Effect of pH of Silane Solution on the Adhesion of Polyimide to a Silica Substrate

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Synopsis

We show that the pH of the aminosilane solution has a significant effect on its efficacy as an adhesion promoter. Furthermore, the maximum adhesion is observed to be in the pH range close to the natural pH of the dilute silane solution. It would be interesting to extend this kind of study to other silanes as well as to various coating materials.

INTRODUCTION

The role of silanes as primers or coupling agents to promote adhesion of polymeric coatings to mineral substrates has been the subject of a number of recent investigations.[1-13] A variety of techniques have been used to study the interactions of silanes at interfaces. It has been known that the mechanical strength of adhesion of polymeric coatings on substrates is influenced by various factors: (i) substrate topography, (ii) chemical nature of substrate, adhesion promoter and polymer, (iii) method of silane deposition and subsequent treatments (e.g., baking, rinsing, etc.), (iv) curing conditions of coatings, and (v) environmental exposure (humidity, chemical treatments, etc.). For a recent detailed review, see Ref. 6. In an aqueous medium, the structural properties of γ-APS (γ-aminopropyltriethoxysilane) are known to be sensitive to the pH of the silane solution.[2,5-7,9,10,14] Recently, Boerio et al.[7,10,14] have reported the structures for γ-APS films deposited on iron and aluminum mirrors using reflection-infrared spectroscopy. They reported "bent" geometries with "upside-down" structures for γ-APS molecules that were deposited from aqueous media under very low and very high pH conditions. Such bent structures would reduce the extent of molecular interaction with the coating, and, concomitantly, one would expect a net reduction of the "practical adhesion" of the coatings. The term practical adhesion is defined as the force or work required to detach a coating from the substrate.[15,16]

Recently, adhesion of polyimide coatings to a silica surface using silanes as adhesion promoters has been studied,[4,12,13] but the effect of pH has not been reported. In this paper, we describe the use of peel strength measurements to study the effect of pH of γ-APS solution on the practical adhesion of polyimide coating to silica surface.

EXPERIMENTAL

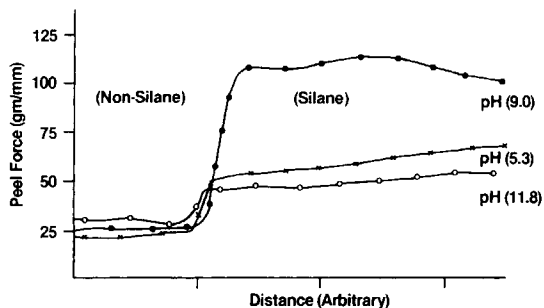The aminosilane (γ-APS of Union Carbide) was dissolved in distilled water

Fig. 1. Peel adhesion of polyimide to silica surface with and without silane (γ-APS) adhesion promoter. The nonsilane region of the wafer did not receive any treatment, whereas the silane region of the wafer was immersed in aqueous γ-APS solutions of varying pH. Typical plots obtained at pH values of 5.3, 9.0, and 11.8 are given.

(0.01% by volume). An oxidized (plasma) silicon wafer was immersed in the aqueous silane solution for four minutes. The pH of the silane solution was varied between 2 and 12 by dropwise additions of glacial acetic acid or dilute sodium hydroxide, respectively, to the freshly prepared aqueous silane solution and was measured using a digital pH meter. Dupont PMDA–ODA polyamic acid solution in NMP (N-methyl pyrrolidone) was used to coat the silica wafers. The coatings were then thermally cured up to 400°C in a nitrogen atmosphere. Typical coating thickness for fully cured films was 34 ± 2 μm. Apropos, there was some variation in polyimide thickness from the center to the edge of the wafer, but the peel results here refer to the area where thickness was uniform. Adhesion strength measurements were performed using a home-built peel tester, and the measured values refer to 90° peel at ambient conditions. The peel force of the polyimide coating is measured in grams per millimeter.

RESULTS AND DISCUSSION

In Figure 1, we present a plot showing the peel force (g/mm) of the polyimide coating to silica substrate plotted as a function of distance (arbitrary length). Prior to applying polyimide coating, a portion of the wafer (the silane region) was treated with aqueous silane (γ-APS) solution at a given pH, while the remaining area (the nonsilane region) was exposed to air only (see Fig. 1). This configuration enabled us to measure the peel force of the coating on the same substrate with and without adhesion promoter. After the polyimide coating was fully cured, the peel test measurements showed marked differences between the silane and nonsilane regions. For example, the peel force in the nonsilane region is about 20–30 g/mm. This range is due to wafer-to-wafer variations. However, in the silane-treated region, the peel force is much higher than from the nonsilane region. A sudden jump in the peel force values is noticed between the two regions. Apropos, there is some variation in peel force as a function of distance, which might be due to variation in thickness of the polyimide coating.

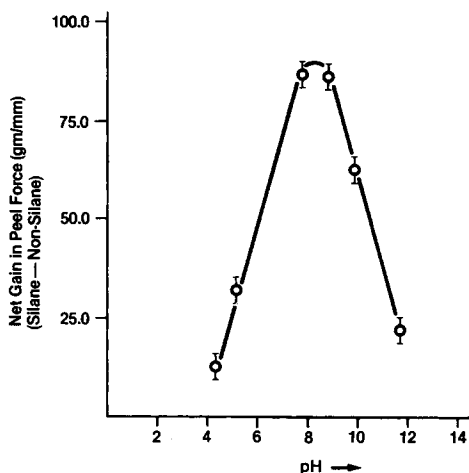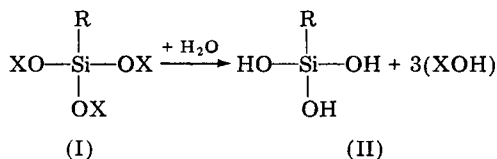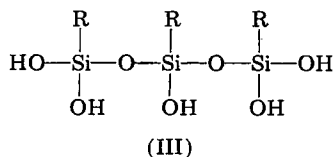In Figure 2 we show the net gain in the peel force per unit width after γ-APS

Fig. 2. The peel force difference between the silane- and non-silane-treated regions of the wafer plotted as a function of pH of γ-APS solution. The curve represents extrapolation of the data point.

treatment vs. the pH of silane solution. Net gain refers to the difference between the peel force of polyimide coating in the silane-treated and non-silane-treated areas of the wafer. It is clear that the net peel force is maximum around pH 8, and is less on either side of this range (see Fig. 2). It is interesting to note that the pH range corresponding to the maximum peel force coincides with the natural pH of the dilute γ-APS solution. The natural pH of γ-APS dilute (0.01%) aqueous solution is 8.0, but it may vary with concentration of silane. In order to explain the observed peel force variation with pH of γ-APS, let us briefly examine the interaction of γ-APS with both the substrate and the coating.

It is generally agreed[1] that in aqueous medium, γ-APS (structure I) undergoes rapid hydrolysis and produces reactive silanol groups (structure II) as given below:
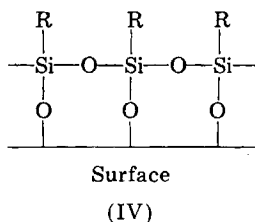
$$\underset{\text{(I)}}{XO\!\!-\!\!\underset{\underset{OX}{|}}{\overset{\overset{R}{|}}{Si}}\!\!-\!\!OX} \xrightarrow{+\,H_2O} \underset{\text{(II)}}{HO\!\!-\!\!\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{Si}}\!\!-\!\!OH} + 3(XOH)$$

In these structures, the R group is $-(CH_2)_3NH_2$ and the X group is C_2H_5. These reactive silanols can rapidly condense among themselves with concomitant loss of water and produce siloxane linkages as given in structure III:

$$\underset{\text{(III)}}{HO\!\!-\!\!\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{Si}}\!\!-\!\!O\!\!-\!\!\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{Si}}\!\!-\!\!O\!\!-\!\!\underset{\underset{OH}{|}}{\overset{\overset{R}{|}}{Si}}\!\!-\!\!OH}$$

Note that the rate of hydrolysis and condensation will depend on the concentration and pH of the silane solution.[6]

Following hydrolysis, the reactive silanols of structure III can further condense with other silanols available at the silica surface (of the substrate).   Finally, after drying or curing covalent linkages are formed with the surface silanols such as those given in structure IV[1]:

$$\begin{array}{ccccc} R & & R & & R \\ | & & | & & | \\ -Si-O-Si-O-Si- \\ | & & | & & | \\ O & & O & & O \\ | & & | & & | \end{array}$$

Surface

(IV)

When overcoated with polyamic acid, the amino groups available from structure IV (through the side group R) would condense with an acid end group of the polyamic acid to produce an imide linkage after thermal curing (structure V).

(V)
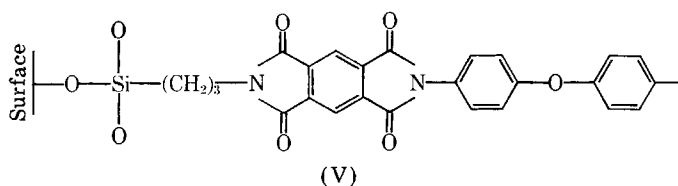
It is structure V[13,17] which is formed in the process and is necessary for achieving adhesion strength.   For acidic or basic media, Boerio et al.[10] have reported structural variations of the γ-APS molecule.   If the pH conditions are such that the free-NH_2 groups (from R) are unavailable, the formation of structure V might be hindered.   That is, under a low pH condition, γ-APS forms a cyclic internal zwitterion (structure VI), and, at high pH, it exhibits a bent geometry with a possible bonding to the surface through both the amino and silanol groups (structure VII).   Here, high and low pH conditions are relative to the isoelectric point (IEP) of the surface.

Surface   Surface

(VI)   (VII)
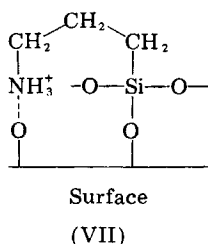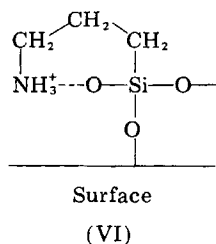
These structures (VI and VII) are more probable on iron and aluminum surfaces since their IEP values are 8.5 and 9.4, respectively, which are much higher than the corresponding IEP value (2.2) of the present silica surface.[18]   In the case of a silica surface, as the IEP value is very low, one would expect the same structure of γ-APS at all pH values greater than 2.2   That is, structure VII might be present for the pH range studied here.   So we are unable to explain the maximum peel force around pH 8 directly in terms of the effect of pH on silane structure alone.   As an alternate possible explanation for the results obtained,

one could propose that the ionic species (viz., sodium, acetate, etc.) present in the acidic or basic additives could influence the formation of chemical bonds at the interface. That is, the additive ions in the γ-APS solution can possibly affect the siloxane as well as imide linkages. However, under natural pH (or without additives), the formation of a stable structure V is more probable, and should result in improved adhesion (cf. above).

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