Journal of Korean Institute of surface Engineering Vol. 32, No. 3, Jun., 1999

EFFECT OF ION BEAM ASSISTED CLEANING ON ADHESION OF ALUMINIUM TO POLYMER SUBSTRATE OF PC AND PMMA

* Sik Chol Kwon, Gun Hwan Lee and Chuel Yong Lee ** Han Bum Goh, Jun Seop Lim and Sung Jin Goh

- * Surface Engineering Laboratory, KIMM, 66 Sang-Nam, Chang-Won, Kyung-Nam, Korea
- ** Aju Engineering Co. Hyunpoong, Dalsung-keun, Daegu, Kyungpook-do, Republic of Korea

Abstract

As metallic surface has its unique lustrous appearance and optical reflectance in visible range of light, the metallization of plastic surface has been an essential drive toward weight reduction for fuel economy and decorations in transportation industry and has been put into practiced from wet chemical-electrochemial to dry vacuum process in view of an environmental effect.

Electron-beam metallization was used in this work with an aim at improving the scratch-proof surface hardness of plastic substrate with metallic finish character. Thin film of Al (1000Å) and SiO₂(7000Å) were metallized on substrate of PC and PMMA and the films were evaluated by pencil test for surface hardness and by cross-cut tape test for adhesion. The ion beam treatment improved around twice as hard as non-treat surface. The ion beam is effect on its hardness and adhesion to surface hardened PC substrate.

1. Introduction

Metallization is a generic process to make a metallic coating on plastics leading to expand the usage of plastics in engineering components in addition to its simple application in the decorative domain as it provides the metallic surface finish. The metallic thin films are usually obtained by evaporation, sputtering and CVD techniques. Fundamental differences between plastics and metals in physical and chemical properties have also created numerous important technical chal-

lenges, which should be overcome prior to industrialization. One major problem is poor adhesion between metal film and plastic surface. Some type of surface modification of polymer is employed prior to metallization in order to improve adhesion. The most commonly used surface modifications are electric dischasrge (corona and plasma) 1) and, more recently, ion-beam treatment²⁾. The other difficult problem is low surface hardness. The ploymer surface hardening is achieved to modify the polymer surface by the chemical technique as like dipping in hardending agent

and the physical one using ion-beam. The metallic film on plastics is so thin that it can be hardly protective from a mechanical damage such as scratching with steel wool in cleaning operations. To protect the metallic coated plastic surface from the exterior damage, the surface should have an enough surface hardness as well as adhesion strength.

In this work, we report on the effect of ion beam as a pretreatment process in metallic coating by electron beam evaporation on PC (polycarbonate) and PMMA (polymethylmethacrylate). Process optimization to improve both of surface hardness and adhesion have been carried out to find its application to plastic surface mirror.

2. Experiment

The two kinds of plastics, PC and PMMA, plates were obtained for this study. They are cut into $250 \times 50 \times 3$ mm as basic substrates. A series of them are surface-hardened by dipping in hard coating agents (*STN21GNTM for PC and ST31PLTM for PMMA) for subsequent coating. And glass plate is used as reference substrate for comparison with plastic substrate.

Al was deposited from wire (>99.9) onto substrate surface by electron-beam evaporation in vacuum chamber at a pressure of 8×10^{-6} Torr. Prior to deposition, all the samples were cleaned in detergent, washed in deionized water and dried at room temperature. The samples were placed at a distance of about 50cm from evapora tion source and the high frequency ion beam

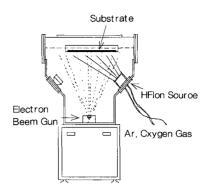


Fig. 1 Schematic diagram of ion beam-assisted evaporation system

source was placed at 60° from the sample normal as depicted in Fig. 1. Ion cleaning was conducted with oxygen ion at accelerating voltage of 1KV for 8min. The total dosage of 0^{2+} ion was 1.4×10^{17} /cm² in our measurement of ion current density with Faraday cup.

The film deposition of Al and SiO₂ was controlled to be 1000 Å for Al and 7000 Å for SiO₂. The thickness was measured and controlled by using a quartz crystal monitor. During deposition, Ar (>99.999) and O₂(>99.9) ions were accelerated at 0.5KV for Ar and 0.1KV for O₂ ions for ion-beam-assisted process and their total dosages were controlled to be $8.25 \times 10^{16} / \text{cm}^2$ for Ar⁺ ions and $3.13 \times 10^{16} / \text{cm}^2$ for O²⁺ ions.

The property of film was measured by pencil test for surface hardness³⁾ and by cross-cut tape test for adhesion⁴⁾ according to ASTM specifications. The hardness is expressed as number by dividing each hardness scale into two divisions ranging from 9H to 6B. And "O" is value denoting the measurement unavailable due to rupture after pencil stroke.

In cross-cut tape test, a lattice pattern with eleven cuts in each direction is made in the film

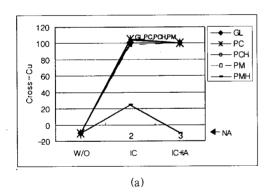
^{*} STN21GN™ for PC and ST31PL™: Trade name of LG hardening agent product

to the substrate, pressure-sensitive tape is applied over the lattice and then removed. The cross-cut adhesion value is denoted by numbers of grit to substraste attached. The NA is also expressed in the data where the coating has flaked before tape is applied.

3. Results and Discussion

3. 1. Effect of ion beam on adhesion

Fig. 2 showed the effect of ion-beam-assisted cleaning and deposition on the adhesion of Al thin film to five kinds of substrates employed in this experiment. The no-adhesion points denoted by (NA) are observed on all the surfaces with no cleaning treatment. It indicates that ion beam



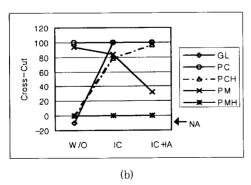
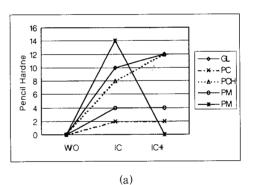


Fig. 2 Cross-cut Adhesion Measurements of (a) Al (b) SiO₂ Thin film on Various Surfaces treated with Ion-Beam

treatment is effective means in removing the contaminants from the substrate surface and providing surface active for good adhesion as proposed by K.L.Mittal⁵⁾. It is well understood that ion beam treatment improves adhesion as of its effect on surface modification of polymer due to mechanical interlocking, the elimination of weak boundary layers, electrostatic attractions and chemical bonding. The adverse effect of ionbeam-assisted cleaning and deposition on PMMA and surface-hardened PMMA with hard coating agent should be extensively investigated with XPS about the formation of new chemical species for the poor adhesion. Several investigators 6-8) considered the prime importance of subsequent overlayers which provide nucleation and



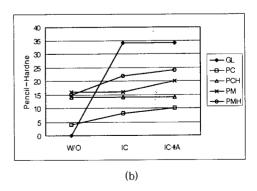


Fig. 3 Surface Hardness Measurements of (a) Al (b) SiO₂ Thin film on Various Surfaces treated with Ion-Beam

chemical bonding sites responsible for adhesion problem.

The effect of ion-beam on the adhesion of SiO₂ film on five different surfaces was depicted in Fig. 3. It is generally agreed as evidenced on glass and hardened-PC that ion-beam-assisted cleaning and deposition contribute to strong adhesioin of film to substarte as ion bombardment induces dehydrogenation and cross-linking of the surface region^{9, 10)}.

Contrary to Al film deposition, SiO₂ film deposition on PC and PMMA surfaces treatment showed excellent adhesion without ion-beam. Especially, ion-beam. Especially, ion-beam treatment has no effect on adhesion of SiO2 film to PC while it has adverse one to PMMA. Comparing with hardened-PC and -PMMA, ion-beam treatment showed positive effect on the adhesion of SiO₂ film to hardened-PC but it demonstrated negative one to hardened-PMMA. Considering the hardening of PMMA with ST31PLTM, it is conclusive that the surface became modified and inert to subsequent coating of Al and SiO₂. The poor adhesion may be associated with the residual stress involved in hardening and ion-bombarding PMMA surface.

3. 2. Effect of ion beam on surface hardness

The effect of ion-beam-cleaning and deposition of Al and SiO₂ film on surface hardness were shown in Fig. 4 and Fig. 5 respectively. It was found that the samples coated with SiO₂ showed around two times as high as those coated with Al all over the process parameters. It is basically related with higher hardness of SiO₂ than Al. The lowest hardness appeared on Al film deposited

over five substrates untreated with ion-beam. It represented a similar trend of adhesion as shown previously in Fig. 2. The film hardness can be defined as a capacity to resist against external load. Thus it is also affected by factors such as substrate hardness, adhesion strength, and residual stress11). Therefore the lowest hardness on untreated surface was considered as of poor adhesion at interface. The ion-beam treatment was predominantly effective on glass rather than others as it was hard enough to support film. In a same sense, the high hardness was evidently observed on the hardened-PC when comparing with bare surface of PC. But more research is necessasry for the explanation of hardness improvement in hardened-PMMA as mentioned above.

4. Conclusions

Various plastic materials were employed as substrates to find out the optimum surface modification by ion-beam to provide surface with high hardness as well as good adhesion to metallic or oxide coating. Polycarbonate (PC) and Polymethle-methacrylate (PMMA), and their hardened PC and PMMA were used to investigate the effect of ion-beam-assisted cleaning and deposition on the hardness and adhesion of 1000 Å thick aluminum and 7000 Å thick silicon oxide film. Ion beam treatment increases surface hardness around two times as higher as untreated surface and much better improvement in adhesion when deposition of Al and SiO2 film are concerned. The hardening of PC showed beneficial effect to hardness and adhesion but hardening of PMMA remain question about poor adhesion.

Reference

- R.W. Burger and L. J. Gerenser, Metallized Plastics, Plenum Press, New York, pp179–193 (1992)
- H. V. Boenig, Plasma Science and Technology,
 By Cornell University Press, Ithaca, New York, pp199-239 (1982)
- 3. ASTM designation: D-3363-92a
- 4. ASTM designation: D-3359-78
- K. L. Mittal, J. Vac. Sci. Technol., 13, 19 (1976)
- 6. L. J. Gerenser, J. F. Elman, M. G. Mason, and

- J. M. Pochan, Polymer, 26, 1162 (1985)
- 7. J. M. Pochan, L. J. Gerenser, and J. F. Elman, Polymer, 27, 1052 (1986)
- 8. L. J. Gerenser, J. Adhes. Sci. Technol., 1, 303 (1987)
- J. M. Burkstrand, Appl. Phys. Lett. 33, 387 (1978)
- J. M. Burkstrand, J. Vac. Sci. Technol. 16, 1072 (1979)
- M. D. Thouless and H. M. Jensen, Adhesion Measurement of films and coatings, by K. L. Mittal, VSP, Utrecht, The Netherlands, pp95– 102 (1995)