^{15} ions/cm^2 or greater. The significant increases of the Al/PTFE adhesion and the Cu/PTFE adhesion appear to be the results of chemical structural changes of PTFE surface, formation of chemical bonding at metal/PTFE interface, and the increased roughness on the PTFE surface caused by Ar^+ irradiation. The extreme surface roughness appears to be the primary source of the increased adhesion in the metal/PTFE systems. It was also determined that the adhesion strength with the Crystal Bond/PTFE samples increased with increasing the ion dose to a certain level. Furthermore, the ion irradiation with an O_2 environment enhanced the adhesion of the Crystal Bond/PTFE beyond that without an O_2 environment. The increase of Crystal Bond/PTFE adhesion is primarily due to the increased surface area and mechanical interlocking at the interface because of the surface roughness of PTFE.

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