# Enhancement of Chromium-to-Polyimide Adhesion by Oxygen DC Glow Treatment Prior to Roll-Sputter Seeding

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ABSTRACT

Roll sputter systems are being used to deposit a variety of metallic thin films onto plastic webs. Polyimide can be coated with a thin layer of chromium and copper to produce a plating strike layer for circuitizing flexible substrates. Adhesion is one of the most important aspects of a strike layer since lifted circuitry normally results in shorts. In the present investigation, to enhance adhesion, an oxygen DC glow discharge was incorporated to treat the polyimide surface prior to deposition of chromium. Oxygen DC glow power, gas pressure, and web speed were varied to determine their effect on adhesion of subsequently deposited metals. Adhesion was observed to be inversely proportional to $O_2$ pressure and web speed and proportional to DC power. The maximum web temperature attained at various DC glow processing conditions is compared to the resulting metal adhesion.

## INTRODUCTION

Pattern plating of circuitry is often used in producing flexible electronic packages such as Tape Automated Bonding (TAB) integrated circuit carriers. Thin metal films serving as seed (strike) layers are deposited onto dielectric materials such as Dupont 200H Kapton® films (a cast polyimide made from pyromellitic dianhydride, PMDA, and oxydianaline, ODA, precursors) in a roll format. Two layer TAB tape circuitization normally involves photo-lithographically patterning a resist layer onto the seed layer followed by plating.

Roll sputtering systems are being used to deposit a variety of metallic thin films onto plastic webs. For example, formation of the seed layer used for TAB tapes consists of direct current (DC) planar magnetron sputter deposition (performed sequentially) of thin chromium (25 nm) and copper (600 nm) layers onto one side of a Kapton web. This process is then repeated for the second side of the web. The chromium serves as an adhesive layer between the polyimide and the copper. Good adhesion of the strike layer to the plastic web is crucial in preventing lifted lines and subsequent circuit failure. However, design and reliability criteria have driven the adhesion requirements to higher levels than can be attained by the above two-metal process.

To further enhance adhesion, it is common to treat the polyimide surface with an oxygen plasma prior to metal deposition. It is known that such a treatment forms various polar groups such as C= O, -OH, and -COOH at the polyimide surface [1], increasing surface energy. Katnani, et al. [2] have demonstrated a correlation between the degree of polyimide surface treatment in an $O_2$ rf plasma, determined using measurements of water contact angle and x-ray photoelectron spectroscopy (XPS), and adhesion of chromium to the polyimide. However, using a remote plasma treatment, downstream from an oxygen plasma generated at microwave frequencies (2.45 GHz), Blackwell, et al. [3] found an inverse relationship between adhesion and extent of treatment. This behavior was attributed to formation of a weak boundary layer at the polyimide surface. This finding is consistent with mechanisms proposed by Tead, et al. [4] for polystyrene surface modification, which suggested that reducing the contribution of ion bombardment to plasma surface modification (absent in the downstream configuration) results in an enhanced degree of chain scissioning events relative to crosslinking events.

DC glow treatment is an alternative to rf and remote-microwave plasma processing techniques. A large negative bias is applied to an electrode in a vacuum chamber. Electrons ejected from this electrode collide with gas particles leading to dissociation into reactive neutrals and ionization. Reactive neutrals, ions, and photons, all components which cause modification of polymers, interact with the web surface. For example, it has been shown that Kapton webs immersed in a DC glow discharge are subjected to bombardment by ions with average kinetic energies around 10 eV [5]. The purpose of

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the present investigation was to measure the effect of variation in DC glow parameters (pressure, gas feed flow rate, and power) on Kapton surface wettability and adhesion of subsequently deposited metal films.

## EXPERIMENTAL

Plasma treatment and in-situ (and in-line) sputter deposition was performed in a roll sputter coater described in a previous report [5]. Differentially pumped sections prevent oxygen from migrating into the sputtering chamber and causing metal film contamination. The web used in this study was a 30.5 cm wide roll of Dupont 200H Kapton film. Two electrodes were used at different times in the course of this study, installed in the plasma module of the roll metallizer system. These replaced a microwave plasma applicator used in previous experiments [3]. One was a circular electrode with a 33 cm diameter. The other was rectangular with sides of 25.4 cm (along the direction of web motion) and 35.6 cm (perpendicular to the direction of web motion). The web passed at a distance 7.6 cm from the surface of the electrode. Because of obvious symmetries, the rectangular electrode is inherently more uniform with respect to web treatment.

The sputtered web was cut into 25.4 cm x 38 cm panels and blanket acid-copper plated to achieve a final copper film thickness of 7.6 microns. Etch mask decals, 1.0 mm wide, were placed on the panels to act as a mask for etching the copper in $FeCl_3$. $KMnO_4$ was used to remove the chromium layer. Final etched-line widths were 0.75 mm. An Instron Model A1026 tensile tester was used to measure the force required to remove the line from the polyimide surface, using a 90° peel test.

Web temperature excursions were measured using 0.051 mm chromel-alumel thermocouples attached to the web in a line perpendicular to the direction of web travel. These thermocouples were transported with the web through the plasma.

DC power, oxygen pressure, and web speed were varied to produce samples for metal adhesion testing. The experimental matrix was constructed using pressures of 100, 125, 150, and 250 mTorr, with powers ranging from 45 to 225 watts in 45 watt increments. Web speed varies inversely with the web's residence time in the plasma.

Optical emission from the plasma was monitored using a Jerrel-Ash model 1233 spectrometer and a Princeton Applied Research model 1460 optical multichannel analyzer configured with a PAR model 1456 detector. Relative oxygen atom number densities were determined by monitoring the emission spectral intensity from neutral atomic oxygen at 845 nm. Argon was added (2% by volume) as an actinometer [6,7] using the emission line at 750.4 nm.

## RESULTS AND DISCUSSION

Initially, the operating ranges of power, system pressure, and gas flow rate were explored to determine conditions under which uniform and stable plasmas could be maintained. Unstable, flickering plasmas occurred at pressures above 600 mTorr. The system produced very stable plasmas at all pressures below 600 mTorr, throughout the entire range of power and flow conditions investigated.

Wettability improved with plasma treatment. Advancing DI water contact angles decreased from 63° for untreated films to a minimum value (with thorough treatment) on the order of 5° to 10°.

Figure 1 shows results of 90° peel tests performed on samples treated at various DC power levels for two different web speeds and two different pressures, using the circular electrode. Greater peel strengths were achieved for treatment at the lower of the two pressures. For the lower web speed, at each pressure, adhesion increased with increasing power. At the highest web speed, at the higher pressure, no significant change in adhesion with power variation was observed. Reduced web speed resulted in better adhesion.

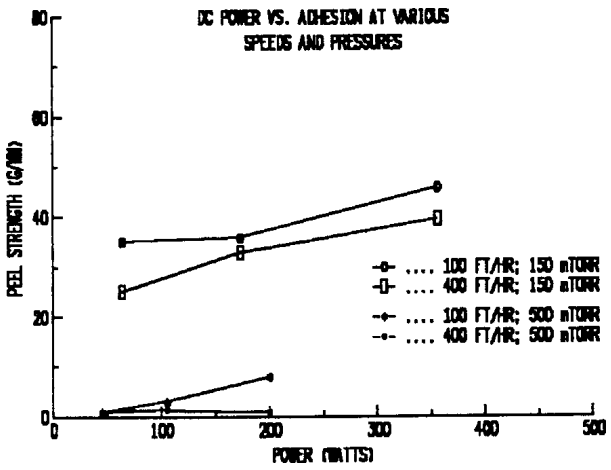


Figure 1. DC glow power versus resulting line adhesion at various web speeds and plasma pressures for circular electrode.

Figure 2 shows a plot of peel strength versus power for experiments performed at additional pressures at a constant web speed using the rectangular electrode. As was observed using the circular electrode, greater adhesion resulted under treatment conditions of higher power and lower pressure. To explain these responses requires an understanding of the effects which variations in DC power and chamber pressure have on O atom densities, ion densities, and energies of ions

striking the Kapton surface. Increasing power results in a greater degree of $O_2$ dissociation and ionization. A thorough study of parametric effects on ion energies and densities for plasmas generated in this system is the subject of another report [5].

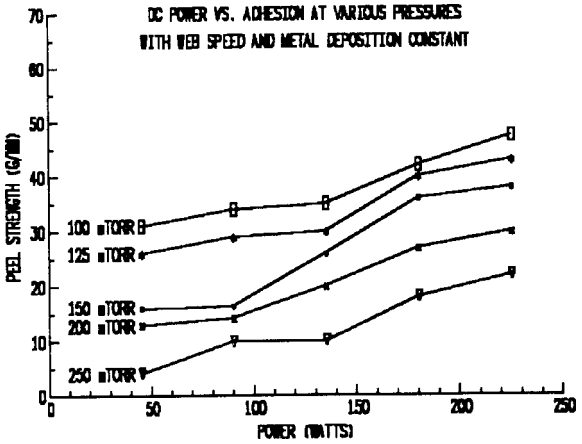


Figure 2. DC glow power versus resulting line adhesion at various pressures with constant web speed for rectangular electrode.

Figure 3 shows peel values versus relative oxygen atom number densities in the plasma for films treated using various DC powers and chamber pressures. For a given pressure, both O atom concentration and adhesion increase with increasing power. It is not clear, however, whether improved adhesion results from higher O atom concentration or variation in other plasma parameters (e.g. number and energy of ions striking the web) induced by increasing DC power level. Clearly, as the pressure is varied, there is no universal correlation between O atom concentration and adhesion.

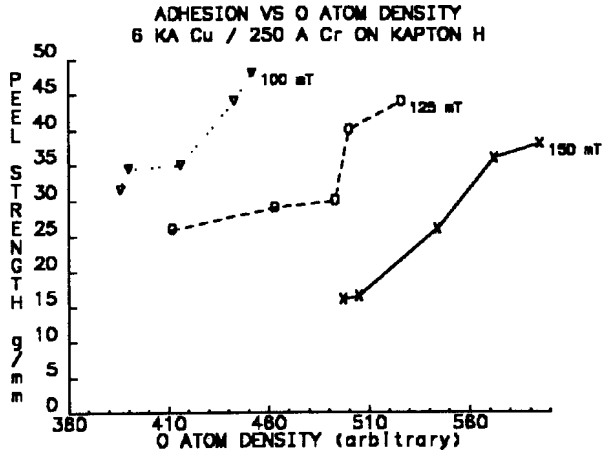


Figure 3. Oxygen atom density versus line adhesion at various pressure and power levels. At a given pressure, greater power results in higher O atom density.

Values for ion densities and sheath potentials were obtained using a Langmuir probe as previously reported [5]. The sheath potential is the voltage difference between the plasma and the web and determines maximum energy of ions striking the web surface. The flux of ions to the web surface is proportional to the density of ions in the plasma. Hence, the energy delivered to the web surface by incident ions is proportional to the product of the ion density and sheath potential. Figure 4 shows peel values versus the product of ion densities and sheath potentials. The trend shown in Figure 4 suggests that a greater degree of ion bombardment (greater product of ion density and sheath potential) results in higher peel values. Although oxygen atoms contribute chemically [2] to improved peel values, the significance of ion bombardment is evident. This is consistent with studies by Pappas, et al. [7] using ion beam irradiation of polyimide surfaces to improve Cu/Cr-to-polyimide adhesion. Adhesion was observed to improve with increasing ion dose.

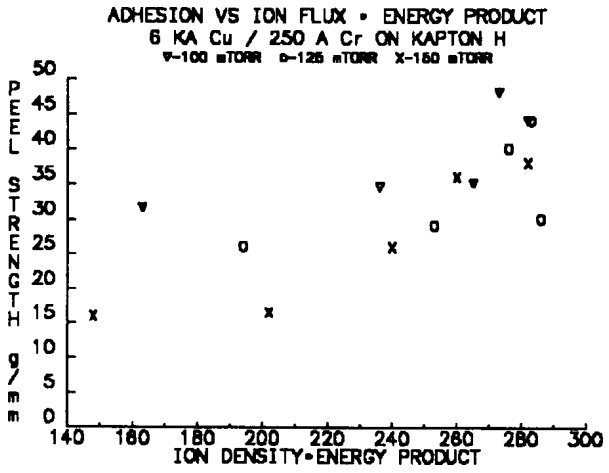


Figure 4. The product of ion density and energy versus line adhesion at various pressure levels.

In a separate study [3], pretreatment was conducted in the same roll metallization system, but downstream from an oxygen microwave plasma in place of the DC plasma system. In the downstream configuration the web was not exposed to bombardment by energetic ions. Treatment using this configuration resulted in lower peel strengths than obtained for untreated films. It was suggested that this resulted from the formation of a weak boundary layer during treatment. This is proposed to result from a reduced amount of chain scission events relative to crosslinking events as suggested to occur during plasma treatment with lower degrees of ion bombardment, [4], i.e., lower average ion kinetic energy and/or lower flux to the web.

Changes in web temperature profiles with varying power and pressure are consistent with trends observed for metal to Kapton adhesion. These results may be explained in the same manner as adhesion changes in that web temperature increases as the product of ion energies and densities at the web surface increases [5]. Figures 5 and 6 depict the temperature effects of power and pressure respectively. Increasing power results in increasing web temperature while increasing pressure results in decreasing temperature. Figure 7 indicates a general trend between web temperature and resulting adhesion at any given pressure. It also shows that high temperatures are not necessarily required to induce adequate adhesion. Different levels of adhesion can be attained at a given temperature by the combined effect of power and pressure. To study this further, an oxygen plasma was generated on a cathode located opposite the metallizer's chill drum. A low system pressure and a power density of 0.47 W/cm$^2$ was maintained. This represents a 50% increase in power over the highest level of previous experimental trials for temperature profile and adhesion measurements. Adhesion values of 66 g/mm were obtained with a maximum temperature of only 25°C as shown in Figure 8. Similar powers and pressures at the DC glow section would have yielded temperatures well over 120°C, with similar adhesion.

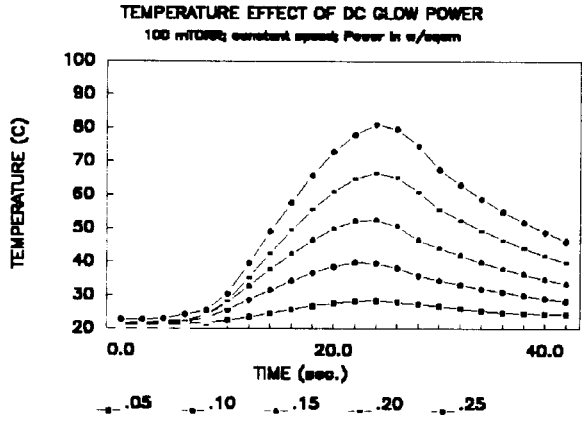


Figure 5. Web temperature profiles for various DC glow powers at constant web speed and plasma pressure.

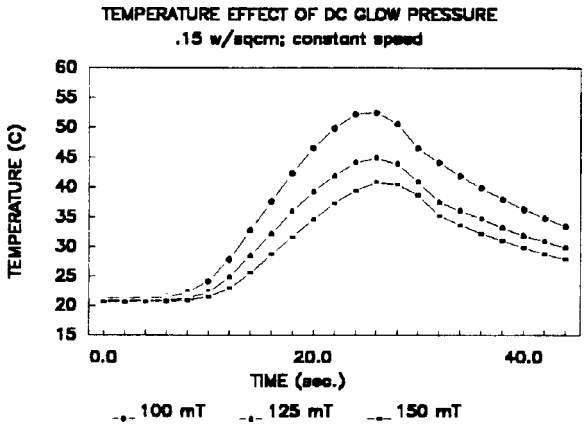


Figure 6. Web temperature profiles for various DC glow pressures at constant web speed and DC power.

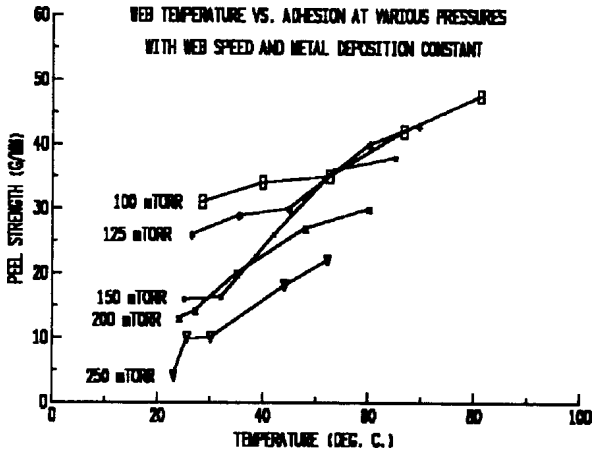


Figure 7. Line adhesion versus maximum temperature attained during DC glow process at various pressures. Five different power levels were examined at each pressure. At a given pressure greater power results in higher temperature.

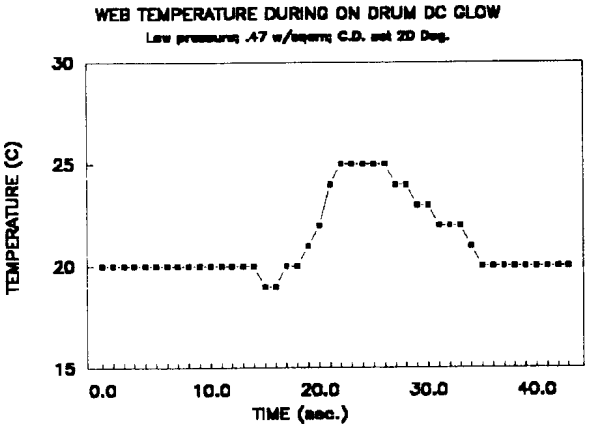


Figure 8. Web temperature profile during "on drum" DC glow for temperature control.

Excessive web temperature during DC glow treatment may have negative impact on other finished web properities such as dimensional stability and heat creasing. Characterization of material heat creasing during metal deposition is purely subjective due to the inconsistent nature of heat crease formation. Heat creasing is related to the interaction of many processing factors and inherent web properties. However, under a constant set of deposition conditions with the raw material lot kept constant, trends in heat creasing were observed relative to plasma processing conditons. Heat crease formation was observed to follow temperature excursions in plasma treatment. Higher powers and lower pressures induce more creasing during deposition, unless temperature is controlled by some means of heat sinking (i.e. on a chilled drum). It appears that some amount of adhesion must be sacrificed to produce material without heat creases.

## CONCLUSIONS

Oxygen DC glow treatment for improving metal-to-polyimide adhesion has been implemented and characterized in a roll metallizer. It was found that adhesion varied directly with applied power and inversely with gas pressure. Web temperature profiling showed similar trends. Both effects appear to be related to the relative degree of web ion bombardment. It was determined that plasma processing conditions which result in improved adhesion may negatively impact other properties of the finished material. The formation of heat creases during in-situ deposition has shown to be related to plasma processing parameters. The adhesion measurements were performed soon after deposition and may not represent material performance under environmental stressing. This is the subject of further studies.

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