

Polyamic Acid Interactions with Aminopropylsilane Surface Conditioners on Metal

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Synopsis

Grazing incidence infrared analysis reveals that metal surfaces of Ag, Al, Cu, Cr, and Al/Cu or Al/Cu/Si alloys interact with APS solutions of natural pH (10.4) to produce passivating siloxane films. These films restrict polyamic acid interaction with metal and amine functionalities, so that covalent attachment of the amic acid to the surface, through the adhesion promoter, does not occur. Instead, imidization appears to proceed in a normal fashion above a siloxane interfacial region which is coordinated to the metal surface by amine-metal interactions.

INTRODUCTION

Recently, we investigated the interaction of polyamic acids at metal/metal oxide surfaces¹ and found that reactive metals such as copper and silver form salts that slow thermal imidization, and decompose the polymer during high temperature curing.² In contrast, and to different degrees, unreactive metals as gold, aluminum, and chromium order amic acids on the surface and allow thermal imidization.

When polyamic acids are employed as a dielectric coating in microelectronics, direct metal-amic acid interaction is rare. Here, the metal usually comprises only a portion of a composite, and adhesion promoters, such as aminopropylsilanes, are generally encountered to bond the amic acid to the remaining substrate, usually silicon dioxide or silicon nitride.³

We have therefore extended our study of polyamic acid interactions to the surfaces of metal films that have been treated with hydrolyzed 3-aminopropyltriethoxysilane (APS) solutions. Boerio and co-workers have used external reflection infrared spectroscopy to characterize thin organic films on metal surfaces⁴ and have evaluated APS solutions on iron, copper, and aluminum^{5,6} deposited at different pH ranges. At the natural pH of 0.1% APS solution (pH 10.4), and using the short immersion times normally encountered in semiconductor fabrication, they found an asymmetric SiO absorption near 1100 cm^{-1} , and amine bicarbonate species which absorbed at 1570 , 1470 , and 1300 cm^{-1} . The bicarbonate species was observed only in the presence of CO_2 ; however, Cu I and II ions were also found on the copper substrate.

METHOD

In a similar fashion we spin applied aqueous 0.1% APS solution to metallic films of aluminum, silver, chrome, copper, and aluminum/copper, and alumi-

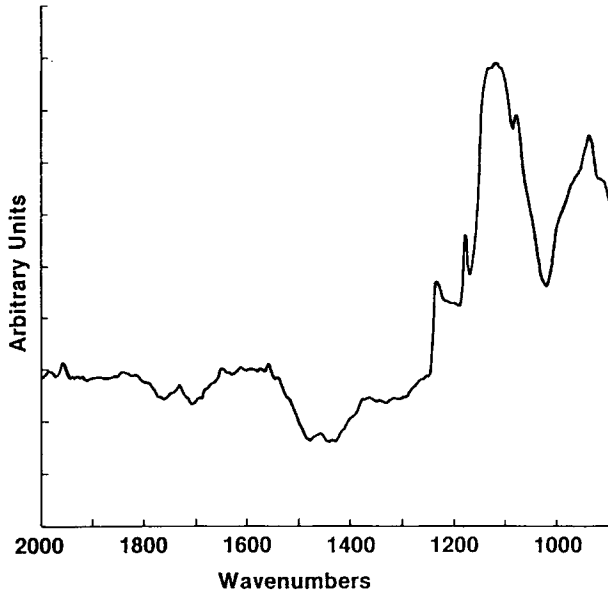


Fig. 1. Grazing incidence infrared spectrum of a typical aminopropylsilane (APS) film on metal (Al, Ag, Cu, Cr, etc.).

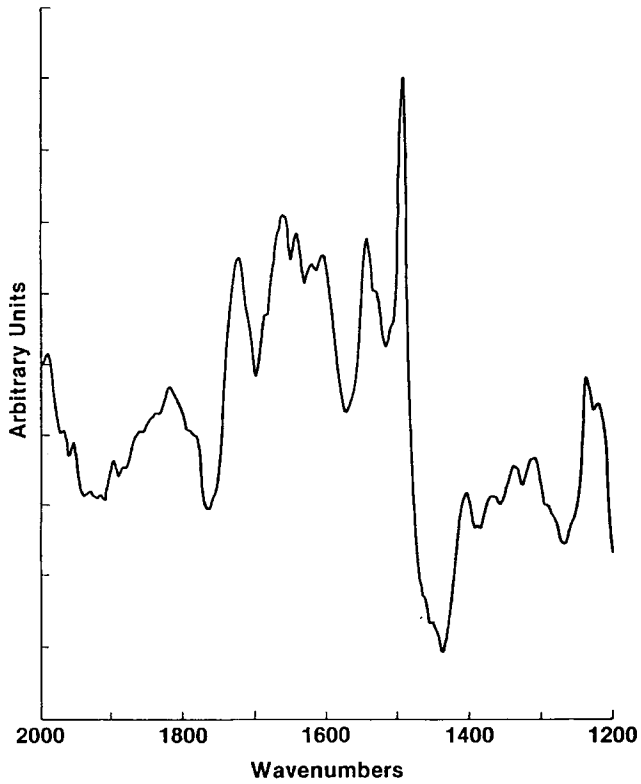


Fig. 2. GI-FTIR spectrum of a polyamic acid film on APS deposited on chrome.

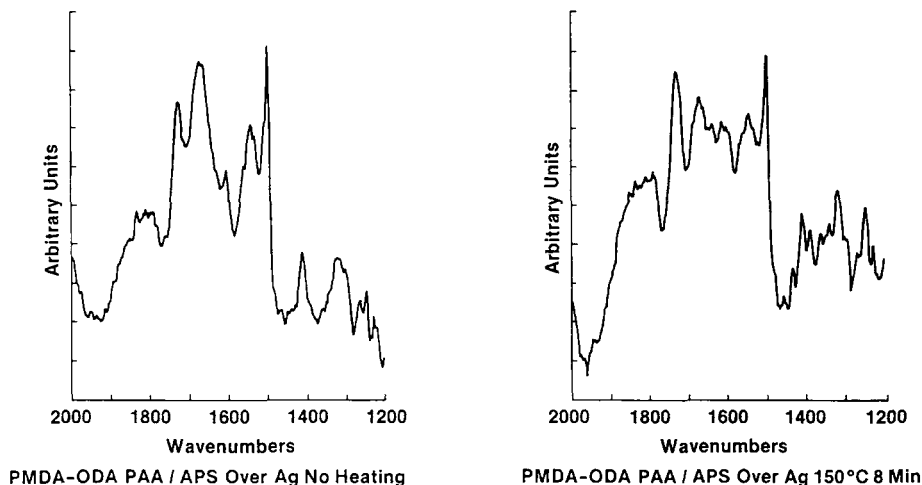


Fig. 3. GI-FTIR spectrum of a polyamic acid film on APS deposited on silver.

num/copper/silicon alloys, vapor deposited as thin films on silicon wafers. All of these films gave similar infrared reflection spectra characteristic of Si-O polymers with little observable NH absorption in the deformation region (1600 cm^{-1}), and no apparent bicarbonate formation (Fig. 1). Baking these siloxanes at 110°C for 5 min did not significantly alter the films.

A dilute solution of pyromellitic dianhydride (PMDA)-oxydianiline (ODA) type polyamic acid in *N*-methylpyrrolidinone (NMP) was spin-applied over these adhesion promoter films and the samples were analyzed by the infrared reflection technique. Surprisingly, in each case, the observed difference spectra (Figs. 2-7) reveal significant carboxylic acid functionality (1720 cm^{-1} carbonyl),

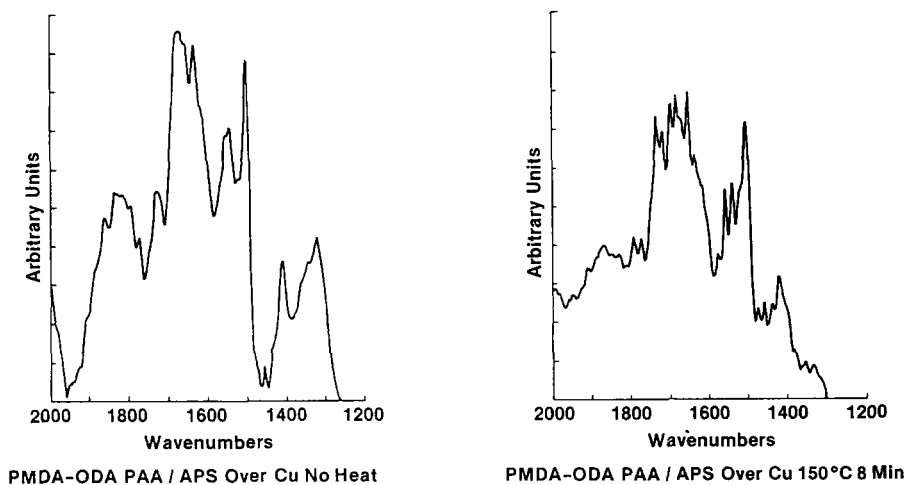


Fig. 4. GI-FTIR spectrum of a polyamic acid film on APS deposited on copper.

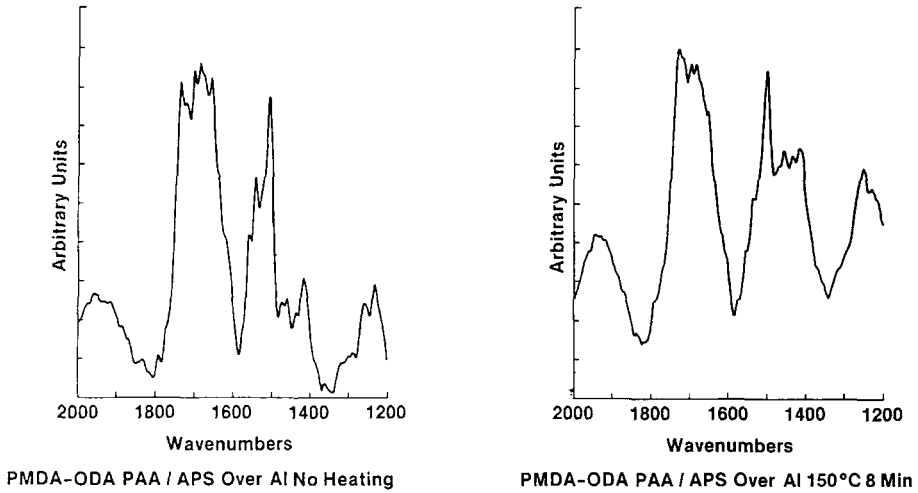


Fig. 5. GI-FTIR spectrum of a polyamic acid film on APS deposited on aluminum.

indicating that amine carboxylic acid interactions (observed in APS-treated silicon dioxide or nitride) are not significant on these surfaces. The carboxylate shielding-metal interactions which were observed on bare metal surfaces are also not apparent. Therefore, instead of direct acid-amine salt formation (which is the major initial adhesion interaction on APS-treated Si-O surfaces), or direct acid-metal salt formation (as occurs when contacting amic acids to silver, copper, or lead), the metal-APS surfaces appear passivated to amic acid attack.

DISCUSSION

These observations reveal that the polar amine-metal-metal oxide coordination, which adsorbs APS from solution onto the metal surface region, is

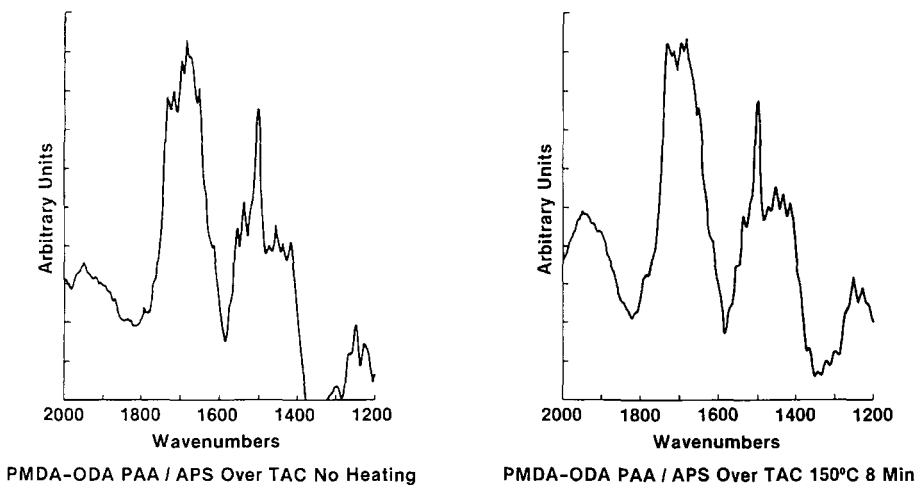


Fig. 6. GI-FTIR spectrum of a polyamic acid film on APS deposited on Ti-Al-Cu.

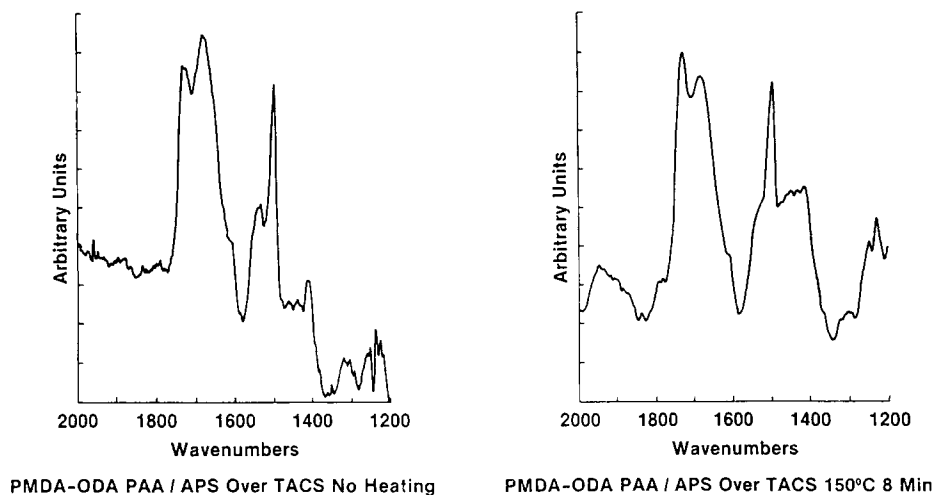


Fig. 7. GI-FTIR spectrum of a polyamic acid film on APS deposited on Ti-Al-Cu-Si.

strong, and probably not reversible, as it is on silicon oxides. Apparently, once the amine ligand is adsorbed, siloxane formation via silanol condensation creates a polymeric covering over a metal-amine core, shielding the amine complexes from carboxylic acid interaction with the amic acid.

This metal passivation by APS explains the generally poor adhesion strength of amic acid-metal interfaces that use APS in an adhesion promotion step. Simply stated, the covalent Si-O and C-N-C bonding interactions, observed on silicon oxide surfaces, are not observed on the metals studied, obviating covalent attachment of the amic acid to the substrate. Instead, an amine-metal surface region appears isolated from a polyamic acid polymer region by a siloxane-rich polymer interface (Fig. 8).

Thermal curing of the amic acid films on these passivated surfaces leads directly to condensation (Figs. 9-14), where acid and amide carbonyl groups ($1725, 1680\text{ cm}^{-1}$) react to form the imide ($1775, 1735\text{ cm}^{-1}$). Interestingly,

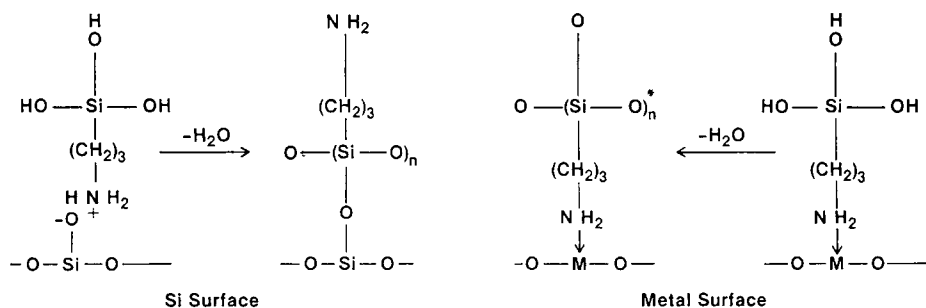


Fig. 8. Probable differences between APS adsorbed from solution on a silicon/silicon oxide surface and a metal/metal oxide surface.

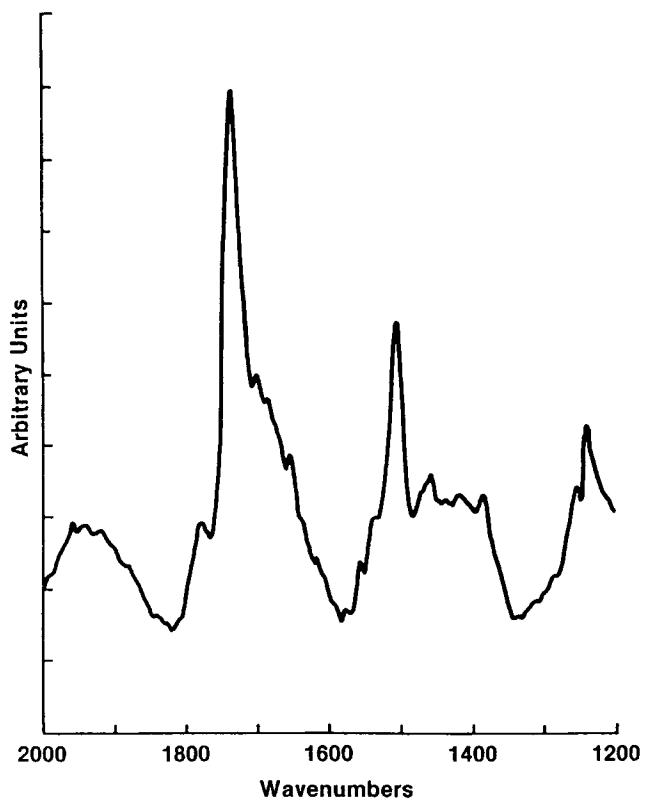


Fig. 9. GI-FTIR of PAA/APS heated to 200°C on Al.

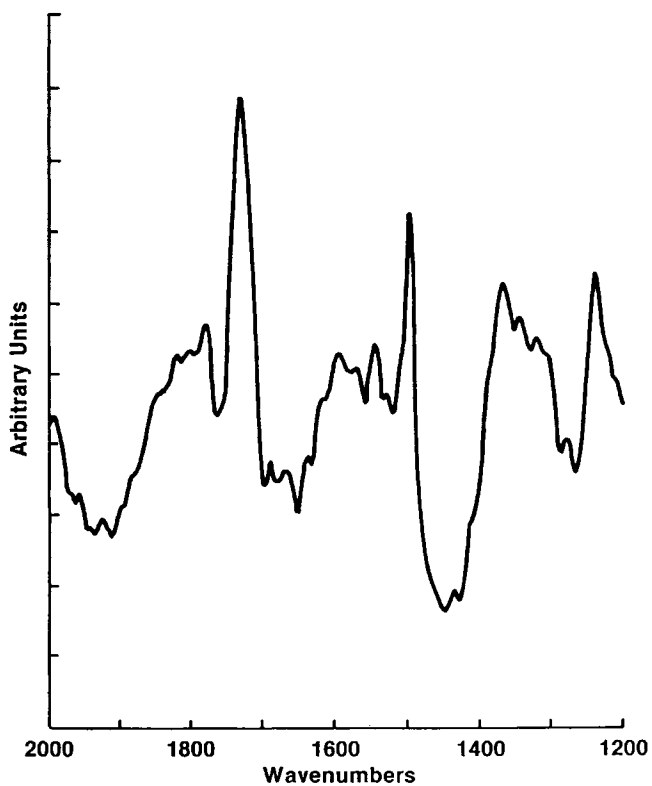


Fig. 10. GI-FTIR of PAA/APS heated to 200°C on Cr.

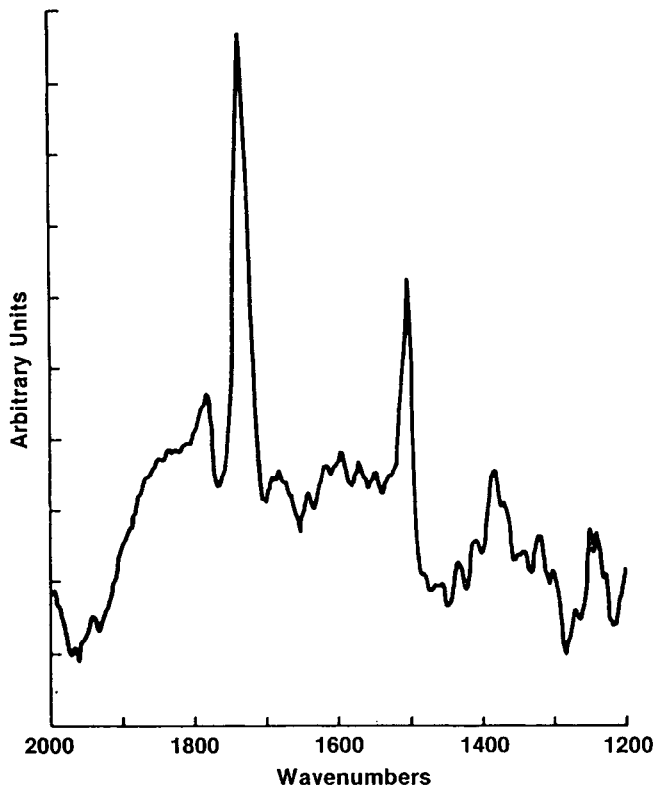


Fig. 11. GI-FTIR of PAA/APS heated to 200°C on Ag.

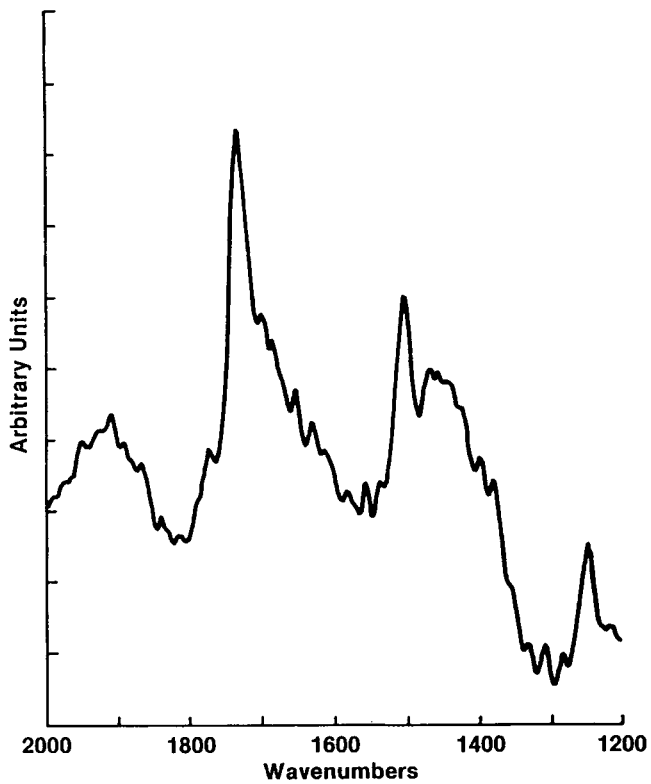


Fig. 12. GI-FTIR of PAA/APS heated to 200°C on Cu.

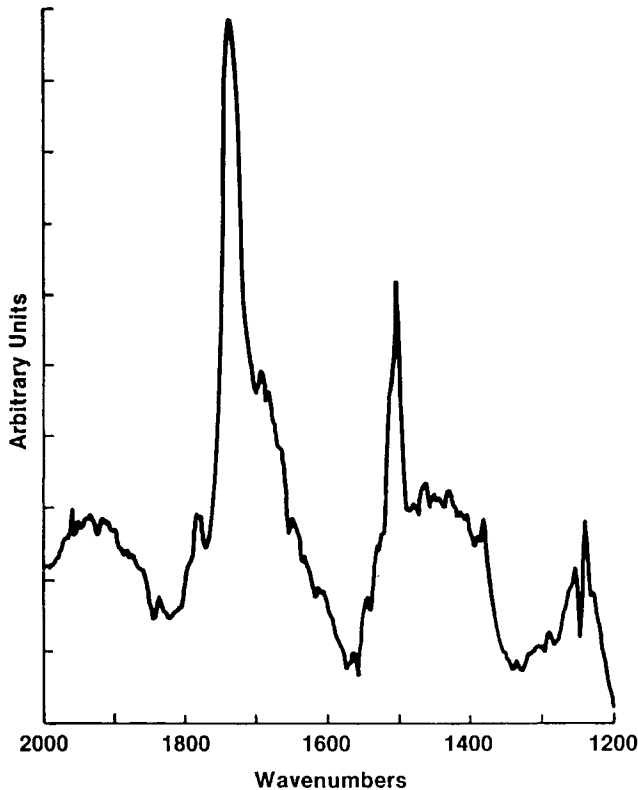


Fig. 13. GI-FTIR of PAA/APS heated to 200°C on Ti-Al-Cu.

copper-APS-PAA regions, and to some extent Al-APS-PAA regions, appear more complex, yielding a spectrum of partially cured material (150°C) with carbonyl doublets (1790, 1770; 1735, 1715; 1695, 1680 cm^{-1}), that produce one imide after thermal cure. The nature of these doublets are as yet undefined. Boerio's findings of Cu ions in the siloxane films is not reflected in amic acid carboxylate salts in the amic acid polymer.

EXPERIMENTAL

Reflective metal surfaces were prepared by vacuum evaporation of pure copper, silver, aluminum, or chromium onto the surfaces of polished silicon wafers. Alloys were prepared by sequential metal evaporation followed by annealing for 20 min in nitrogen at 400°C. A 0.1% aqueous solution of 3-aminopropyltriethoxysilane was prepared in deionized water and aged for 1 h. This solution was puddle applied to the metal surfaces, allowed a 30-s reaction period, and spun dry at 4000 rpm for 2 min. Polyamic acid films were immediately deposited by spin application of a 4% solids solution of a commercial PMDA-ODA polymer (duPont product 5057) diluted with *N*-methylpyrrolidinone (NMP).

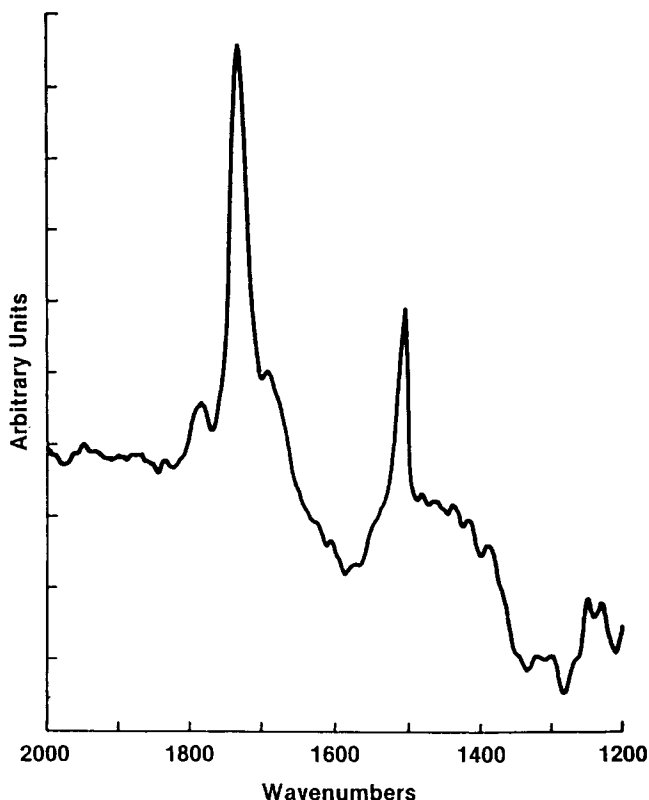


Fig. 14. GI-FTIR of PAA/APS heated to 200°C on Ti-Al-Cu-Si.

Treated surfaces were puddled with the polymer, allowed to stand for 1 min, and spun at 4000 rpm, 4 min.

Spectra were recorded using a Harrick Scientific Inc. reflection accessory with germanium polarizer in the beam of a Digilab FTS-14C FTIR, operated in the single beam mode at resolution 4 cm^{-1} , using 1000 scans under nitrogen purge. A nontreated gold film was used to reference each treated film. Grazing incidence angle was 75° , with parallel polarized analyzer.

CONCLUSION

Grazing incidence infrared analysis reveals that metal surfaces of Ag, Al, Cu, Cr, and Al/Cu or Al/Cu/Si alloys interact with APS solutions of natural pH (10.4) to produce passivating siloxane films. These films restrict polyamic acid interaction with metal and amine functionalities, so that covalent attachment of the amic acid to the surface, through the adhesion promoter, does not occur. Instead, imidization appears to proceed in a normal fashion above a siloxane interfacial region which is coordinated to the metal surface by amine-metal interactions.

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