

Effect of Polyimide Thickness on Its Adhesion to Silicon Nitride Substrate with and without Adhesion Promoter

INTRODUCTION

The adhesion of polyimide (PI) to a variety of mineral substrates is of crucial importance as polyimide has found applications in the microelectronics industry¹ because of its low dielectric constant and high thermal stability. Adhesion enhancement of PI coatings using adhesion promoters has been the subject of few recent investigations.²⁻⁵ Earlier, we had reported⁴ on the effect of pH of γ -aminopropyltriethoxysilane (γ -APS) solution on the adhesion of PI coating, and here we discuss the effect of PI coating thickness on its adhesion to silicon nitride (Si_3N_4) surface with and without γ -APS as the adhesion promoter.

It should be pointed out that the word "adhesion" here signifies "practical" adhesion which is defined as the force or the work required to remove a coating from the substrate.⁶ Apropos, it is interesting to mention that, as far as the interfacial adhesion is concerned, that should not be affected by the thickness of the coating as the interfacial interactions act over very short distances vis-a-vis thicknesses normally used. So it becomes imperative here to distinguish between the practical adhesion and interfacial adhesion. In our study, we have used silicon nitride as the substrate and the practical adhesion was measured in terms of peel strength.

Earlier, Croll had reported on the effect of polymer coating thickness on its practical adhesion (peel strength); but no adhesion promoter was used, and also he did not study polyimide as the overcoat.⁷ Croll found that the practical adhesion of epoxy coatings decreased with increasing thickness and at a certain critical thickness (t), the energy due to internal strains became greater than or equal to the interfacial strength and thus culminated in a spontaneous peeling of the coating. This behavior was explained in terms of increasing internal stress with increasing thickness. The genesis of internal stress has been argued in terms of solvent loss with the concomitant shrinkage of the coating during drying. Recently, some stress measurements on polyimide coatings as a function of temperature have been reported, but no attempt was made to correlate the stress level with the peel strength.⁸

EXPERIMENTAL

The PI coating material used in this study was DuPont PMDA-ODA polyamic acid in NMP (*N*-methyl pyrrolidone) and γ -APS was obtained from Union Carbide as A1100 silane. Polymer coatings were applied on precleaned (Argon plasma) Si_3N_4 wafers. It should be mentioned here that the ESCA⁹ results show the presence of oxygen on this surface; in other words, it is really silicon oxynitride. The following procedure was used to apply the PI coatings:

(i) A portion of the wafer was immersed 2 min in a 0.01% γ -APS solution in distilled water, and, subsequently, dried at room temperature under nitrogen atmosphere.

(ii) The wafer was then fully dipped in a polyamic acid solution in NMP and cured in successive steps as follows: 85°C for 10 min, 150°C for 30 min, 200°C for 30 min, 300°C for 30 min, and 400°C for 30 min under dry nitrogen atmosphere.

Multiple coatings were applied to attain the desired thickness, as single coat under these conditions gave only $\sim 10\text{-}\mu\text{m}$ -thick coating. The coating was scribed at 1/16 in. separations all the way to the wafer and the coating thickness was measured using Alpha Step equipment at various places. The peel strength measurements at 90° were carried out using a home-built peel tester; the peel test configuration is shown in Figure 1. As the adhesion in the nonsilane region is relatively poor, so the peel could be initiated in this region.

RESULTS AND DISCUSSION

Figure 2 illustrates the peel test data obtained on polyimide coatings deposited on silicon nitride wafers with and without the adhesion promoter. Since lower half of the Si_3N_4 wafer

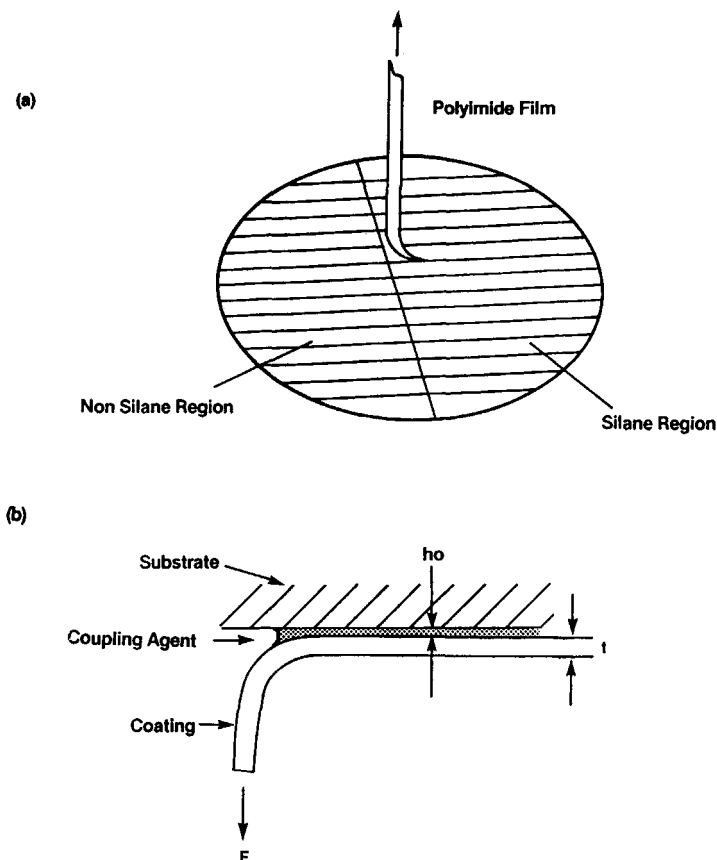


Fig. 1. (a) Peeling of polyimide coatings from the wafer. The coating was scribed at 1/16 in. separations. The nonsilane and silane regions are indicated. (b) Peel test configuration showing the substrate, coupling agent, and the coating materials.

was first treated with 0.01% γ -APS solution, the present peel test configuration first measured the adhesion in the nonsilane region followed by measurement in the silane region. Figure 2 illustrates the peel test plots for three wafers with coating thicknesses 10, 28, and 50 μm . It is clear from the results that this silane promotes adhesion of polyimide to silicon nitride at all thicknesses, but the peel strength is much greater at 50 μm thickness than at 10 and 28 μm thicknesses. The interaction of silane with silicon nitride is not well understood. However, as we pointed out earlier that ESCA showed the presence of oxygen, so the silanol groups (after hydrolysis of A1100) could react on this surface as on SiO_2 surface,⁴ or there may be a new interaction because of the presence of nitrogen. In any case, more detailed study is needed to understand the interactions involved. As for the interaction of polyamic acid (precursor to polyimide) with A100, this has been discussed by the authors⁴ and by others.⁵

In Figure 3, the peel test data for the nonsilane region are plotted as a function of the coating thickness. Although it appears that the peel force is maximum at $\sim 15 \mu\text{m}$, but considering the accuracy of peel data, it may not be a real effect. So we are inclined to believe that the peel force decreases linearly with thickness, an observation akin to that made by Croll for other polymer coatings.⁷ For the present PI coatings, the extrapolated thickness for spontaneous peeling is around 65 μm . In the same figure, we also present the peel force data in the silane region. It is interesting to note that the peel force rises gradually with increasing thickness of the polyimide coating when the coupling agent is present, which is a completely different behavior from that observed in the nonsilane region of the wafer.

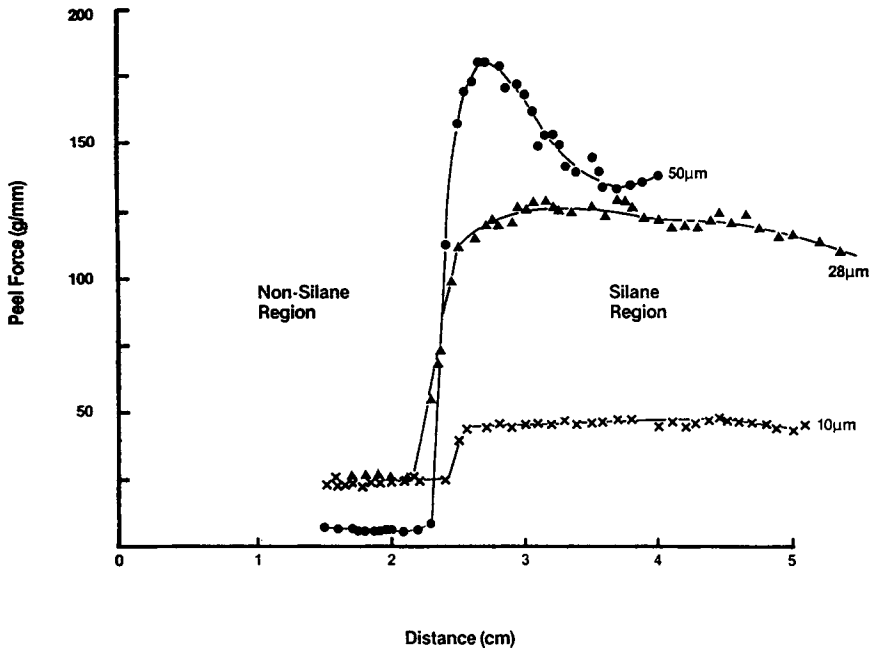


Fig. 2. Peel force (g/mm) vs. distance (cm) for polyimide coatings to silicon nitride wafer. The peel force variations with thicknesses are presented for both nonsilane and silane regions of the wafer.

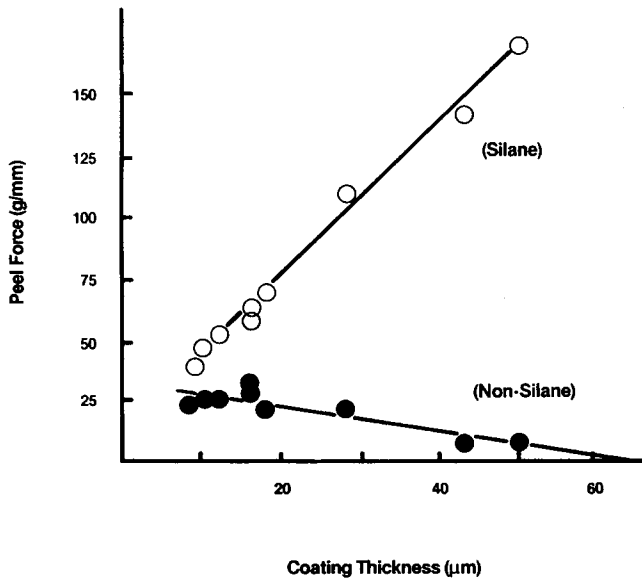


Fig. 3. Peel force (g/mm) vs. thickness of the polyimide coating for the nonsilane and silane regions.

Before discussing the results, it should be added here that there are three different terms that contribute to peel force: (i) interfacial work of adhesion, (ii) stresses created in the PI coating, and (iii) presence of silane coupling agent.

For the nonsilane region, only the first two terms [cases (i) and (ii) are applicable] and the peel force variation with thickness (t) can be explained using Kendall's energy balance expression¹⁰:

$$F/w = \Gamma - tE\epsilon^2/2 \quad (t > 0) \quad (1)$$

where Γ = interfacial work of adhesion, E = Young's modulus of the coating, ϵ = shrinkage strain, w = width of the coating, and, t = thickness of the coating.

According to this expression, the peel force decreases linearly with increasing thickness of the coating. The peel force would be expected to be zero at a particular coating thickness when

$$\Gamma = tE\epsilon^2/2 \quad (2)$$

It would be interesting to calculate the critical thickness value, but it is not possible as the values for the requisite parameters are not available. However, from the results in Figure 3 the critical thickness appears to be around 65 μm .

For the silane (γ -APS) treated region, the effect of coating thickness on the peel force is complex, and eq. (1) has to be modified possibly with the addition of a third term. Following the approach given by Bikerman,¹¹ for the adhesively bonded joints, the extension of the coupling agent by the applied force (F_m) at which rupture starts (due to yield of the coupling agent) in the peel test is given by

$$F_m/w = Ct^3 h_0^3 \quad (3)$$

$$C = 0.3799\sigma_m(E/E_1)^3 \quad (4)$$

where h_0 , σ_m and E_1 represent the thickness, tensile strength, and Young's modulus of the coupling agent. Equation (3) represents the peel force variation of the PI coating in the presence of adhesion promoter. According to this, the peel force is expected to vary as t^3 . This is close to a linear rise in thickness, as is found in our experiment (see Fig. 3). We should add here that the exact thickness of the silane layer used in this study is not known, but we believe it must be very thin as the concentration used (0.01%) was very low. In any case, a detailed study of the effect of silane layer thickness (concentration of silane solution) on the adhesion of polyimide (as a function of thickness) is in order.

SUMMARY

We have shown that the effect of polyimide thickness on its adhesion depends on whether or not the adhesion promoter is used. Without the adhesion promoter, the adhesion decreases with increasing thickness and this is explained in terms of increasing internal stresses. However, in the presence of adhesion promoter, the behavior is dramatically different, i.e., the practical adhesion increases with increasing thickness of the coatings.

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Received March 20, 1984

Accepted November 16, 1984