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Humidity effect on polyimide film adhesion

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A 90° peel tester with substrate heating capability has been built to evaluate the adhesion strength of polyimide film to silicon substrate. The peel strength of polyimide film is not only a function of film thickness or peeling rate, but also a function of ambient humidity. A mechanism is proposed. The peel strength decreases with increasing relative humidity due to the hydrolysis of polyimide, reaches a minimum, and then increases with increasing relative humidity due to the hydrogen bonding at the weak boundary layer. In a high-humidity environment, peel crack tips are attacked by moisture and result in weak adhesion measurement. Water adsorbed by polyimide film near the crack tip and diffused into the peel crack tip is the main mode of moisture attack. The peel behaviour of polyimide film at the elevated temperature is almost the same as peeling at room temperature in a low-humidity environment.

1. Introduction

Polyimides are known to be an important class of high-temperature polymers with good dielectric properties for application in the fabrication of high-density multilayer chip packages [1–3]. Successful use of polyimide as an insulating layer requires that the fully cured polyimide films maintain interface integrity with various organic, inorganic and metal surfaces under process conditions. The adhesion depends on the chemistry and physics of the interface, and also on the stress in the film and substrate [4]. Adhesion plays a very important role in building up multiple layer structures. Poor adhesion of polyimide at the interface induces moisture penetration and a loss in its passivation function. It is, therefore, of utmost importance to understand factors that contribute to the initial adhesion, and thus adhesion degradation, and take appropriate steps to improve the interface reliability.

The polyimides most often used in industry are those derived from the polyamic acid precursors. These polyimide precursors are similar as far as their reactive groups are concerned. The reactive groups R and R′ affect the acid strength of the amic acid moiety, which, in turn, affects the reactivity with the substrate surface and the resulting adhesion. The imidization reaction in all cases is the same, involving the loss of water with the closing of the imiding ring, as shown in Fig. 1 [5].

Humidity stability of adhesion is an important requirement in microelectronics applications. The thermodynamics of a polymer–inorganic interface system suggests that if only secondary forces are acting across the interface, water will desorb the polymer film from the inorganic surface, as described by Kinloch *et al.* [6]. Therefore, water must be prevented from reaching the interface in concentrations high enough to displace the polymeric film, or primary bonding must be established at the interface to resist the water. Gledhill *et al.* [7] propose that there is a critical water concentration in the polymer layer below which weakening of the adhesion does not occur. This critical water concentration has also been suggested in a more recent work [8], where a relative humidity of about 25% appears to be the point above which substantial degradation of the adhesion occurs. The water permeation through polyimide was also investigated by Sacher and Susko [9]. The concentration of absorbed water was found to depend on the relative humidity and not on the temperature or sample thickness, reaching a maximum of one water molecule per repeat unit at 100% RH.

In this study, the peel adhesion test was chosen as the adhesion measurement standard because of its reproducibility and reliability. The peel force, which represents the work needed to peel off a film from a substrate, is influenced by mechanical factors, i.e. film and substrate properties such as film thickness, yield strength, Poisson ratio, and stiffness, as well as the fundamental adhesion between the film and substrate. Peeling adhesion of polyimide film has been evaluated extensively, (e.g. [10–12]). However, peeling of polyimide in different humidity environments has not been reported. The effects of relative humidity on the peeling test have been investigated extensively in this study.

2. Experimental procedure

Silicon wafers with ⟨100⟩ orientation were prepared as follows. First, they were cleaned by solvent treatment: dipped in a ultrasonic bath with trichloroethylene, acetone, and methanol for 10 min, respectively.

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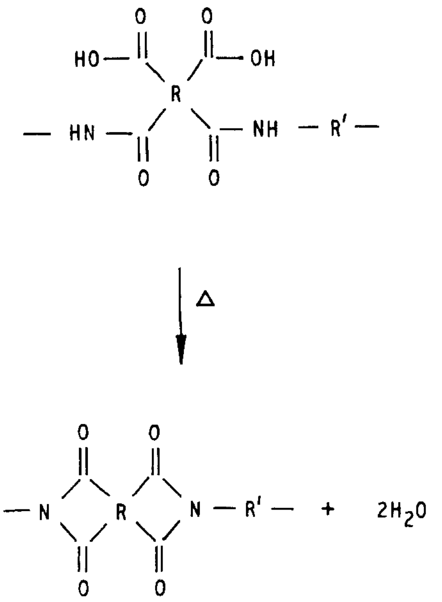

Figure 1 Polyamic acid (PAA) thermal imidization.

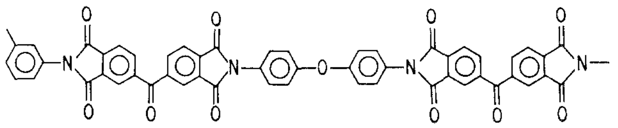

Figure 2 Molecular structure of polyimide BTDA/ODA/MPD (Dupont PI-2555) upon imidization.

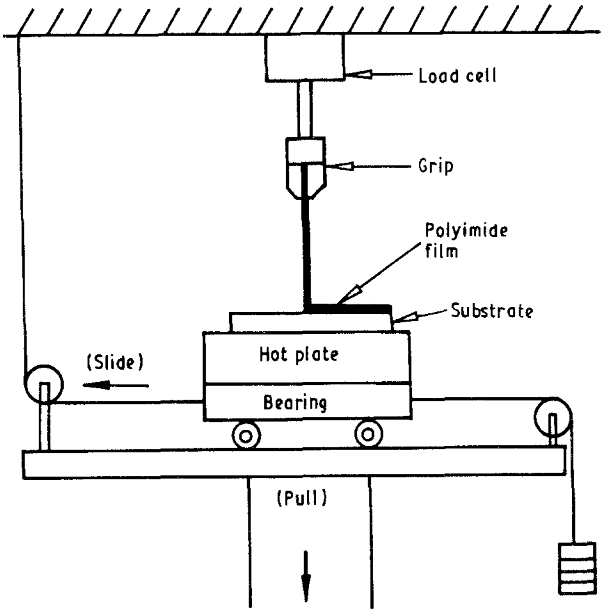

Figure 3 Schematic diagram of a 90° peeling apparatus with heating and self-aligning capabilities.

Then the wafers were immersed in a 10% hydrofluoric acid solution for 5 min, followed by a deionized water rinse to remove native oxide layers. Finally, they were dried by prepurified nitrogen and immediately spin coated. Polyamic acid of benzophenone tetracarboxylic di-anhydride/4,4-Oxydianiline/*m*-phenylene diamine was used (Dupont Pyralin PI-2555). The molecular structures of the polyimide (BTDA/ODA/MPD) are shown in Fig. 2. Polyimide precursor with 16% solid content in N-methyl-pyrollidone (NMP) were spin-coated on cleaned silicon wafers at 2500 r.p.m. and baked for 30 min at 80 °C in an oven to remove NMP solvent. Multiple coatings were applied to obtain the desired thickness with a 20 min bake at 80 °C between each coat. The final curing procedure was conducted at 130 °C for 30 min, 200 °C for 30 min, 300 °C for 30 min, and 400 °C for 45 min on a hot plate. The peel strengths of the polyimide films were measured on a self-designed peel tester. The tester was constructed using a special design apparatus with substrate heating capability (shown as Fig. 3) to maintain a 90° peel angle during peeling of the entire film. The peel force is measured by using a 1 kg load cell with 0.1 g resolution and the measured force is transmitted to a personal computer for data processing. After the polyimide films were fully cured, they were cut into 3 mm wide peel strips using a sharp scalpel. The peel initiation ends were wrapped in a Scotch-tape for ease of handling in a peel tester. The peel strengths were measured by averaging at least five 3 mm wide strips of polyimide films. The relative humidity was measured using a Vaisala relative humidity meter with 2% RH accuracy and 0.1% RH resolution. The relative humidity in the laboratory during testing was in the range 50%–60%, and the temperature was in the range 20–24 °C. The lowest relative humidity condition of 7% RH was controlled by flushing the enclosed peel tester with dry nitrogen. The highest humidity condition of 93% RH was controlled by passing dry nitrogen over a water reservoir. All the samples were stored in a vacuum desiccator before peel analysis to prevent moisture absorption by the polyimide films. The locus of failure was characterized using scanning electron microscopy (SEM) on both peeled polyimide and substrate peeled surfaces.

3. Results and discussion

The peel strength of a 14.3 µm thick polyimide film as a function of relative humidity is shown in Fig. 4 with 0.5 mm min^{-1} peeling rate. From this figure, a minimum peel strength is seen to exist at about 55% RH and a high peel strength both in very high and low humidity conditions, and no plateau was found in this relation either under low or high humidity conditions. Fig. 5 shows the same relationship as in Fig. 4, but with testing procedures from high humidity to low humidity and reverse humidity conditions. These results show that the peel strength varies with humidity and this phenomenon is reproducible and independent of the testing procedures. The bonding of polyimide film and substrate may occur by two different mechanisms at high and low humidity ambient. The peel strength at various ambient humidities as a function of peeling rate is shown in Fig. 6. A linear relationship between peel strength and peeling rate on a logarithm scale are found in low-humidity conditions of 30% RH. The same results were also reported by Oh *et al.* [13]. With increasing ambient humidity, the peel strength decreases at the peeling rate of 5 mm min^{-1}. However, when the humidity is above 60% RH, in the lower peeling rate conditions, the peel

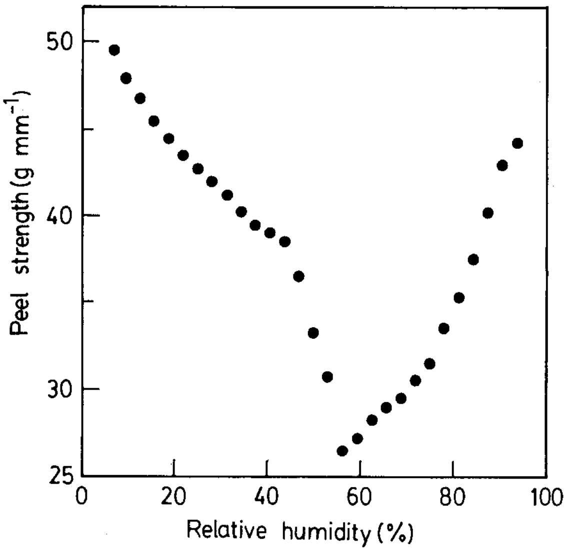

Figure 4 Peel strength of 14.3 μm thick polyimide film with a peeling rate of 0.5 mm min^{-1} as a function of relative humidity.

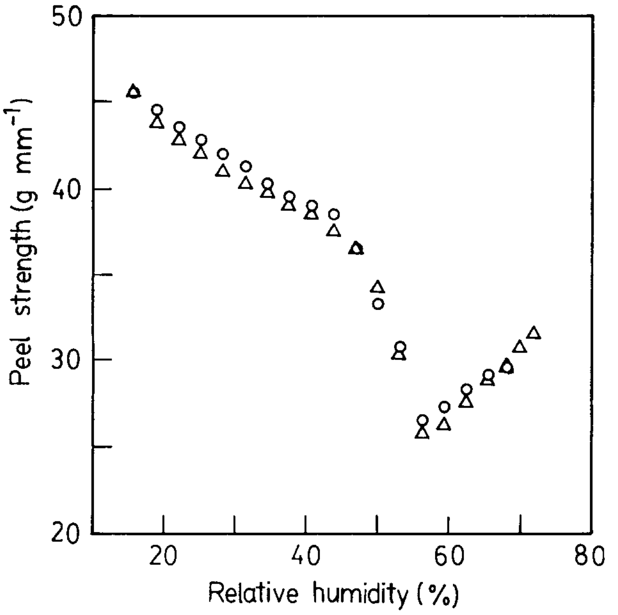

Figure 5 Peel strength of 14.3 μm thick polyimide film with a peeling rate of 0.5 mm min^{-1} as a function of relative humidity. (○) Transition from high to low humidity, (△) transition from low to high humidity.

strength increases with increasing ambient humidity. Figs 4 and 5 show the consistency of the results with a peeling rate of 0.5 mm min^{-1}.

An hypothesis is proposed to explain this interesting phenomenon. Because covalent bond formation and breaking are not easily reversible, the phenomenon shown in Fig. 5 is unlikely to be induced by any covalent bond between the polyimide and substrate. Water is adsorbed on non-hydroscopic oxides as hydroxyl groups M–OH (M = substrate) and as molecular water held by hydrogen bonding to the surface hydroxyls [14]. Extensive studies of the adsorption of water on amorphous silica were made by Hair [15] by means of infrared spectroscopy. These spectral developments correspond to the formation of more isolated surface silanols and silanols close enough to hydrogen bond. Water adsorption on other non-hydroscopic

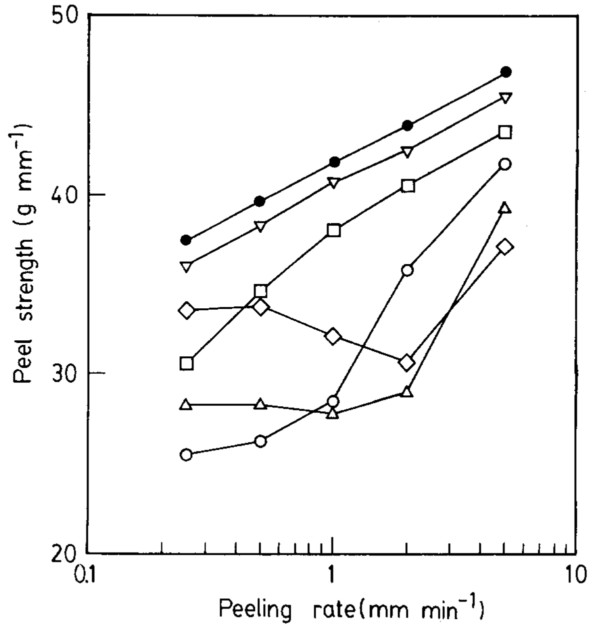

Figure 6 Peel strength of 14.3 μm thick polyimide film under various relative humidity conditions as a function of peeling rate at 23 °C. RH: (●) 30%, (▽) 40%, (□) 51%, (○) 60%, (△) 70%, (◇) 82%.

oxides is at least qualitatively similar, i.e. there are surface hydroxyls that sometimes interact with each other and are sites for molecular water adsorption. At least a monolayer of water is present on the substrate during the preparation of a spin-coating polyimide specimen. Even if a sample was prepared with a perfectly dry surface, water could penetrate to the interface by diffusion through the polymer. Once water molecules cluster at a polyimide interface, they are capable of hydrolysing any physical bond that can conceivably be formed between polyimide and silicon or silicon oxides. Direct grafting of monomers to the substrate during polymerization has been reported [16]. Although such a process can produce intimate contact between polymer and substrate, the ultimate M–O–C bond is readily hydrolysed and cannot resist water penetration. Hence, the less moisture affecting the interface, the higher will be the bonding strength between polyimide and substrate. The phenomenon of higher peel strength at higher humidity could be explained by the following proposals. The adhesion strength of the weak boundary layer is widely accepted as shown in Fig. 7. From the work of Buchwalter and Greenblatt [10], the locus of failure in peeling of PMDA/ODA polyimide from an SiO_2 substrate was in the polyimide. In this case, as determined by Auger electron spectroscopy (AES), the failure locus was about 2 nm into the polyimide film. Similar behaviour in the locus of failure is also seen in polystyrene (PS) on S-glass without amino–propyltriethoxy–silane (APS) adhesion promoter [17].

In BTDA/ODA/MPD polyimide, there are more carbonyl (>C=O) groups than PMDA/ODA series polyimides. The carbonyl groups could form hydrogen bonds with water to bridge the weak boundary layers, as shown in Fig. 8. When the water content reached a certain critical value, the hydrogen bonding

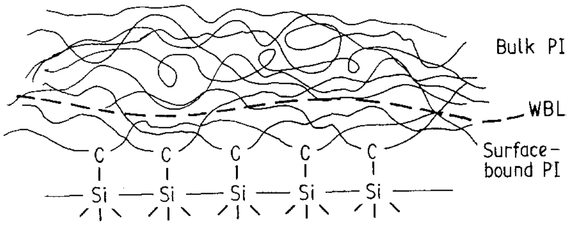

Figure 7 Schematic representation of locus of failure in polyimide on a silicon substrate by a weak boundary layer.

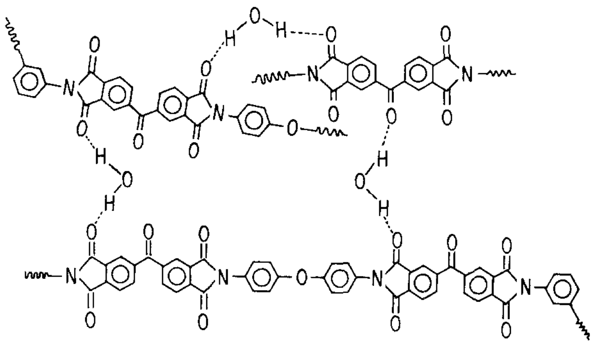

Figure 8 Schematic representation of hydrogen bonding induced by water at a weak boundary layer in polyimide.

could act as the main force in a weak boundary layer. Hence, a sufficient water content could produce a higher adhesion strength in high relative humidity ambient. The formation of a weak boundary layer was suggested by Buchwalter [18], in the case of polyamic acid coated on to the non-APS-treated substrate, the polymer has occasion to orient during the spin application process as well as during the cure schedule, at least through the 130 °C bake. Therefore, it is likely that the individual polymer chains are oriented parallel to the substrate surface and will still continue to order and pack during the imidization process. This ordering process may create a weak boundary between the oriented, surface-bound polyimide chains and the bulk polyimide. The peel strength shown in Fig. 4 could be considered to be a compromise between hydrolysis and a hydrogen bonding mechanism.

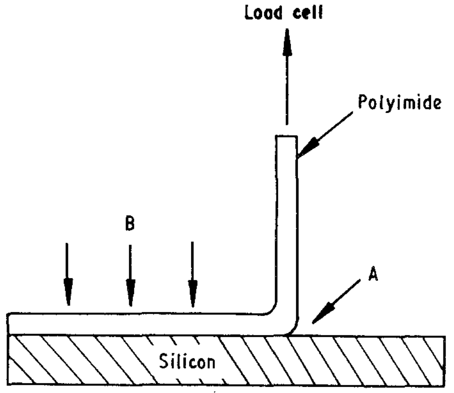

Figure 9 Schematic peel strip diagram. A, water ingress at the crack tip; B, water ingress through the film.

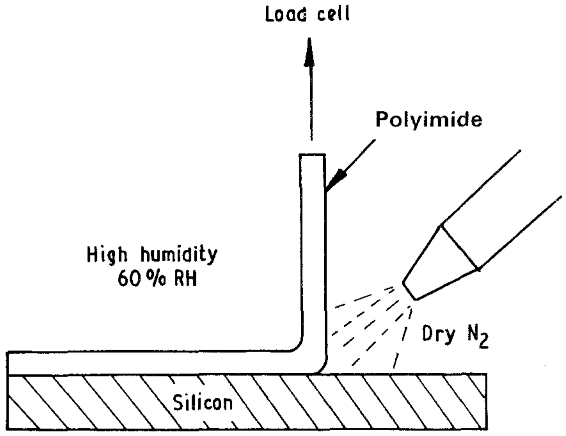

Figure 10 Schematic drawing of a local dry atmosphere at the peel crack tip.

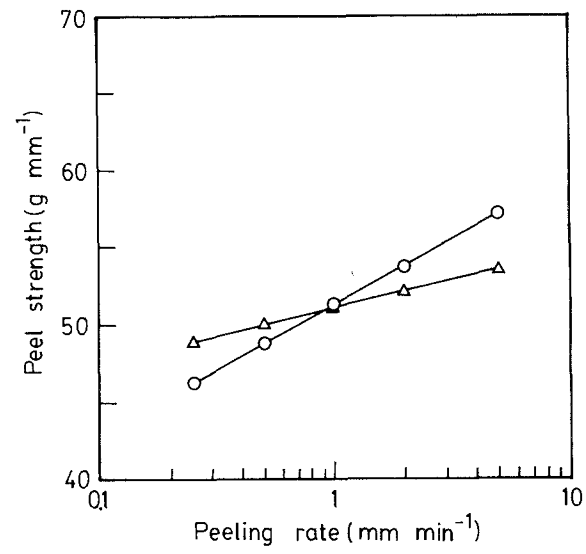

Figure 11 Peel strength of a 14.3 μm thick polyimide as a function of peeling rate in (○) a low relative humidity of 12.5% RH ambient and (△) a local dry atmosphere at the peel crack tip.

Because the data show a dramatic dependence of the peel strength on the ambient humidity, it would be interesting to know how the moisture attacks the specimen. There are three modes of moisture attack according to Buchwalter and Lacombe [8]. The most likely way is direct moisture attack at the peel crack tip or coming from the top of an unpeeled film. Fig. 9 shows a schematic diagram of a peel strip under steady state conditions. To distinguish between these two modes, a local dry atmosphere was constructed by blowing dry nitrogen at the peel crack tip as shown in Fig. 10. The relative humidity of the local area is about 8% RH. The flow rate of dry nitrogen is controlled at 0.25 standard cm h^{-1}, so the peel strength could not be affected by this small flow of nitrogen. The peel data of a localized dry atmosphere and an entirely low-humidity ambient of 12.5% RH are shown in Fig. 11. The results show that there is almost no difference between a localized dry atmosphere and an entire low humidity. This revealed that the most important path of moisture attack on the specimen was directly at the peel crack tip, because the concentration of absorbed water was found to depend on the relative humidity only. It is well known that polyimides, once exposed to water, take up between 2% and 5% by weight of moisture. Even when polyimide absorbed water to its saturation content, the amount of water diffused to interface was still very small. Mittal and Lussow [19] have shown that in the case of photoresist adhesion to SiO_2, the diffusion coefficient of a basic solution at the interface is about 8×10^{-6} $cm^2 s^{-1}$ depending on the interface adhesion, while the average diffusion coefficient through the photoresist film would be less than 1×10^{-9} $cm^2 s^{-1}$. However, for most polyimides, the diffusion coefficient near room temperature falls in the range 2×10^{-9}–7×10^{-9} $cm^2 s^{-1}$ [20]. The water diffusion behaviour at the interface between polyimide and substrate has not been reported. However, the data reported for a photoresist can be used as a reference. Therefore, surface adsorption of moisture at the crack tip dominates the humidity effect. The effect of absorbed moisture in the polyimide on adhesion strength, i.e. path B as shown in Fig. 9, is small.

The variation of peel strength with temperature in a laboratory ambient was reported by Hu and Chen [21], and shown in Fig. 12. In the discussion above, the moisture adsorption played an important role in the peeling test. Similarly, an experiment of peeling at elevated temperature in a low-humidity ambient of 12.5% RH was conducted. Fig. 13 shows the peel strength of a 14.3 μm polyimide film as a function of temperature at low-humidity ambient with a peeling rate of 0.5 mm min^{-1}. The results show that there is no apparent difference in peel strength from 30–70 °C. Fig. 14 shows peel strength at 22 and 80 °C as a function of peeling rate in a low humidity of 12.5% RH. The results show that the peeling behaviour is similar at both temperatures. Therefore, the peeling behaviour is almost the same between peeling at

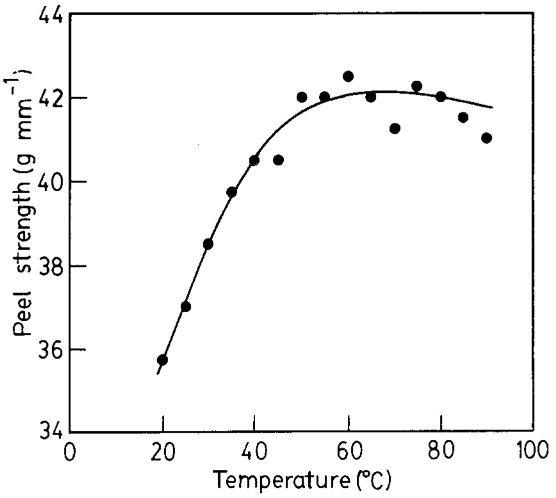

Figure 12 Peel strength of a 12.8 μm thick polyimide film as a function of substrate temperature. Peeling rate 0.5 mm min^{-1}.

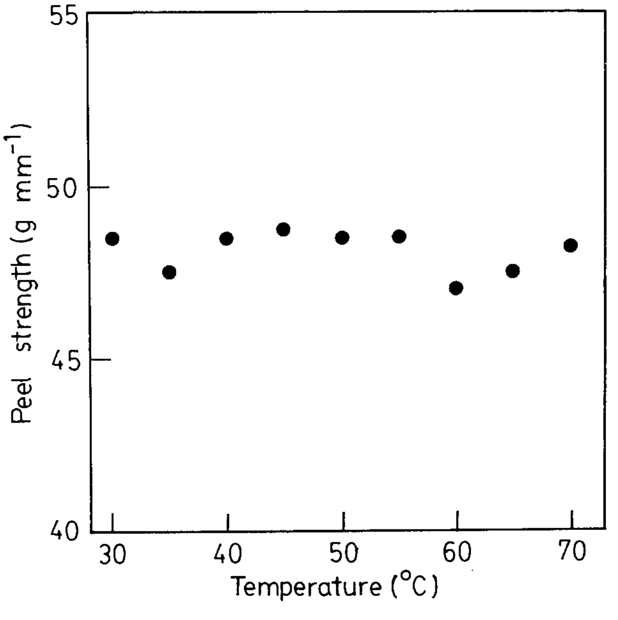

Figure 13 Peel strength of a 14.3 μm thick polyimide film with a peeling rate of 0.5 mm min^{-1} in an ambient of 12.5% RH as a function of substrate temperature.

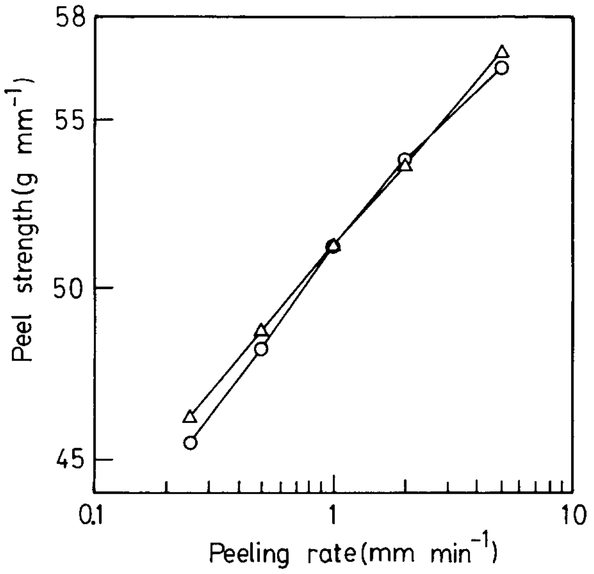

Figure 14 Peel strength of a 14.3 μm thick polyimide film as a function of peeling rate in a low humidity of 12.5 % RH at (○) 80 and (△) 22 °C.

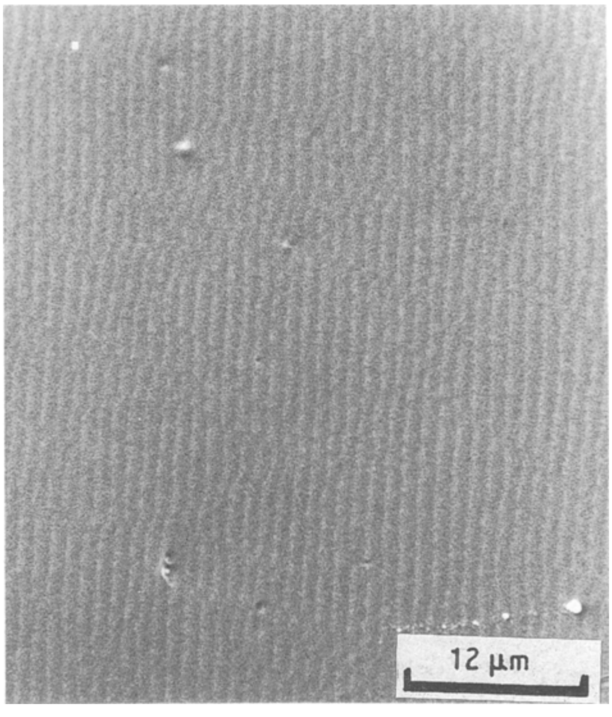

Figure 15 Scanning electron micrograph of the peeled polyimide film surface of a 23.3 μm thick film peeled in a low humidity of 15% RH.

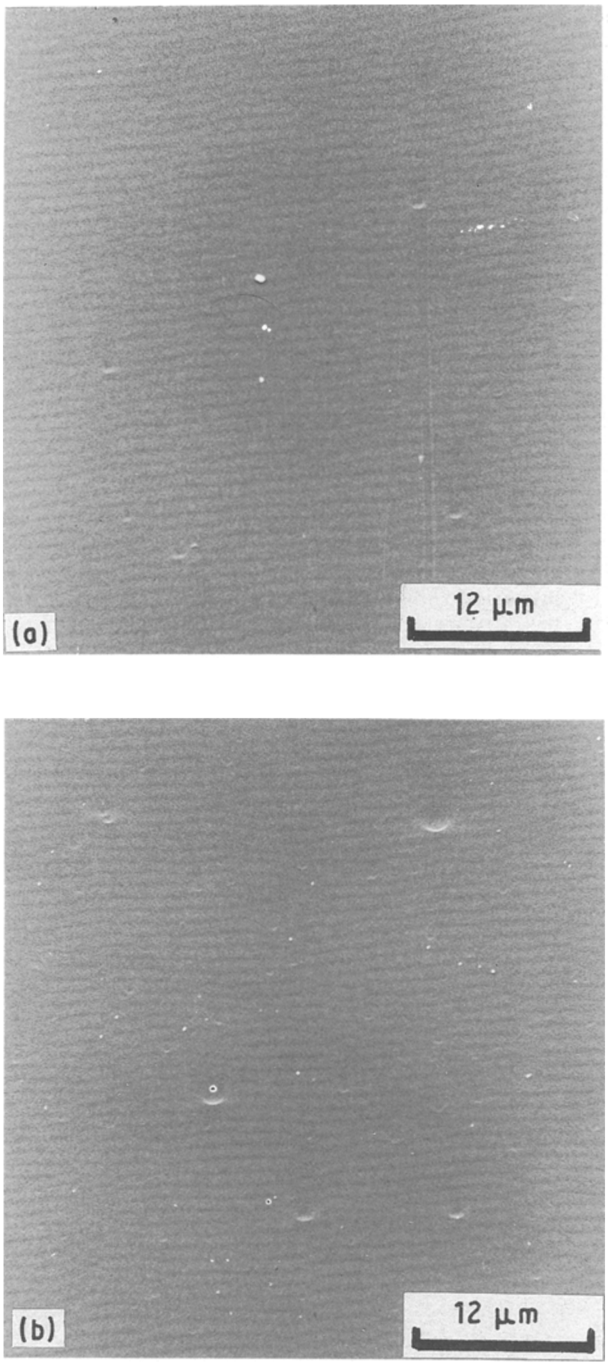

Figure 16 Scanning electron micrographs of the peeled 14.3 µm thick polyimide film with (a) a local dry atmosphere at the peel crack tip, and (b) on peeling at 80 °C in a 12.5% RH ambient.

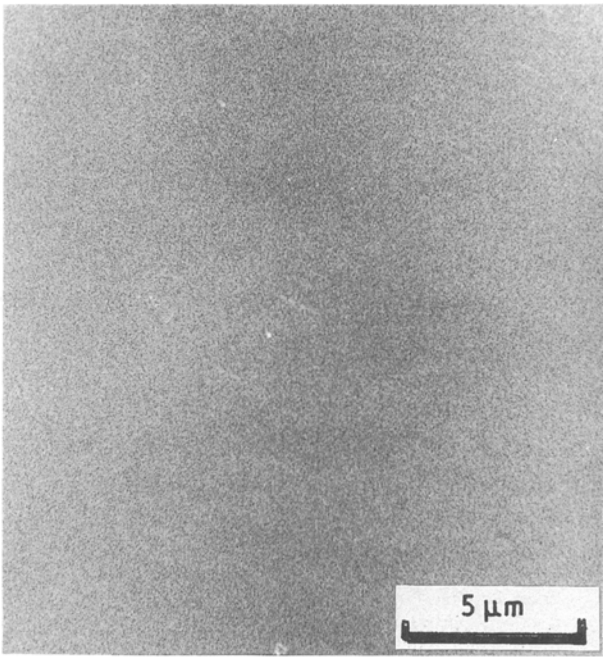

Figure 17 Scanning electron micrograph of the peeled 13 µm thick polyimide film in an ambient of 50%–60% RH at a peeling rate of 5 mm min^{-1}.

elevated temperature and at room temperature when testing is carried out in a low-humidity ambient.

Scanning electron micrographs of the failure surface of peeled polyimide films (Fig. 15) illustrate that, with strong adhesion during peeling in a low-humidity environment, the peel crack propagates with a discontinuous stick–slip process. Peel crack propagation is a moment-controlled process with a stress concentration at the peel crack tip. Thus, during the peel test, the peel force increases as the radius of curvature of the peel strip at the peeling edge decreases, until the stored strain energy exceeds the fracture resistance of the weakest bond at or near the interface [22, 23]. During this stage, the peeling rate is less than the imposed machine rate, owing to the progressive bending of the peeled strip. Fig. 16 shows the peeled surfaces of the local dry atmosphere at the peel front and low humidity at an elevated temperature. The average striation spacing of the polyimide is about 1.0–1.2 µm. With a low interfacial adhesion strength, as shown in Fig. 17 for a high-humidity peeling system, bond breaking before the development of local plastic hinges leads to rather continuous peel propagation without the formation of striations.

4. Conclusion

The peeling of polyimide film from silicon with a native oxide surface has been evaluated by a 90° peel tester. The measured peel force is consistent and reproducible. The peel force at high humidity, low humidity, and elevated temperature with varying peeling rate have been explored and measured.

In a high-humidity environment, crack tips are attacked by moisture and result in weak adhesion measurement. The moisture effect could be reduced by peeling in an enclosed environment with low humidity. When peeling occurs in a moderate humidity environment, the peel strength was reduced, caused by moisture increase with decreasing peeling rate. The peel strength is not only a function of film thickness or peeling rate, but also a function of ambient humidity: it decreased with increasing relative humidity, reached a minimum at about 55% RH, then increased with increasing relative humidity. No plateau was found in the relation of peel strength versus relative humidity, either under low- or high-humidity conditions. Moisture adsorption on a polyimide film near the crack tip and diffusion into the crack tip is the most important mode of moisture attack. Even on peeling at elevated temperature, the moisture mostly dominates the entire peeling behaviour.

after peeling at high temperature or low humidity. For a low interface adhesion strength, such as peeling in a high-humidity environment, no striations were observed.

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