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*Thin Film Adhesion: Effect of Glow Discharge on Substrate

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ABSTRACT

Glow discharge treatment of soda lime glass and silica substrates prior to depositing copper films in oil-free ultra high vacuum as well as in conventional vacuum has been found to increase film adhesion suggesting that gross contamination removal is not the only effect of importance in this method of improving film adhesion. There is evidence from Auger electron emission spectroscopy for sorption of gas from the discharge into the substrate surface layers. Desorption of gases from the substrate also appears to take place. A difference in electron emission from a variety of insulating surfaces following glow discharge was observed in a scanning electron microscope, the sign of the change depending on the nature of the discharge gas. No sputtered material from system components could be detected on the substrate and there was no detectable micro-roughening nor net surface electric charge.

INTRODUCTION

POOOR ADHESION BETWEEN thin films (less than $1\ \mu\text{m}$ thick) and the substrates on which they are deposited is a recurring problem, for example in microcircuit and optical applications¹. The technique of subjecting the substrate to a low-pressure glow discharge before film formation has long been used to improve adhesion but has not gained universal acceptance. The present work confirms that glow discharge treatment of a variety of insulating substrates prior to vacuum deposition of metal films greatly improves film adhesion and results are presented for the adhesion of copper films to soda lime glass substrates. It was therefore of interest to investigate the effect of the discharge on the substrate surface, using a variety of techniques, with a view to indicating its suitability for various applications.

EXPERIMENTAL

The glow discharge was produced by applying a 50 Hz AC high tension (4.5 kV peak to peak) between aluminium ring electrodes in a gas at a pressure of 0.01-0.1 torr (total discharge current in the range $0.6\text{-}2.4 \times 10^{-5}$ amperes per square millimetre of electrode area) and was sustained for a period of 15 minutes. The substrate, located in the positive column of the discharge, was

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shielded from direct line of sight of the electrodes. This arrangement minimized the chance of substrate bombardment by high energy positive ions and electrons².

Two types of vacuum system were used: a conventional, unbaked, silicone oil-diffusion pumped system having a residual pressure of 10^{-5} torr (mainly water vapour) and an oil-free, getter-ion pumped stainless steel ultra high vacuum system which received a 10 hour bake at 250°C to achieve a residual pressure of 10^{-9} torr. The discharge was maintained in a flow of gas in the conventional system but was maintained in a static gas pressure in the UHV system. Mass spectrometric analysis indicated that the residual pressure in the UHV system consisted mainly of carbon monoxide, carbon dioxide and water vapour with total hydrocarbon in the low 10^{-11} torr range. In both systems one half of the substrate area was masked from the discharge. After pumping away the discharge gases, the film was evaporated on to the whole area from a hot source. This enabled a direct comparison of the effect of the discharge on film adhesion to be made. The arrangement for glow discharge treatment and metallizing the substrate in the UHV system is illustrated in Figure 1.

Two methods of pre-cleaning the glass substrates were used: one involved several steps, the main features being a rub with a slurry of magnesium hydroxide (pharmaceutical grade), treatment with Decon 75 detergent (Medical-Pharmaceutical Developments Ltd., Shoreham-by-Sea, Sussex) in an ultrasonic bath and a final isopropanol vapour rinse; the other simply involved immersion in dilute nitric acid followed by rinsing with distilled water in a Soxhlet extractor (*i.e.* a method involving no organic agents).

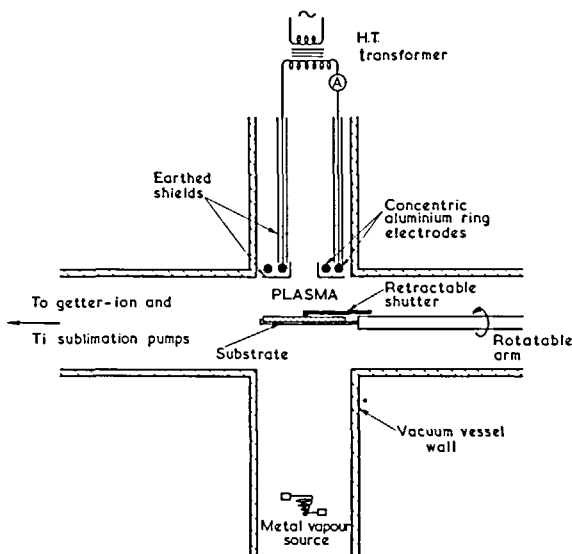


Figure 1. Arrangement for glow discharge treatment and metallizing of substrate in ultra high vacuum. Scale: metal vapour source to substrate distance approx. 70 mm.

Film adhesion was assessed by glueing brass rods vertically to the film using a fast-setting cyanoacrylate adhesive (Eastman 910) and, using a Tensometer and load cell, measuring the force applied horizontally to the rod required to pull the film from its substrate¹. As applied this is essentially a tensile test of the adhesion; a simple stress distribution has been assumed in deriving film adhesion values which should therefore be regarded as approximate.

RESULTS AND DISCUSSION

In Figure 2 values of the adhesion of about twenty copper films (thickness range 0.3 to 0.8 μm) vacuum deposited on soda lime glass substrates under various conditions are plotted against time elapsed from when the films were prepared. Little difference was found within the scatter of the values between films aged in the atmosphere and in vacuum, nor between the two types of precleaning used.

Films prepared in the UHV system, on surfaces not subjected to glow discharge, have a higher adhesion than those prepared in the conventional system and retain a higher adhesion with time.

When glow discharge is applied, the difference between the two vacuum systems is less apparent, but the arithmetic means of the adhesion values in both systems are markedly higher and remain high with time although there is still a gradual overall decrease. There was no detectable difference in the improvement of film adhesion between air and nitrogen discharges.

It may be noted that for both vacuum systems films formed on substrates which had been exposed to the discharge were markedly more scratch

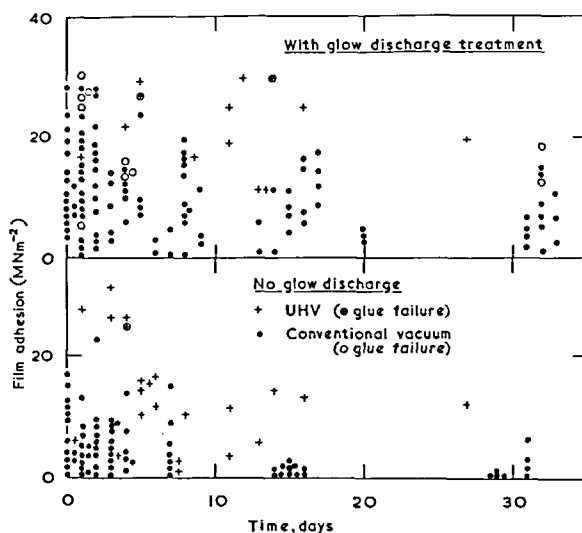


Figure 2. Ageing of the adhesion of thin copper films to soda lime glass substrates prepared under various conditions.

resistant. However, scratch resistance is not considered to be simply related to adhesion³.

The glow discharge arrangement used subjects the substrate to bombardment by low energy positive ions and electrons, and exposes it to excited atoms and molecules and to various radiations. In the following sections some possible effects of this complex plasma on the substrate surface and their relative importance in influencing film adhesion in our experiments are considered. Such effects may of course be closely interrelated.

Alteration of Chemical Composition of Substrate Surface Layers

Samples of soda lime glass and silica substrates were exposed over half their areas to glow discharges in a number of gases in the two vacuum systems. The substrates were then removed from the vacuum systems and the exposed and masked surfaces examined by Auger electron emission spectroscopy. This sensitive surface technique gives an element analysis of approximately the first three atomic layers only and is capable of detecting sub-monolayer concentrations.

All samples from both vacuum systems showed a high surface carbon concentration (50% or more), the remaining elements being mainly silicon and oxygen. In the case of samples from the conventional vacuum system the carbon level was lower on the area exposed to the glow discharge while the reverse was the case for the UHV system. The analysis could not distinguish whether the carbon was in elemental form or combined, *e.g.* as oxide or hydrocarbon, although its desorption in several cases under the influence of the analyzing electron beam (which made quantitative analysis difficult) suggested that it was in compound form. However, contamination of the samples with carbonaceous material due to the unavoidable exposure to the atmosphere complicates the picture because of the possibility of differential contamination of glow discharge treated and untreated surfaces from the two systems; no definite conclusion can therefore be drawn with respect to carbon concentration at the substrate surface immediately after glow discharge in the systems.

No sodium could be detected in the surface layers of any of the soda lime glass specimens and the indicated calcium concentration was only one percent or less. This was probably due to a leaching effect by the pre-cleaning treatments.

It may be noted that ellipsometric measurements on glass and silica surfaces showed changes following glow discharge treatment which may be interpreted in terms of compositional changes of the surface layers⁴.

Removal of Organic Contamination: Although glow discharge can remove organic contamination (*e.g.* several molecular layers of radioactively labelled stearic acid were removed from steel surfaces⁵ and can therefore "clean" a surface, the fact that the glow discharge still improves adhesion on a baked-out surface in an oil-free UHV system indicates that such gross contamination removal is not the only factor of major importance.

Formation of Polymeric Films etc: It is well known that highly cross-linked polymeric films can form on surfaces exposed to electron and ionic bombardment in the presence of organic molecules⁶ and moreover that metal atom sticking coefficients might be expected to be high on such films⁷. However, improved adhesion as a result of glow discharge treatment is still observed in UHV where such polymeric film formation on the substrate should not be significant. It is possible, however, that dissociation in the discharge of light carbon-containing molecules (e.g. CO, CO₂, CH₄, etc.) present in the vacuum system may lead to the formation of carbonaceous film on the substrate surface⁸. The concentration of water vapour in the discharge may determine the extent to which such a film could form—the production of hydrogen and oxygen atoms in the plasma tending to retard its formation. Such an effect might account for the results of the Auger analyses of these surfaces, i.e. that, subject to the uncertainty in the analyses due to atmospheric exposure mentioned above, there was a higher carbon concentration on the glow discharge treated relative to the untreated surfaces in the baked UHV system in contrast to the unbaked conventional system.

Deposition of Extraneous Material on the Substrate: There was no evidence from the Auger analyses of samples from both vacuum systems of any material (e.g. aluminium, titanium, stainless steel constituents) being sputtered on to the substrate from the surroundings and which might have led to an enhanced nucleation density and adhesion of the subsequently deposited film.

Gas Sorption-Desorption: It seems probable that under the influence of the discharge there will be desorption of gaseous species (e.g. water) from the substrate and also that both adsorption on the surface and sorption into the substrate of new gas species will take place^{2,9}. In the case of discharges in spectroscopically pure nitrogen at a static pressure in the UHV system, mass spectrometric analysis immediately after removal of the bulk of the gas at the end of the discharge period showed that the original partial pressures of residual gases had been enhanced and that, in addition, nitric oxide and ammonia had been formed, indicating interaction of the plasma with exposed surfaces. The Auger analyses indicated a nitrogen content of 0.1-0.3% on the glow discharge treated silica and soda lime glass surfaces and as much as 2% in the case of a silicon single crystal with an air oxide layer; traces of nitrogen were also found on glow discharge treated diamond.

The decrease in copper film adhesion with time (Figure 2) may result from the diffusion of gases, e.g. H₂O, CO₂ from underlying layers in the substrate to the copper-glass interface. When the substrate is subjected to glow discharge it is possible that the surface layers are denuded of these gases which are perhaps replaced by other products from the discharge which may then act as a barrier to diffusion of these gases from deeper layers to the interface resulting in the slowing in the rate of decrease in adhesion observed.

Alteration of Substrate Surface Topography

- It seemed possible that the discharge could sputter surface components to different extents leading to micro-roughening and “keying” of the subsequently deposited film. Using multiple beam interferometry no difference in surface roughening of glass greater than 3 nm peak to peak could be detected. It was also found that if one half of a single crystal face of silicon or of magnesium oxide was subjected to a glow discharge in nitrogen in the UHV system, it had an identical reflection high energy electron diffraction pattern to the untreated half. The patterns exhibited sharp Kikuchi lines with only occasional strong Laue spots indicating a high degree of surface smoothness¹⁰. However, it must be pointed out that it is experimentally difficult to detect changes in topography of the order of atomic dimensions and these may be important in influencing adhesion.

Alteration of Electrical and Electronic Properties of Substrate Surface

Although it is known that there is some disturbance of the electrical properties of insulating materials by the discharge^{2,11}, in the particular case of soda lime glass no net electric charge could be detected to a limit of 10^{-13} coulombs mm^{-2} by electrometer probe techniques¹². While this latter observation involved exposure of the sample to the atmosphere after glow discharge, it has since been confirmed in this laboratory¹³ using a sensitive electrometer probe sited in the conventional vacuum system that provided the electrodes were electrically floating an AC glow discharge produced no detectable net charge on a variety of insulating substrate surfaces mounted on an earthed metal backing. In fact exposure of about one minute to the glow discharge removed any charge remaining on the insulating surfaces from their previous chemical cleaning and handling. Substrate materials examined included soda lime glass, silica and various plastics.

The following observations indicate that the glow discharge can alter the surface electronic states of insulating materials¹⁴. If one half of a glass substrate, for example, is subjected to the discharge and the whole then examined in a scanning electron microscope operated in the emissive mode a different emission of electrons is obtained from the two halves. When an air or oxygen discharge is used the emission from the area exposed to the discharge is enhanced; when nitrogen, hydrogen, water vapour or argon are used the emission is decreased. This effect has been observed on a variety of insulating substrates including silica, magnesium oxide and diamond and persists after long exposures to the atmosphere.

A possible explanation of the altered emission in the case of glass and other insulators containing oxygen is that under the influence of the energy of the discharge and the presence of excited atoms, gas atoms are sorbed into the glass surface (*cf.* Auger evidence above). If the sorbed atoms are electron acceptors (*e.g.* oxygen) then the density of electrons in excited energy states is increased by a process of electron transfer from the doubly charged oxygen

ions of the glass to the sorbed atoms, and these electrons are more easily ejected under the influence of the incident primary electron beam in the microscope, leading to an enhanced emission. A decrease in the number of electrons in excited energy states compared with the untreated glass will occur when the sorbed gas atoms (*e.g.* nitrogen, argon) displace oxygen from the glass. The persistence of the effect is in accordance with the expected long lifetimes of electrons in such excited states.

However, it should be noted that an improvement in copper film adhesion to glass is obtained for both air and nitrogen glow discharges so that the effect on film adhesion may relate to a change in surface emission characteristics but not directly to the sign of the change. Some authors do however report that glow discharges in air and oxygen are more effective than those in other gases in increasing the adhesion of aluminium films to glass⁹. It is interesting, also, that heating the glass to 250°C in the UHV system after glow discharge destroyed the improvement in film adhesion and that heat treatment also eliminated the difference in electron emission observed in the scanning electron microscope. Heating would be expected to restore the normal population of electrons in excited states in the glass.

Effect of Glow Discharge Treatment of the Substrate on Film Microstructure

While differences in the optical transmission or reflectivity of films formed on surfaces exposed to and masked from the glow discharge were clearly visible, it was difficult to detect really marked differences in the film microstructure. Transmission electron micrographs indicated a tendency to more continuous film formation in the early stages of growth on substrates which had been subjected to glow discharge (illustrated in Figure 3 for the case of tin depositing on carbon). This suggests a tendency to denser

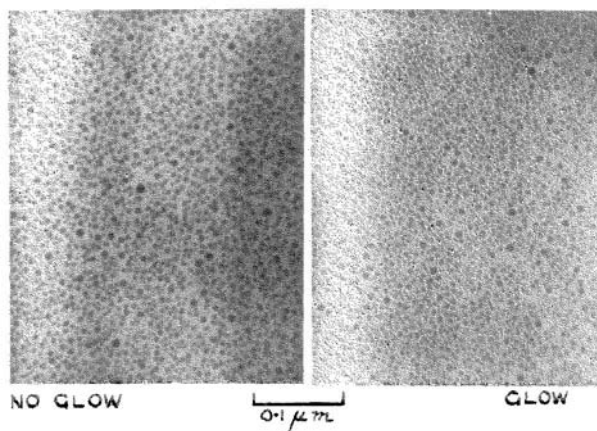


Figure 3. Typical transmission electron micrographs showing effect of glow discharge treatment of a carbon film substrate on the subsequent nucleation and growth of a tin deposit.

In the case of no glow discharge pretreatment the tin deposit is concentrated in circular, isolated islands of about 7 nm average diameter (dark spots). With glow discharge pretreatment the tin appears to be distributed between islands and a more continuous background film.

nucleation and enhanced lateral growth of metal islands and is similar to but not so marked as that observed on surfaces which have been charged either by direct polarization or by electron bombardment^{15, 16}.

This effect may be interpreted in terms of a larger number of sites on the treated surface at which metal atoms can be trapped after impingement and surface migration. These sites of stronger binding may act as "pinning" sites for the film crystallites and contribute to the enhanced adhesion. Such sites may be formed in any alteration of surface chemical composition, topography or electronic character discussed above.

SUMMARY AND CONCLUSIONS

The complex action of glow discharge treatment of insulating substrates in improving metal film adhesion has been considered in terms of alterations to the substrate surface chemical composition, topography and electrical or electronic properties.

Surface Chemical Composition: Removal of gross contamination (*i.e.* "cleaning") is not the only factor of importance; sorption of gases from the plasma has been observed and desorption of gases and vapours from surface layers seems probable; there is no evidence for material from the vacuum system components being sputtered on to the substrate.

Surface Topography: No micro-roughening could be detected within the limits of the techniques used.

Surface Electrical and Electronic Properties: No net surface electric charge was detected but the electron emission was altered, the sign of the change depending on the nature of the discharge gas.

It is concluded that the action of a glow discharge under clean conditions relates to changes in the chemical composition (particularly gas concentration) of the substrate surface layers and to the consequent modification of the electronic state of the surface. These changes may improve film adhesion through formation of additional "pinning" sites and increasing the overall strength of bonding at the interface.

From the point of view of the practical applications of glow discharge treatment in improving thin film adhesion to dielectric substrates the following conclusions may be noted from this work.

1. When glow discharge is applied to the substrate there is little advantage to be gained from using an oil-free UHV system as compared to a conventional system.
2. The chemical composition of the substrate surface may be altered and changes in its optical properties are usual.
3. No micro-roughening of the substrate takes place on a detectable scale so that the technique may be used where it is necessary to preserve the original surface topography.
4. While there is no net surface electrical charging of the substrate, alterations to the number of electrons in excited energy states appear to take place and may be a disadvantage in certain microelectronic applications.

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