



MULTIPLE MIRROR TELESCOPE OBSERVATORY

Smithsonian Astrophysical Observatory and Steward Observatory, University of Arizona

Reply to: MMT Observatory
University of Arizona
Tucson, Arizona 85721
(602) 621-1558

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Glow Discharge Cleaning — Review and Recommendations

Barry A. Sabol

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Abstract

A summary of literature concerning the glow discharge cleaning of glass substrates for evaporative aluminum coatings is combined with an overview of glow discharge physics to provide a foundation for the design of the Upgrade/Conversion glow discharge system. Measurements taken and procedures currently used at the Steward Observatory Sunnyside facility as well as areas of concern for the Upgrade/Conversion system are included in the appendices.

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I. Introduction

A recent survey of the literature on glow discharge cleaning has found confusing accounts of the cleaning process, contradictory interpretation of experiments, and disagreement over fundamental processes. These problems are due, in part, to the unfortunate timing of the discovery that much of the cleaning action is provided by disassociated oxygen. Also contributing is considerable confusion and disagreement in the plasma physics of glow discharge.

The most extensive studies on the cleaning action of glow discharge were done by Holland.^{1,2,3} The importance of oxygen in the cleaning process was evidently not realized until late in his series of papers. Consequently, much of his work on the cleaning action of ion and electron bombardment is tainted with effects due to chemical reactions with oxygen. Most subsequent studies pertaining to substrate preparation for evaporative coatings are short and provide insufficient detail. Reports on the glow discharge designs of recently constructed large aluminization chambers^{4,5,6} are basically recitations of Holland's recommendations.

Physically, the process is an extremely complex one and, for the most part, cannot be modeled by an idealized plasma. Particle species are numerous, even in a single, inert discharge gas. Electrons, ions, and neutrals each have two or more classes of velocity distributions. The discharge is not in thermodynamic equilibrium so that thermal velocities differ from species to species. A multitude of excitation and ionization mechanisms are responsible for maintaining the discharge. Disagreement over experimental studies reflects the general difficulty in isolating effects in a plasma and the particular difficulties of low particle energies and plasma sheath formation (which screens charged objects from the plasma—including probes).

This report attempts to summarize the consistent features of this confusing literature into a coherent picture of the cleaning process that can lead to an informed design for an AC glow discharge system for the 6.5 m and 8 m aluminization chambers. The fact that glow discharge cleaning of astronomical mirrors is successfully accomplished regularly without such attention to detail may suggest that current designs are adequate. Nevertheless, careful scrutiny of the process seems warranted because: (1) the reduced spacing of the glow ring to mirror surface from one mirror radius to about $1/4$ mirror radius, (2) the cost, labor, and downtime associated with the aluminization procedure preclude normal testing and debugging periods, and (3) there is considerable potential for heating the substrate and/or cryopumping components during the discharge, mostly to the detriment of the aluminization process.

An attempt was made to assign particle energies, number densities, and temperatures to the various regions of the glow and to describe their variation with voltage and pressure. In spite of numerous investigations of various aspects of the discharge process, there are very few "good" data pertaining to these issues and most of them pertain to noble gases rather than oxygen. It is interesting that the glow discharge, which is relatively simple to produce, is such an enormously complex phenomenon.

This report will hopefully aid the reader in the realm of physical insight as it did the author. Modeling information, on the other hand, remains scarce. The final section presents some testing procedures that may alleviate this deficiency.

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II. Adhesion

"Aged" glass (exposed to air) has a surface layer of OH groups that can retain neutral water molecules by covalent hydrogen bonds and/or a layer of fatty acids, as noted by Bateson.⁷ The contamination layer is not removed by chemical cleaning but can be removed by sparking, flaming, heating, or glow discharge in the presence of oxygen. Once treated, the surface should be in a highly reactive state because of the exposed OH groups which are not removed by these methods. In a clean vacuum, the deposited vapor can react chemically with the OH centers displacing hydrogen.

Holland¹ found laboratory examples of this behavior when he compared the surface properties of glass fractured in vacuum to that of glass fractured in air. The vacuum fractured surfaces absorbed silicone vapors from the diffusion pump oil while those fractured in air showed no absorption of silicone—even after glow discharge cleaning. He concluded that the "aged" surfaces are covered with OH⁻ ions that are not removed by the glow and that screen out the silicone.

Glow discharge cleaning of substrates has been practiced for many years. The first applications to the aluminization of astronomical mirrors were done by John Strong^{8,9} who used air as the discharge gas. Later attempts by other workers to improve the process using pure inert gases led to poor results. Since then, several investigators have found that the presence of oxygen in glow discharge cleaning is necessary for improved adhesion. Figure 1 shows the results of one such study¹⁰ for gold films. Holland² mentions poor adhesion of aluminum films when the discharge gases were hydrogen and argon rather than air. There are other reports, however, in which the use of argon produces somewhat more favorable results.

Bateson⁷ also found that the presence of oxygen (even in well degassed vacuum systems) plays an additional role in adhesion. Residual oxygen is gettered during deposition by chemisorption with aluminum, and as the deposited layer builds its character changes from oxide to metallic lattice as the oxygen in the region becomes depleted. These results may be connected to those of Mattson¹¹ who found that the surface roughness of aluminum films deposited in the presence of oxygen at 20 Å/sec increased dramatically when the oxygen partial pressure reached 2×10^{-6} torr (Figure 2). Films deposited similarly in argon showed no such increase. This may indicate that the "wall" gettering at this evaporation rate is insufficient to deplete the oxygen level at this partial pressure which leaves the coated substrate gettering a critical amount of oxygen throughout deposition.

Aluminum bonds well to its oxide and the oxide bonds well to glass. This is also the case for the more reactive metals such as chromium, titanium, and tantalum while noble metals, such as silver and gold, adhere poorly to glass. An oxide bond can grow after deposition through diffusion of oxygen from the film surface to the film-substrate interface. An example of this improvement in time is shown in Figure 3.

Sandwich structures are often used to enhance adhesion. Common examples are silver, gold, or aluminum over chromium. The delay between deposition of the two films must be kept at a minimum to prevent an oxide layer from forming on the chromium.

Aluminum coatings prepared by evaporation in sequence from several sources² tend to have a laminar structure of metal and oxide films.

Substrate heating due to charged particle bombardment or radiant heating also leads to improved adhesion. In the case of aluminum, however, reflectivity degrades with increasing substrate temperature². This effect may not be significant at 10-20°C above ambient. Nevertheless, substrate heating should be kept at a minimum and as uniform as possible.

In summary, improved adhesion of aluminum films to glass substrates is due to removal of the surface layer of fatty acid/water, the conversion of the substrate to a reactive state, and the presence of a small partial pressure of oxygen to react with the arriving vapor to produce the oxide bond.

III. Physical Structure of the Discharge

The following description includes ideas and results from several sources^{13,14,15} and refers to DC glow discharges in a glass or ungrounded tube.

Three figures are used to portray the basic characteristics of the glow discharge. Figure 4 describes the electrical breakdown of some gases. Figure 5 shows the structure of the discharge in terms of light intensity, voltage, electric field strength, and net space charge. Figure 6 gives the current-voltage behavior over a current range of several orders of magnitude.

The breakdown voltages of some gases (Paschen curve—Figure 4) are given as a function of pd (pressure \times anode-cathode distance). The minimum of the Paschen curve can be understood as follows: If, at constant d , the pressure is increased, the electrons cannot gain enough energy for ionization between collisions without raising the accelerating voltage. Lowering the pressure at constant d reduces the number of collisions to the point where the number of ions necessary for discharge cannot be supplied without raising the electron voltage. The same idea applies when varying d at constant pressure.

At a pressure below a few torr, the discharge structure becomes apparent in a series of dark spaces between glowing regions (Figure 5). This series of zones is the resulting steady state condition of the plasma. They are arranged to satisfy the criteria for overall charge neutrality, equal current through the discharge cross-section, and other conservation conditions. In a conceptual sense, $I = \text{current density} \times \text{area} = \sum n_i q_i v_i A$ for the various species and $I = \text{constant}$ can be satisfied by different values of n_i and v_i (as the zones attest). Arc discharges and other constrictive plasma phenomena display variations in the area, A .

Cathode Region

The cathode dark space is a region of high electric field, high particle velocities (v), and low particle densities (n). If the tube were at high vacuum, the electric field would be constant across the anode-cathode distance, d , (cold cathode—no thermoionic emission). Instead, the plasma has arranged itself so that the majority of the potential difference (the cathode fall) is concentrated over a distance, d_c , the dark space length.

In terms of the Paschen curve (Figure 4), as the voltage comes up to breakdown values (for a particular pressure), the value of the anode-cathode distance (d) yields a point on the curve that may be in either direction from the minimum voltage. After breakdown and for a considerable current range (10^{-6} - 10^{-3} amps, normal glow region—Figure 6) the electrode voltage and the effective anode-cathode distance (dark space length— d_c) have changed so that the discharge is operating at the Paschen minimum. This is the optimum configuration in which the necessary ionization is produced to maintain the current.

The cathode dark space contains the driving mechanisms for conductivity production in the rest of the discharge. At the cathode, the electrons required to maintain the discharge are supplied by positive ion bombardment. The cathode glow (Figure 5) is caused by the recombination of these ions with slow electrons. The "slow" electrons dislodged by the incoming ions are accelerated out of the dark space, becoming the "fast" or primary electrons. This leaves a net positive space charge in the cathode vicinity due to the ions, which causes a large voltage gradient so that most of the tube voltage is taken up in the cathode fall. Current in this region is supplied mainly by the ions flowing to the cathode. Elsewhere in the glow, most of the current is due to electron flow.

Some of the electrons accelerated out of the cathode region contribute to ionization in the dark space (mainly the lower energy part of the electron distribution). These electrons (which lose energy in collision), other low energy electrons produced by ionization, and thermal electrons contribute to further ionization. Eventually, the ionization multiplies quickly over a short range creating the negative glow.

Many of the fast electrons, however, penetrate all the way to the anode (depending on pressure) by virtue of their decreasing collision cross-section with increasing energy. For example, in a 700 V argon discharge the electrons have a range of 5.0 cm at 1.0 torr and 100 cm at 1.0 mtorr.

The interactions in the dark space and negative glow are poorly understood. There is significant disagreement on how much ionization occurs in the dark space. Also, no one seems to know whether the ions that bombard the cathode originate in the negative glow, in the dark space, or both. Estimates cover both extremes.

The behavior in the cathode vicinity that accounts for the normal and abnormal glow regions of the current-voltage graph (Figure 6) is interesting. The normal glow region is characterized by the fact that raising the supply voltage raises the current but has little effect on the discharge voltage (230 V aluminum). This is because the cathode glow only partially covers the electrode area at the low current end. As the supply voltage is raised, the area of the cathode glow increases while the current density remains constant in accordance with $j/p^2 = \text{constant}$ (Figure 7). This behavior continues until the cathode glow fully covers the electrode area. Referring to the Paschen curve (Figure 4), since pd_c is at optimum value ($= (pd)_{min} = \text{constant}$), the dark space length, d_c is inversely proportional to pressure in the normal glow region. Extending the dark space all the way to the anode, however, extinguishes the discharge.

Once the cathode glow is of maximum area, increasing the supply voltage raises the discharge voltage. This marks the beginning of the abnormal glow region (Figure 6) where most glow discharge cleaning is done. Here, neither j/p^2 nor pd_c are constant. The current density increases with rising supply voltage while the dark space length, d_c , decreases (V_c rises). The cathode region assumes the characteristics which at breakdown would represent the left-hand portion of the Paschen curve (Figure 4).

In the abnormal glow region the effect of gas pressure (at constant V_c) on the ion energy distribution is small. As previously mentioned, raising V_c at constant pressure causes the dark space to decrease in thickness. As a result, a relatively larger proportion of high energy ions will reach the cathode. A sample energy distribution for Ar^+ ions is given in Figure 8. Most have energy less than 0.20 V. Ions with similar cross-section (such as Ar^{++}) arrive at the cathode with higher energy. Figure 9 shows that approximately 12% of the Ar^{++} ions arrive at the cathode with $V \sim V_c$ (although the percentage of ions that are Ar^{++} is not given). The energy distribution of the secondary electrons emitted at the cathode is, however, only weakly dependent on the incident ion energy. Ranges are 3-4 eV for argon, 3-9 eV for neon, and 4-12 eV for helium.

Continuing to raise the supply voltage raises the discharge voltage and current density until cathode heating changes the nature of the discharge through increased electron production (thermoionic emission). The conditions for arc discharge are met (Figure 6) and the cathode glow contracts into an arc.