Improvement of adhesion of copper on polyimide by reactive ion-beam etching

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In this paper we describe the effect of oxygen-reactive ion-beam etching of a polyimide film to enhance its adhesion to an overlying, subsequently deposited copper film. The adhesion strength of the copper to the polyimide could be increased by as much as a factor of 25 as a result of the etching. Near the etching condition which resulted in optimum strength, the failure mode at the polyimide/copper interface changed from adhesive failure to tensile failure. The latter occurred at the "roots" of a "grass-like" surface structure of the ion-etched polyimide film.

Introduction

The adhesion of copper to polyimide (PI) is largely due to mechanical interlocking, which in turn depends on the structure of the Cu/PI interface. Therefore, one way to improve Cu/PI adhesion is simply to roughen one surface or the other. This turns out to be a great deal more complicated than one would immediately suppose. In what follows we describe what we have learned by roughening PI surfaces with reactive ion beams prior to deposition of the overlying Cu.

Experiments

Used in this study were Kapton PI films and films formed by spin-coating du Pont 2540 onto silicon. Oxygen gas reactive ion-beam etching (RIBE) was carried out at various energies (500, 1000 eV), ion-current densities (0.4, 0.6, 0.8, 1.0, and 1.2 mA/cm^2), and etching times (5, 10, 15, 20 min). The system which was used has been described elsewhere [1]. The chamber base pressure was 2×10^{-6} torr and the operating oxygen gas pressure was 2×10^{-4} torr. Most of the ion-beam etching was performed on the upper surfaces of the films. Ion-beam etching was also performed on cross-sectional slices (normal to their surfaces) of the films. Two methods were used to prepare cross sections. In the first, the sample was sliced with a razor blade. In the second, the surface was masked by a glass slide and then etched, creating a 10-μm-deep step. The side of the step (the cross section) was then subsequently etched by a beam which was oriented normal to it. Ion-beam etching in argon was also carried out to

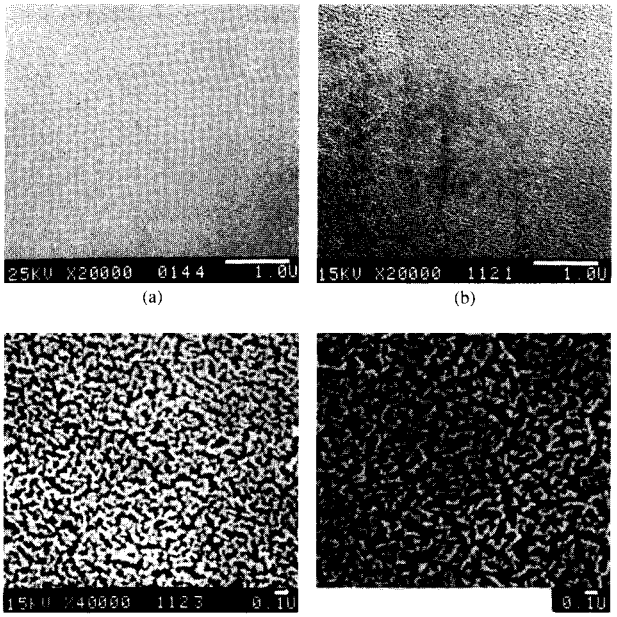


Figure 1

Scanning electron micrographs of a PI film, illustrating surface morphological changes with various amounts of O_2 reactive ion-beam etching (RIBE): (a) Unmodified PI. (b)–(d) After 1, 3, and 5 min of O_2 RIBE, respectively. (Beam energy = 1000 eV; beam density = 1.2 mA/cm^2.)

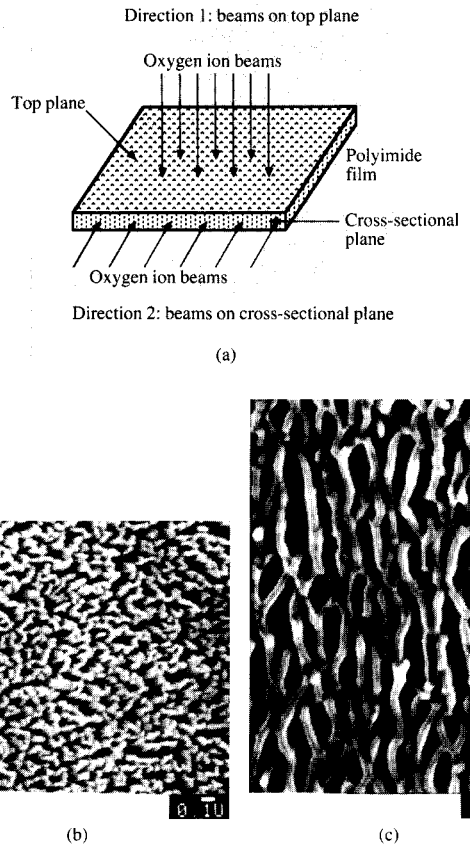


Figure 2

Scanning electron micrographs of a Kapton PI film after O_2 RIBE for 5 min at the same beam energy (the PI film formed by spin-coating gave closely similar results for both orientations): (a) Geometry of the film and beam directions. (b) Grass-like structure on the top plane of the film, tilted 30° under the scanning electron microscope. (c) Plate-like structure on its cross-sectional plane.

compare the surface morphology with that produced by etching in oxygen.

After etching, the surface morphology was observed by scanning electron microscopy (SEM). X-ray photoemission spectroscopy (XPS) was used to investigate the surface compositional differences of the PI films before and after etching. The XPS experiments were performed in an angle-resolved mode at a glancing angle in order to increase sensitivity.

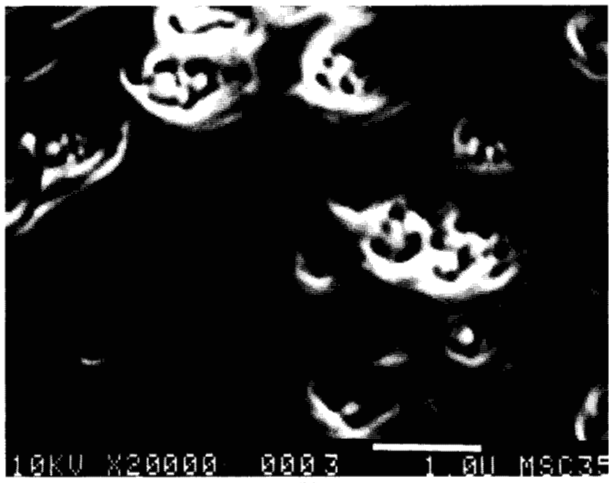
Cu films were deposited on the PI films by thermal evaporation. Stripes which were 1 mm wide, 20 mm long, and 20 μm thick, used for peel-testing, were deposited by using Al sheet masks. Peel-testing (at 90°), to measure the peel strength of the Cu/PI interface, was performed using an Instron machine.

Results and discussion

• *Morphological changes*

The surface morphology of the PI films changed substantially with beam energy, ion dose (beam current density times etching time), and beam direction. **Figure 1** shows the surface morphological changes with various ion doses (etching times) at a beam energy of 1000 eV. The unetched surface of the PI film was very smooth, but at the initial stage of etching with low ion doses, etch pits formed. These etch pits evolved to surface cracks during further ion etching, and grew deeper and propagated, leading to the development of grass-like and plate-like structures at the top plane [direction 1 in **Figure 2(a)**] and the cross-sectional plane [direction 2 in Figure 2(a)] of the PI films, respectively. **Figures 2(b)** and **2(c)** show the grass-like and plate-like microstructures which were observed. The structures became deeper and wider at higher beam energies and larger ion doses as a result of chemical reaction and surface erosion by chemical and physical effects of the reactive oxygen ion beams. To separate the effects of physical ion bombardment in the O_2 RIBE, argon ion-beam etching was performed at the same beam conditions as the O_2 RIBE. The surface

(a)



(b)

Figure 3

Scanning electron micrographs of a PI film after ion-beam etching in argon for 15 min at the same beam energy (a) on its top plane and (b) on its cross-sectional plane.

Table 1 Composition analysis for unetched and O_2 RIBE (1000 eV, 1.2 mA/cm^2, 15 min) specimens.

	Detector angle	*Elements*					
		Carbon			*Oxygen*		*Nitrogen*
		C=O	*C–N, C–C*	*C–O*	*O–C*	*O=C*	
Theoretical			75.9		17.2		6.9
Unetched	80°	8.4	30.3	36.5	4.9	12.3	
			75.2 (total)		17.2 (total)		7.5
O_2 RIBE	80°	17.7	25.1	29.4	6.6	14.5	
			72.2 (total)		21.1 (total)		6.7

morphology of argon-etched PI shown in **Figure 3** is totally different from that of the former. Regardless of ion-beam conditions, the latter caused the formation of larger surface etch pits. One important fact is that no differences were found between the top plane and the cross-sectional plane. It is known that argon physically sputters the oxygen and nitrogen from PMDA–ODA-type PI.* When we placed a PI film in the region outside the electrodes in an RF-oxygen plasma, etching still occurred (without ion bombardment) but no grass-like structure developed. Hence we conclude that the formation of the grass-like and plate-like structures requires both the presence of reactive oxygen ions or molecules and bombardment by ions.

The chemical reaction of an oxygen plasma with PI (on the negatively biased electrode) has been studied previously [2–4]. The oxygen ions strike the PI surface and abstract a hydrogen atom, leaving behind a radical which may be attacked by the reactive species: oxygen ions and molecules. The subsequent attachment of oxygen weakens the carbon–carbon bond by about 25%, thus enhancing the degradation of the PI by chain scission [2–4]. Our XPS results show that O_2 RIBE oxygenates the PI and decreases its carbon and nitrogen concentrations. **Table 1** indicates the percentage composition of C, O, and N for unetched and O_2 RIBE (1000 eV, 1.2 mA/cm^2, 15 min) specimens.

• *Reasons for the morphological changes*

Several suggestions have been made regarding the surface structure which results from O_2 RIBE. Rangelow et al. [5] suggested that the appearance of the grass-like structure is caused by metal compound contamination, in that case by Al contamination caused by sputtering of the reactor walls during oxygen reactive ion etching. Kogoma and Turban [3] concluded that a surface which has been exposed to O_2 RIBE is partially covered by a deposited material ($C_nH_mO_x$), which obstructs the etching reaction and causes surface roughness. However, neither indicates why different morphologies should be found at the top and the cross-sectional planes of the PI film formed by spin-coating.

In our XPS studies, the detection angle (see **Figure 4**) between the detector and the specimen was set at 80° to enhance the detectability of the electrons emerging from the top portion of the grass-like structure. There were no measurable metallic surface impurities, which is also consistent with the view that metal contaminants acting as a mask are not responsible for the surface roughness. The XPS results also show that the oxygen concentration after O_2 RIBE increases from 17.2 atomic % to 21.1 atomic %, while the nitrogen and carbon concentrations decrease. The carbon concentration is reduced from 75.3% to 72.2%, while that of the carbonyl carbon approximately doubles; as a result, chain scission is enhanced.

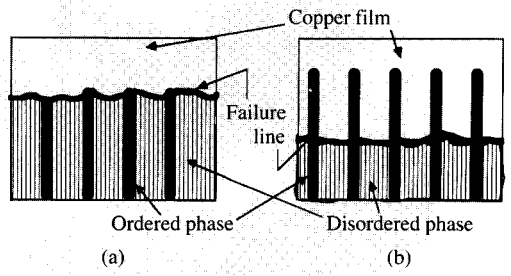
* P. Ho, IBM Research Division, T. J. Watson Research Laboratory, Yorktown Heights, NY, private communication.

The morphology of PMDA–ODA has been investigated by numerous groups using scattering [6] and diffraction [7]. It is obvious that an appreciable long-range crystalline morphology does not exist in thermally imidized PI films. The structure can be described as crystalline only in highly extended chain segments. The lateral alignment of chain segments is ordered in a smectic fashion along the chain axis for several monomer units, as reflected by a coherence length from the intramolecular reflection of some 50–60 Å up to 120 Å. Also, it is presumably ordered along the vertical direction of the PI film. We expect that the etch rate for the ordered phase is less than that for the disordered phase because of its higher density and more efficient bonding. In our studies, after small surface asperities were developed due to the sputter yield differences between the ordered and the disordered phases, surface asperities would grow into grass-like structure during further etching.

• *Adhesion of Cu on polyimide*

The peel strength of Cu on the unmodified PI film surface was found to be 2.5 ± 0.3 g/mm, the average for 30 samples. Its failure mode was found to be adhesive failure at the interface of the unmodified PI and Cu films. The peel strength was so low that an unmodified PI film region was used to initiate peeling in the peel-testing of an O_2 RIBE-modified PI film. For the O_2 RIBE-modified PI film, two types of failure mechanisms were found: adhesive failure at the PI/Cu interface, and tensile failure in the PI film itself. As illustrated in **Figure 5(a)**, at the early stage of etching, etch pits and surface cracks were initiated and the failure mode was adhesive failure at the interface. The peel strength was substantially increased due to the mechanical interlocking. For example, the peel strength measured after O_2 RIBE at 500 eV/0.2 mA/cm^2/5 min was 70 ± 5 g/mm (based on 10 samples), which was more than 25 times that of unmodified PI films. This was the optimal condition found for increasing the bond strength.

Substantially larger ion doses resulted in a deeper "grass-like" structure with thinner "blades" and fewer blades per unit area. Peel-strength tests indicated that the mechanical bonding between the blades and Cu is very high, and the weak points are at the "roots" of the long, thin blades, resulting in a drop in peel strength to about 22 g/mm (the average for 10 samples) because of tensile fracture of the blades at their roots. This result corresponded reasonably well with simple calculations: Assuming a blade diameter of 0.3 μm and an ultimate tensile strength of 35 kg/mm^2 for



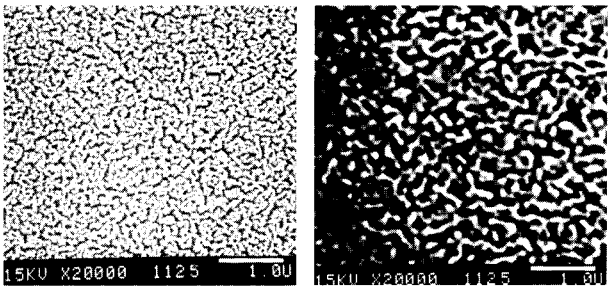
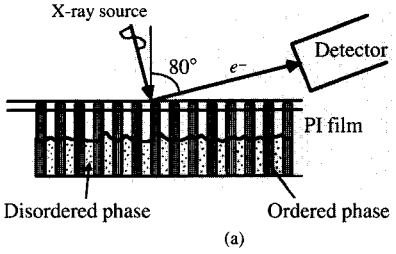


Figure 5

Schematic diagrams of (a) adhesive and (b) tensile failure modes; and scanning electron micrographs of a PI film which had been subjected to O_2 RIBE for 5 min at the same beam energy, (c) before and (d) after peel-testing.



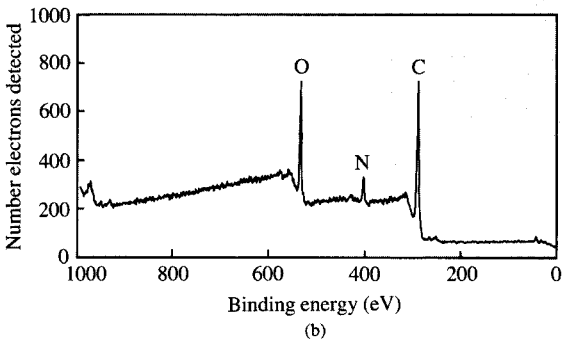


Figure 4

XPS system with angled specimen stage (a), and a typical spectrum for a complete energy scan (b).

the PI, the load required to break each blade was calculated to be 0.003 g times the number of blades (~6000) per mm, or ~20 g/mm.

Figure 5(b) shows the other of the two inferred failure modes; shown in **Figures 5(c)** and **5(d)** are scanning electron micrographs of the surface of a PI film which had been subjected to O_2 RIBE before and after peel-testing. Numerous scanning electron micrographs were obtained which clearly demonstrated the removal of the blades from modified PI film surfaces and their embedding in the peeled copper films. Regarding the adhesion, there are critical etching conditions which cause the failure mode to change from adhesive failure to tensile failure. Further studies are being carried out to determine the O_2 RIBE conditions for achieving optimal adhesion.

Summary

The top and cross-sectional planes of the polyimide films which were examined in this study assumed grass-like and plate-like structures, respectively, upon exposure to oxygen-reactive ion-beam etching.

Etch pits were developed at the early stage of etching, which evolved to surface cracks and subsequently to the grass-like and plate-like structures.

The main reason for these morphological changes is believed to be the structural inhomogeneity of the polyimide films, involving crystalline and other phases. The grass-like and plate-like structures could not be accounted for solely on the basis of physical ion bombardment. A combination of chemical reaction with oxygen ions, hydrogen abstractions by molecules and ion bombardment, and chain degradation appeared to be necessary to cause the observed surface modification.

The adhesion to a polyimide film of an overlying, deposited copper film could be improved by mechanical interlocking. However, excessive exposure to oxygen-reactive ion-beam etching resulted in a low peel strength because of failure at the "roots" of the thin, long "blades" of the resulting grass-like surface structure of the polyimide film.

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