

반응성 기체를 첨가한 저 에너지 이온빔 처리에 의한 고분자와 금속 간의 계면 접착력 증가에 관한 연구

이지석*·서용석*·김한성*·강태진*

Enhanced Interfacial Adhesion between Polymers and Metals(Cu) by Low Energy Ion-beam Irradiation with Reactive Gases

Jiseok Lee, Yongsok Seo, Hansung Kim and Taejin Kang

Abstract

Using a low-energy Ar⁺ ion-beam with and without reactive gases, polymers such as chemically stable poly(tetrafluoroethylene) (PTFE) and poly(ether ether ketone) (PEEK) films were modified to have special surface features. The adhesion strength between the polymers and the copper was significantly improved because of both changes in the surface topography and chemical interactions due to polymer surface functionalization (oxidation and amination). The surface modification altered the failure mode from adhesive failure for the unmodified polymer/Cu interface to cohesive failure for the surface-modified polymer/Cu layer interface..

Key Words: ion beam irradiation, interfacial adhesion, fracture toughness.

1. Introduction

While poly(tetrafluoro ethylene) (PTFE) is an ideal material for microelectronic applications because of its many desirable properties, the chemical stability of PTFE makes it difficult to form a chemical bond with a functional group on the surface, which is definitely needed for the deposition of metal films, such as copper, onto a PTFE film to be used in such applications. Many experimental studies have been done to improve the adhesion between PTFE and copper metal. Though they have their own merits, wet processes are not always the choice for the PTFE surface functionalization because of the complex processes and pollution and solvent recycling problems. Since vacuum technologies can change the chemical or the physical properties only at the polymer surface without affecting the bulk properties, these technologies have been intensively investigated.

Plasma treatment is one of them, but its effect is not so much remarkable.

Recently, we developed a novel process, low-energy ion-beam irradiation under a reactive gas environment, for polymer surface modification.(1,2) For a strong adhesion between the copper metal layer deposited by thermal evaporation and the PTFE surface, functionalization of the PTFE surface and control of the surface topography are two crucial factors. In this study, we have demonstrated that PTFE surface modification by low-energy Ar⁺ ion-beam with and without a reactive gas caused special surface features which significantly enhance the adhesion strength between the evaporated copper layer and the modified PTFE surface. It is shown that the nitrogen containing functionality provided by the reactive ion beam irradiation interacts more favorably with the copper layer than oxygen containing functionality.

The incorporation of functional groups on the

polyetheretherketone (PEEK) surface and the surface topology change were also studied and compared to those of PTFE. For PEEK, dominance of the former was evident because the lap-shear strength initially increased with the irradiation. The special surface features significantly enhanced the adhesion strength between the evaporated copper layer and the modified PEEK surface. However, the decrease in the surface roughness with ion-beam irradiation implies a decrease in adhesion strength due to a smaller contact area, and the shear strength due to topology change also slowly decreased after a long time irradiation.

2. Experimental

2.1 Materials.

A commercial PTFE sheet and a copper sheet with thickness of 0.05mm were used. Argon, ammonia and oxygen gases of 99.99% purity were used.

2.2 Ion-beam Apparatus.

The reactive low-energy ion-beam irradiation system is fully described elsewhere. (1,2) It was composed of a conventional ion-beam system, a reactive gas feeding system, and a stand for the polymer samples. The working pressure in the reaction chamber was kept under 10⁻⁴ Torr. The Ar⁺ ion-beam was generated from a 5-cm cold, hollow cathode ion source, and its potential energy was maintained at less than 1keV. Reactive gas was constantly injected from the bottom of the chamber. The flow rate of the reactive gas was 3 sccm, which was controlled by a mass flow controller (MassFlo 9121).

2.3 Surface Characterization.

The AFM images were obtained using a multimode scanning probe microscope (Digital Instruments, Inc.). The ESR spectrometer used was a Bruker ESP300 operating in the X-band microwave frequency range. The XPS spectrum was recorded using a Surface Science 2803-S spectrometer (hν=1.5keV). Scanning electron microscopy (SEM)

observations of the samples were performed on a Hitachi S-2500C.

2.4 Interfacial Adhesion.

A copper layer of about 200 nm in thickness was thermally evaporated onto the PTFE film by using a vacuum thermal evaporation technique. The deposition was carried out under a pressure of 10⁻⁶ Torr and at a deposition rate of about 2 Å/s. The copper deposited surface was adhered to a copper sheet by using an epoxy adhesive. The assembly was cured at 100°C for 6 hours and was then subjected to a T-peel adhesion test using an Instron Universal Testing Machine (model 4204) at room temperature. A crosshead speed of 10 mm/min was used. All the reported results are averages of at least ten measurements.

3. Results and Discussion

In Figure 1, it is shown that PTFE surface modification by low-energy Ar⁺ ion-beam with and without a reactive gas caused special surface features which significantly enhance the adhesion strength between the evaporated copper layer and the modified PTFE surface.

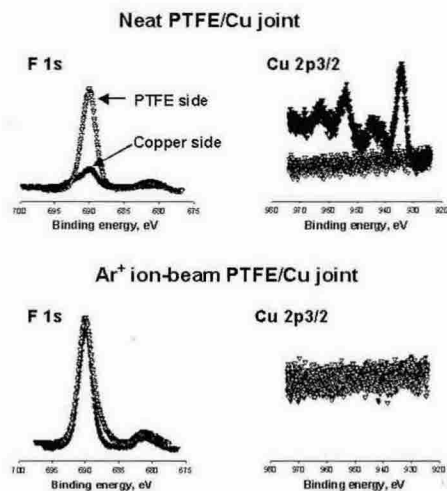


Figure 1. XPS spectra of the peeled-off surfaces. Empty and filled symbols represent the PTFE side and the copper side, respectively.

It is shown that the nitrogen containing functionality provided by the reactive ion beam irradiation interacts more favorably with the copper layer than oxygen containing functionality.(Figure 2)

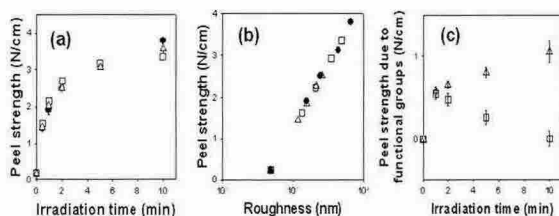


Figure 2. (a) Peel strength for the adhesion joint vs irradiation time, (b) the peel strength due to the surface roughness, and (c) the peel strength due to chemical interactions (● = Ar⁺ only, □ = Ar⁺ + O₂, △ = Ar⁺ + NH₃).

The change in the surface topography is the dominant factor deciding the adhesion with the copper layer while chemical interactions due to surface functionalization also contribute significantly. Surface modification by reactive ion-beam irradiation alters the failure mode because of the topography change and the surface functionalization. (Figure 1) This is peculiar to PTFE. For these reasons, a reactive low-energy ion-beam appears to be a very effective and environmentally favorable process for improving polymer/metal adhesion.

We also applied the low energy ion-beam irradiation method to modify the surface of PEEK to improve the adhesion between PEEK and copper. Surface modification was done by using an Ar⁺ ion-beam irradiation with and without a reactive O₂ gas. The contact angle decreased with the irradiation time owing to the increased hydrophilicity. Incorporation of oxygen onto the surface layer occurred through depletion of hydrocarbons in benzene rings. The XPS results showed that hydrophilic groups were formed on the PEEK surface during the modification process. Incorporation of oxygen in the surface layers and

emergence of the COO⁻ group with the depletion of hydrocarbons made the surface quite hydrophilic. Differently from the case of PTFE, the surface became smoother with increasing ion-beam irradiation time. (Figure 3)

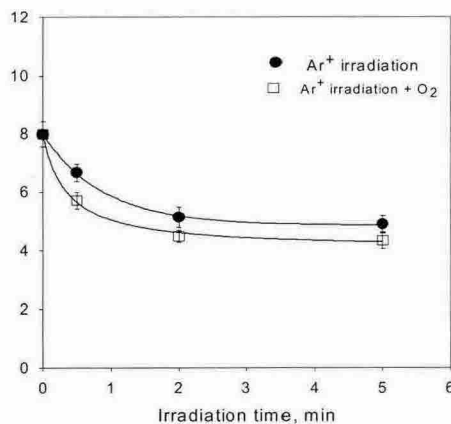


Figure 3. The surface roughness of ion-beam irradiated PEEK with the irradiation time; only Ar⁺ ion-beam irradiation (●), Ar⁺ irradiation with reactive O₂ gas (□).

The incorporation of functional groups on the PEEK surface and the surface topology change have opposite effects on the adhesion strength between PEEK and copper. (Figure 4)

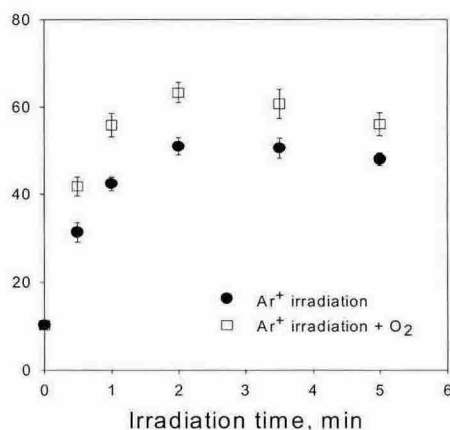


Figure 4. The adhesive strength of ion-beam irradiated PEEK/Cu with the irradiation time; only Ar⁺ ion-beam irradiation (●), Ar⁺ irradiation with reactive O₂ gas (□).

Dominance of the former was evident because the lap-shear strength increased with the irradiation time (hence, the induction of functional groups on the surface) while the contact surface area decreased. The lap-shear strengths of the irradiated PEEK/copper system were significantly improved (five and six times for Ar⁺ ion-beam irradiation only and Ar⁺ ion-beam plus O₂ gas irradiation, respectively).

4. Conclusion

In PEEK, the contact angle decreased with the irradiation time owing to the increased hydrophilicity. Incorporation of oxygen onto the surface layer occurred through depletion of hydrocarbons in benzene rings. The lap-shear strengths of the irradiated PEEK/copper system were significantly improved, but failure occurred at the interface. The surface became smoother with increasing ion-beam irradiation time. The incorporation of functional groups on the PEEK surface and the surface topology change have opposite effects on the adhesion strength between PEEK and copper. Dominance of the former was evident because the lap-shear strength increased with the irradiation time while the contact surface area decreased.

In PTFE, the contact angle increased with irradiation time owing to the effect of roughness. The XPS results showed that defluorination, oxidation, and amination occurred on the PTFE surface during the modification, the degree of which was explained by radical concentration measurement. The surface of ion-beam irradiated PTFE showed a grass-like structure by the sputtering effect of collision of ions. The adhesion strength increased with irradiation time. It is surprisingly higher than the previously reported adhesion strength between the PTFE treated with remote hydrogen plasma and the deposited copper layer. From the XPS analysis, the failure occurred in the inner layer of the PTFE (cohesive failure) rather than at the interface between the PTFE and copper (adhesive failure) for the modified PTFE/copper.

Acknowledgement

This work was supported by the SRC/ERC program of MOST/KOSEF (R11-2005-065).

References

- (1) H. J. Kim, K. Lee, Y. Seo, S. Kwak, S. Koh, *Macromolecules*, 2001, 34, 2546; b) H. J. Kim, K. Lee, Y. Seo, *Macromolecules*, 2002, 35, 1267
- (2) S. Kim, K. Lee, Y. Seo, *Langmuir*, 2002, 18, 6185.