Some comparisons in the application of End-Hall and Cold Cathode ion sources in the conversion of SiO to SiO_2

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ABSTRACT

Silicon dioxide has many desirable properties as a coating material for the visible and near IR spectrum. These include low index, high transmittance, good adhesion, and environmental durability. The deposition of the material from solid discs or granular forms using an electron beam gun tends to have a fluctuating angular distribution. This causes reproducibility problems in some critical optical coating processes. Silicon monoxide can be evaporated from a resistance source with a highly reproducible deposition pattern, but it does not have the low index and high transmittance required. We report on attempts to develop processes which convert the SiO to SiO_2 during deposition by the use of ion assisted deposition. The additional oxygen must be supplied in a sufficiently energetic process to provide the material conversion during or after the SiO deposition on the surface to be coated. The deposition rate (10Å per second), the uniformity, and the repeatability of the processes must also be adequate for the production of the product at an economical rate. These experiments have been done with both an End-Hall and a Cold Cathode ion source. A comparison of the results and behavior observed with each type of ion source are reported along with recommended process parameters to be used with each.

Keywords: Silicon Oxides, Ion Assisted Deposition, End-Hall Ion Source, Cold Cathode Ion Source

1. INTRODUCTION

Silicon dioxide (SiO_2) is widely used as a low index material for visible and near infrared thin film coatings. Common practice has been to deposit SiO_2 from granular material or solid plates in an electron beam gun. These processes are notorious for "tunnelling" wherein the evaporation/sublimation creates cavities that tend to be more favored evaporation areas than the surrounding areas and become deeper while the other areas are not eroded. This instability results in a changing rate and angular distribution of the evaporated material. This in turn causes non-reproducible results in the deposited layers. The more demanding coatings can be severely hindered by these effects. We reported earlier[1] on alleviating these problems by evaporating SiO and further oxidizing it with ion assisted deposition (IAD). SiO evaporates/sublimes readily from a resistance source and is found to have a very reproducible distribution and rate from a properly configured source. We currently use an R. D. Mathis Company SO-23185 source which has internal baffles to insure uniform output at the source aperture. The problem is then to oxidize this straw colored SiO to the clear SiO_2 ("gold") that is desired. This is like the tale of Ruplestiltskin turning "straw into gold." At elevated temperatures and a slow enough rate, this oxidation can be accomplished by deposition of the SiO in an oxygen background. However, in most applications of the type of interest for production, rates of 10Å per second are not feasible because full oxidation does not take place at practical temperatures and pressures. A solution to this problem is to use IAD to provided the needed activated and energetic extra oxygen. We will describe our experience with two appropriate IAD sources which we have used to convert SiO to SiO_2.

2. ION GUNS

Our experience to date has included three types of Ion Guns: the Ion Tech gridded Kaufman gun, the Denton Cold Cathode CC-102R, and the Commonwealth Scientific Mark II End Hall source. In all cases, our process speed is limited by the rate at which we can deposit the materials and obtain the desired properties. This rate is limited in turn by the ion current density which can be provided. We therefore want to operate the ion guns at the highest beam power practical. We also have learned from the literature and our own observations that there is an upper limit on the electron volts (ev) of the ions. Excess ev will cause damage to the deposited materials

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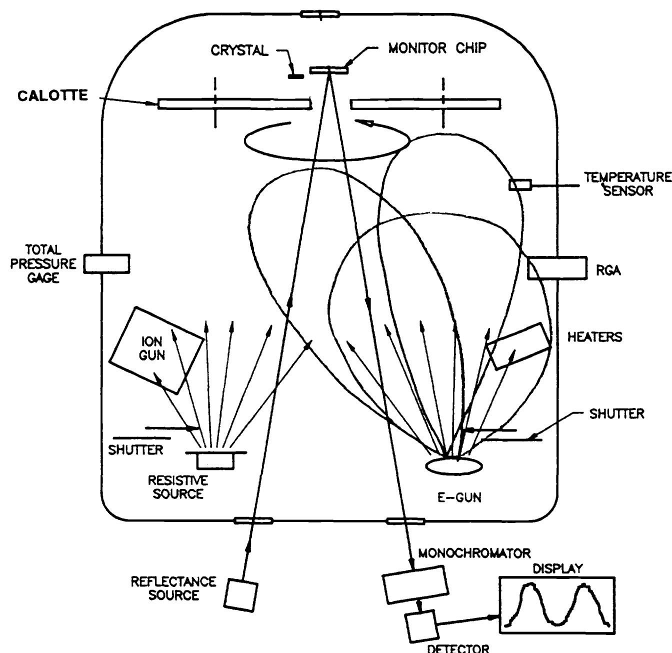

Fig. 1. Typical box coater chamber configuration illustrating the variable distribution directions and amounts found when depositing SiO_2 from an E-gun.

and therefore to the optical properties, particularly absorption. The power density of the ions cannot practically be increased by added voltage beyond some point such as 300ev. Our principal requirements for the SiO to SiO_2 conversion are processes which run for many hours. It is our understanding (and experience) that the filaments and grids of the Kaufman type source could not be expected to survive the full power oxygen operation required, and therefore we made no attempt to use these guns in the present case. The Cold Cathode gun was said to "prefer" operation with oxygen over argon because of sputtering effects. Therefore, our first efforts were with the Cold Cathode gun. The End Hall gun has some similar characteristics to the Cold Cathode and was also developed into a satisfactory solution to our requirements. In both cases, we operate at the maximum power capability of the guns consistent with stable and long term operation. The general configuration of the chambers used is shown in Fig. 1.

2.1 Cold Cathode Source

The cross section of the Cold Cathode Source is seen in Fig. 2. The only papers of which we are aware on this gun are in the references[1-5]. A molybdenum anode is surrounded by an aluminum cavity which is in turn surrounded by a ring of permanent magnets which produce an axial magnetic field. The gas is admitted to the gun chamber through six (6) small orifices below the anode ring by a gas flow controller. The gun is water cooled. It can be biased to offset the voltage of the whole system with respect to ground, but we have no experience with this; we have only operated at zero bias volts. There is a tungsten neutralizer over the aperture which we typically operate at its maximum current of 20 amps. The neutralizer voltage will range from 12 volts upward with age. The filament will last more than 10 hours and is very easy and inexpensive to replace, so that it is not as big a problem as in a Kaufman gridded type source. The power supply has three controls: neutralizer amps, bias volts, and drive amps. There are additionally displays of drive volts and beam amps. We set the neutralizer to maximum current, the bias to zero (but not off), and control only the drive volts through the drive current and the gas flow.

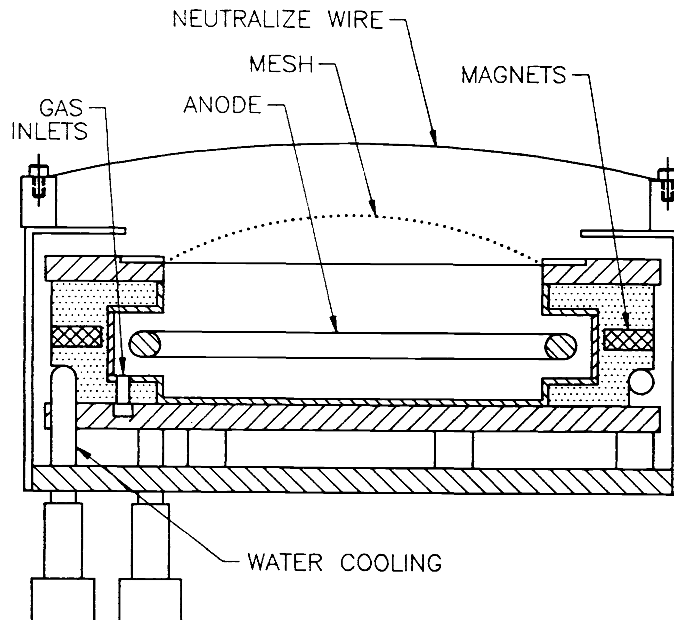

Fig. 2. General cross section of the Denton CC-102R Cold Cathode ion source used in this work.

The ion source is aimed for best uniformity of result on the rotating calotte. The aim point is approximately midway between the points on the calotte which are directly over the silicon monoxide and titania sources.

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These sources have uniformity masks a few centimeters below the calotte and directly over the sources. The titania is evaporated from an electron beam gun diagonally opposite the silicon monoxide source and used as the high index material.

2.1.1 Cold Cathode Source Characteristics

The behavior of the Cold Cathode Source is a strong function of the gas pressure, flow conditions through the Cold Cathode cavity, the neutralizer emission, and the "cleanliness" or surface conditions inside the ion source cavity.

The gas to the source passes through a gas flow controller before it enters the source. The flow controller is calibrated for oxygen flow in standard cubic centimeters per minute (SCCM). When another gas is used the calibration would be different. Figure 3 shows the chamber pressure with indicated oxygen and argon flow in one of our Balzers BAK760's with no deposition or IAD in process. The dashed line in Fig. 3 shows how this changes with deposition and IAD with oxygen ions. The silicon monoxide getters the oxygen very readily and effectively increases the pumping speed of the overall system.

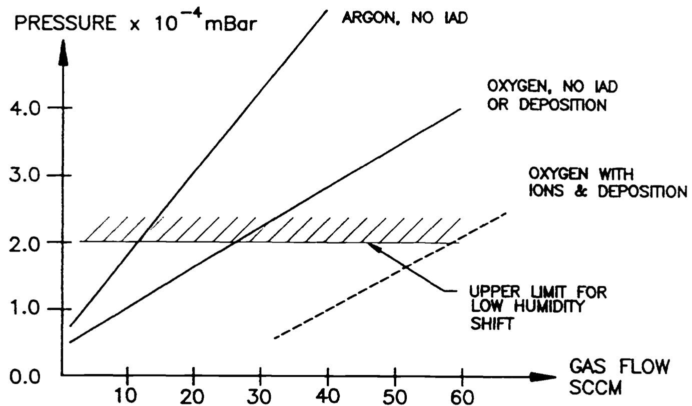

Fig. 3. Chamber pressure versus indicated gas flow in a Balzers BAK760 with and without oxygen IAD and SiO deposition. Upper limit on chamber pressure to produce no humidity shift in coatings is shown from our experience.

We assume that the drive voltage is somewhat linearly related to the actual output beam voltage and similarly that the drive amps is related to the beam amps. The drive voltage is primarily a function of the drive amps applied and the gas flow through the source. Figure 4 shows this relationship. There is also a significant effect of source cleanliness by which we mean the state of deposits which build up in the cavity with use. We find it necessary to clean the source periodically as we will describe below.

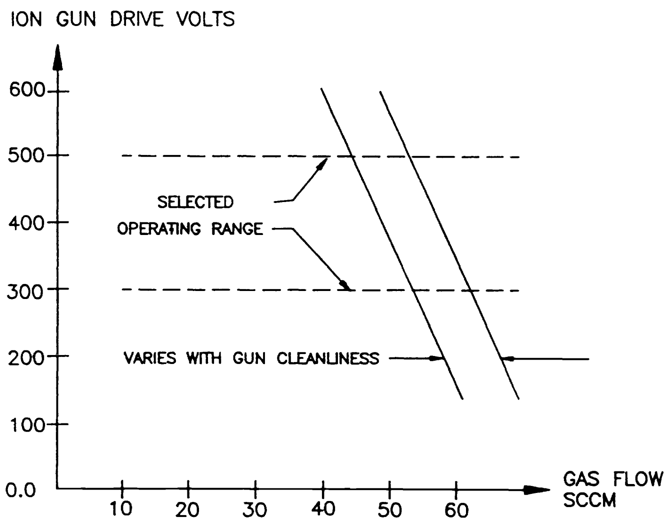

Fig. 4. Operating conditions of drive volts versus gas flow for the CC-102R source in a Balzers BAK760 chamber.

When operating the source with argon, we found that the drive voltage decreased with neutralizer amps up to some current and then increased with additional current. When oxygen was used the same general behavior was seen, but the maximum available neutralizer current of 20 amps was reached before an inflection was observed. We believe that the lowest drive voltage at a maximum drive current is desirable in our application. We therefore wonder if it would be beneficial to have an extended neutralizer capability to reach the drive voltage minimum with oxygen.

If the source is operated without enough neutralization, we observe sparks on the substrates and fixturing, and arcing indications on the source power supply. We have seen no ill effects of excess neutralization, so we always apply the maximum available. We observe that, if the pressure in the cavity of the source drops too low, the drive voltage increases and at some point the source will arc. This seems to disrupt the steady operation of the ion beam conditions, and therefore we avoid this condition if at all possible.

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Our early experiments with the largest standard aperture supplied with the source pointed to the desirability of keeping the drive volts below 400 for minimum absorption in the films and above 300 for maximum densifying effect. We prefer to operate between 300 and 400, but can get reasonable results up to 500 drive volts. This is indicated in Fig. 4. We seldom approach the lower limit of 300 with the large aperture because the gas flow required for that with the typical source conditions and the resulting chamber pressures would be too high to allow the production of the desired robust films.

Our more recent use of the sources in a 1100mm chamber have been with a reduced aperture in the ion source. This increases the pressure inside the source cavity while decreasing the chamber pressure for a given gas flow. In this configuration and in this chamber, the operating conditions are typically: 20-40 sccm oxygen flow, 1000ma drive current, 250-300 drive volts, and resulting chamber pressure of $1\text{-}3 \times 10^{-4}$ mbar. This seems to produce results which are equal to or better than the larger aperture results.

The ion source is water cooled. When operating at the high powers which we use, if the neutralizer is turned off, one can observe the molybdenum anode to be glowing a dull red. We believe that we accidentally operated the source without water cooling at one time and that this partially demagnetized the magnets of the source. The result of the lower magnetic field is to increase the drive voltage under otherwise constant conditions. Since we find this very undesirable, we think that operation without water cooling is to be avoided. The magnets are expensive to replace. We have also experimented with a higher current power supply and seemed to have overheated and damaged the magnets at about 2000ma of drive current.

2.1.2 Cleaning the Cold Cathode Source

As mentioned above, the source accumulates a buildup of coating within the cavity. This causes the drive volts to increase with otherwise constant conditions. When the volts get out of the selected operating range, it becomes necessary to clean the source. The deposits observed range from yellow to brown and green, and they can be quite hard in some cases and somewhat chalky in others. An analysis of the deposits in the cavity of the source showed molybdenum (probably oxide) to be dominant with only traces of aluminum. The molybdenum electrode erodes with use and is clearly the source of the deposits. We had expected that aluminum oxide would be dominant, and were therefore surprised at this result. We have also noticed that the molybdenum anode ring may erode in the region near the gas inlet holes to the cavity. This is most noticeable at the hole nearest the gas source where the pressure and gas flow are assumed to be the highest. The gas inlet holes in the aluminum base plate of the cavity also show significant erosion which is greatest nearest the gas source. When these effects become too severe, we replace the components.

We use three different techniques for cleaning. One is to disassemble the cavity and abrade away the deposits with ScotchBright, if necessary emery paper, and/or fine bead blasting. We have been advised to strive for a smooth surface to avoid points for arcing. The second approach is to sputter clean the source with argon before loading the chamber for a coating run. This avoids disassembly and can be effective between chamber cleanings. The sputter cleaning takes about 1/2 hour. The third technique is to operate the source during deposition with a mixture of 25% Argon with the 75% Oxygen as described in section 2.2.1 on the End-Hall source. This tends to clean the source as it performs its normal IAD function, but at this time we still manually clean the Cold Cathode source frequently, since the argon is not as clear a benefit here as with the End-Hall gun.

2.1.3 Results with the Cold Cathode Source

We have used this deposition arrangement and technique extensively for the production of stacks ranging from 40 to 90 layers of silicon dioxide and titania. Insignificant spectral shift with changing humidity can be achieved using this IAD system. Without IAD, we typically may see a 15 to 20nm spectral shift. The deposition conditions of such a run using the large aperture might be: 225 degrees Celsius, 10Å per second for both materials, 48 SCCM of oxygen through the ion source, 450-500 drive volts, 1.0 drive amps, 20 amps for neutralizer, and the chamber pressure would be mostly in the range of 1.4 to 2.0x10-4 mbar. The silicon monoxide layers getter more than the titania and therefore the higher chamber pressures are associated with the titania. These films also pass the adhesion and severe abrasion tests of MIL-C-675. The resulting index of the

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silica is about 1.50. We have found that the conditions which give little of no humidity shift with this type of coating are not necessarily compatible with some laser damage requirements. Additional oxygen is required to reduce the laser damage and give an index of about 1.46, but the humidity shift will partially return, perhaps 6-8nm.

We have generally been able to achieve good and repeatable uniformity over a full chamber diameter calotte by the use of masks. However, the ion source parameters must be reasonably stable or the uniformity can be seen to have some changes. The ion beam has a distribution which is clearly more concentrated on the axis of the beam. It appears that if an adequate amount of ions reach the less bombarded areas, the excess ions in the more bombarded areas are not detrimental. We have had some indication that this is less true when the drive volts are in the high (500V) region. The hypothesis is that some ion etching may be occurring at the higher drive volts and thereby the thicknesses of the layers are slightly reduced at the center of the beam impingement area.

2.2 End-Hall Source

The End-Hall source has many similarities to the Cold Cathode source described above and some differences. Figure 5 illustrates the general configuration. Kaufman and Robinson[7] and Cuomo, Rossnagel, and Kaufman[8] describe these sources in some detail, but we will also give a brief description here for the convenience of the reader. The gas to be ionized is admitted to the throat of the anode at a controlled flow rate. Electrons from the AC current heated cathode bombard the gas. A high voltage is applied to the anode and ionization of the gas occurs. The magnetic field in the anode region is primarily axial which enhances the affectivity of the electrons. The ions are accelerated upward from the anode. Electrons from the cathode also serve as the neutralization for the ion beam.

It can be seen that the cathode is similar to the neutralizer of the Cold Cathode source. The magnetic fields and gas feeds are similar also. The anode configurations are different in detail, but similar in function. The major difference seems to be that the gas is confined to a smaller space where ionization occurs in the End-Hall source described here. This allows lower ion voltages at lower gas flow rates and therefore lower total chamber pressures.

2.2.1 End-Hall Source Characteristics

The source which we have used has limits of: 5000ma of drive current, 175 anode or drive volts, 50 sccm gas flow, 25 amps of cathode or neutralizer current. We have chosen: 4000ma drive current, 120 anode volts, and 19 amps starting cathode current.

The controller/power supply is automated to start the discharge and then control the beam to preset values. A starting anode voltage and gas flow are preset, we use 130 volts and 20 sccm. Upon starting, the controller heats the cathode, stabilizes the gas flow to the preset value, and brings up the anode voltage until the discharge starts. After a number of seconds, the controller adjusts the system to the chosen running values set on the knobs of the controller. In principle, the controller then

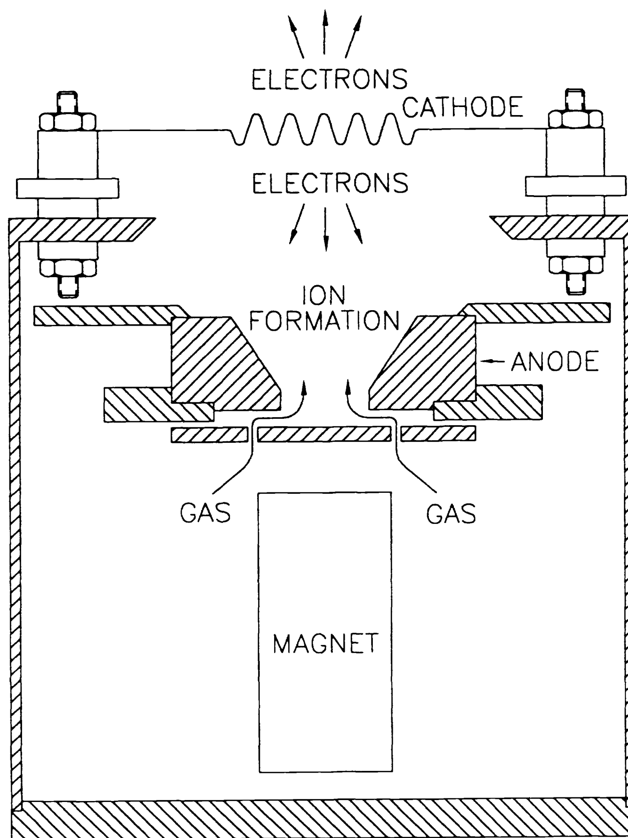

Fig. 5. General configuration of the Commonwealth Scientific End-Hall ion source used in these studies.

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maintains the ion beam at constant volts and current. The voltage is controlled by the gas flow in a servo loop, the drive current is maintained by a current control loop, and the neutralizer has a third loop which attempts to maintain neutralizer current.

We initially had great difficulty in achieving stable operation of this system. At first we were concerned about cleanliness of the source-head components, gas leaks in the interface of the head to its mounting plate, and coating on the cables in the chamber. We did find it necessary to shield the ion source from the electron gun cabling near the baseplate of the chamber to overcome noise and interactions. However, our other concerns above turned out to be inconsequential. As long as all of the electrical connections are good and no major coating buildups occur on insulators leading to the head, we have had no difficulties with the head.

The controller is another story. Since our need is to get the maximum ion current density practical at an acceptable voltage from the source, we operate at the limits of the system capability. The three control loops seem to fight each other. We were only able the achieve stable operation after making two changes to the control system. First we removed the neutralizer/cathode power control from the controller and replaced it by a manual Variac control. We now set the cathode current to about 20 amps before starting the source and leave the Variac set for the rest of the day. This provides satisfactory results and the longest cathode life (about 10 hours). The current through the cathode does drop to the 15 amps range toward the end of its life, but the source operation is stable until the cathode burns out. The second thing we found necessary was to properly compensate the current control loop for stability. As chamber conditions change such as evaporation of a gettering material, the current and gas flow controls see transients. If the compensations are not correct, this well lead to oscillations and/or the gas flow going full open with no control.

With the changes mentioned, we find very stable operation at 4000ma and 120 volts. When transients occur, the current may go near 5000ma. If it exceeds 5000ma it tends to loose control and get "locked-up." We therefore operate at 4000ma to leave it just enough headroom to accommodate normal process transients.

The anode parts and gas distributor plate are made of non-magnetic stainless steel. When operating with oxygen, these surfaces develop a brown or orange color and we seem to have observed decreasing system stability. We experimented with 50/50% and 25/75% mixture of Ar/O_2 and found the 25/75% most stable.

2.2.2 Cleaning the End-Hall Source

We have been very pleased to find that the cleaning needed for this source when we use the 25/75% mix is very easy. When setting up for a run and before installing a new cathode, we scrub the cone of the anode and the exposed spot on the gas distributor plate with ScotchBright and vacuum out the dust produced. This only takes a minute.

The cathodes are a consumable item which we replace before every long run. It is important to be sure that good electrical contact is made, particularly with the spring fingers of the push-on connectors. This seems to be hypersensitive if the controller has not been modified as we have done to remove the neutralizer control loop.

2.2.3 Results with the End-Hall Source

We find the End-Hall source with the control system as we have modified it to be quite stable, reproducible, and easy to maintain. The beam gives good results and uniformity over a 1150mm diameter calotte when aimed at about the 70% radius. The densification and oxidation of the SiO/SiO_2 seems slightly better under the same conditions as the Cold Cathode source, otherwise most of the same results are obtained. The effects of gettering are not as apparent here since the End-Hall source seems to achieve higher beam current with less gas flow. The make-up oxygen supplied to keep constant chamber pressure is probably greater with the End-Hall source.

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3. CONCLUSIONS

Both the Cold Cathode and End-Hall sources have allowed us to obtain the desired results of producing good SiO_2 from SiO at high rates for many layers. Figure 6 shows and example of the low humidity shifts which can be obtained along with fully oxidized films. This full densification, however, usually requires about half the rates of deposition or twice the ion densities which we have been describing here.

After some modifications, this particular End-Hall source has proved to be very stable. The Cold Cathode source changes somewhat with operating time due to erosion of the anode and gas distributor plate and resulting deposits. There is further development in progress to enhance the stability of the Cold Cathode source over long processes.

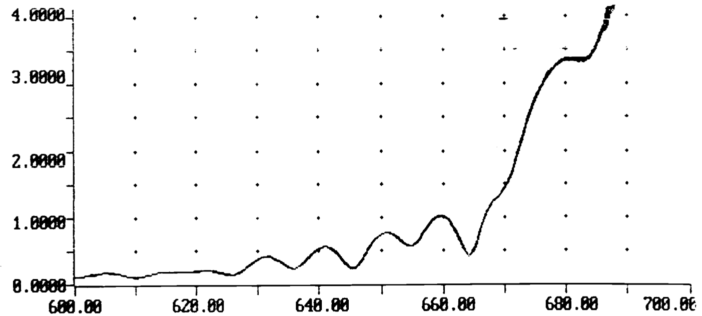

Fig. 6. Optical density versus wavelength for two scans of an IAD coated sample with the Cold Cathode source at near 0% and 100% humidity showing negligible shift.

Our previous work with gridded Kaufman sources showed that TiO_2 tended to be damaged to the point of some absorption by ions in excess of 200ev while SiO_2 was not adversely affected by 600ev. The mean ion ev of the End-Hall source has been estimated[8] to be 60% of the anode voltage and by similarity the Cold Cathode source may be about 60% also. This would lead to the estimation that the End-Hall source was providing about 72ev ions and the Cold Cathode about 200+ev. If the drive currents for the two sources can be compared at 4000ma and 1000ma respectively, this implies a relative ion power of 72x4 to 200x1 or 288:200. This is consistent with our observations in that the End-Hall seems somewhat stronger, but not overwhelmingly so. It appears that the End-Hall source is challenged to operate at a higher anode voltage for more beam power up to the point of film damage (200ev/.60) while the Cold Cathode source is challenged to operate at a lower anode voltage (333V) to avoid damage. The Cold Cathode source starts in a desirable range but tends to build toward a higher than desirable anode voltage as internal deposits build up.

Both sources have proved usable but have some room for improvement as provided by the manufacturers. Our present needs and desires would be best met by a system which operated stably at about 300 drive volts and at least 2000ma of drive current. Both of these sources seem to provide the basis for further developments in that direction.

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