Atomic Force Microscopy Study of Rubbed Polyimide Films

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ABSTRACT: The surface of rubbed polyimide films was studied as a function of the film thickness and applied load using atomic force microscopy (AFM). Three dominant consequences of rubbing on the film topography were observed: scratches confined to the near surface of the film, tears that extended to the substrate, and strings of islands or droplets aligned parallel to the rubbing direction. Tears, found only in films less than 50 nm thick, varied in areal density and shape due to variations in the film thickness, rubbing load, and adhesion to the substrate. Strings of droplets aligned in the rubbing direction were seen on most samples without discernible dependence on the thickness or rubbing load. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1470–1477, 2001

Key words: polyimide; rubbing; atomic force microscopy (AFM); thin polymer films; polyimide rubbing films; load and thickness effect

INTRODUCTION

Polyimide films are widely used as alignment layers in the liquid crystal display industry. When unidirectionally rubbed with cloth, the polyimide films are capable of orienting liquid crystals into monodomains over large areas. Since the quality of the alignment of the liquid crystal determines the quality of the device, rubbed polyimide films have been the object of much interest.[1]

Much of the research on rubbed polyimide films has focused on the influence of the rubbing parameters on the alignment of molecules within the film and on changes induced at the surface of the film.[2–4] Near-edge X-ray absorption fine structure (NEXAFS), surface second-harmonic generation, and infrared absorption studies have shown that rubbing aligns the molecules on the surface in the rubbing direction.[5–8] The depth to which the orientation penetrates into the film has been found to be <6 nm, although one study found penetration as far as 60 nm.[8] The penetration and completeness of this alignment saturate at higher rubbing loads or longer rubbing distance.

In this study, atomic force microscopy (AFM) was used to investigate the surface topography of rubbed polyimide films as a function of the film thickness, applied load, and nature of the substrate in an effort to understand the mechanism of molecular alignment as affected by the rubbing process. As rubbed polyimide films thinner than ~20 nm have not previously been studied with AFM, the features observed here are of interest for direct comparison with results obtained by other methods.[8–10]

EXPERIMENTAL

The poly(amic acid) diethyl ester of biphenyltetra-carboxylic dianhydride–*p*-phenylenediamine (BPDA–
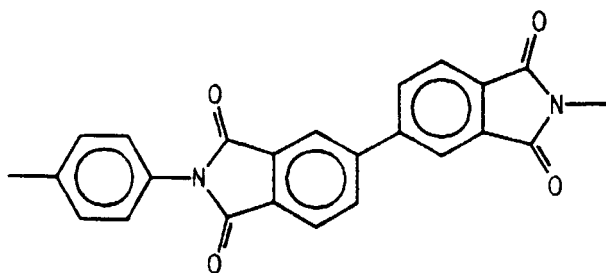
Figure 1   Sketch of the BPDA–PDA chemical repeat unit.

PDA) (Fig. 1) with a molecular weight of approximately 30,000 was deposited as films of varying thickness, spin-coated from solutions in 1-methyl-2-pyrrolidinone (NMP) onto mica, silicon, and glass substrates. Mica substrates were prepared by cleaving the top layers from a mica slide with tape, to provide a clean surface. In some cases, the mica was then heated using a heat gun to approximately 100°C to drive off water. This was done in an effort to decrease the tendency of these films to dewet the mica surface. Glass substrates were cleaned with acetone, water, and ethanol rinses. Polished single-crystal silicon substrates were prepared using a piranha etch (H_2SO_4 80%, H_2O_2 20%), followed by rinsing with water and ethanol. Film thickness was controlled by changing the solution concentration or spinning speed. These films were then imidized in an oven where the temperature was increased to 300°C at a rate of 1°C/h under flowing N_2. The samples were kept at 300°C for 1 h and then cooled to room temperature at a rate of 1°C/h. The films were then rubbed by first placing them face down on a velour cloth (Fig. 2). A known weight was applied to exert a laterally uniform load between the surface of the polyimide and the cloth. To affix the sample to the weight, the sample was affixed with double-sided tape to a small sheet of metal, 5.6 cm^2 in area. This assembly was placed face down on the velour. The mica pieces used as substrates were sufficiently thin (no more than 0.3 mm in thickness) that the pressure exerted on them was essentially the same as that over the entire metal sheet. Four different weights were then used (100, 20, 10, and 6.6 g) to effect four different loads (18, 4, 2, and 1 g/cm^2) over the surface area of the metal sheet to which the sample was attached. The cloth was pulled unidirectionally beneath the film at a rate of 30 cm/min for a distance of 30 cm.

AFM studies were performed in the tapping mode (TMAFM) using a Nanoscope IIIa (Digital Instruments). On samples with films spun onto silicon, the film thickness was measured by optical ellipsometry, where ~10% variation in the film thickness was found laterally across the film. AFM measurements of the depths of tears in the film that reached to the substrate were averaged over a single sample to give an independent measure of the thickness for those films. Films on mica substrates were used for most of these investigations because the atomically flat surface of the mica allowed any surface features to be attributed to the polyimide film alone and not to the substrate. The bare mica surfaces, as prepared for film deposition, are without steps over areas of at least (40 μm)^2. Films on silicon and glass substrates were also observed, to study the effects of possible substrate specific interactions. One sample for each set of parameters (thickness, rubbing load, substrate) was tested, and many randomly chosen sites were imaged on each sample. In total, approximately 8000–12,000 μm^2 of the surface was measured in images larger than 10 μm^2 on a side and between three and six images, each 1 μm^2 on a side, were taken on each sample.

RESULTS

The surfaces of the as-prepared BPDA–PDA films were, on average, flat with random fluctuations in height, exhibiting a mottled texture, where there is a nonuniform variation of the height of the surface. This gives the appearance of small islands or droplets randomly arranged on a randomly undulating surface (Fig. 3). Other researchers have seen similar features on different polyimide film surfaces.[11–14] This topography was found to be independent of the film thickness with
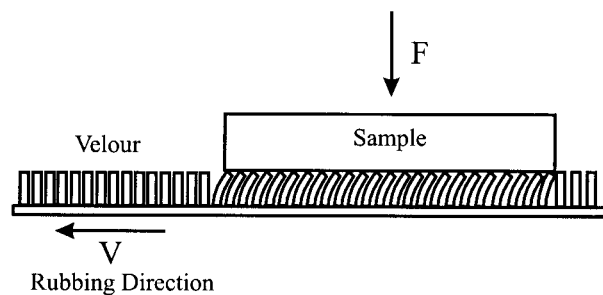

Figure 2   Diagram of the rubbing procedure. The sample is placed face down on the velour with a known force F applied. The velour is then pulled out from under the sample unidirectionally with contant velocity V.
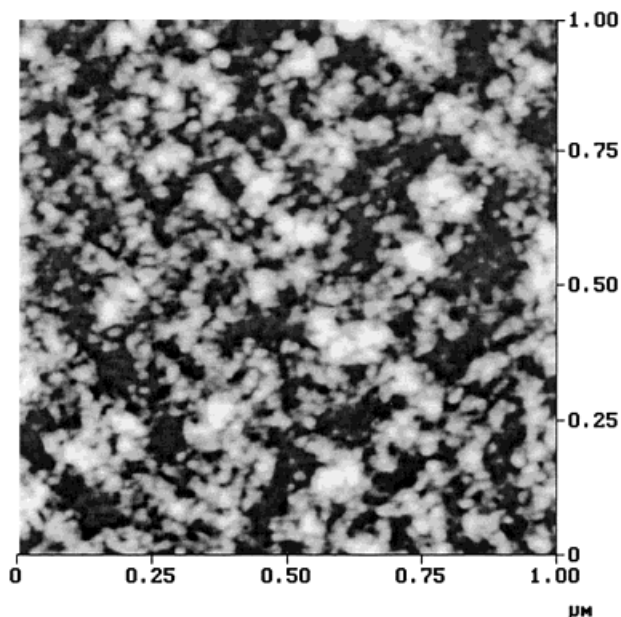
Figure 3 TMAFM image of the pristine polyimide film surface. Note the spherically appearing polyimide islands, randomly arranged, atop hills and valleys of 1–3 nm height. This image is representative of the surface films which are more than about 10 nm thick.

the exception of the very thinnest of samples, wherein the amplitude of these fluctuations becomes larger. In some cases, the films appear to dewet the mica surface with circular patches, exposing the very smooth underlying mica. Apparently, either before or during curing, the solution which dries to become the film has pulled away from the surface of the mica, leaving small bare patches of mica. The mica can be identified by its atomically flat nature, in contrast to the undulating surface of the polyimide film. We have seen in our preparation and subsequent AFM imaging of these films that dewetting of the film tends to decrease in severity if the substrate is heated above 100°C before deposition of the polyimide in solution. Thus, this dewetting may be caused by an excess of water on the surface. These depressions in the film remain unchanged with rubbing.

Films were then rubbed, as described previously. Scratches were seen on all samples, regardless of substrate type, thickness, or rubbing load (Fig. 4). This is consistent with other results where the scratches on rubbed polyimide films were found and where the relationship to rubbing strength was briefly studied.[12,13] A distribution in the depth of the scratches was seen for each film. The areal density of scratches varied across the surface of the film. The scratches have a charac-

teristic topography, as shown in Figure 4(b), comprising a groove in the film nested between two ridges, and bear a striking resemblance to furrows in a plowed field as discussed by Jin and Unertl.[15] In that study, these researchers created scratches similar to those seen on rubbed polyimide surfaces by dragging an AFM tip across the surface. As scratches were not formed for applied loads less than the yield stress of the polyimide, and due to the shape of the scratches, these researchers explained this phenomenon as "microplowing," as opposed to microcutting or microcracking.

The two ridges of the scratches observed on these rubbed films are often higher than the cen-
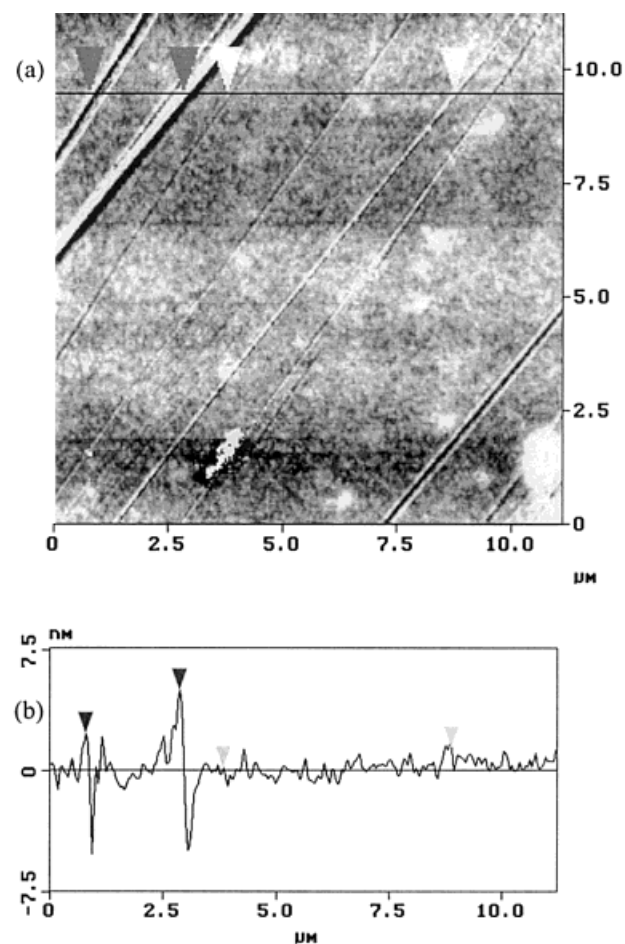

Figure 4 TMAFM images of scratches on a 175-nm-thick polyimide film rubbed from upper right to lower left with a 20-g/cm^2 rubbing load: (a) a variety of scratches, from the deep scratches in the upper left to the lighter scratches in the center of the image; (b) a crosssection along the line marked in (a), showing the triangular shape of the scratches. The markers indicate the positions of each of four scratches on the graph and on the image.

tral groove is deep, and they are often of different heights themselves. The depths of the grooves are usually 1–5 nm below the average surface level of

(a)

(b)

(c)

the film, although they have been observed to be as shallow as 0.5 nm and as deep as 33 nm. The ridges are typically 2–6 nm above the average surface level of the film, although ridges as high as 49 nm have been observed.

In the case of thinner films (<30 nm thick) on mica, tears as well as scratches were evident (Fig. 5). These tears are wide, deep depressions in the film, having widths varying from those of the widest scratches to nearly 5 microns. In contrast to scratches, the tears are relatively flat at the base [Fig. 5(b)] and are usually shorter than the scratches, terminating in a large buildup of the polyimide. The tears sometimes exhibited a series of these "pile-ups" for distances up to 50 microns or longer; a portion of such a region is shown in Figure 5(c). Within the tear, the topography is at least as flat as is the surface of the rubbed polyimide film, although not as flat as bare mica. In fact, in the bottoms of a few tears, scratches were observed. The roughness within the tears may be scratches in the mica itself, since bare mica rubbed under similar conditions is heavily scratched.

AFM measurements showed that the average depth of the tears in films on mica often exceeds the thickness of similar films spun on silicon (as measured by ellipsometry) by 3 ± 1 nm. Some of the variation in these measurements may be due to the fact that the height of the film surface itself varies by as much as 3 nm, as can be seen in Figures 3 and 8. For each sample measured, however, this difference between the thicknesses is in the same direction, that is, the tear depth is always deeper than is the ellipsometric thickness. This suggests either that the adhesion of the polyimide film to the mica substrate is sufficiently strong that cohesive failure occurs in the mica or that there are variations in the actual thickness of the film.

The fractional area of the sample that is torn varies both with the film thickness and the rub-
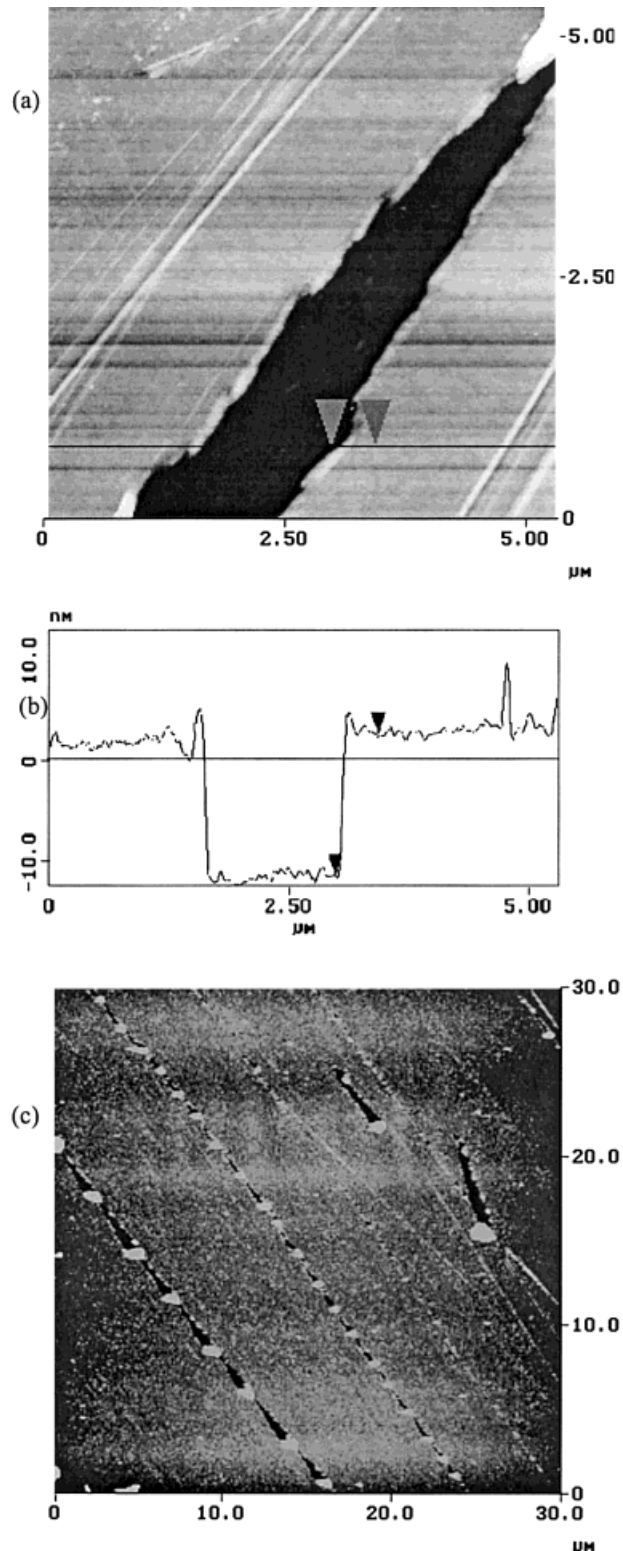
Figure 5   (a,b) TMAFM image and cross section of a tear on a 16-nm-thick film (as measured by average trough depth), rubbing load = 20 g/cm^2. Note that the trough bottom is flat as opposed to triangular in the cross section. The vertical distance between the two markers is 14 nm. The rubbing direction on this image is upper right to lower left. (c) An area on a 6-nm-thick film, rubbing load = 4 g/cm^2, where the tears have formed head-to-tail, making long chains. On this sample, the tears are also smaller, in general, than in the previous image. The rubbing direction is upper left to lower right.
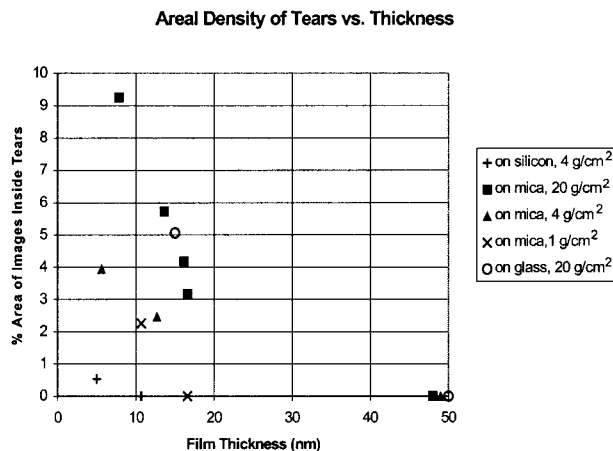
Areal Density of Tears vs. Thickness

Figure 6   A graph of area occupied by tears on the film surface versus film thickness. Film thickness is measured by averaging the depths of all tears found in the film or by ellipsometry in the absence of tears. Note the general trend of a decreasing tear area with increasing thickness and decreasing rub load.

bing load. Shown in Figure 6 are the average areas of observed tears as functions of the film thickness. Different loading conditions are shown. Each point on the graph is the average of areal densities of tears taken from multiple images on the same sample. The total area imaged for each point varied from 4000 to 12,000 μm^2, and each imaging area was a square between 10 and 40 μm on a side. Error bars are not shown because the standard deviation of the data points was extremely large due to large variations in the tear areas per image over a single sample. Qualitatively, the data suggest that for thick films the number of tears is independent of the applied load.

The substrate was also found to influence the characteristics of the tears (Fig. 7). Polyimide films on glass and silicon substrates have different tear shapes from those of the films on mica substrates, most likely due to different interactions between the substrate and polyimide. Tears on the glass surface have a larger width-to-length ratio than on either mica or silicon where the tears are long and thin [Fig. 7(c)]. Again, the cross sections measured through the images [Fig. 7(b,d)] show that the tears have a flat bottom. Nonetheless, the area taken up by tears for films on glass follows a similar dependence on the thickness and on the rubbing load as that of the films on mica, although differing somewhat in the absolute amount of area removed.

Another feature often found on the rubbed surface is the arrangement of the hemispherical polyimide islands, which are found randomly arranged on the unrubbed surface, along a preferred direction, roughly parallel to the rubbing direction (Fig. 8). This gives the surface a grooved appearance, as the islands are lined up in long chains, with grooves between the chains. The depth of the grooves between the chains of islands is ~0.5–1 nm. The spacing between the adjacent strings of islands is ~10–40 nm, approximately the width of one island. Similar strings of islands were seen by Kim et al.[13] on films of HT210 polyimide, but these were found to be spaced about 100 nm apart, much farther apart than observed here. Also, the islands observed in that study were seen to coalesce and become wider with an increasing rubbing load. In our study, however, no dependence on the nature of this topography on film thickness, rubbing load, or substrate was found. Features of comparable size to the aligned chains of islands in this study were also found by Pidduck et al.[12] in rubbed films of the Probimide 32 polyimide. However, these features also exhibited a strong dependence on the rubbing load. Differences between the results of these studies and ours may be attributable to differences in the type of polyimide used or in the experimental procedure.

Not all the islands on a rubbed surface are aligned into chains. In fact, many areas exist where a scratch is surrounded by randomly arranged islands or where only a strip of islands is aligned and the areas bordering the strip are not. Also, a few 1-μm^2 areas have been observed with two slightly different orientations of grooves [Fig. 8(b)].

DISCUSSION

In thick films, the action of buffing the polyimide surface produces an alignment of the polyimide chains at the surface. Grazing incidence X-ray scattering (GIXS) and NEXAFS have shown that the orientation of chains at the surface is quite high and that the orientation propagates only several nanometers into the film.[5,6] The bulk modulus of BPDA–PDA is 6.1 GPa.[16] If we consider now the force involved in the buffing process, if all the fibers were in contact with the polyimide surface, then a load of only 1 GPa would be expected.[17] However, if not all the fibers are in contact with the surface, as shown by Kikuchi et al.,[18] then the load at the fiber tips can

easily exceed the yield stress of the polymer, plastically deform the polymer, and produce an orientation of the chains.
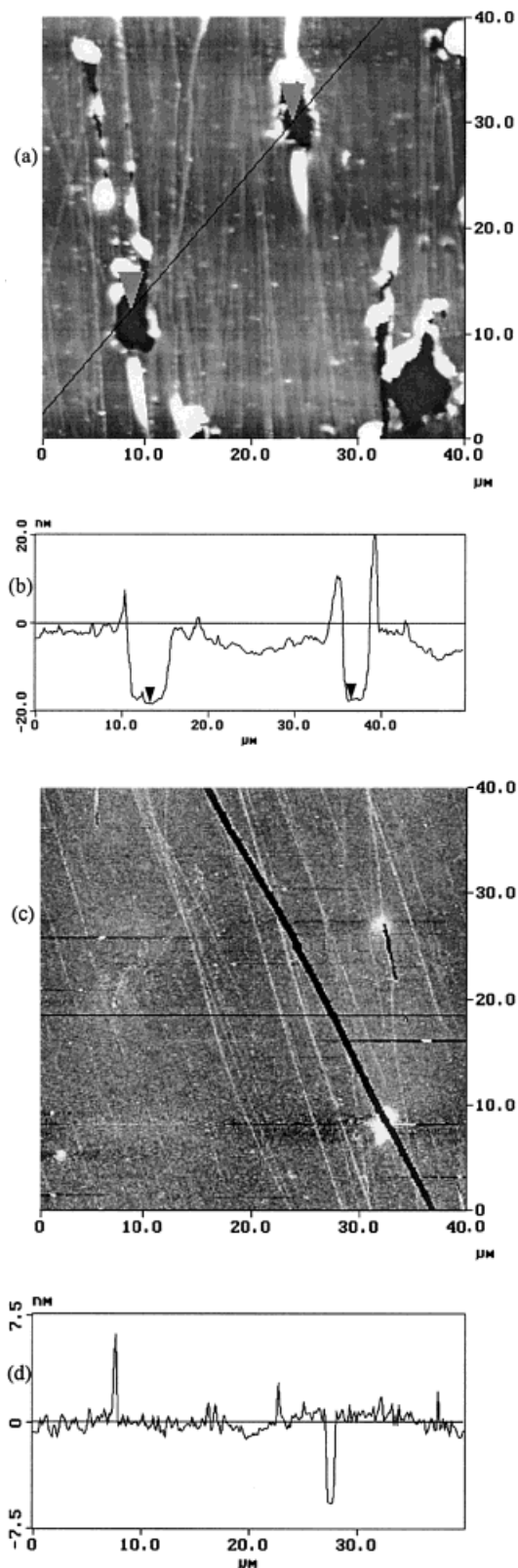
Now, as the film gets thinner, the alignment of the BPDA–PDA chains parallel to the surface increases markedly.[19] In fact, the alignment of chains parallel to the surface is sufficiently high so that the morphology of the film is planar and is similar to the turbostatic structure exhibited by graphite. This planar alignment of the chains will make the film more susceptible to the shear deformation placed on the film during buffing. Consequently, in thin films, the response of the polymer to buffing will be greater. This is in keeping with the results of these studies.

If we now consider the extent to which the surface deformation propagates into the film, the planar orientation of the chains will serve to increase this distance. Consequently, as the film thickness is decreased, the force exerted in the buffing process will be sufficiently large and propagate over a sufficiently large depth into the film so as to cause a catastrophic failure of the entire film, that is, scratching or tearing of the film, when the film thickness is comparable to the deformation distance from the surface. This effect would, as observed here, become more severe with decreasing film thickness.

An additional factor that enters into the deformation of the BPDA–PDA films is the stress that is inherent in the film during preparation. Films are solution-cast in amic acid or amic acid ester. Complete removal of the solvent is not possible due to the strong association of the solvent with the polymer. Upon imidization or curing, there is a significant volume reduction due to the solvent loss and the loss of either water or an alcohol upon cycloimidization. This volume reduction occurs only in the film thickness due to the adhesion of the chains to the substrate surface. This, in turn, gives rise to the orientation of the chains parallel to the surface and also causes the film to be under stress. This stress, coupled with the applied load during buffing, is sufficient to overcome the adhesion of the polyimide to the surface, resulting in the failure observed. In general, how-

Figure 7 (a) TMAFM image of typical tears on a glass substrate, film thickness 15 nm, rubbing direction from bottom to top. Note that these tears have a larger width-to-length ratio than that of the usual tear on mica and lack the single, distinct mound of material at the terminus. (b) Crosssection through the line marked on (a). (c) Tears on a silicon substrate. (d) Crosssection through the line marked in (c). Note the flat-bottomed nature of these tears.
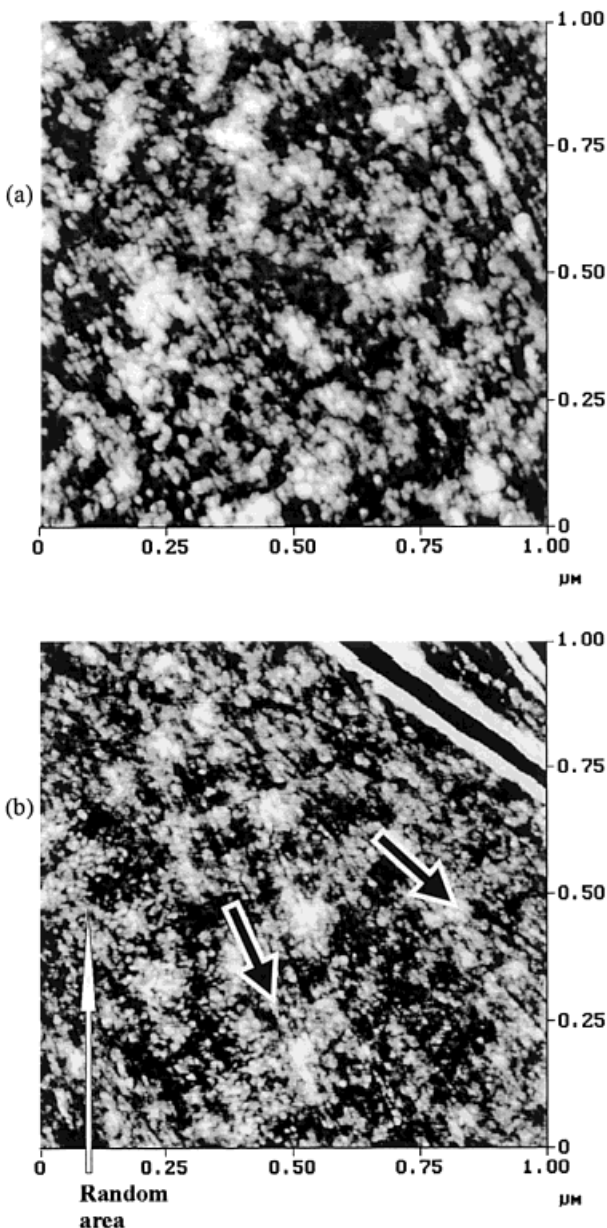
Figure 8 TMAFM images of the rubbed polyimide surface. White areas are 3 nm higher than are the black areas. Note how in (a) (rubbing load = 4 g/cm^2) the islands, which in the unrubbed film were randomly dispersed, are now aligned into chains. (b) Rubbing load = 1 g/cm^2. Two stripes of chained islands, along two slightly different directions (indicated by black arrows), adjacent to patches of random islands (indicated by white arrow). Note also the presence of a scratch in the upper right-hand corner. The rub direction in these images is from upper left to lower right.

ever, the adhesion of the chains to the surface will tend to retard the orientation of the polymer in response to an applied deformation.

The results shown in this study also point to another important aspect of the buffing process, which is that the deformation and orientation do not occur uniformly across the surface. It is not possible from these studies or others to determine whether this nonuniform deformation results from imperfections in the film or from nonuniform contact of the fibers at the surface. Nevertheless, it is very apparent that failure occurs at random points across the surface. This nonuniform deformation is fully consistent with previous GIXS and NEXAFS studies, where, in the former, an average surface orientation was observed and, in the latter, a partial orientation of the molecules at the surface was found.[5,6] As long as the average separation distance between areas where marked orientation occurs is less than or comparable to the correlation length of the liquid crystals (typically microns in size), then monodomain formation of the liquid crystals is possible. It is also clear that failure of the film by scratching or tearing will only serve to reduce the amount of orientation of the liquid crystals.

A characteristic feature of the tearing processes is the buildup of the polyimide at the terminus of the tear. Frequently, multiple sequential tears are observed in the buffing direction. This is reminiscent of a stick-slip process, where the buildup of the polymer becomes sufficiently large so that the applied load is not sufficient to continue the tear. Rather, the tear stops, and a new tear is initiated. In fact, the recoil of the fibers on the cloth from the "mounded" polymer may be sufficiently strong to initiate another tear.

The occurrence of tears and the implications of their occurrence has a bearing on the research of others on films less than 50 nm thick by other methods. In those studies, it is either found or assumed that the orientation of the molecules will be uniform through the depth of films less than about 15 nm thick.[4–7,20,21] As the above discussion asserts, the occurrence of troughs upholds this assumption. Also, since these other studies average over comparatively large areas of the surface, they are unable to discover what localized features may be affecting phenomena such as liquid crystal alignment and pretilt angle. Some studies compared results from films with thicknesses less than 20 nm with those with greater thicknesses.[6,19,21] The knowledge of the occurrence of tears and other irregularities in these thinner films could influence how the results of these studies are interpreted, as thicker rubbed films will not exhibit the same surface irregularities and film defects as those of thinner ones. Also, one study

found that the thickness of a 10-nm-thick film decreased by nearly a nanometer due to rubbing, as measured by ellipsometry. The tears found in our research may explain or give a possible mechanism for this decrease in thickness.

Probably the most curious feature of the surface deformation is the appearance of the string of droplets or islands of the polymer in the buffing direction. While it can be argued that such features are similar to a stick-slip deformation process that involves only the polymer at the surface, a more in-depth study is necessary to provide a quantitative explanation.

In conclusion, three types of failure in our rubbed polyimide films were found: scratches, tears, and strings of islands aligned along the rubbing direction. The tears show a definite dependence on the rubbing load and film thickness, whereas the aligned strings of islands show none. It is suggested that local overshearing of the film is responsible for the formation of tears. The presence of tears and scratches may inhibit liquid crystal alignment. It is apparent that the deformation of the surface is quite heterogeneous.

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