

PLATING IN A CORONA DISCHARGE

R. D. Wales

Materials Sciences Laboratory
Lockheed Palo Alto Research Laboratory
Palo Alto, California

ABSTRACT

It has been demonstrated that boron can be deposited on a suitable substrate in a corona discharge. Application of high-voltage electrical energy across a gaseous hydrogen-boron halide mixture forms ionized/activated states, resulting in the deposition of metallic boron. The deposition process is electrochemical in nature, the boron being deposited cathodically.

INTRODUCTION

Literature on electric discharges is quite extensive. However, most of this literature concerns the nature and properties of discharges taking place in stable gas systems. Detailed discussions of electrical discharges are presented in several books^(1, 2, 3, 4). Relatively little information is available concerning chemical reactions initiated and sustained by electrical discharges. Arc reactions are basically thermally initiated reactions deriving their thermal energy from the arc and thus are not applicable in the present sense. Glow discharges have been utilized for the polymerization of organic materials and the deposition of oxide films. The formation of pure boron powder⁽⁵⁾ and the decomposition of diborane⁽⁶⁾ and boron trichloride⁽⁷⁾ have been studied in a glow discharge. No references have been located concerning chemical reactions initiated and sustained by a corona discharge.

Those references^(8, 9, 10) which refer to the utilization of a corona discharge to catalyze, or cause, a chemical reaction do not in fact utilize a corona discharge. The discharge utilized in these references has an odd resemblance to a glow discharge, but is actually a suppressed spark. Thus, the discharge goes through the phenomena of spark buildup without, however, generating a spark. Direct current cannot be used in these systems since the buildup of charge at the insulated electrodes quenches the discharge, and a reverse cycle is necessary to remove this charge and reinitiate the discharge.

A corona discharge is, essentially, intermediate between a glow and an arc discharge being, however, a low current phenomenon. Glow discharges are generally generated at low pressures while an arc is generally a high-pressure phenomenon. The gas is ionized more or less uniformly throughout the system in a glow discharge. An arc is obtained when a narrow path of ionized particles is generated between two electrodes, resulting in a low resistance path which further aggravates the situation until extremely energetic particles exist in the narrow path. A corona discharge is not as pressure-dependent and is obtained at a small electrode which is opposed by a much larger electrode. There is a very large

change in field through the corona, but very little change over the remaining distance to the opposing electrode. Most studies of corona discharges have been in inert gas systems, and have been generated at a point electrode.

This study has been directed toward the determination of the feasibility for depositing a coating, e.g., boron, on a suitable substrate in a corona discharge. A further object has been to determine some of the critical parameters and a possible indication of the mechanism and characteristics of this technique for coating the substrate material.

EXPERIMENTAL WORK

A schematic diagram of the system used in this study is indicated in Fig. 1. The system pressure was controlled with a Cartesian Manostat 6A (Manostat Corporation) and a Welch mechanical pump Model 1402 (W. M. Welch Manufacturing Company). The discharge was initiated and sustained with a 7,000/12,000 V Jefferson luminous tube outdoor-type transformer (Jefferson Electric Company) connected to 60-cps 110-V power source through a Variac variable transformer.

To determine the effect of alternating and direct current, an RCA CR 212 half-wave rectifier was added to the circuit. At the same time a resistance bridge, a current measuring resistor, and an ammeter were added to the circuit. A schematic of the circuit is presented in Fig. 2. The resistance bridge consisted of six 2-W 2-megohm resistors (R_2) and one 2-W 1,000-ohm resistor (R_1), all in series; the total voltage being 11,775 times the voltage across the 1,000-ohm resistor. The current measuring resistor was a 2-W 10.075-ohm resistor. The voltage measurements were made with a Hewlett-Packard Model 130B oscilloscope, and alternating current measurements were made with a Simpson Model 378 milliammeter.

The reactants utilized in this study were hydrogen, helium, or argon, and boron tribromide. The hydrogen was passed through a "De-oxo" unit (Engelhard), through a drying column of magnesium perchlorate, and then through a flowmeter. After the flowmeter, the hydrogen was split into two streams, one of which was bubbled through the boron tribromide, and then recombined into one stream before entering the reaction chamber or cell.

The temperature of the bubbler, and of the cell, was controlled by wrapping each (and the associated gas lines) with heating tape and controlling the power input with a Variac variable transformer.

The system was maintained at or below atmospheric pressure for this study, with most of the data being obtained at 2 to 3 in. of mercury below atmospheric pressure.

Tungsten wire was chosen as the substrate material. This wire was cleaned by passing it successively through a train consisting of concentrated nitric acid, a distilled water rinse, and an acetone rinse.

Using the hydrogen-boron tribromide reactant system and 60-cps alternating current to develop a corona, approximately a dozen cell designs were tried. The cell design which appears to be the most satisfactory is pictured in Fig. 3. This cell consists of a 2-in.-long pyrex glass tube with a neoprene o-ring inside each end and wrapped with eight turns of 3-mil tungsten wire along the tube length such that the wire is parallel and concentric to the axis of the tube. The wire is 0.9 cm from the axis. This assembly is then inserted in a 5-in.-long pyrex glass tube 1.5-in. in diameter and supported such that the tubes are concentric. A tungsten wire lead is then extended out of the tube, and neoprene rubber stoppers inserted in each end. Each stopper has a capillary tube through its center such that there are approximately 3 in. between the capillaries, and the filament enters and leaves the cell through these capillaries. The reactants also enter (and leave) the cell through the stoppers.

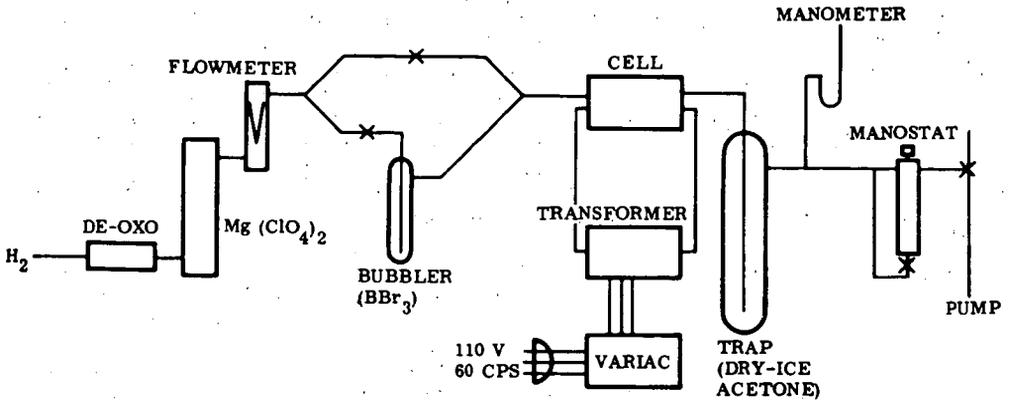


Fig. 1 Schematic of System Utilized for Plating in a Corona Discharge

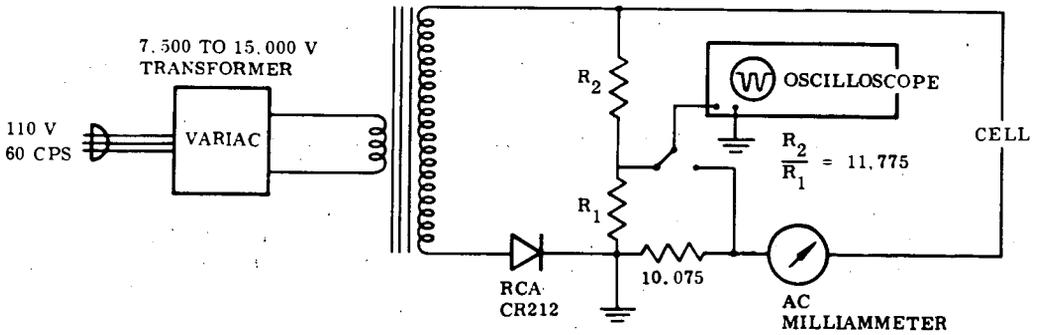


Fig. 2 Schematic of Power Input and Measuring Circuit Used With the Corona Discharge Plating Apparatus

PRIMARY VARIABLE CONSIDERATIONS

Deposition Utilizing Alternating Current

Hydrogen and boron tribromide vapors were used to obtain a coating of boron on 1-mil tungsten wire in a corona developed with 60-cps alternating current. It was determined that, at about 70 and 350 mA/cm², no coating is obtained when the cell (and reactants) are at room temperature, while a coating of boron is obtained if the temperature is raised to approximately 100° C. At higher current densities, the coating is concentrated in nodules. If enough power is supplied to heat the filament to a dull red glow, a good coating is obtained in the hot zone. At lower current densities, a more uniform coating is obtained, depending upon the reactant ratios and flow rates. Thus, hydrogen was bubbled through boron tribromide at a rate of approximately 400 ml/min, and the system was maintained at approximately atmospheric pressure. When the boron tribromide was maintained at about room temperature and at a total hydrogen flow rate of about 1.5 liter/min, the corona was discontinuous along the wire and boron deposited in the area of the coronas to give discrete coated and uncoated areas. With a hydrogen flow rate of about 400 ml/min and a plating time of about 10 min, a much smoother coating was obtained. There was some tendency for the corona to break into discontinuous sections, which resulted in a nonuniform buildup of boron.

When the boron tribromide was heated to about 30° C and the hydrogen flow rate was maintained at 400 ml/min, the corona was somewhat more continuous and the coating nearly uniform. However, the coating was not nearly as smooth as in the previous example.

There was also a tendency for the formation of corona points on the opposing electrode system with a resulting deposition of boron under the corona.

Deposition Utilizing Direct Current

Using hydrogen and boron tribromide as reactants to obtain a deposit of boron on 1-mil tungsten wire in a corona developed with half-wave rectified 60-cps alternating current, no deposit was obtained when the 1-mil wire was the anode. However, a coating was obtained when the 1-mil wire was the cathode. Good, continuous corona and boron deposits were obtained when the corona was initiated in a large excess of hydrogen (the hydrogen flow was then decreased to the desired amount after about 5 min).

The coating is quite uniform and has an orange peel appearance at 2,000X magnification. Some of the morphology of the substrate is apparent at high magnification (e.g., die marks). The voltage requirements for a particular current increased as the hydrogen flow decreased, increasing from more than 1,000 V peak to about 7,000 V peak as the excess hydrogen was decreased in these runs.

Attempts to utilize pure dc power were unsuccessful. The power supplies available were designed to deliver several hundred milliamperes and had relatively coarse controls. Thus, as the corona was initiated, the power supplies did not allow sufficient control, resulting in "runaway" or burning in two of the substrate wire.

Deposition Utilizing Argon and Helium

Using helium instead of hydrogen, a coating was obtained, but arcing was much easier and thus lower current (and lower flow rates) were necessary. Peak voltages of 7,000 to 8,000 V were used.

Using argon instead of hydrogen required higher voltage (with lower currents) and resulted in the formation of corona points under which boron was deposited to give whiskers. Peak voltages of about 9,000 V were used. Whiskers greater than 6 mils long and about 0.5 mil in diameter were obtained before discontinuing these experiments.

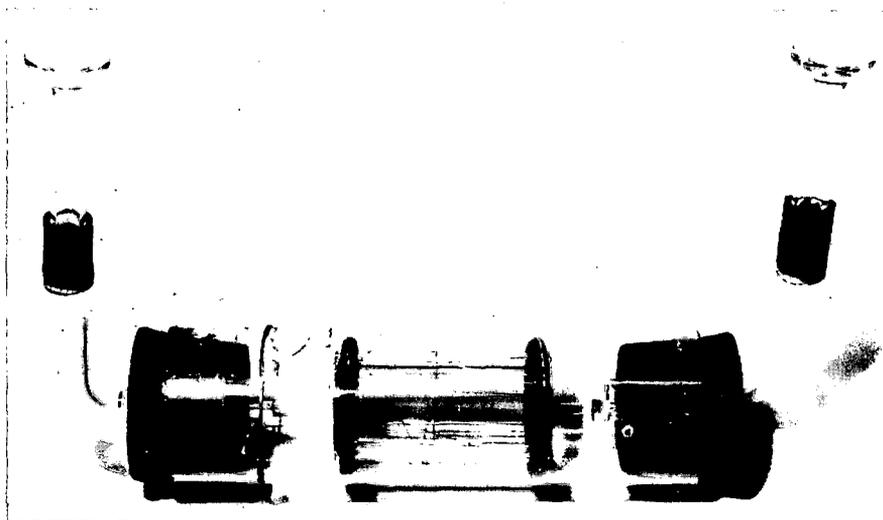


Fig. 3 Reaction Cell Used for Plating in a Corona Discharge

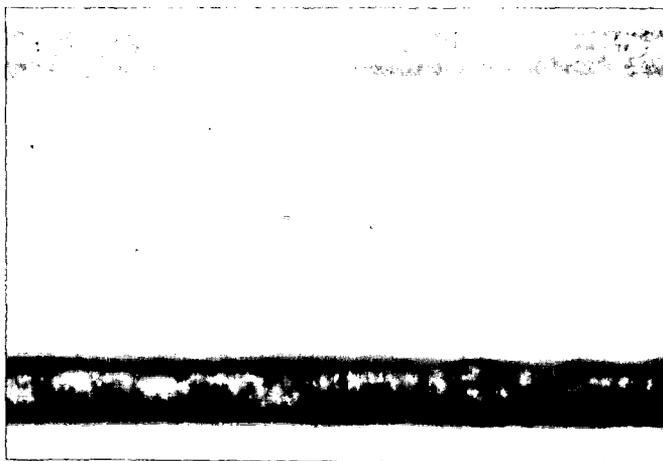


Fig. 4 Boron Deposit on 1-mil Tungsten Wire, Run 28-1,
Tungsten Substrate Material at Top (340 \times)



Fig. 5 Boron Deposit on 0.5-mil Tungsten Wire,
Run 35-1 (450 \times)

Bromine was a product when helium or argon was used while hydrogen caused the formation of hydrogen bromide.

Discussion

(1) Cell Design. The reaction cell should be designed so that the concentration of reactants and products is essentially constant throughout the cell to give a more uniform corona and deposit. The electrode geometry and separation are to some extent dependent upon the power requirements, which are in turn dependent upon the resistance heating effects in the filament and upon the arcing probability. Thus, in practice, the current in the filament should not be great enough to heat the filament excessively. With this current limitation, the electrode separation is dependent upon the arcing probability and should be great enough to level out any small variations in electrode separation which could cause the current to concentrate in a small region. Furthermore, to obtain a uniform corona around the filament, the opposing electrode should be concentric around the filament. If the power input is not pure direct current, a "motoring" effect results if the opposing electrode is a wire coiled around the filament. That is, a vibration or circular oscillation will be induced on the filament. Therefore, the opposing electrode has been made up of a group of connected electrodes arranged concentrically around the filament and parallel to it in order to minimize the "motoring" effect. The opposing electrode could also have been a metal cylinder or screen, but in order both to observe the filament and be able to operate at reasonable electrode separations (reasonable voltages), interconnected parallel wire electrodes were selected.

(2) Mechanism of Deposition. The results obtained indicate that the mechanism of boron deposition in a corona discharge is cathodic. In this type system, electrons are generated and repelled from the cathode while positive ions are drawn to it. At the anode, positive ions are generated or electrons are drawn to it. Thus, the boron radical is positively charged and drawn to the cathode where it is deposited as elemental boron.

Helium and argon were used to determine if the boron tribromide was ionized directly, or if its ionization was a secondary reaction. Table I indicates some of the ionization levels for these gases. Helium in a corona discharge has only one or two potential (or ionization) levels, and these are quite high. However, helium is ionized at lower applied voltages than most gases because the electrons generated at the cathode have only elastic collisions with helium atoms until they acquire enough kinetic energy from the field to ionize the helium. Argon has a potential (or ionization) level which is relatively low (about half that of helium) but higher than the ionization levels for hydrogen. In helium the system was very susceptible to arcing, while in argon higher voltages were required with some susceptibility to arcing. In hydrogen arcing was not such a problem because of the many types of inelastic collisions possible and the consequent tendency to decrease the electron energy and concentration. Boron was deposited in all three systems. However, in hydrogen, hydrogen bromide was obtained while bromine was obtained in both argon and helium. Deposition was slightly easier and there was a slightly increased rate of deposition of boron with an increased tendency to arcing in helium and argon. The difference, however, was not sufficient to be due to direct reaction with the free electron, and indicates that the boron tribromide is ionized by collision with ionized particles rather than electrons or the field. Thus, the mechanism includes: (a) the ionization (or activation) of the hydrogen (helium or argon), (b) the collision or exchange of energy of the ionized particle with boron tribromide to result in (c) the formation of a positively charged boron radical and hydrogen bromide (or bromine), (d) the transport of the charged boron radical to the cathode in the field, and (e) the electrochemical deposition of boron on the cathode.

It is apparently necessary to add a small amount of kinetic (thermal) energy to aid the deposition in hydrogen. However, this reactant system offers certain advantages over helium or argon systems. That is, with hydrogen, there are apparently more ionized or activated particles with fewer electrons and consequently less likelihood of creating conditions conducive to arcing.

Table 1. Ionization Levels for Helium, Argon, and Hydrogen(2, 11)

Gas	First Excitation Potential (eV)	Ionization Potential (eV)			Metastable Level (eV)
		I	II	III	
He	20.5	24.5	54.1		19.7
A	11.6	15.7	27.7	40.7	11.5
H ₂	11.5	15.4			11.9
H	10.2	13.5			10.15

(3) The Corona. In the high-field region near the substrate wire, positive ions can attain high energies and the secondary electron emission process is quite efficient. These secondary electrons will start electron avalanches, which will in turn produce many positive ions, which produce more avalanches, etc. At low pressures, diffusion of the electron avalanches spreads the glow and distributes the positive space charge so that the discharge is not quenched. Diffusion does not take place at higher pressure, and a localized dense space charge extinguishes the corona. The extinction lasts until the positive space charge diffuses to the electrode and the last ions reinitiate the discharge, resulting in a periodic corona with a frequency dependent upon the field and the velocity of the positive ions.

With the negative wire (cathode), the ionization increases first with distance from the wire, reaches a peak, then drops sharply. That is, the electrons move out from the wire and produce relatively stationary positive ions between themselves and the wire, thus weakening the field at greater distances. The maximum ionization occurs at several ionizing free paths from the wire, and there is a dark space between the wire and the luminous glow. Furthermore, as mentioned, at low pressures the lateral diffusion of electron avalanches spreads the corona over the wire surface. Because the value of the coefficient of electron emission is important, and because the glow will not be uniform if the coefficient of electron emission varies over the surface of the wire, the glow may settle in patches of greater or lesser luminosity and at high pressures will appear as a single small area of corona. The corona may exhibit a marked flickering near threshold because the positive ion bombardment may change the effective coefficient of electron emission by denuding the surface of its gas film. The discharge thus decreases or ceases in that region, resuming again when the surface has recovered. At low pressures and voltages well above the threshold value, the corona is fairly steady.

In this work it was necessary to clean the substrate wire so that there were no variations in the coefficient of electron emission along the wire, and thus a localization of the corona into points. During deposition the corona was distributed over the substrate wire in a uniform manner. However, the discharge was periodic as indicated in the above discussion. That is, the sheath (of light) along the wire was not of a uniform brightness, but consisted of brighter and darker areas which seemed to move along the wire in a somewhat random manner, but which appeared periodic in nature at a given point on the wire.

SECONDARY VARIABLE CONSIDERATIONS

Experimental Work

The deposition system was that previously described. The tungsten wire was cleaned as before, then placed in the cell. The corona was then initiated in excess hydrogen and maintained for about 5 min, or until the corona was continuous or nearly continuous along the substrate electrode, before the conditions were changed to give boron deposition. This initial "cleaning" process was effected with hydrogen flowing at about 160cc/min through the boron tribromide at about 26° C and with hydrogen flowing through the bypass line at about 270cc/min. The electrical input during this time was about 17 mA peak and about 4,700 V peak for 1-mil tungsten wire and about 5,600 V peak and 4.5 and 11.0 mA peak for 0.5-mil tungsten wire.

Results

(1) Deposition on 1-mil Tungsten Wire. Some of the results obtained are presented in Table 2. The corona was maintained continuously in all runs. A picture of the filament obtained in Run 28-1 is shown in Fig. 4. In Run 28-1 the current fell from an approximate initial value of 12.3 mA peak to about 3.5 mA peak in about 9 min, after which it was nearly constant. The peak voltage changed from 6,900 to 13,190 V. The filament obtained in this run is apparently the desired type, although not of optimum thickness.

Table 2. Some Effects of Varying Process Conditions With 1-mil Tungsten Wire Substrate

Run	Vacuum (in. Hg)	H ₂ flow bubbler (cc/min)	H ₂ flow bypass (cc/min)	Current peak (mA)	Voltage peak (V)	Time (min)	Temp. BBr-3 (°C)	Comments
17-3	2.3	160	—	14.2	6,800	40	26	Corona uniform for about 6 min then broke up. Coating not uniform, large nodules formed, due to discontinuous corona.
23-1	1.2	40	35	16	6,700	30	26	Corona fairly uniform, substrate etched, no coating.
23-3	1.4	80	—	13.6	8,100	58	26	Corona fairly uniform, coating fairly uniform, final diameter of about 1.2 mil.
25-1	2.3	50	40	14.2	6,100	7	—	To attain 47° C.
		50	—	13	7,900	42	47	Overheated substrate in areas. Coating thick and mostly rough.
28-1	2.6	50	40	12.3	6,900	5	—	To attain 70° C.
		50	—	3.5	13,200	78	70	Good coating, final diameter 1.33 mil.

The data obtained in the experiments presented, and in other similar experiments, indicate that:

- (a) the voltage requirements increase as the boron tribromide to hydrogen ratio increases.
- (b) The voltage requirements increase as the system pressure increases.
- (c) The substrate is etched with little or no boron deposited as the boron tribromide to hydrogen ratio decreases.
- (d) The corona tends to break up into points at high flow rates, resulting in nonuniform boron deposits.

Good coatings were obtained at high boron tribromide to hydrogen ratios and relatively low currents.

(2) Deposition on 0.5-mil Tungsten Wire. Some of the results obtained are given in Table 3. The corona was maintained continuously in Runs 30-1 and 30-2. The power input was discontinued in all remaining runs until the boron tribromide and the cell has attained the desired temperature. The currents and voltages indicated for all runs below 35 are approximate since no adjustments were made once the run had begun.

The effects of operating conditions are similar to those observed for deposition on 1.0-mil tungsten wire. However, the decreased heating effects of the 0.5-mil wire necessitate heating the cell to about 200°C to prevent condensation of the boron tribromide.

In Run 31-1, an apparently desirable coating was obtained at the ends of the reaction zone while the central portion of the filament was quite nodular. In Run 31-1 the peak current was 6.2 mA, falling to about 1.8 mA at the end of the run. During this time the peak voltage changed from 12,480 V to about 15,780 V.

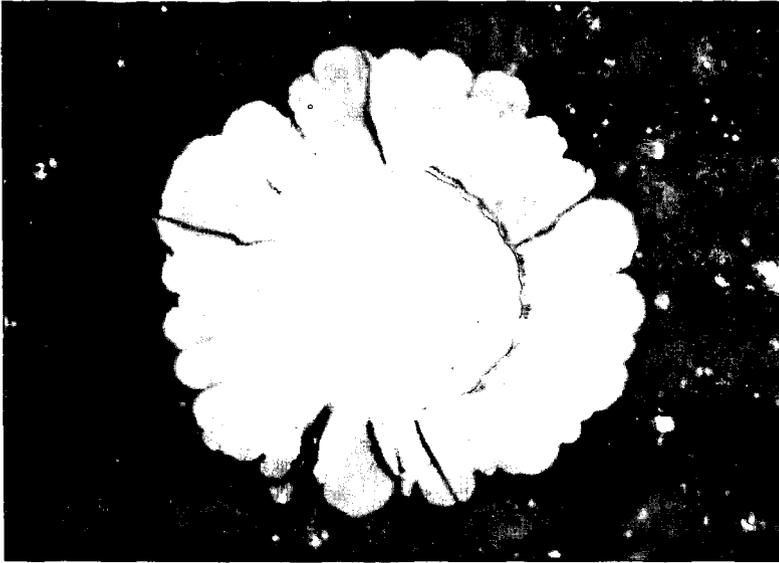
Runs 35-1 and 35-2 yielded filaments having uniform coatings of boron. The coating, as shown in Fig. 5, had ridges along its surface resembling die marks on wire. Figure 6 shows a cross section of filament from Run 35-1 in normal and in polarized light. The higher magnifications indicate that the markings on the surface are reflections of the markings on the substrate in almost a one-to-one ratio. Furthermore, there is no indication of boride formation. However, polarized light indicates some anisotropic properties similar to pyrolytic graphite. The material seems softer and much darker than that grown by gas plating techniques. Although there are some unidentified lines, x-ray data indicate that the coating is amorphous boron with no borides in the filament.

Cursory examination of the surface for a few of the substrates has indicated surface finishes varying from the ridged (die marks) through smooth to an orange-peel-type finish, while the filaments obtained have had surface finishes ranging from ridged through smooth to nodular. Therefore, the substrate surface is a critical factor in determining the appearance and surface of the final filament.

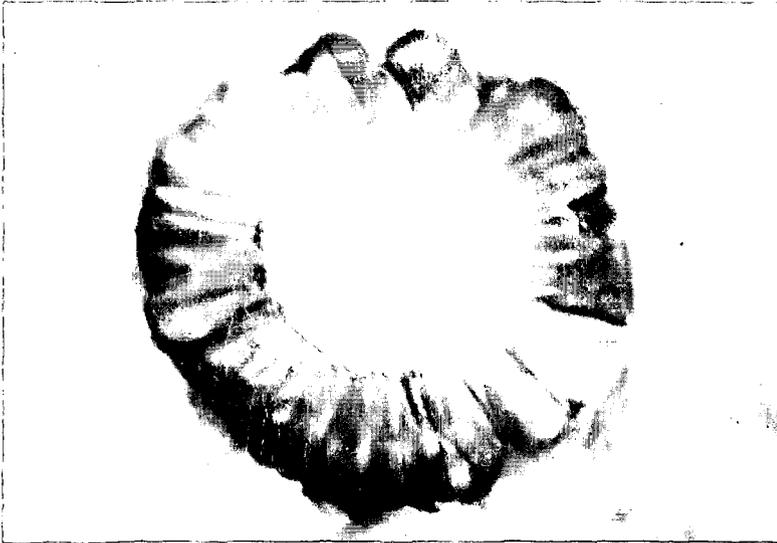
(3) Effect of Morphology of the Substrate. The 0.5-mil tungsten substrate wire has been examined after various stages in the process. Some of the results are presented in Table 4.

It has been determined that the liquid cleaning train cleans and slightly etches the wire, and the high hydrogen corona etches the wire as indicated in Table 4. At low peak currents the die marks were etched away, but the surface has a very rough orange peel finish. Using both high and low currents consecutively, a much smoother orange peel finish is obtained.

Boron deposited on wire etched to an orange peel finish gives a coating similar to that pictured in Fig. 7. The morphology of boron deposited on variously etched wire verifies the hypothesis previously presented in that the coating morphology and growth structure are directly dependent upon the morphology of the substrate.



(a) Normal



(b) Polarized Light

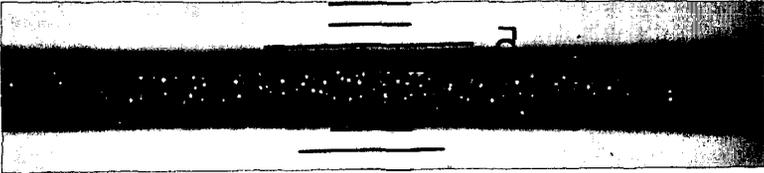
Fig. 6 Cross Section of Filament Obtained by Plating in a Corona Discharge, cf. Fig. 5 (3,000 \times)

Table 3. Some Effects of Varying Process Conditions With 0.5-mil Tungsten Wire Substrate

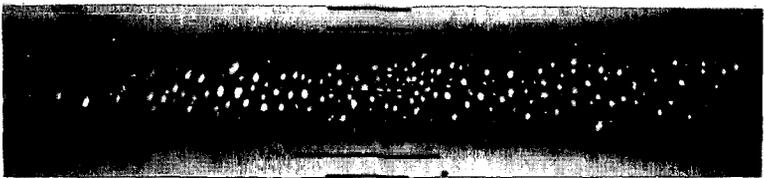
Run	Vacuum (in. Hg)	H ₂ flow bubbler (cc/min)	Current peak (mA)	Voltage peak (V)	Time (min)	Temp. BBr ₃ (°C)	Temp. cell (°C)	Approx. flow rate BBr ₃ (ml/hr liq)	Comments
30-1	2.7	50	4.0	12,200	19	64	-	7.0	Final thickness - 0.94 mil, substrate - 1/4 mil, coating appears porous, flakes off fairly easily, BBr ₃ condensed in cell.
30-2	3.0	50	1.0	13,000	30	67	111	6.8	Final thickness - 0.68 mil, substrate - 0.3 mil, coating a little better than Run 30-1, BBr ₃ condensed in cell.
31-1	2.6	50	1.8	15,780	27	58	175	-	Final thickness on ends 1.2 mils, in center - 1.7 mils, coating as desired on ends, uniform and nodular in center. BBr ₃ condensed in cell.
33-1	2.7	50	3.0	8,830	20	48	215	3.5	Final thickness - 0.8 mils uniform coating, somewhat nodular, mostly as ridges or "wrinkles." No BBr ₃ condensed in cell.
34-1	2.5	50	1.0	11,770	22	63	210	4.0	Final thickness on ends 0.9 mil, in center - 0.7-2 mil, substrate 0.4 mil on ends. Coating on ends about like Run 30-2, coating in center nonuniform with large nodules separating short lengths of uniform ridged or "wrinkled" coating.

Table 3. (cont'd)

Run	Vacuum (in. Hg)	H ₂ flow bubbler (cc/min)	Current peak (V)	Voltage peak (V)	Time (min)	Temp. BBr ₃ (°C)	Temp. cell (°C)	Approx. flow rate BBr ₃ (ml/hr liq)	Comments
35-1	2.5	50	2.0	Start 6,120 End 9,420	20	52	205	4.9	Final thickness 0.9 mil, substrate thickness 0.5 mil, coating uniform with ridges which have the appearance of die marks on drawn wire. Coating coherent but appears to be poorly bonded to substrate.
35-2	2.6	50	4.0	Start 6,950 End 7,770	8	53	204	4.9	Coating about same as in Run 35-1.
36-3	2.5	50	8.0	Start 7,800 End 8,420	20	54	236	4.0	Rough, nodular coating, thickness > 1 mil.
39-2	2.5	50	2.0	Start 6,690 End 7,680	24	52	225	3.5	Final thickness approx. 1 mil. Coating uniform, very small nodules with some "nodes."



(a) 604x



(b) 1,230x

Fig. 7 Boron Deposit on 0.5-mil Tungsten Wire, Run 52-1,
cf. Table 4

Table 4. Some Effects of Various Process Conditions Upon Morphology

Run	H ₂ flow bubbler (cc/min)	H ₂ flow bypass (cc/min)	Temp. BBr ₃ (°C)	Temp. cell (°C)	Current peak (mA)	Voltage peak (V)	Time (min)	Comments
-	0.5 mil tungsten wire untreated							
46-1	0.5 mil tungsten wire after cleaning train only							
46-2	160	270	-	-	4.6	6,450	5	Dirty, not too smooth, die marks. Clean, some etching; die-marks plainly visible microscopically.
46-3	160	270	-	-	7.6	6,190	5-1/2	Corona not uniform for first 3 min, some pitting, die-marks faintly visible.
46-4	160	270	-	-	7.6	6,190	4	Corona good from beginning; outside visible corona apparently no change, in corona surface uniformly etched quite rough with no die marks.
47-1	160	270	-	-	7.5	6,190	2	Corona not uniform for first 2 min. surface has orange-peel finish, no die marks.
47-2	95	270	-	-	7.8	5,010	5	No apparent surface change.
	95	270	-	-	3.0	4,830	3	Corona fair.
48-1	95	270	-	-	7.6	5,200	5	Corona nonuniform, surface fairly smooth, die mark visible.
	95	270	-	-	2.0	4,460	3	Corona fair
48-3	95	270	-	-	7.0	4,950	4	Surface has orange peel finish, smoother than 46-4.
	95	270	-	-	2.0	4,460	5	Corona fair
52-1	160	270	-	-	7.6	6,320	3	Surface about like 48-1, die marks faintly visible.
	95	95	to heat cell and BBr ₃ ; power left on; at temperature in 3 min; made no power adjustments					
	50	0	53	235	Final 0.4	Final 11,580	18	Coating uniform except for a couple of areas, coating of approximately 0.05-mil nodules, final diameter approximately 0.8 mil.

Table 5. Some Effects of Various Process Conditions

Run	H ₂ flow bubbler (cc/min)	H ₂ flow bypass (cc/min)	Temp. BBr ₃ (°C)	Temp. cell (°C)	Current peak (mA)	Voltage peak (V)	Time (min)	Comments	
61-1	160	270	-	-	7.6	6,190	2	Coating mostly uniform. Final diameter 1.1 mil.	
	Started heating cell and BBr ₃ ; power left on; made no power adjustments								
	95	95	32	H ₂ flow constant for 2 min					
69-2	50	0	51	H ₂ flow and temperature constant				Coating on inlet side good. Final diameter 1.1 mil. Outlet side had many large nodules.	
	at end of run								
	160	270	-	235	0.4	11,520	21		
	Shutdown for 11 min								
71-1	Started heating cell and BBr ₃ ; power left on; made no power adjustments								
	95	95	37	95	6.5	7,620	2		
	50	0	55	230	4.9	8,540			
	Final								
	3.1								
9,970									
15									
7.6									
7,180									
4									
Started heating cell and BBr ₃ ; power left on; made no power adjustments									
3									
2									
8,930									
Final									
10,400									
10									

Table 5 (Continued)

Run	H ₂ flow bubbler (cc/min)	H ₂ flow bypass (cc/min)	Temp. BBr ₃ (°C)	Temp. cell (°C)	Current peak (mA)	Voltage peak (V)	Time (min)	Comments	
71-2	160	270	25	-	7.6	7,060	4	Coating even and uniform. Final diameter 0.60 mil.	
	Started heating cell and BBr ₃ ; power left on; made no power adjustments								
	95	95	34	-	6.3	7,430	3		
73-1	50	0	54	235	-	-	6	Coating uniform. Final diameter 0.75 mil.	
	Final								
	3.0								
	7.6								
74-1	Varied conditions as in Run 61-1 except final BBr ₃ temperature 71° C and current not allowed below 2.0 mA								
	At end of run								
	160	270	24	220	2.0	20,800	16	Coating uniform and even except for one area. Final diameter 1.0 mil.	
	Started heating cell and BBr ₃ ; power left on; made no power adjustments								
	95	95	38	215	6.2	7,800	2		
50	0	71	235	5.0	8,540	5			
Current maintained at 2.0 mA									
Final									
27,860									

(4) Variation of Plating Conditions. Combining the information obtained in the previous tests, several runs were made using variations of the plating conditions. Some of the results obtained are presented in Table 5 and in Fig. 8.

The current-time and voltage-time characteristics for two runs are indicated in Fig. 8. The filament obtained in Run 73-1 (Table 5) was evenly and uniformly coated similar to the filament pictured in Fig. 7. Except for one defect, the filament obtained from Run 74-1 (Table 5) was evenly and uniformly coated similar to the filament pictured in Fig. 7. As indicated in Fig. 8, the defect probably occurred after an elapsed time of about 21 min at a cell voltage of about 23,600 V.

The results obtained indicate that the best process conditions and plating procedure for boron deposition on a stationary 0.5-mil tungsten wire are as indicated in Fig. 8.

Discussion

The morphology of the deposit obtained reflects, in general, the morphology of the substrate. The coating is essentially amorphous in nature although there is indication of anisotropy.

One set of operating conditions giving a satisfactory coating of boron on tungsten is presented graphically in Fig. 8. In general, good coatings have been obtained at high boron tribromide-to-hydrogen ratios and relatively low currents. Furthermore, if the flowrate is too great, the corona tends to break up into points, resulting in nonuniform deposits.

Other effects of varying operation conditions which suggest limitations for deposition, and which also tend to verify the mechanism for deposition presented previously, include:

- (a) The voltage requirements increase as the boron tribromide to hydrogen ratio increases.
- (b) The voltage requirements increase as the system pressure increases.
- (c) The substrate is etched with little or no boron deposited as the boron tribromide-to-hydrogen ratio decreases.

CONTINUOUS BORON DEPOSITION ON A MOVING FILAMENT

Experimental Work

A system was designed, assembled, and tested for continuous boron deposition on a moving filament. Figure 9 is a schematic of the apparatus. The design resembles that for the batch plating process (Fig. 1). The filament is pulled through the system with a Graham constant speed motor. The spool is mounted on a shaft and suspended in such a manner as to offer minimum friction. The seal and electrical contact between cells is a unique arrangement such that the filament moves through the seal in a vertical direction without breaking the seal.

The power for the cells has been obtained in a manner similar to that used for the batch plating process (Fig. 2). There has been a considerable problem with 60-cycle pickup in the measurement system. Shielding and grounding at various critical positions were necessary to eliminate this problem.

Hydrogen-boron trichloride was chosen as the reactant system. The reactant mixture has been obtained by bubbling hydrogen through boron trichloride maintained at about -20°C . The reaction cells have not been heated externally, and the vapor flow was split between all three cells.

The etching cell was not utilized as such, and was eventually converted to use for cleaning the substrate filament by the hot-wire technique. Thus, the chemical cleaning train was eliminated. Hydrogen only was passed through the cleaning cell and the substrate heated to

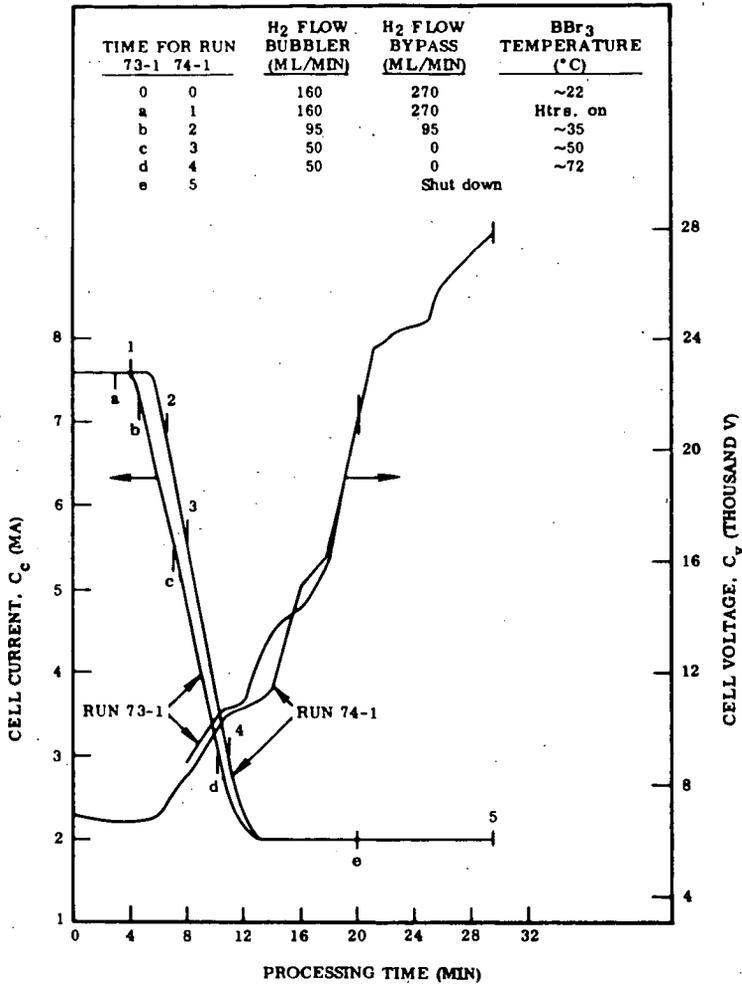


Fig. 8 Electrical Characteristics During Deposition of Boron on 0.5-mil Tungsten Wire in a Corona Discharge

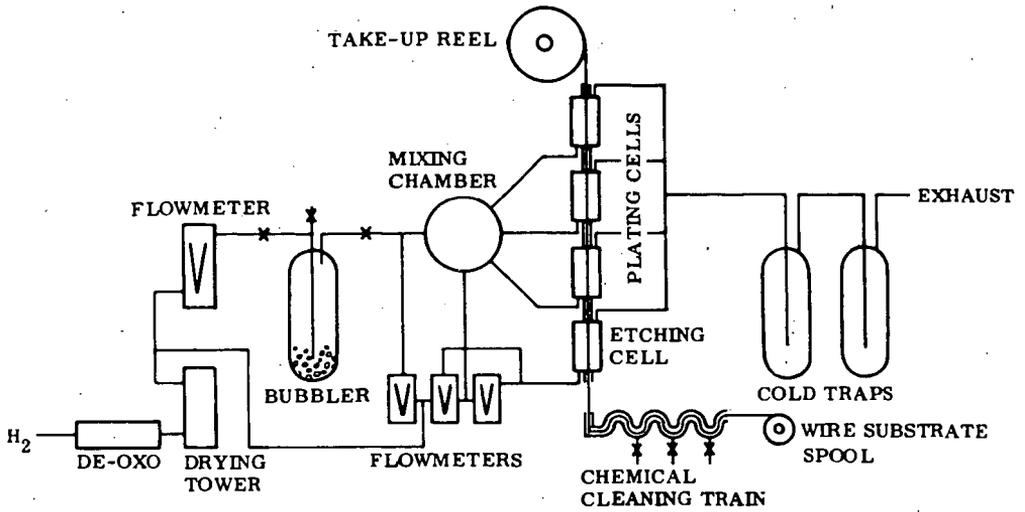


Fig. 9 Schematic of Continuous System for Plating in a Corona Discharge

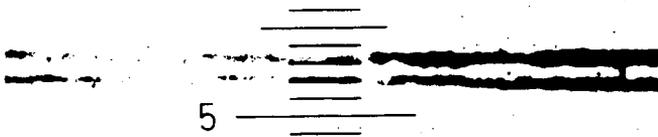


Fig. 10 Boron Deposit on 0.15-mil Tungsten Wire, Continuous System (600 \times)

a red heat in this cell using dc power. Tests performed in this system have utilized both 0.5-mil and 0.15-mil tungsten substrate.

Results

(1) AC Pickup. The use of shielded leads and wire cages around the transformers has, with the use of 1,000 ohm current measuring resistors, virtually eliminated the ac pickup.

(2) Deposition on 0.5-mil Tungsten Wire. Satisfactory results have been obtained at a hydrogen flow rate through the bubbler of about 100 cc/min and additional hydrogen at a flow rate of about 350 cc/min. Hydrogen is flowing through the cleaning cell at about 140 cc/min and the wire is cleaned by resistance heating at a dc voltage of about 70 V and a DC current of about 320 milliamperes. Some of the results obtained are indicated in Table 6.

Using only one cell, at a filament speed of about 3.6 in./min a coating about 0.25-mil thick was obtained; at a filament speed of about 14.4 in./min, a coating about 0.05-mil thick was obtained.

Using two cells, there was some problem in maintaining the corona in the second cell. At a filament speed of about 3.6 in./min a coating about 0.7-mil thick was obtained in the areas where a good corona was maintained. At a filament speed of about 14.4 in./min and a current input to the second cell of about half that to the first cell, a coating about 0.07-mil thick was obtained.

(3) Deposition on 0.15-mil Tungsten Wire. The 0.15-mil tungsten substrate wire was cleaned by the hot-wire technique at hydrogen flow rate of about 140 cc/min and at a dc power input of about 208 V and 90 mA. While the input vapors were split between the three plating cells, only one cell was utilized for plating studies. Some of the results are indicated in Table 7.

The best results were obtained at a filament speed of about 5 in./min with a hydrogen flow rate through the bubbler of about 70 cc/min, and additional hydrogen at a flow rate of about 350 cc/min. To maintain a uniform corona, it was necessary to switch the power on and off relatively slowly during the run. Under these conditions a coating thickness of about 0.17 mil was obtained.

There is apparently some difference in either the morphology of the 0.15-mil substrate as compared to the 0.5-mil material, or less effect by this substrate upon the morphology of the deposit. Although the morphology of the material deposited on 0.5-mil tungsten appeared similar to that indicated in Fig. 5, the morphology of the deposit on the 0.15-mil tungsten appeared more like that indicated in Fig. 4. Figure 10 indicates the morphology usually obtained on 0.15-mil tungsten substrate. The total diameter of this sample is 0.4 mil.

Discussion

An apparatus has been presented, and tests performed, indicating the feasibility of depositing boron on a continuously moving substrate in a corona discharge.

Although no tests were made for verification, the results obtained with the 0.15-mil substrate indicate that the substrate diameter also effects the operating conditions, probably through buildup of the positive ion sheath to such an extent that the corona cannot recover after being quenched. This effect is possibly related to the similar effect of high flowrates on larger substrates noted in the previous section. The effects might be explained by postulating a higher concentration of boron radicals around the smaller substrate simply through volume considerations, and around the larger substrate through an increased concentration resulting from increased availability due to higher flowrates. The charged species would tend to remain in the volume near the substrate because of the greater effects of the electrical field.

Table 6. Some Effects of Varying Process Conditions With 0.5 Mil Tungsten Substrate in a Continuous System

Run	Filament Speed (in./min)	H ₂ flow (cc/min)			Cell no. 1		Cell no. 2		Comments
		Cleaning	Bubbler	Bypass	Voltage peak (V)	Current peak (mA)	Voltage peak (V)	Current peak (mA)	
85-4	3.6	140	100	350	7,000	16	-	-	Good corona, final diameter - 1 mil.
85-5	3.6	140	100	350	7,000	17	7,200	18	Corona not good in 2nd cell, final diameter in uniform portions - 1.9 mils.
87-1	14.1	140	100	350	6,600	5.8	-	-	Apparently very faint but good corona.
					6,000	12.5	-	-	Corona broke up as power increased, then formed good corona, final diameter 0.6 mil.
87-2	14.4	140	100	350	6,000	12.5	6,720	6.4	Corona good in Cell 1, weak but apparently good in Cell 2. Final diameter 0.64 mil.
					6,000	12.5	6,960	17.5	Cell 2; Corona broke up with increasing power and did not improve before heating occurred.

Table 7. Some Effects of Varying Process Conditions With 0.15 mil Tungsten Substrate in a Continuous System

Run	Filament Speed (in./min)	H ₂ flow (cc/min)			Cell no. 0		Cell no. 1		Comments
		Cleaning	Bubbler	Bypass	Voltage dc (V)	Current dc (mA)	Voltage peak (V)	Current peak (mA)	
88-3	0.8	140	100	350	218	85	6,000	12	Corona as discontinuous 1/8 in. strips, some heating of substrate, could get good corona by switching on full power, but new wire had breaks in the corona, in good corona areas total thickness 0.6 mil.
88-5	5.1	140	70	350	208	90	5,200	-	Maintained good corona by switching power on and off slowly, total thickness 0.5 mil.
89-2	5.1	140	120	350	208	90	7,100	14.6	Corona poor with some heating of wire.
89-3	5.1	140	120	350	208	90	7,200	14.0	Corona good, after short time wire began to heat.
90-4	5.1	140	120	350	208	90	7,400	14	Could get good corona by switching on full power, but new wire had breaks in the corona.

CONCLUSIONS

Chemical reactions can be initiated and sustained by a corona discharge. Boron has been deposited on a tungsten wire substrate in a corona discharge at relatively low temperatures. The deposition process is electrochemical in nature, the boron being deposited cathodically, and the mechanism for the reaction is indicated to be of the form:

- (a) Emission of electrons from the cathode
- (b) Ionization (or activation) of hydrogen, argon, or helium, and production of secondary electrons which in turn ionize more hydrogen, etc.
- (c) Collision of ionized hydrogen, argon, or helium with boron tribromide and exchange of energy
- (d) Formation of positive boron radicals and hydrogen bromide or bromine
- (e) Transfer of the positive boron radical to the cathode
- (f) Electrochemical reaction of the boron radical to form an essentially amorphous deposit of boron

The morphology of the deposit is essentially the same as the morphology of the substrate. There is no interaction of the boron with the tungsten and there is apparently some anisotropy of the deposit.

The corona discharge during deposition is not essentially different from a corona discharge developed in an inert gas system, and the same criteria and properties are extant. Like a corona discharge in an inert gas, the coefficient of electron emission and the ability of the electrons to diffuse along the wire are most important in obtaining a uniform corona, and thus a uniform deposit, on the substrate. Furthermore, if the sheath of positively charged boron radicals becomes too dense, the corona is quenched and will not recover fast enough to prevent the breakup of the corona into points.

ACKNOWLEDGEMENT

This work was supported by the U. S. Air Force Contract AF 33(615)-2130, and was based upon an idea presented by J. B. Story. The filament cross-sections were prepared by W. C. Coons and the continuous system was operated by Barbara Traina. Grateful acknowledgement is also made to R. N. Varney, M. E. Sibert, and A. E. Hultquist for many helpful discussions of gas discharges in general and of corona discharges in particular.

REFERENCES

1. N. A. Kapzow, "Elektrochemische Vorgänge in Gasen und in Vakuum," Veb Deutscher Verlag der Wissenschaften, Berlin, 1955
2. S. C. Brown, "Basic Data of Plasma Physics," The Technology Press of MIT and John Wiley and Sons, Inc., New York, 1959
3. E. J. Helland, The Plasma State, Reinhold Publishing Corporation, New York, 1961
4. L. B. Loeb, Electrical Coronas, Univ. of Calif. Press, 1965
5. L. Ya. Markovskii, V. I. L'vova, Yu. D. Kondrashev, Bor. Trudy Konf. Khim, Bora; Ego Soedineii, 36-45 (1958) cf. FTD-MT-64-427, Foreign Technology Division, A. F. Systems Command, 1965
6. W. V. Kotlensky and R. Schaeffer, J. Am. Chem. Soc. **80**, 4517 (1958)
7. R. T. Holzmann and W. F. Morris, J. Chem. Phys. **29**, 677 (1958)
8. N. R. Dibelius, J. C. Fraser, M. Kawahata, and C. D. Doyle, Chem. Engr. Progress, **60**, No. 6, 41-44 (June 1964)
9. S. J. Lawrence, Chem. Engr. Progress, **60**, No. 6, 45-51 (June, 1964)
10. J. A. Coffman and W. R. Browne, Scientific American, **212**, No. 6, 90-98 (June 1965)
11. N. A. Lange, Editor, Handbook of Chemistry, 10th Ed., 111, McGraw-Hill Book Company, Inc., N. Y. 1961