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DEVELOPMENT ON HIGH TEMPERATURE
INSULATION MATERIALS

Part III. Deposition and Properties of Pyrolytic Aluminum
and Silicon Nitrides

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Westinghouse Research Laboratories
Technical Report AMPL-TR-66-320- Part II

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FOREWORD

This report was prepared by Westinghouse Research Laboratories, R&D Center, Pittsburgh, Pa. 15235, under USAF Contract No. AF 33(615)-2782. This contract was initiated under Project 7371, "Applied Research in Electrical, Electronic, and Magnetic Materials," Task 73-101, "Dielectric and Related Materials." The work was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, Paul W. Dimiduk(MAYT), Project Engineer.

This report covers work conducted from June 1965 to June 1967. The report was submitted in July 1967.

Persons engaged on this project include the following technicians: C.L. Jones, F.A. Kerin, J.L. Benedict, and E.A. Jones.

The authors wish to acknowledge the splendid efforts of Mrs. Mary L. Theodore of the Analytical Chemistry Section and Mr. Robert C. Kuznicki of the X-ray Diffraction Section of these Laboratories.

This technical report has been reviewed and is approved.



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ABSTRACT
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Pyrolytic aluminum nitride has been deposited on refractory electrical conductors using $\text{AlCl}_3 \cdot \text{NH}_3$ as the source material. Effects which pressure, temperature and rate of deposition have on electrical and other properties of deposits have been determined. Density of deposited coatings approach that of the calculated value. However, they still contain residual chlorine, causing electrical properties to fall short of what is expected of dense high purity AlN.

Pyrolytic silicon nitride has been prepared from gaseous mixtures of silane and ammonia under varying conditions of temperature and pressure. Adherent, relatively soft, amorphous films have been deposited on substrates heated in the 700° to 800°C range while hard crystalline coatings of α - Si_3N_4 have been obtained in the vicinity of 1250°C. Coatings, which are both hard and amorphous, have been deposited at ~1000°C and have been characterized by a number of techniques.

High temperature dielectric property tests of aluminum and silicon nitrides have indicated good high temperature resistivities with some samples, but considerable variability existed among samples. Measurements on aluminum nitride in particular, have indicated the presence of impurity conduction. Silicon nitride coatings seem to demonstrate more consistently high resistivities which make this material a potentially useful dielectric at 800° to 1000°C at low voltages.

Studies of the conduction across gas spaces, due to thermionic emission at high temperature, indicate this effect is very important in high temperature insulation systems. Solid insulating barriers do not prevent, but only modify such conduction, since the insulation surface is also a thermionic emitter.

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1. INTRODUCTION

With the advancement of science and technology the temperature at which electrical conductors are called upon to operate efficiently and reliably has been increasing. So much is this so that only the higher melting materials can be considered for some projected high temperature applications. Possible conductors for very high temperature use are molybdenum, tungsten, platinum and graphite. As with ordinary conductors these, too, must be provided with an effective electrical insulation. This insulation must of course have adequate thermal stability and electrical properties at the intended high use temperatures ($\sim 1100^{\circ}\text{C}$) of the refractory conductors. Added to these requirements is the formidable one of being able to completely seal the conductor, thereby protecting it from air or other atmospheres with which it reacts at its contemplated use temperature.

Two materials, which from an examination of their bulk properties, appear to be potentially effective high temperature electrical insulators are aluminum and silicon nitrides. The chemical resistance of these nitrides is very good, being essentially unaffected by concentrated acids at room temperature. They are attacked only very slowly in boiling acids and alkalis. Their rate of oxidation is very slow at 1100°C . When exposed to air at high temperature, dense adherent films of the metal oxide form on their surface retarding further oxidation. The d-c resistivities of sintered aluminum¹ and silicon nitride³ bodies at 1000°C are reported to be 10^5 and 10^6 ohm-cm, respectively. The coefficient of linear expansion of aluminum nitride² in the $100^{\circ}\text{--}1000^{\circ}\text{C}$ range is $5.7 \times 10^{-6}/^{\circ}\text{C}$ which matches fairly well that of molybdenum and tungsten. The expansion of silicon nitride is somewhat lower, having a value of $2.5 \times 10^{-6}/^{\circ}\text{C}$ in approximately the same temperature range. As a result of this low thermal expansion and good thermal conductivity they have excellent thermal shock resistance.

Most of the nitride materials heretofore prepared and on which the above properties were determined were sintered or hot pressed structures. Materials in this form are not readily adapted for use, or for evaluation, as electrical insulation for capacitors or wire conductors. Materials for such applications should have as low a porosity as possible, should be essentially free of impurities and be in the form of films or coatings having thickness in the mil range. To obtain such specimens, chemical vapor deposition techniques were used, producing what has come to be known as pyrolytic coatings. These were applied to molybdenum, tungsten, and graphite in the form of rods, plates, foils or wire coils.

The effects which processing variables, such as rate and temperature of deposition and type of substrate, have on the properties of the deposited films were investigated. Properties examined were the composition, crystal structure, microstructure and oxidation resistance of the films. Such physical properties as flexibility and degree of adhesion of the film to the substrate were examined. The temperature dependence of such electrical properties as resistivity, breakdown strength, dielectric constant and loss factor of the coatings were determined. An effort was also made to measure the effectiveness of the two nitrides as high temperature oxidation protection coatings for molybdenum substrates.

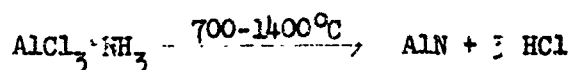
2. EXPERIMENTAL

2.1 Pyrolytic Deposition of Aluminum Nitride

Aluminum nitride powder has been prepared by vaporization of aluminum in a nitrogen atmosphere at temperatures of 1800° to 2000°C^1 and by striking a d.c. arc between high purity aluminum electrodes in nitrogen gas.² Aluminum nitride has been deposited on graphite substrates by thermal decomposition of $\text{AlCl}_3 \cdot \text{NH}_3^4$. More recent literature describes the formation of very thin (up to 25 micron) films by passing gaseous ammonia and AlCl_3 over hot substrates.^{5,6}

The present work has used the solid, volatile, aluminum chloride-ammonia complex, $\text{AlCl}_3 \cdot \text{NH}_3$, as the starting material for the deposition of pyrolytic aluminum nitride. This, in the earlier part of the project, was

prepared separately and introduced in the reaction chamber as such but later work showed that it may be prepared directly in the deposition apparatus by passing dry ammonia gas over sublimed AlCl_3 . The apparatus is shown in Fig. 1. It is constructed of quartz tubing with Vycor joints. Pyrolytic deposition of aluminum nitride using $\text{AlCl}_3 \cdot \text{NH}_3$ as the starting material is represented by the equation:



The substrate to be coated was suspended from 2 hooks in the cap of the apparatus by way of molybdenum or tungsten wires. It was heated to the desired temperature by means of an external r.f. coil. Temperature was measured by means of an optical pyrometer. The starting material in the cup at the bottom of the apparatus was heated, in the area of 150° to 300°C , using a small heating mantle. The vapor pressure of the $\text{AlCl}_3 \cdot \text{NH}_3$ complex varies from 0.02 torr at 160°C to 760 torr at 420°C . Substrates coated were molybdenum, tungsten and graphite rods, plates, foils or wire coils. Films have been deposited at substrate temperatures ranging from 700° to 1400°C . Pressure during deposition has been varied from about 20 microns in a continuously pumped system to atmospheric pressure where a flow of ultrapure nitrogen was used as a carrier gas. Pressure was varied by attachment to a vacuum source and/or an inlet gas source by appropriate valve manipulation. Variations in the temperature to which the substrate was heated during pyrolysis had the most significant effect on the composition and properties of deposits obtained. Variation in pressure during deposition appeared to affect such properties as uniformity of coating thickness and texture of its surface.

2.1.1 Deposition of Aluminum Nitride in a Continuously Pumped System

First attempts to form aluminum nitride by the pyrolysis of $\text{AlCl}_3 \cdot \text{NH}_3$ were made in a continuously pumped system. The pressure in these experiments varied from 20 to 250 microns which developed from the vapor pressure of the starting material and from by-product HCl. Both horizontal and vertical reaction tubes were used in these experiments. However no cost-

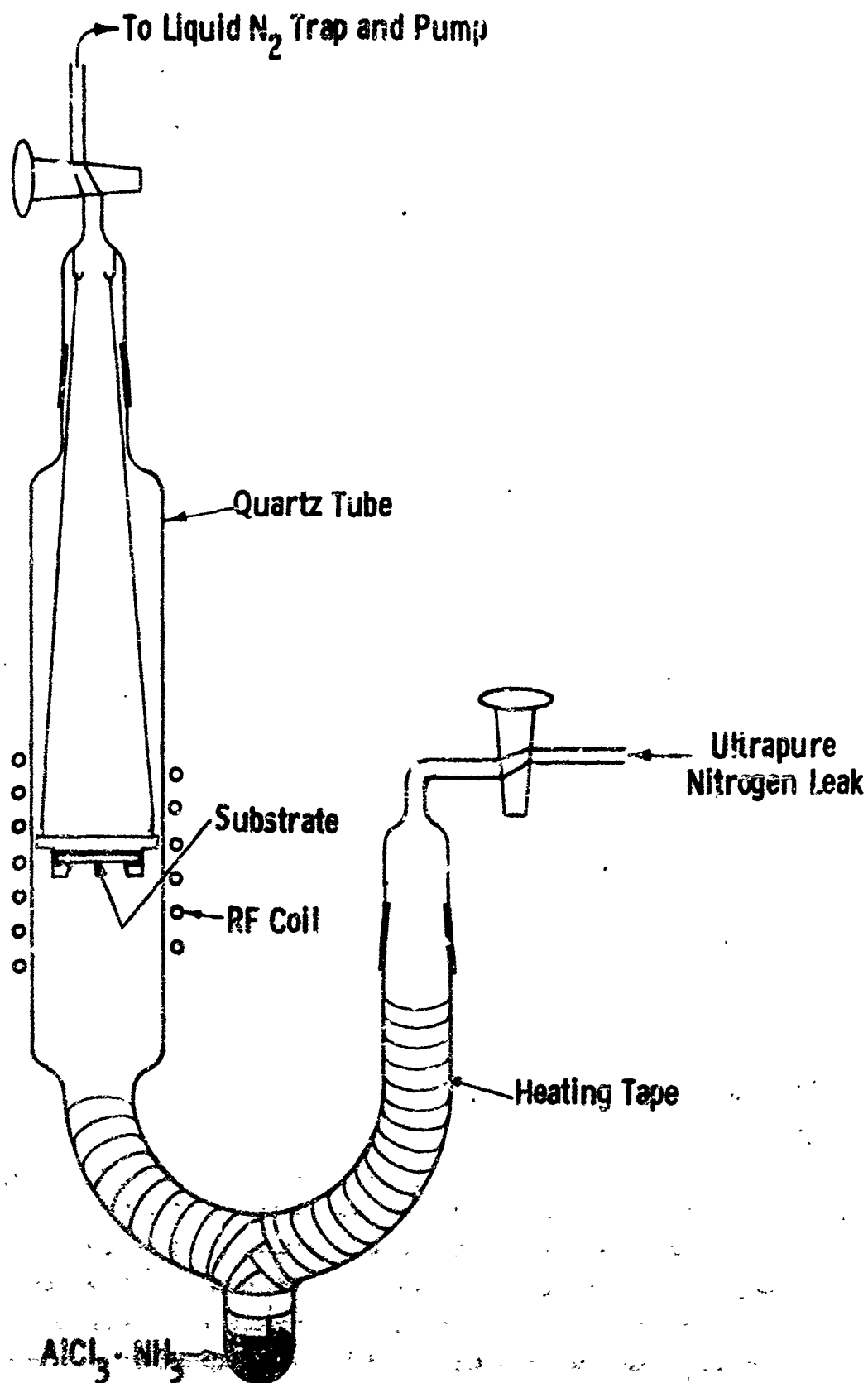


Fig. 1-Flow apparatus for vapor deposition of aluminum nitride

ings satisfactory for measuring electrical properties were obtained. Most substrates were only partially coated and the thickness of all coatings was very nonuniform. Occurrence of poor adhesion was more prevalent than in coatings applied at higher pressures. Some molybdenum rods, poorly coated in a continuously pumped system containing undiluted $\text{AlCl}_3 \cdot \text{NH}_3$ vapors, are shown in Fig. 2.

2.1.2 Deposition of Aluminum Nitride Using Carrier Gases at Atmospheric Pressure

For the purpose of achieving a more effective delivery of reactant vapors to the entire substrate surface, a flow of carrier gas was passed over the heated starting material and then to the vicinity of the hot substrate. Carrier gases tried were ultrapure hydrogen, ultrapure nitrogen and mixtures of nitrogen and dry ammonia. Nitrogen was the most convenient to use and gave results at least as satisfactory as the others. Ammonia was added to the nitrogen carrier gas in an effort to eliminate or reduce chlorine contamination of aluminum nitride deposited from $\text{AlCl}_3 \cdot \text{NH}_3$. Hydrogen was examined as a carrier gas with the same purpose in mind. Both nitrogen and hydrogen were used at the rate of 0.1 liter per minute. Flows of both NH_3 and N_2 in their mixtures were varied from 0.1 to 0.3 liter per minute. The use of NH_3 caused increased production of ammonium chloride "soot" which tended to clog stopcock openings; NH_3 appeared to have no effect on the chlorine content of the deposits. The chlorine content of these deposits is of the order of 0.5%. With hydrogen as the carrier gas, reddish-gray coatings were obtained indicating partial reduction to aluminum.

The use of ammonia as the carrier gas suggested the preparation of $\text{AlCl}_3 \cdot \text{NH}_3$ in situ rather than preparing it separately and then adding it to the deposition apparatus. This was done by adding resublimed AlCl_3 to the cup of the apparatus and then passing NH_3 over it before heating the substrate. The resulting product was liquid at 150°C and was easily volatilized indicating that it is the 1:1 complex which is formed. No difference was noted in the coatings formed from this material and those deposited using the already prepared complex.

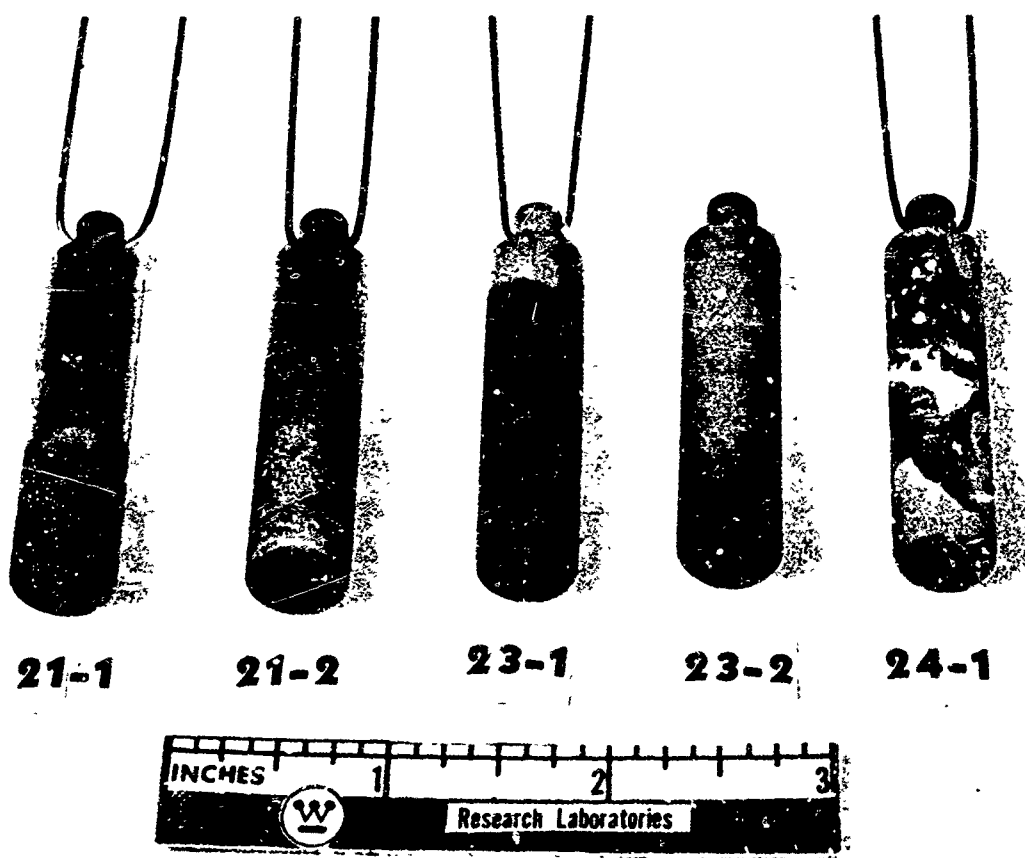
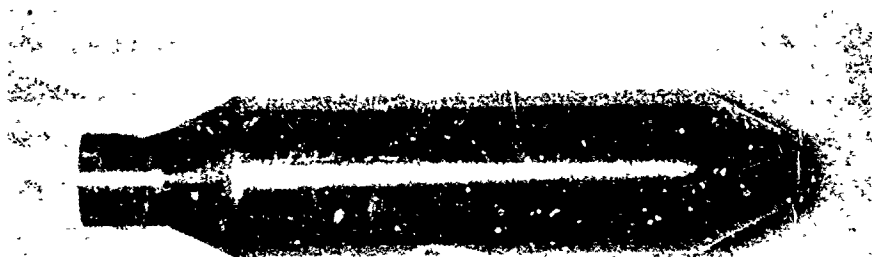


Fig. 2 Molybdenum Rods Partially and Fully Coated with Aluminum Nitride in a Continuously Pumped System Containing Undiluted $\text{AlCl}_3 \cdot \text{NH}_3$ Vapors

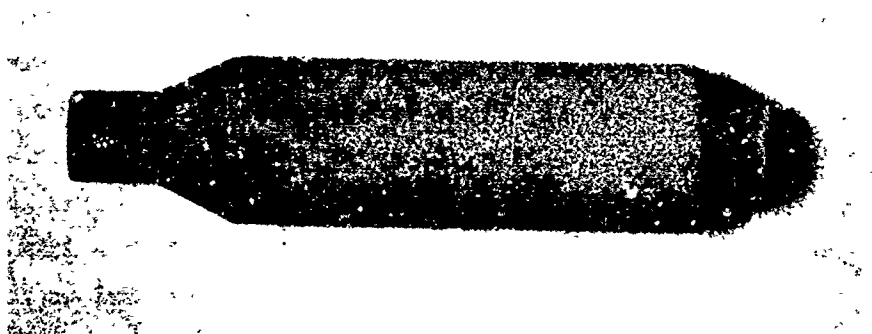
The general procedure for the deposition of AlN using nitrogen as the carrier gas at atmospheric pressure was to first heat-clean the substrate for 20 minutes by bringing it to 1500°C at a pressure of 1 to 2 microns in the deposition apparatus. The substrate was allowed to cool in vacuum before the system was brought to atmospheric pressure with nitrogen. Starting material was then added to the cup in the U portion of the reaction apparatus. The system was alternately evacuated and flushed with nitrogen several times before starting a 100 ml/min. flow of N₂ which was allowed to escape from the system through a mercury bubbler. The substrate was brought to the desired temperature before the heating mantle became hot enough to melt and vaporize the starting material. With the temperature of the starting material at 250-300°C, molybdenum and tungsten rods were completely coated with 1.5 to 3 mil films within one hour. Thickness of the film over the length of 2" x 1/2" diameter rods varied within 1 to 3 mils. Higher starting material temperatures increased the deposition rate but also gave greater variation in thickness and roughness to the film. In Fig. 3 are shown molybdenum rods coated in this manner at various substrate temperatures. Because of the ready availability and relative ease of cutting molybdenum, most of the deposition work was done with this material rather than with tungsten. Graphite was also used as a substrate material but radial cracking of the coating was quite common as the substrate cooled from deposition temperature to room temperature.

2.1.2.1 Effect of Substrate Temperature on Properties of Aluminum Nitride Deposited at Atmospheric Pressure

Three substrate temperature ranges were examined in studying the properties of aluminum nitride films deposited at atmospheric pressure. These were 700°-800°, 1000°-1300° and 1300°-1500°C. In the lowest temperature range, smooth transparent insulating films were obtained. In the middle temperature range, where most of the deposition work was done, hard opaque films were formed. In the higher part of the 1300°C-1500° range, either nothing deposited, or that which did, was in the form of beads which made only a small area of contact with the substrate. They were therefore easily rubbed off. Examples of these coatings on molybdenum rods are shown in Fig. 3.



LH-62-2 - 750°C



LP-58-2 - 1250°C



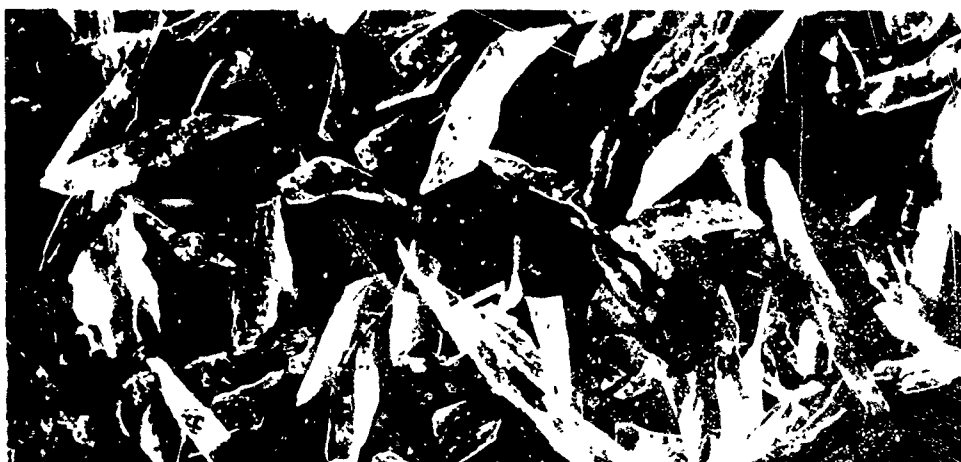
LH-59-2 - 1450°C

Fig. 3 Molybdenum Rods Coated with Aluminum Nitride at Various Temperatures by Carrying $\text{AlCl}_3 \cdot \text{NH}_3$ Vapors over the Rods at Atmosphere Pressure (2X)

Coatings deposited at 800°, 1000° and 1300° were examined regarding their x-ray diffraction patterns, infrared spectra, hydrolyzability and electrical properties. Differences between properties of material deposited at 800° and 1000° are greater than those between the 1000 and 1300° coatings. It should be mentioned that, desirable as it might be, it was not possible to determine all properties of a coating deposited at any one temperature on a single sample. For example, electrical properties were determined on thin coatings deposited on 1/2 inch diameter molybdenum rods, about 2 inches long. But to obtain samples of sufficient quantity, free of the substrate, for elemental and other analyses, it was necessary to deposit very thick coatings on molybdenum wire coils. Samples which were cracked off the coils by bending and stretching the coils are shown in Fig. 4. The 800°C material is translucent while those deposited at higher temperatures are opaque. As the opaque deposit grows thicker than 1 to 2 mils, nodules become evident on the surface of the coating. That the growth of these nodules actually began right at the substrate surface can be seen from the photograph of the fractured AlN coating in Figure 5. Such nodule growth has also been noted in the deposition of pyrolytic graphite.⁷ They are believed to originate from nucleation centers around foreign particles, or irregularities in the substrate surface. As the growth continues, projections grow out from the nodules. One particularly large projection is shown in Fig. 6. It is very likely that the temperature at which new material is being deposited on these extended projections is lower than that at which the deeper deposit took place. As a result, there conceivably could be some differences in the overall composition of thick and thin coatings deposited at the same nominal temperature. These differences could be significant in relating electrical properties of thin (1 to 2 mil) films with other properties determined on coatings which were 10 mils thick or greater.

2.1.2.1.1 X-Ray Diffraction Analysis

Photographs of the x-ray diffraction patterns of 800°, 1000° and 1300°C coatings are shown in Fig. 7. The pattern of the 800° material shows the presence of two crystalline phases. The sharp lines correspond



800°C



1000°C



1300°C

Fig. 4 Aluminum Nitride Cracked off Molybdenum Wire Coils on which it had been Deposited at Atmosphere Pressure (8X)



Fig. 5 Fractured Aluminum Nitride Surface Showing Nodule Growth (50X)



Fig. 6 Growth Projection from Nodule on Surface of Thick Coating (100X)

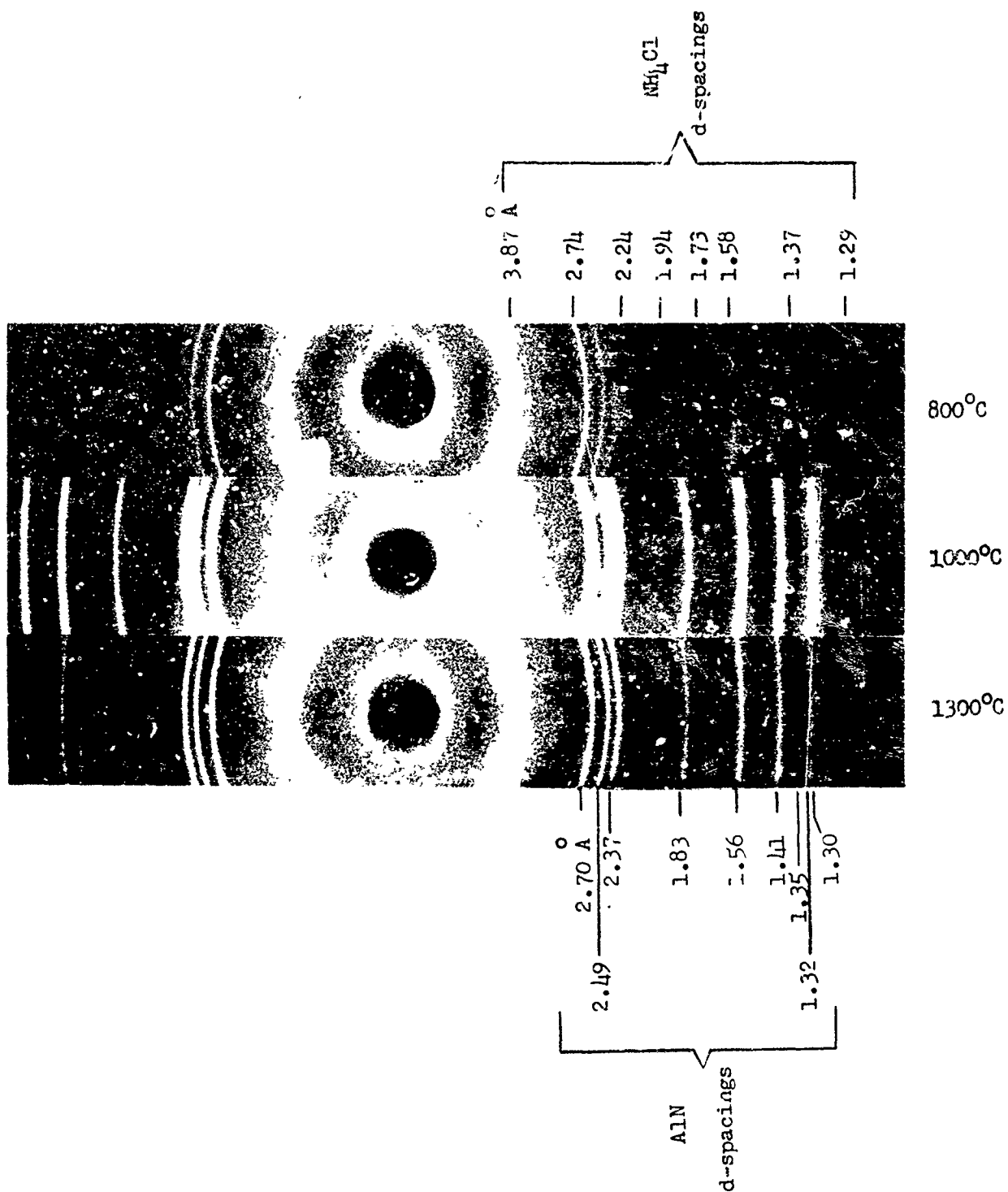


Fig. 7 X-Ray Diffraction Patterns of Aluminum Nitride Deposited at 800°, 1000° and 1300°C

to a crystal having the simple cubic NH_4Cl structure. More diffuse lines of AlN are also present. Ammonium chloride, which sublimes at about 335°C , probably was not present in the coating as deposited at 800°C , but could have been subsequently formed by hydrolysis of the powdered sample. No NH_4Cl lines are present in the patterns of the 1000° and 1300°C coatings; only the AlN structure is present. The lines in the pattern of the 1300° material are much sharper than in the 1000° deposit, indicating an increase in the orientation of the crystal structure as the deposition temperature increases.

2.1.2.1.2 Infrared Spectra

Infrared spectra were obtained on the 800° , 1000° and 1300°C aluminum nitride deposits using Nujol mulls between NaCl plates. These are shown in Fig. 8. Here, too, there is evidence of considerable amounts of ammonium chloride in the coatings deposited at 800°C . This is indicated by the sharp absorption at 7.2 microns, between the 2 Nujol peaks, and lesser NH_4Cl bands at 6.2, 5.8, 5.2 microns, and several in the 3 to 3.5 micron region. The very strong broad band centered at 14 microns is characteristic of AlN . In the spectrum of the 1000° material, the 7.2 micron band, and all of the lesser NH_4Cl bands are much weaker than in the 800° deposit. The AlN band in the 12 to 15 micron region is still strong. In the spectrum of the 1300° deposit the 7.2 micron band, as well as the other NH_4Cl bands, has disappeared leaving only the Nujol and AlN absorption. Spectra for Nujol and for NH_4Cl are given in Fig. 9 and 10 for comparison.

Once again, these spectra do not necessarily point to the presence of NH_4Cl as such in the coating as deposited. It probably results from one, or more, incompletely condensed materials still containing hydrolyzable chlorine and nitrogen.

2.1.2.1.3 Hydrolyzability

In removing the coated substrate from the deposition tube, it sometimes came in contact with the tube walls, picking up some particles of by-product ammonium chloride. This was especially true of wire coil substrates. To remove any trace of NH_4Cl picked up in this manner, the

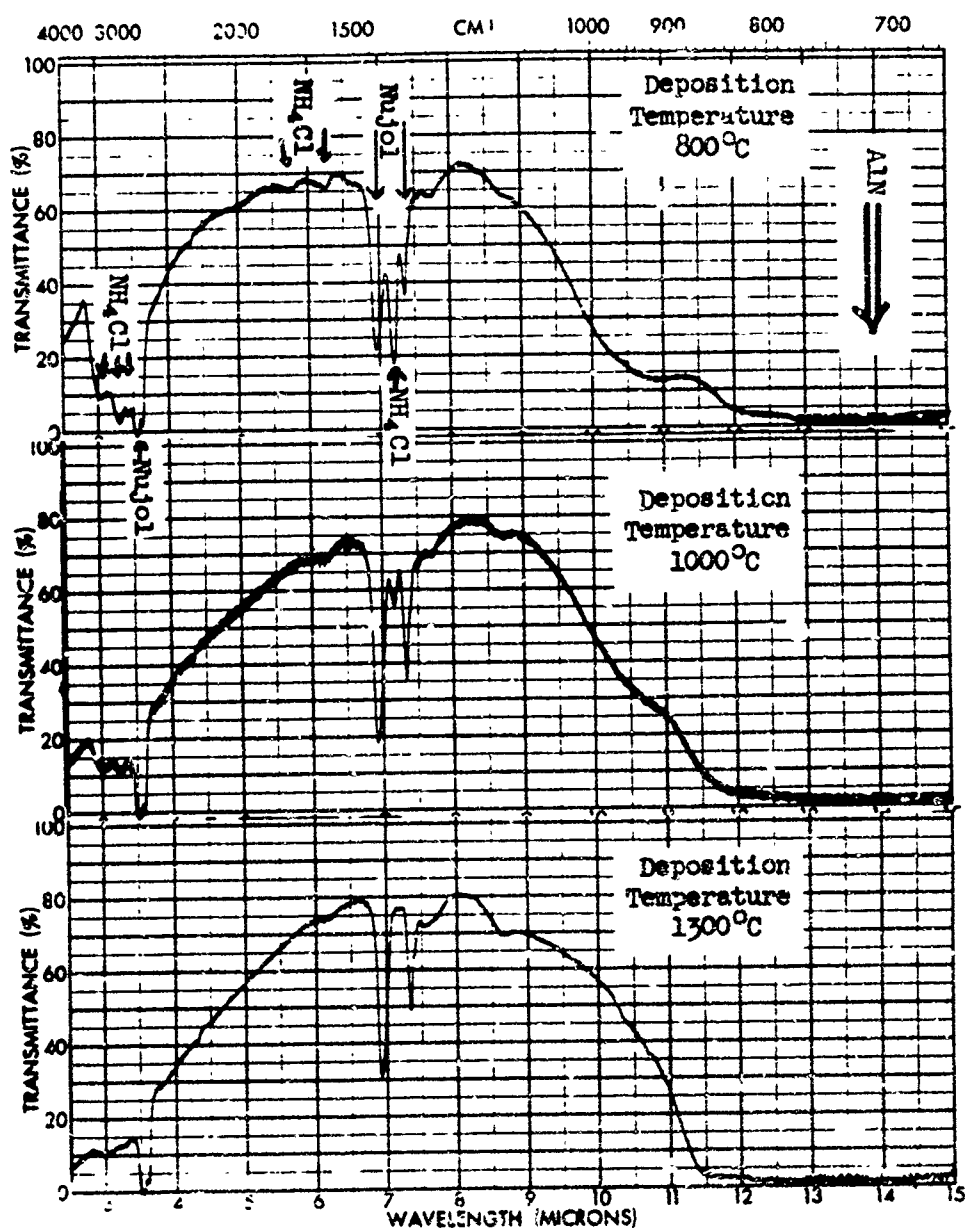


Fig. 8 Infrared Spectra of Aluminum Nitride Deposited at 800°, 1000° and 1300°C (Nujol Mull on NaCl Plates)

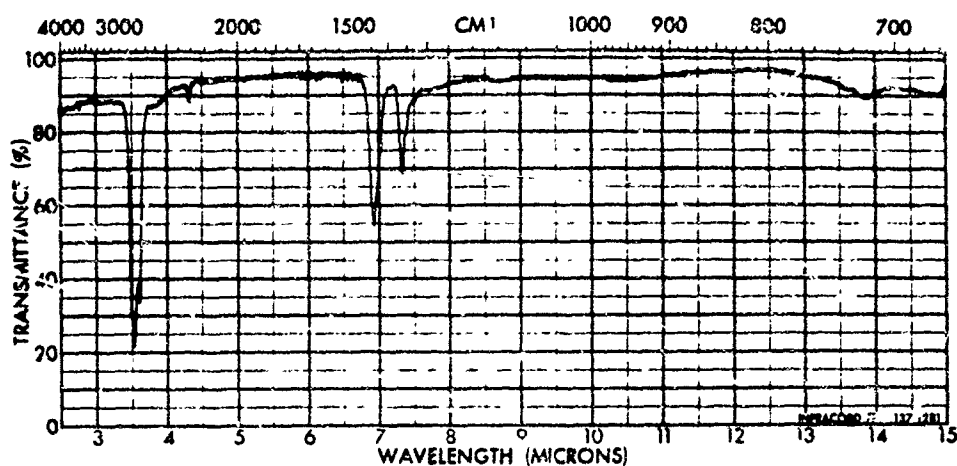


Fig. 9 Infrared Spectrum of Nujol on NaCl Plates

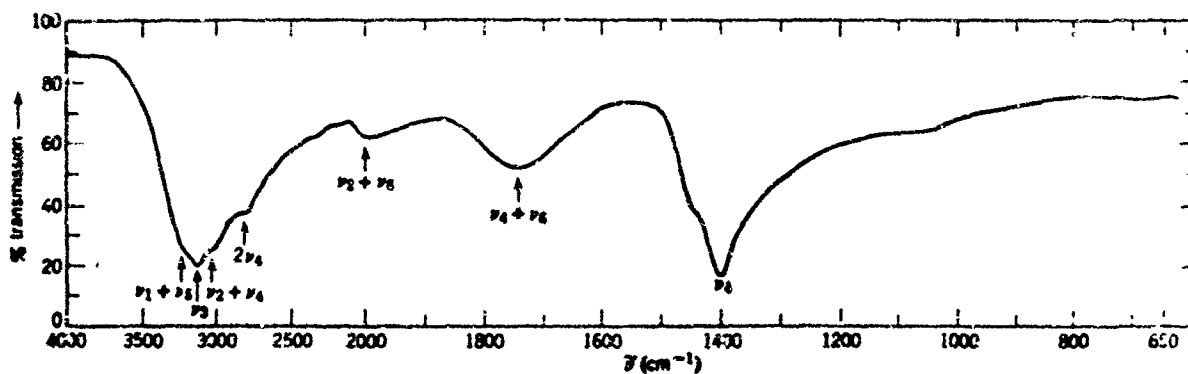


Fig. 10 Infrared Spectrum of Pu_4Cl Sublimed onto NaCl Plates
(From "Infrared Spectra of Inorganic and Coordination Compounds" by Kazuo Nakamoto, John Wiley & Sons, New York (1963))

coated coil was washed several times with deionized water. On one occasion, after thoroughly washing an 800°C coating, the coil was left for about an hour in deionized water in a stoppered vial. Upon opening the vial, a strong odor of ammonia was detected. The water was replaced and the procedure was repeated. Again a strong odor of NH_3 developed, suggesting poor hydrolytic stability of coatings deposited at 800°C. This same washing and soaking was repeated with coils coated at 1000° and 1300°C. No ammonia odor was detected.

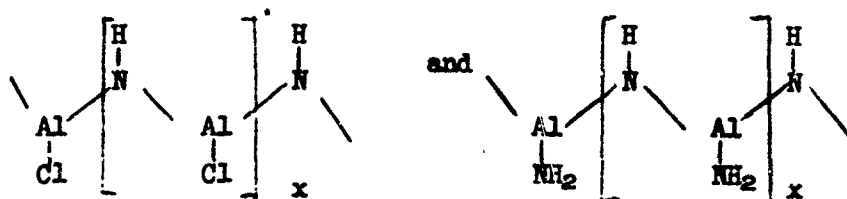
A somewhat more exact measure of the hydrolytic stability was then obtained. Samples of aluminum nitride coated on molybdenum wire coils at 800°, 1000° and 1300°C were washed rapidly with deionized water to remove any NH_4Cl picked up on being removed from the deposition tube. After drying at 130°C, they were finely ground, weighed and soaked in 25 ml of deionized water. After 1 hour in water with intermittent shaking, aliquots for ammonia and chloride ion determinations were removed using a pipette fitted with a filter stick. Ammonia content was determined colorimetrically by the use of Nessler's reagent. Absorbance was measured at 4000 Å using a Beckman Model DU spectrophotometer. The aliquot for chloride ion determination was diluted with a mixture of methanol and acetone and then acidified with 1:1 H_2SO_4 . It was titrated with 0.0025 N AgNO_3 using glass and silver electrodes. After 8-1/3 hours, aliquots were again removed for ammonia and chloride determination. Results of these determinations are shown in Table 1. It can be seen

Table 1

Products of Hydrolysis of Aluminum Nitride Deposited
at 800°, 1000° and 1300°C Using $\text{AlCl}_3 + \text{NH}_3$ as Reactants

Deposition Temperature	<u>1 Hour Hydrolysis</u>		<u>8.5 Hour Hydrolysis</u>	
	Moles NH_3 100 gm Sample	Moles HCl 100 gm Sample	Moles NH_3 100 gm Sample	Moles HCl 100 gm Sample
800°C	0.120	0.120	0.160	0.113
1000°C	0.018	0.007	0.042	0.011
1300°C	0.008	0.004	0.031	0.007

that coatings deposited at 800°C are more susceptible to hydrolysis than are the 1000°C and 1300°C coatings. At lower deposition temperatures, the deposit very probably contains incompletely condensed hydrolyzable materials having the general composition:



The presence, and hydrolysis, of the amino-substituted material would account for the higher than 1:1 molar ratio of ammonia to HCl actually found in the hydrolysis products. It is possible that the instability that does occur in the higher temperature coatings is due to the "projection growth" (Fig. 6) which no doubt deposits at lower than nominal deposition temperatures.

2.1.2.1.4 Electrical Properties

Conductivity, loss factor and other electrical properties of aluminum nitride films deposited at 800°C and 1300°C from AlCl_3 and NH_3 vapors are shown in Figs. 11, 12 and 13. As might be expected, the conductivity of the deposits formed at 800°C is fairly high. The d-c value measured at 300°C is $8 \times 10^{-10} (\text{ohm-cm})^{-1}$. Since at this temperature the conductivity vs temperature curve is becoming quite steep, measurements were not made at higher temperatures. The conductivity of the film deposited at 1300°C was measured up to a temperature of 600°C. It is lower, by a factor of 10^4 , than the 800°C deposit. The electrical properties of this film are comparable to those of films previously deposited using the separately prepared $\text{AlCl}_3 \cdot \text{NH}_3$ complex.⁸ The dielectric constant and conductivity values reported here in Figs. 12 and 13 may be in error by as much as 20% due to the uncertainty about the film thickness, which was variable due to roughness of the surface. The surface was in fact so rough that continuity of the deposited platinum electrode could not be maintained at high temperatures (600°C and above).

Curve 579736-B

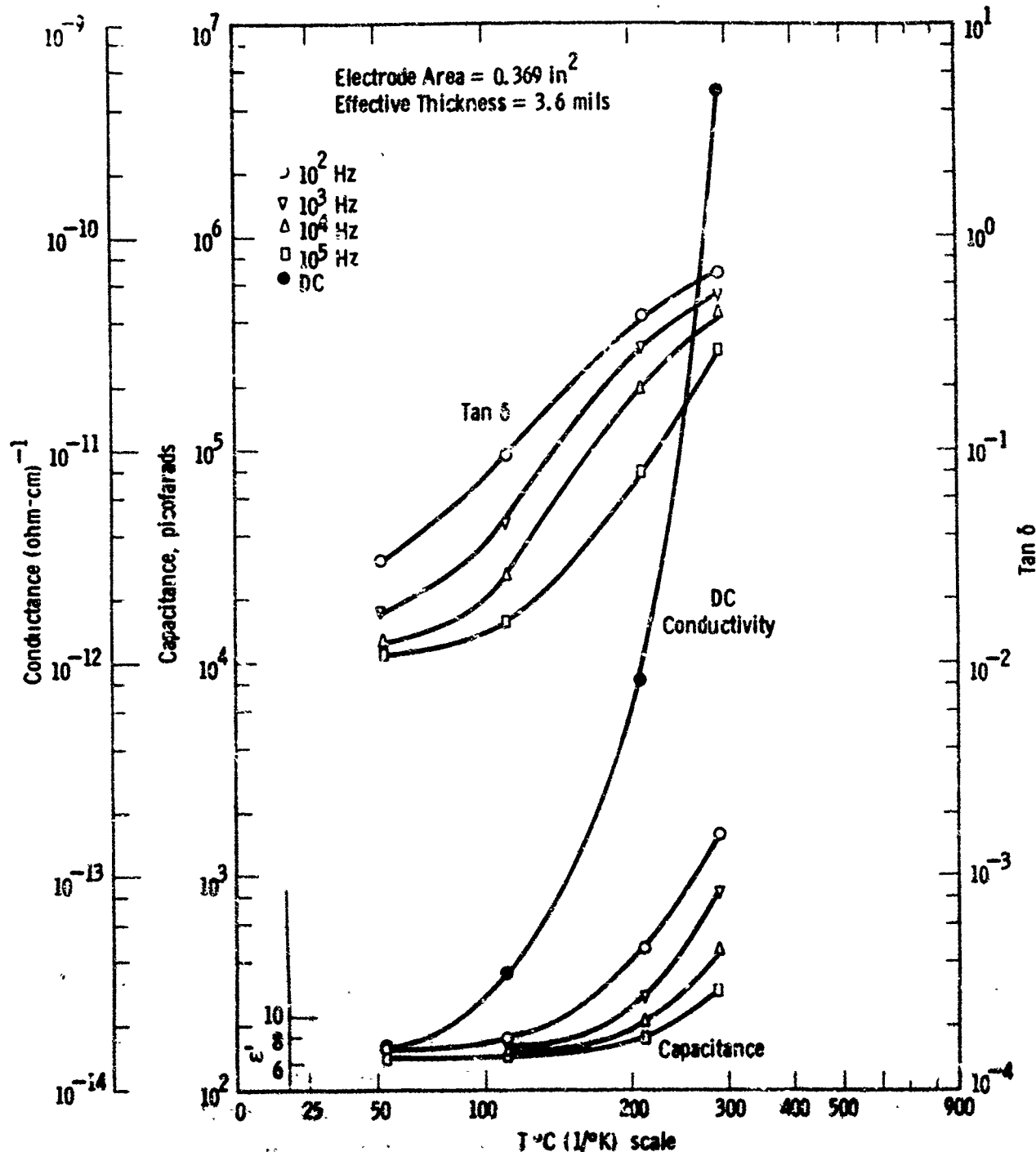


Fig. 11—Dielectric Properties of Aluminum Nitride
Sample LHE2-2, Deposited at 800°C

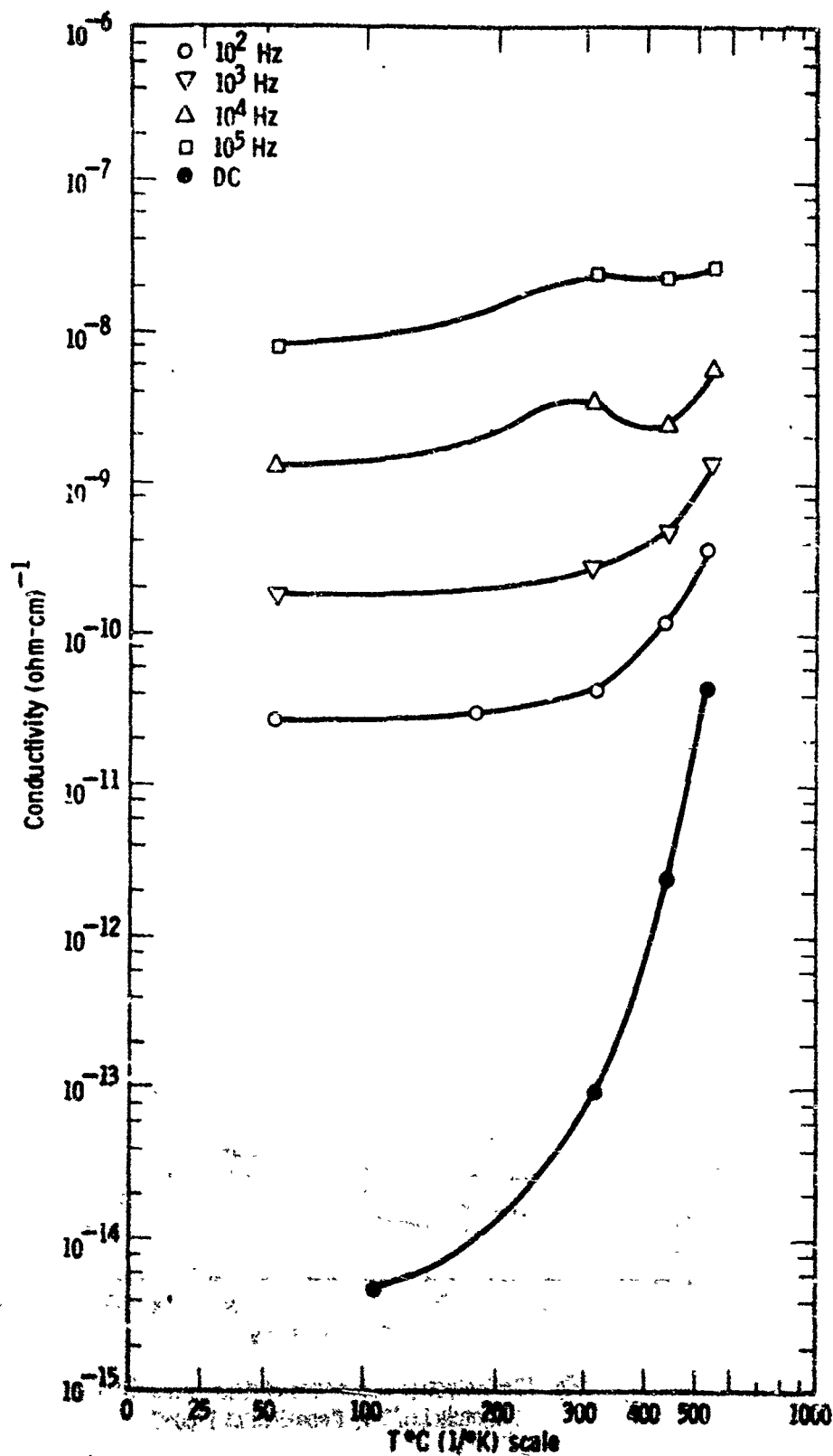


Fig. 12-Conductivity of Aluminum Nitride
Sample LH79-L, Deposited at 1300°C

Curve 579732-8

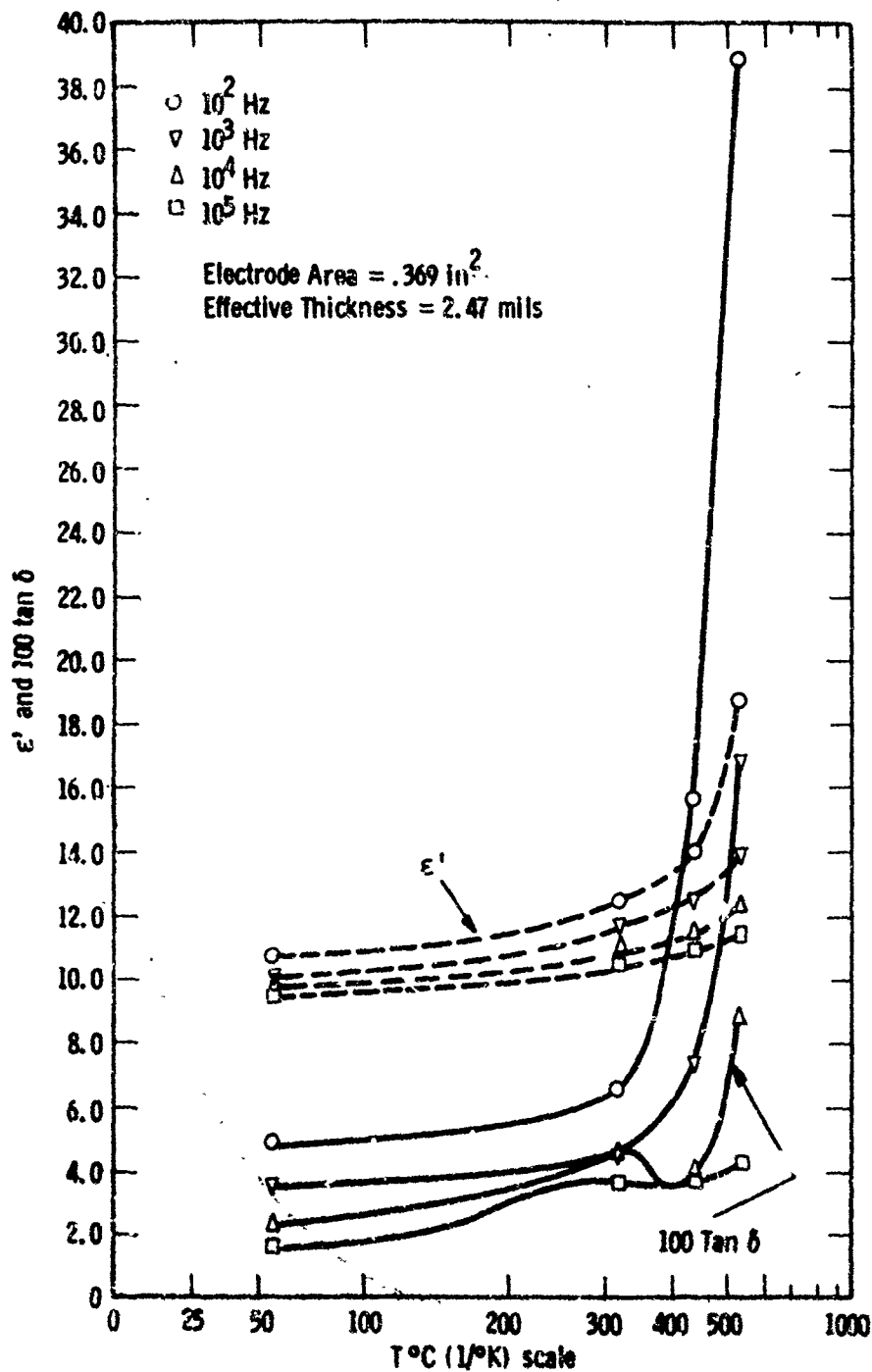


Fig. 13—Dielectric Properties of Aluminum Nitride
(Sample LH79-1, Deposited at 1350°C)

2.1.3 Deposition of Aluminum Nitride at Intermediate Pressures

As described above, one of the early procedures investigated for the deposition of aluminum nitride was that of heating the substrate in a continuously pumped (.01 to .02 torr) system containing undiluted $\text{AlCl}_3 \cdot \text{NH}_3$ vapors. This method gave very nonuniformly coated or only partially coated substrates. More uniform coatings were later obtained by using a flow of nitrogen at atmospheric pressure to carry vapors of the complex over the hot substrate. Properties of coatings deposited at atmospheric pressure were examined quite extensively. The coatings were very hard, brittle, oxidation resistant and afforded considerable oxidation protection to molybdenum substrates. However, the presence of residual chlorine in the coatings was believed to have been the cause of failure to attain the expected excellent high temperature electrical properties of aluminum nitride. Another bothersome aspect of coatings deposited at atmospheric pressure was the development of beaded nodules in coatings one mil thick and greater.

It was suggested that deposition in vacuum would possibly aid in removal of chlorine impurity. Since deposition under continuously pumped conditions did not give satisfactory coverage, a combination of the vacuum and the atmospheric nitrogen flow system was then investigated.

In this procedure aluminum chloride, in the cup at the bottom of the U tube shown in Figure 1, was reacted with ammonia to form a volatile complex which is solid at room temperature but liquid above 150°C . Substrates were given a 20 minute heat cleaning and degassing by heating with an external r.f. induction coil to about 1500°C at a pressure of 5 to 10 microns. Substrates in this case were usually flat molybdenum, and some graphite, plates suspended with their main plane in the horizontal position as sketched in Fig. 1. Examples of these coated plates are shown in Fig. 14. The temperature of the substrate was then lowered to the desired temperature and the pressure was increased to 5 to 10 torr by allowing ultra pure nitrogen to enter the system by way of a controlled leak. The temperature of the cup containing the source material was raised to 150° to 200°C by means of a heating mantle.

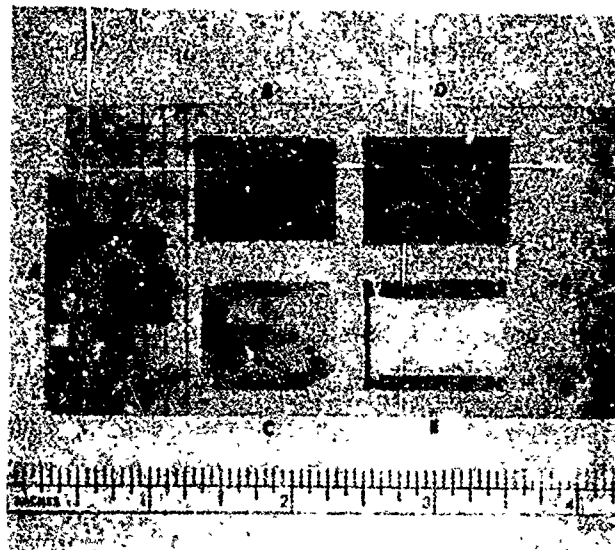


Fig. 14 Aluminum Nitride Deposited on and Isolated from Molybdenum Plates

- A. Four Mil AlN Film Isolated from Molybdenum Plate
- B. and D. Aluminum Nitride Deposited on Molybdenum Plate
- C. Ten Mil AlN Film Isolated from Molybdenum Plate
- E. Reverse Side of Coated Plate

Under these conditions with substrate temperatures of 1100° to 1400°C the rate of deposition can be varied from 1 to 10 mils per hour by varying the temperature of the starting material from 150° to 200°C. As experienced previously, it has not been possible to deposit onto a substrate at temperatures greater than 1400°C. No coating is obtained at this or higher temperatures. Coatings in the 1350° to 1400°C range were obtained by giving the substrate a flash (~ 30 seconds) coating at ~1000°C then raising the generator to full power. With the flash coating on, further deposition takes place at 1350-1400°C. Full power setting on the generator easily heats a bare molybdenum plate or rod to 1600°C but the high emissivity of the coating prevents the flash-coated substrate from attaining this temperature. Depositions applied to lightly sand blasted molybdenum surfaces are quite hard (~8 on Moh's scale), adherent, relatively smooth and generally free of nodules. The lower the rate of deposition the smoother is the surface of the deposit. The uniformity and appearance of these coatings are superior to those formed at atmospheric pressure. As deposited adherently on the molybdenum plate, coatings appear gray but when released from the plate they are white or light tan. Some of these are also pictured in Fig. 14.

Samples for elemental analysis have been cracked from plates or rods by crushing the coated specimen in a hydraulic press. Results of analysis of two different depositions at 1250° to 1300°C are given in Table 2.

Table 2

Elemental Analysis of Pyrolytic Aluminum Nitride

	<u>% Al</u>	<u>% N</u>	<u>% Cl</u>
Theoretical	65.85	34.15	----
LH-103-3	66.2	32.5	0.31
LH-111-2	66.1	33.3	0.32

It can be seen that these samples while containing less chlorine than previous depositions still contain about 0.3% of this impurity. As discussed in Section 2.4 of this report (Figs. 38 and 39), their

high temperature electrical properties are similar to values reported for hot pressed specimens. They are not what is expected for high purity aluminum nitride.

In addition to isolating coatings by crushing the coated substrate in a press, samples of pyrolytic aluminum nitride have been separated from molybdenum plates, (which had been coated on only one side) by dissolving the plate in a mixture of nitric and hydrofluoric acids. Two such isolated coatings are seen in Fig. 14 along with coated plates. The acid has no noticeable effect on the coating.

2.1.4 Composition and Structure of Pyrolytic Aluminum Nitride

It is well known that elemental analysis of these highly refractory and inert materials is very troublesome. Results of nitrogen determination are often less than 1/2 of the actual value. But it is believed that a reliable method of analysis has finally been developed on this project. The procedure of analysis is given in the last paragraph of the section. Two examples of results of analysis of pyrolytic aluminum nitride are seen in Table 2. In these two samples the average of aluminum values is 0.3% higher than theoretical and the nitrogen average is 0.75% low. These analyses indicate that the deposit is AlN. However, chlorine contamination of these materials deposited by pyrolysis of $\text{AlCl}_3 \cdot \text{NH}_3$ at 1300°C and 5 to 10 torr is of the order of 0.3%.

As noted earlier, x-ray diffraction analysis of these deposits show the presence of the hexagonal wurtzite structure which AlN is known to have. Infrared analysis also confirms its presence. Optical (500x) and electron micrographs (6400x) of a cross-sectioned surface of material deposited at atmospheric pressure showed the presence of voids. In Fig. 5 of this report is a 50x photograph of a fractured surface of this material showing the presence of a nodule growth. The occurrence of such nodules has been reported in the structure of pyrolytic graphite and boron nitride. The density of this material, determined on a sample of rather limited size was 2.61 g/cc. Later samples deposited at 1350°C and a pressure of 5 to 8 torr proved to be much more dense. The density

of a 4.35 gram sample accumulated from 4 depositions, by dissolving away the molybdenum plate substrates in a HNO_3 -HF mixture, was found to be 3.13 g/cc. This compares with a value of 3.26 g/cc calculated using the cell dimensions, $a = 3.111 \text{ \AA}$ and $c = 4.980 \text{ \AA}$. An air comparison pycnometer was used.

In the determinations of chlorine in AlN, 0.1 gram of the deposit was dissolved by slowly boiling in 8 ml of 50% NaOH solution. This was acidified with H_2SO_4 and diluted with 100 ml each of methanol and acetone. It was then titrated with AgNO_3 . A blank was run on the reagents in the same manner. For aluminum analysis, again a 0.1 gram sample was dissolved in the same way and then acidified with HCl. Methyl red indicator was added, the solution was brought to boiling, and then neutralized with NH_4OH . The precipitated hydroxide was heated for 1 hour at 1100°C to convert it to the oxide which was then weighed. Nitrogen was determined by covering 0.1 gram of sample with 3 grams of H_2O in a platinum crucible. The crucible was placed in a quartz apparatus through which a flow of nitrogen was maintained. The quartz tube was heated to 700°C for 1 hour and the exit gases were bubbled into $6\text{NH}_2\text{SO}_4$ to absorb liberated NH_3 . This acid was transferred to a micro Kjeldahl apparatus from which NH_3 was distilled into a 5% boric acid solution. The boric acid was titrated with 0.1N HCl.

2.1.5 Oxidation Resistance of Aluminum Nitride Coatings and Protection Offered to Molybdenum

The product of oxidation of aluminum nitride at high temperatures is alumina. Total conversion of the nitride to the oxide would result in a weight gain of 25%. To determine the extent of oxidation of a 4 mil film deposited at atmospheric pressure, it was heated in air at 1000°C for 115 hours. After 90 hours the sample stopped gaining weight. The total increase during this heating was 4% which probably represents the conversion of the nitride surface to alumina.

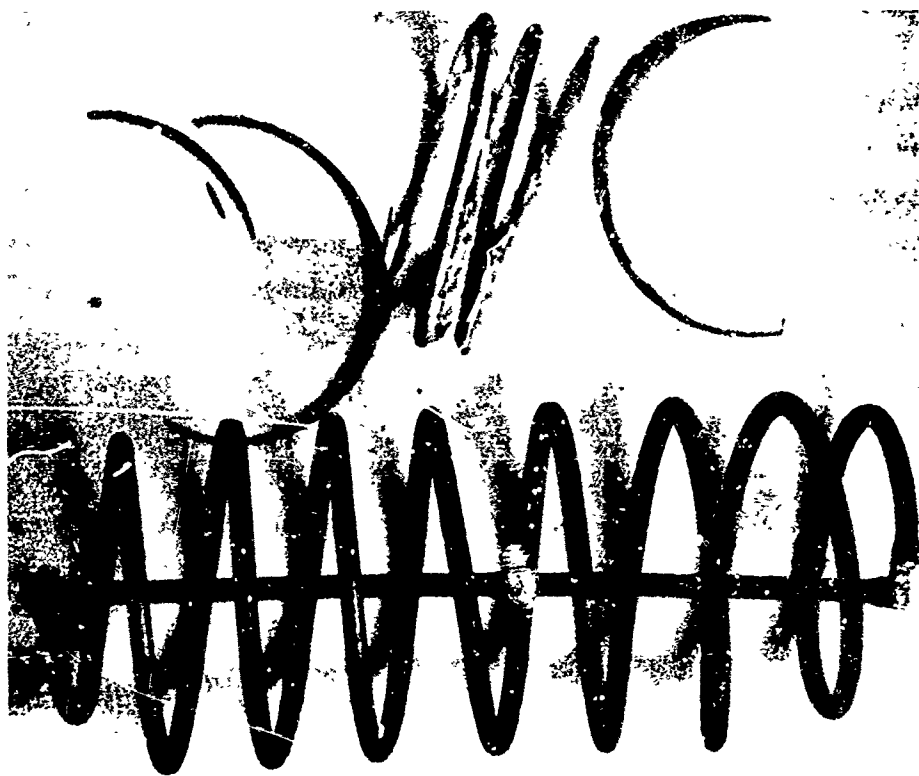


Fig. 15 Molybdenum Wire Coils, Uncoated and Coated with 0.1 Mil Aluminum Nitride after 16 Hours at 700°C in Air (3X)

Table 3
Weight Loss of Aluminum Nitride Coated and
Uncoated Molybdenum Wire Coil in Air at 700°C

	Coated Coil (LH-54-2)		Uncoated Coil	
Weight	3.3960 grams		3.4250 grams	
Area	13.37 cm ²		13.45 cm ²	
Hours at 700°C	Weight Lost		Weight Lost	
	grams	gms/cm ² /hr	grams	gms/cm ² /hr
18	0.0022	1.5×10^{-7}	0.8838	6.1×10^{-5}
25.5	0.0045	2.2×10^{-7}	1.3448	6.5×10^{-5}
41	0.0137	4.1×10^{-7}	2.0482	6.4×10^{-5}
65	0.0431	8.0×10^{-7}	3.0083	5.9×10^{-5}

Molybdenum rods and wire coils coated with aluminum nitride were heated in air at 700°C and above to determine to what extent the coating protects the metal against oxidation. Molybdenum metal begins to oxidize noticeably at 400° and very actively at 600°. Sublimation of the oxide layer begins at about 640°C. Judging from the oxidation resistance of the nitride film itself, a continuous nonporous film should protect molybdenum from oxidation up to 1000°C. A coil made of 0.040 inch molybdenum wire was coated with 0.2 mil of AlN. This coil, along with an uncoated molybdenum coil of similar geometry, was heated at 700°C for 65 hours. The loss in weight of each coil with time is tabulated in Table 3. The weight loss of the uncoated coil is several orders of magnitude greater than that of the coated coil. The rate of weight loss of the uncoated coil is fairly constant at about 6×10^{-5} gm/cm²/hr, but that of the coated coil is initially about 10^{-7} gm/cm²/hr and slowly increases to about 10^{-6} gm/cm²/hr. This increase is the result of the onset of pitting of the wire. During the first 41 hours, corrosion was noted on the rough cut ends of the coil which appeared to contain uncoated crevices. At the 65 hour weighing, pitting was noted on one of the turns. The condition of coated and uncoated coils is pictured in Fig. 15.

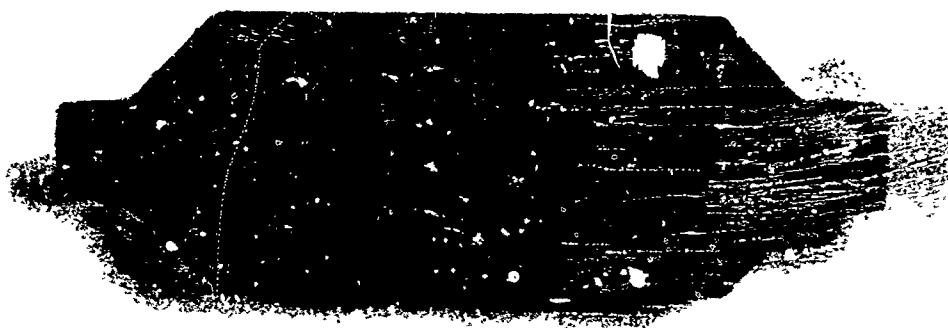
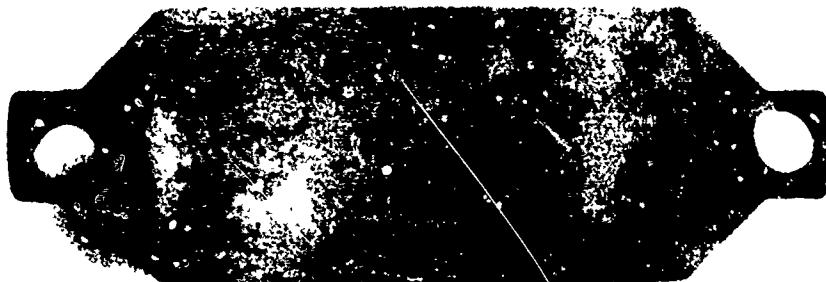
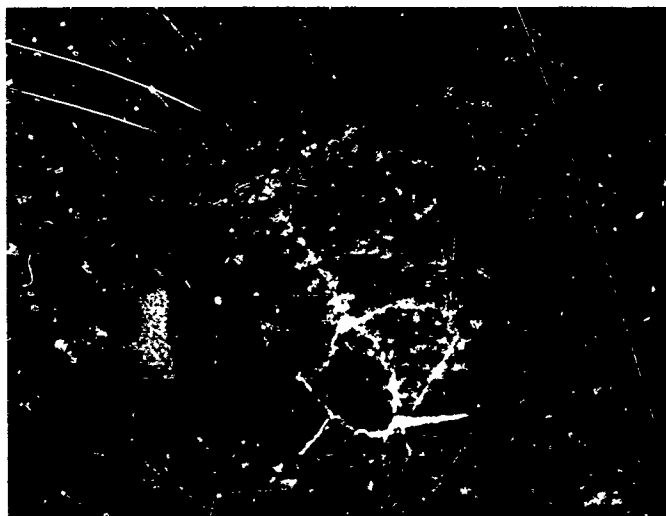


Fig. 16 Aluminum Nitride-Coated Molybdenum Rod Heated 17 Days in Air
at 700°C Showing Corrosion Growth in Hole at Right (3X)



A



B

Fig. 17 A. Aluminum Nitride-Coated Molybdenum Rod Heated in Air for 20 hrs. at 700°, 24 hrs. at 800°, 24 hrs. at 914° and 42 hrs. at 986°C (3X)

B. Corrosive Attack on End of Same Rod After this Heating Schedule (12.5X)

A 1/2 inch diameter molybdenum rod which was given a 3 mil coating of AlN was heated for 17 days in air at 700°C. This is shown in Fig. 16. The only evidence of oxidative attack is a small white growth which can be seen in the interior of one of the suspension holes. Another 1/2 inch diameter rod which had been coated with 6 mils of AlN at a substrate temperature of 1150°C, and a pressure of 5 to 7 torr was heated in air up to 986°C. The heating schedule and cumulated weight change of the coated rod are as follows:

700°C	20 hours	-1.8 mg
800°C	24 hours	--
914°C	24 hours	+2.1 mg
986°C	42 hours	+2.1 mg

The specimen was taken directly from furnace temperature to room temperature for observation and weighing. After weighing, it was put back into the furnace at temperature. In Fig. 17A is a photograph of the rod after this heating schedule. No change was noted in the appearance of the coating after the 700° and 800° heating. After 24 hours at 914°, several fine white lines were visible in the coating at one of the flat ends of the rod. After the subsequent 42 hours at 986°, a break occurred in the coating at this point showing oxidative attack. This break is shown in Fig. 17B.

2.1.6 Flexibility of Aluminum Nitride Films

Six inch lengths of .040" molybdenum wire have been coated with aluminum nitride in thicknesses of 0.5 mils to several mils. These insulated wires were used to check the flexibility of the coating. When wires coated with 0.5 mil films were bent around an 0.8 inch mandrel, general cracking and some chipping occurred. In another evaluation, 5 mil molybdenum foil strips with 0.2 mil coatings and others with much thinner films (0.1 to 1 micron) were bent over mandrels ranging from 3 to 7/8 inches in diameter. The usual diameter increment between mandrels was 1/4 inch. As seen in Fig. 18A, the 0.2 mil film did not show cracking until bent around the 2-1/4 inch diameter. Over the 2 inch mandrel, there was increased cracking and some chipping began.

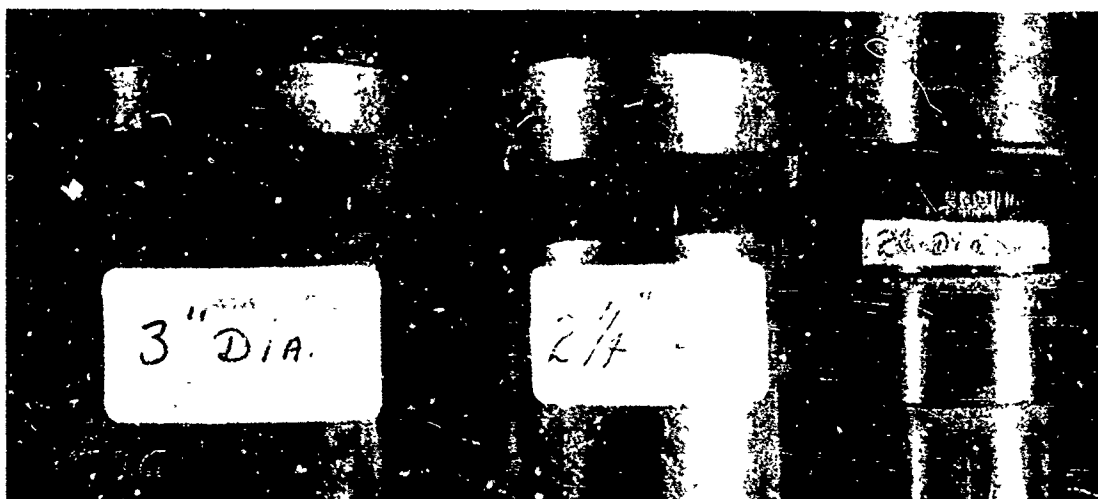


Fig. 18 A. Two Tenth Mil Film of AlN on Molybdenum Foil Showing Cracking when Bent over 2-1/4 inch Mandrel



Fig. 18 B. One Tenth Micron AlN Film on Molybdenum Foil Showing no Apparent Cracking when Bent over 7/8 inch Mandrel

Fig. 18B shows a molybdenum strip having a coating thin enough to show interference patterns. No obvious cracking in this film took place as the mandrel diameter was reduced to 7/8 inch, but when examined under a microscope a few long cracks were apparent.

In applications such as capacitors, where thin coatings are required and where sharp bends are not encountered, the limited flexibility of these coatings probably could be tolerated. They might also be used to insulate coils where these could be formed into the desired shape prior to coating.

2.2 Aluminum Nitride from Reaction of Aluminum with Ammonia

The literature contains several reports of the preparation of aluminum nitride by the nitridation of elemental aluminum. Nitridation has been carried out by striking an arc between aluminum electrodes in an atmosphere of nitrogen²; by vaporizing aluminum at 1800 to 2000°C in a nitrogen atmosphere; and by heating the molten metal to 1000°C in a flow of ammonia gas⁹.

We have made several runs in which molybdenum rods, coated with a layer of evaporated aluminum, were heated to 1250° in a flow of dry NH₃ gas. The rod was suspended in a vertical quartz tube (Fig. 1) through which ammonia flowed at a rate of 0.7 liter /min. The rod was brought to temperature as rapidly as possible (< 5 mins.) so as to minimize the risk of the aluminum beading up or alloying with the rod. No beading was apparent, but alloying did occur as noted below. An insulating film of AlN, about 0.4 mil thick, was obtained on one rod. The film had peeled away from the rod at several spots. An x-ray diffraction pattern of the peeled film showed AlN to be present. When another sample was scraped from the same rod, the sample was contaminated and diluted with substrate metal and an interface alloy. In the complex x-ray diffraction pattern of this sample, alloys having the crystal structure of Mo₃Al and Al₃Mo were detected. Films formed on other rods by this method either contained pinholes or were so thin that probes and electrodes easily pierced them. In these experiments, the operations of vacuum heat cleaning of the rod, evaporation of the aluminum film, and nitridation of the film were carried out separately.

Limitation of time did not permit the construction of an apparatus which would allow all three operations to be carried out without exposing the rod to the atmosphere between operations. One of the problems encountered in this work is the difficulty of obtaining adherent, pinhole-free evaporated aluminum films which are thick enough to produce aluminum nitride films having adequate electrical resistance.

2.3 Pyrolytic Deposition of Silicon Nitride

The early synthetic work on silicon nitride was accomplished by the nitriding of silicon powders or the ammonolysis of silicon tetrachloride followed by heating to produce bulk samples of silicon nitride.¹⁰⁻¹² This was followed by the investigation of Popper and Ruddlesden who prepared structural materials from nitrided silicon.³ The process involved pressing fine silicon powder into the desired shape, partially nitriding to increase the strength of the green body, machining to final tolerances and finally nitriding to as great an extent as possible. This generally resulted in structures which had a high degree of porosity and a relatively large amount of non-reacted silicon. The electrical properties of this material (18-28% porosity) show it to be a good insulator with resistivities of $> 10^{13}$ ohm-cm at room temperature and 10^6 ohm-cm at $\sim 1000^\circ\text{C}$. If the nitrided silicon body was compacted to higher density, however, the conductivity increased. This has been attributed to the presence of nonreacted silicon in the nitrided body.

More recent efforts in the investigation of silicon nitride have been concerned with the preparation of films as passivating layers for integrated circuits and encapsulating materials for devices.^{13,14} Thin films of silicon nitride seem to be well suited to this use since the material is reported to have a high order of chemical inertness and displays resistance to radiation and oxidation at high temperatures. Silicon nitride also acts as a barrier to the diffusion of sodium.¹³ Problems do exist however, in the characterization of silicon nitride. Materials described as silicon nitride in patents and in the chemical literature are sometimes found to be other materials. An example of this is work that was done to deposit silicon nitride as a high temperature dielectric

for use in molybdenum capacitors. After several patents had been issued and a publication had appeared, the authors discovered that the material they had thought to be silicon nitride was in fact silicon dioxide.¹⁵⁻¹⁹ Fortunately, in this case, the authors were quick to point out the error.

The recent interest in silicon nitride as a possible replacement for silicon oxide acting as a thin film on semiconductor devices has resulted in the development of new techniques for the synthesis of this material. These include r.f. sputtering, pyrolysis of silicon tetrachloride in an ammonia atmosphere, vapor phase transport, the pyrolysis of silane and ammonia, and various other methods.¹³ We have independently investigated some of these methods including the $\text{SiCl}_4 + \text{NH}_3$ method, a method involving pyrolysis of a $\text{SiF}_4 \cdot 2\text{NH}_3$ complex, vapor phase transport, and the use of silane and ammonia.⁸

The $\text{SiCl}_4\text{-NH}_3$ method ideally would be thought to follow the reaction as illustrated in Equation 1.



It is known, however, and in fact it is readily observable, that SiCl_4 and NH_3 react even under ambient conditions to give a complex polymeric product possibly containing, in addition to the Si-N bonds expected, Si-Cl, Si-NH, SiNH_2 , various other groupings and impurities such as NH_4Cl . Conditions desirable for good chemical vapor deposition, such as the absence of a gas phase reaction for example, are not readily obtainable except under the most carefully controlled conditions.

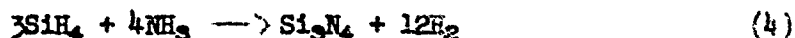
A solid phase complex of SiF_4 and NH_3 , which was reported in 1955 by Miller and Sisler²⁰, was also used to prepare silicon nitride. The complex, $\text{SiF}_4 \cdot 2\text{NH}_3$, after being placed in the reaction apparatus, was volatilized by localized heating, transported into the vicinity of a hot substrate by carrier gases and subsequently pyrolyzed to silicon nitride.

The equations describing this sequence of reactions are shown as Equations 2 and 3.



The by-products shown in Equation 3 would be expected to give rise to problems similar to these found with the use of SiCl_4 and NH_3 .

The system which has been subjected to the most thorough examination has been that which involves the pyrolysis of silane and ammonia. Ideally, this reaction would proceed as shown in Equation 4.



Of the systems considered, this one, due to the absence of solid phase by-products, should proceed with the least chance of by-product contamination. In addition, silane and ammonia do not undergo reaction at ambient or even moderate temperatures, thereby minimizing the possibility of spontaneous nucleation from the gas phase. It should be mentioned, however, that the main disadvantage of working with this system is that silane is a pyrophoric material and must be handled in the absence of air or oxygen.²¹⁻²³

2.3.1 Deposition of Silicon Nitride by the Pyrolysis of Silane and Ammonia

The deposition on a molybdenum surface, of films from silane and ammonia, as it has developed in this investigation can be classified into three categories. These are primarily dependent upon the temperature of deposition and to a lesser extent upon the pressure during the deposition cycle. After a general description of the experimental procedure, the two extremes of temperature under which coatings have been obtained will be discussed along with the properties of the coatings obtained at these temperatures. The solid phase by-product of the reaction will be briefly discussed and a suggested mechanism for the deposition of silicon nitride,

which is based on the pyrolysis of silane and the known physical properties of the coating and by-products, will be developed. Finally, the coatings which are deposited at $\sim 1000^{\circ}\text{C}$ and seem to display the most desirable properties will be discussed in greater detail.

2.3.1.1 Reagents

Carrier grade, ultrapure, nitrogen obtained from Air Products and Chemical Inc., anhydrous ammonia ($> 99.95\%$) and silane (99.9999%) from the Matheson Co., Inc. and trichloroethylene, electronic grade, from Fisher Scientific Co. were among the chemicals used in this investigation. AEX Air Eraser Compound, obtained from Paasche Air Brush Co., Chicago, was utilized for surface sandblasting of a substrate prior to deposition.

2.3.1.2 Apparatus

Originally the apparatus was one constructed with a borosilicate glass manifold and fused silica reactor. This was later modified to the present system (Figs. 19-21) made with a type 316 stainless steel manifold and a water-cooled fused-silica reaction tube attached to the system through O-ring seals. The rotameters, which are connected to the system through Teflon pressure fittings, are calibrated glass tubes with stainless steel and glass floats. Gas flows are controlled by stainless steel needle valves - other valves in the system being stainless steel with Teflon packing.

2.3.1.3 Substrates

Graphite rods, platinum sputtered on fused silica, fused silica slides, platinum foil and molybdenum plate, rod, wire and foil have been used as substrates in these experiments. Difficulty was experienced in uniformly heating molybdenum wire coils in an r.f. field. Since the electrical measurements could more readily be performed on plates or rods, and since the electrical and other physical properties characteristic of the nitride films on molybdenum would be expected to be the same on a wire as found on a plate or rod, it was not deemed necessary to change the method of heating to, for example, resistance heating in order to accommodate the wire.

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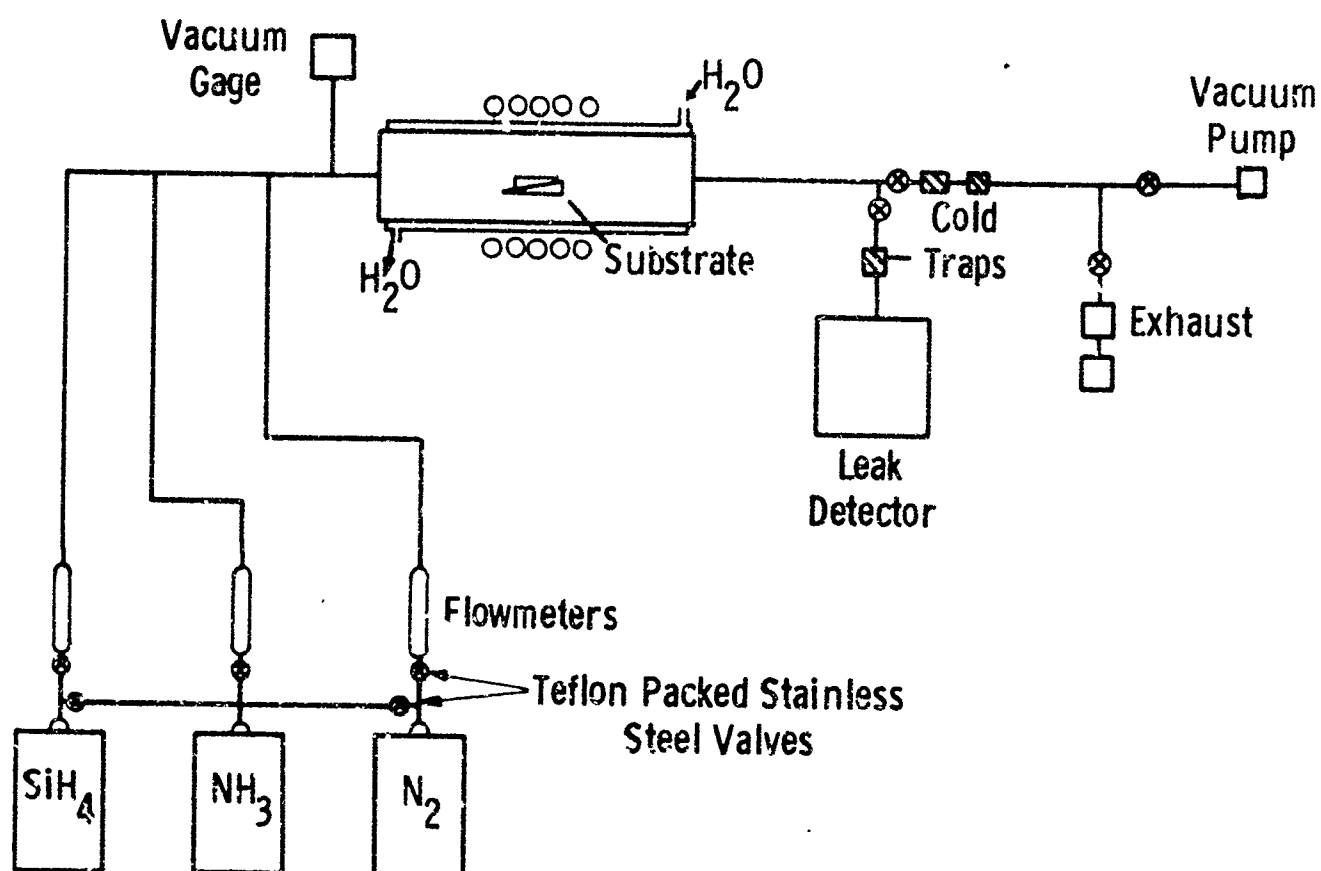


Fig. 19 —Schematic diagram of apparatus used for the deposition of silicon nitride

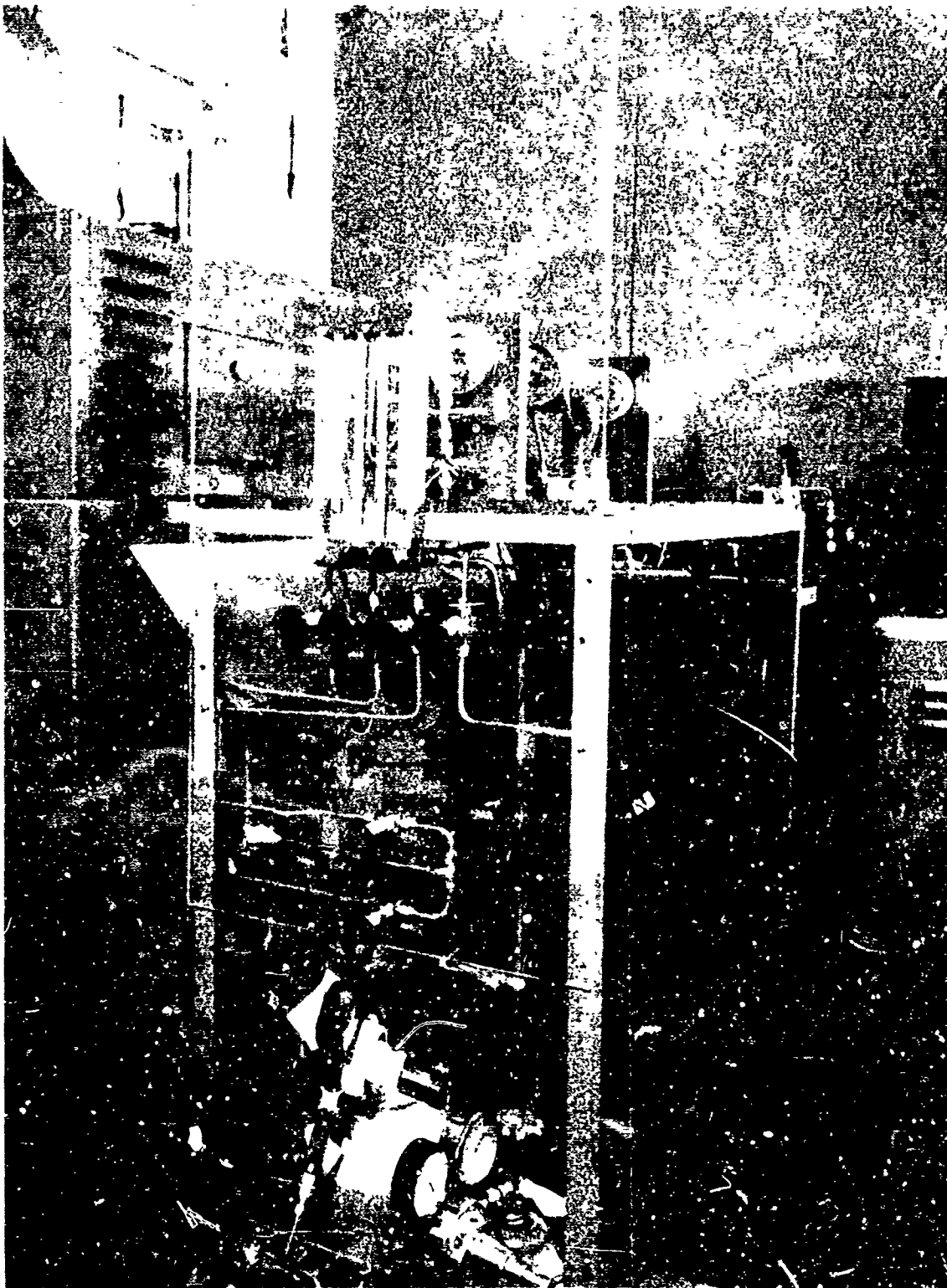


Fig. 20 Apparatus for the Deposition of Silicon Nitride
Showing Purge System and Flow Meters



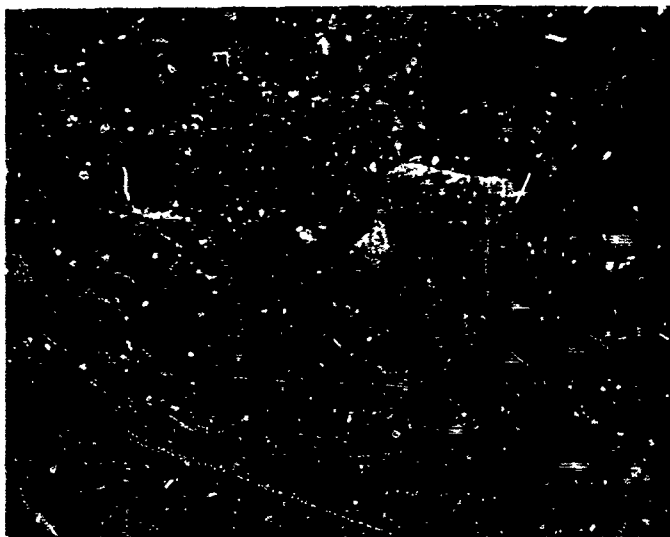
Fig. 21 Apparatus for the Deposition of Silicon Nitride
Showing Traps and Exhaust System

Of the substrates considered, the thermal coefficient of expansion of molybdenum offers a reasonably close match to that reported for silicon nitride (see Table 4). In addition, molybdenum is a favorable high temperature electrical conductor since it can carry the highest current per unit mass of all the refractory conductors. For these reasons most of the recent work on the deposition of silicon nitride has been done with molybdenum, either in the form of plates or rods, as the substrate material.

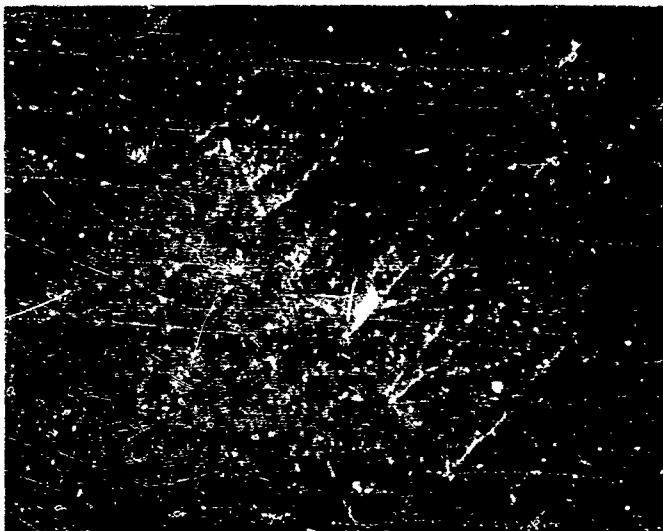
Table 4
Properties of Some High Temperature Materials (24)

Material	Melting Point °C	Density g/cc	Electrical Resistivity Micro ohm-cm	Thermal Expansion $\times 10^{-6}$ °C ⁻¹
Tungsten	3410	19.3	5.5	4.5
Tantalum	2996	16.6	13.5	6.6
Osmium	2700	22.5	9.5	6.6
Molybdenum	2620	10.2	5.2	5.4
Platinum	1773	21.45	10.6	10.2
Silicon Nitride	1900 (decom.)	3.18	1×10^{11}	2.5

It has been experimentally observed that sandblasted and degreased molybdenum surfaces provide a favorable surface for the deposition of silicon nitride. In fact in one experiment a molybdenum plate was partially sandblasted, thoroughly cleaned and coated with pyrolytic silicon nitride. As shown in Fig. 22, the sandblasted area received much more adherent and uniform coating than the area which was not sandblasted. Use of a polished molybdenum substrate generally resulted in a film with poor adherence. As a result of these and similar experiments a standardized surface preparation, that has proven to be satisfactory, has experimentally evolved. This consists of sandblasting the molybdenum substrate followed by several successive ultrasonic degreasing treatments,



A



B

Fig. 22 Micrograph of Silicon Nitride Coated Molybdenum Plates
Showing Junction Between Sandblasted and Polished Surfaces

- A. Left - Sandblasted; Right - Polished (50X)
- B. Top - Sandblasted; Bottom - Polished (12.5X)

each with fresh aliquots of trichloroethylene, rinsing with trichloroethylene and air drying. The substrate is then heat treated just before deposition, as indicated in a subsequent section.

2.3.1.4 Procedure

Typically, the experimental procedure involved placing a cleaned substrate on a susceptor which in turn rested on an inclined fused silica sled. The susceptor generally consisted of a 0.060" or 0.120" thick molybdenum plate. After assembly, the sled, susceptor and substrate were inserted into the reactor and centered in the work coil of the r.f. generator. The reactor was isolated from the atmosphere, purged with nitrogen and then evacuated to a few microns of pressure. Further cleaning of the substrate was then accomplished in vacuo by heating the substrate-susceptor assembly to the vicinity of 1500°C for ten to fifteen minutes. The substrate was then allowed to cool and the pressure in the system was adjusted by metering in the desired quantities of nitrogen, ammonia and silane. (Experiments were done at pressures ranging from a few mm of mercury to slightly above atmospheric pressure). Deposition was initiated by again heating the substrate. The temperature was closely monitored, especially during the early phases of the deposition, and adjusted to maintain as near a constant temperature as possible.

Exhaust gases, which probably contained unreacted ammonia and silane as well as hydrogen, higher gaseous silanes and other complex gaseous by-products formed as a result of the pyrolysis, were passed through a liquid nitrogen trap before being pumped into the atmosphere. (In the case of experiments at slightly above atmospheric pressure, when no vacuum pump was used, the exhaust gases were bubbled directly through a basic alcohol solution to decompose silane before exposure to air; no liquid nitrogen trap was used in this circumstance.) At the termination of a reduced pressure experiment, the system was pressurized with nitrogen and, after a nitrogen flow had been established through the basic alcohol solution, the traps were gently warmed allowing the condensed reactants and by-products to be passed through the basic alcohol solution. In a carefully purged and leak free system no problems were observed using this

technique. It is imperative, however, that care be exercised since even the slightest leak could possibly allow oxygen (b.p. -182.5°C) to condense in the liquid nitrogen trap (b.p. -195.8°C).

2.3.1.5 Deposition at $700-800^{\circ}\text{C}$

A series of experiments conducted with the pressure of the reactor (air cooled) held slightly above atmospheric and flow rates of ~ 0.5 cc/min of silane, ~ 80 cc/min of ammonia and ~ 250 cc/min of nitrogen over a molybdenum substrate held in the vicinity of $700-800^{\circ}\text{C}$ yielded coatings which were metallic gray in color and relatively soft, having a hardness of 6.5-7.5 on Mohs' scale. These materials were characteristically amorphous as determined by x-ray powder data and yielded an infrared spectrum like that shown in Fig. 23. The predominant feature of this infrared spectrum is a very broad band centered at $\sim 950\text{ cm}^{-1}$. The position of this band is in the vicinity of that arising from an Si-N absorption and the broad featureless nature of the absorption is characteristic of material having a low order of crystallinity. Coatings of this material display a relatively high resistivity when tested, at room temperature, with the probes of an ohmmeter. It was found however that these materials could be converted to a conducting material (at room temperature) simply by heating to temperatures in excess of 1000°C . Subsequent x-ray powder data revealed that the material contained a new crystalline phase-silicon. Whether this silicon was formed simply by crystallization of amorphous silicon present in the film or resulted from a disproportionation-crystallization mechanism is not known. It is apparent however that the low temperature deposit, found under the stated conditions, does not display the characteristics of silicon nitride - even though the infrared spectrum is that expected of amorphous silicon nitride.

2.3.1.6 Deposition at $\sim 1250^{\circ}\text{C}$

Under the same general condition of pressure and reactant gas composition, but with substrate temperatures in the vicinity of 1250°C , the deposit obtained is $\alpha\text{-Si}_3\text{N}_4$ as evidenced by x-ray powder data. A Mohs'

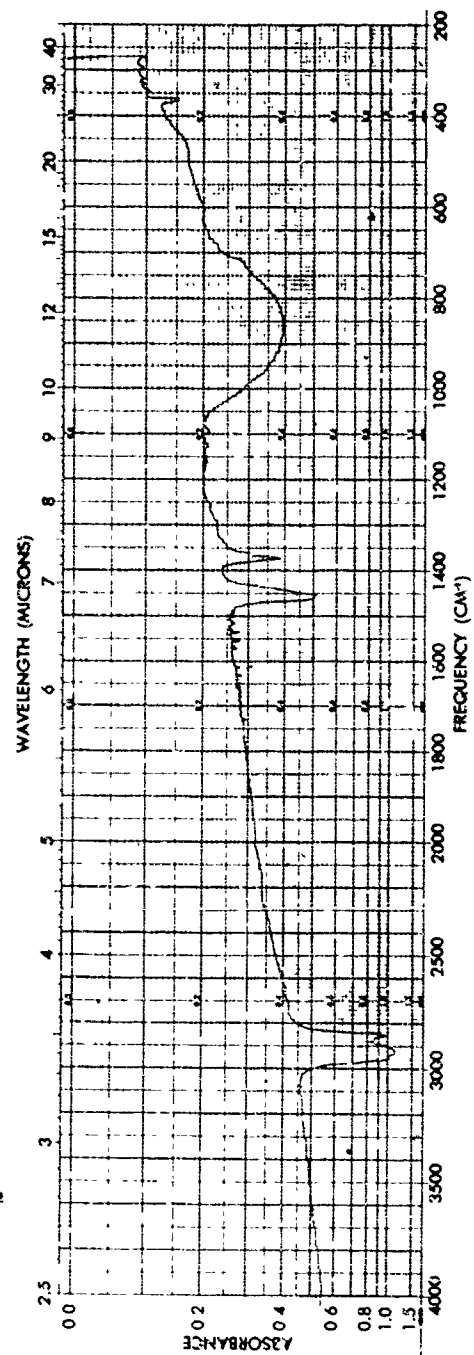


Fig. 23 Infrared Spectrum (Mujol) of Deposit Formed at 700-800°C

hardness test yielded a hardness of > 9 which is in good agreement with the reported values for silicon nitride.⁵ Infrared spectral investigation of this material revealed the spectrum expected from crystalline silicon nitride (Fig. 27). These data are also in good agreement with published spectra of silicon nitride and our own measurements made on commercially available samples of silicon nitride powder.²⁵ In general, the crystalline nitride prepared at 1250°C in our apparatus varied in color from white to light tan, in contrast to the distinctly metallic gray color of the commercial silicon nitride.

One of the interesting observations made during this initial series of experiments with molybdenum substrates concerned an apparent decrease in temperature during deposition. This was the subject of some concern since it could reflect either an actual cooling occurring through an increased emissivity of the coated rod or a decrease in emissivity, causing a change only in the temperature recorded by pyrometry, but not in the actual temperature of the substrate. The resolution of this problem was accomplished by preparing a substrate of a two inch section of one-half inch diameter molybdenum rod, containing a hole which was $1/16$ " in diameter and $3/8$ " deep to approximate a black body cavity. A series of measurements at different temperatures was made on the clean molybdenum surface and the results were compared to those obtained by taking measurements under the same conditions from the hole approximating a black body cavity. This, and a similar rod, were then coated with the high temperature crystalline film of silicon nitride and the low temperature amorphous coating, respectively. The results which are given in Fig. 24 clearly show that both of the coatings have very high spectral emissivities. Therefore, the observed temperature drop of the rod upon being coated is real, not merely apparent.

2.3.1.7 By-products of the Reaction

It was observed that during the course of the early experiments a considerable quantity of material was deposited from the gas phase. This was particularly true of the reactions in which the substrate was held at a high temperature and the flow of gases through the reactor was relatively slow. The material deposited from the gas phase varied in color from

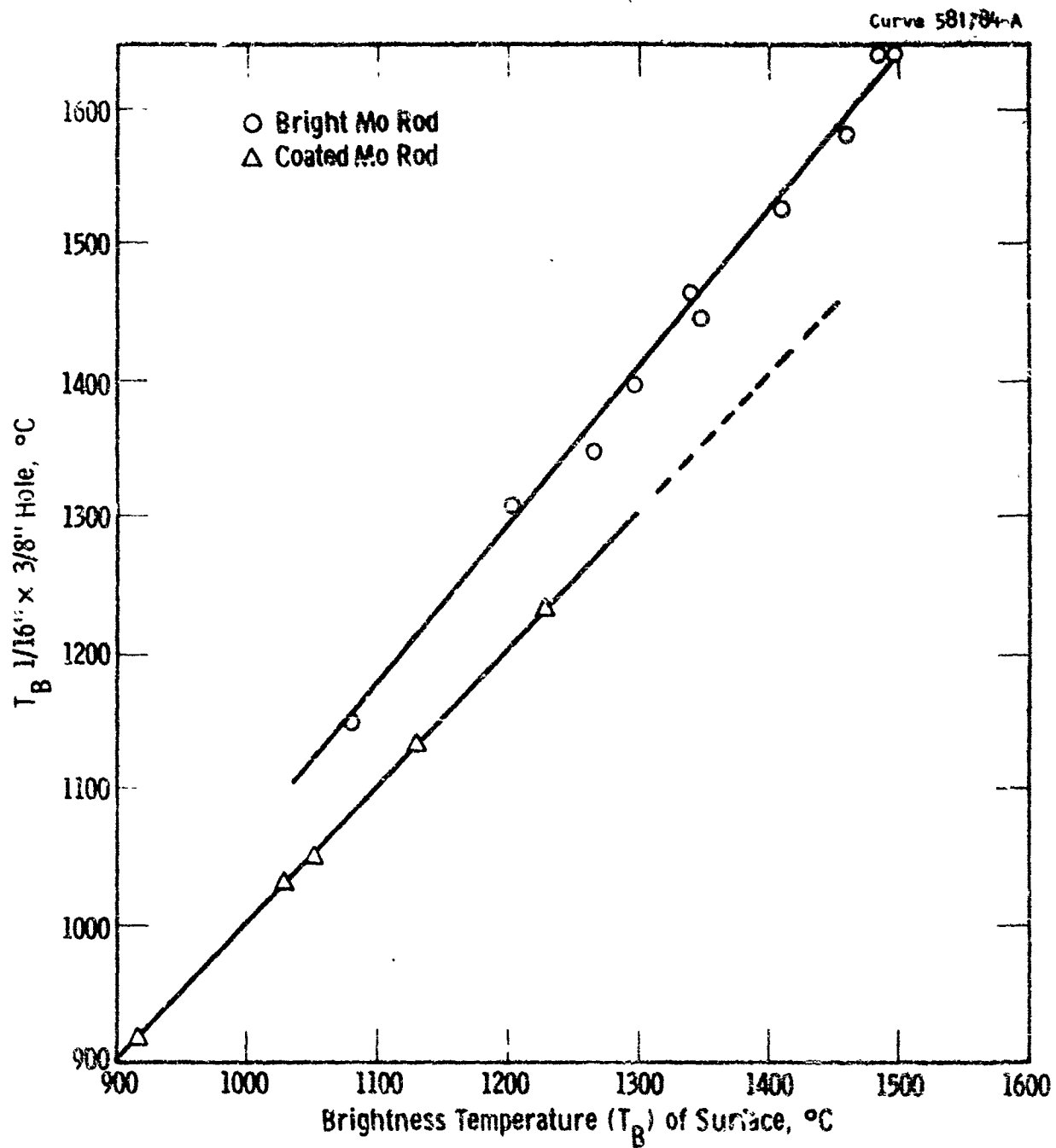


Fig. 24—Brightness Temperature of the Surface Compared to that of a "Black Body Hole" for Uncoated and Coated Molybdenum

dark brown to almost white and yielded an infrared spectrum like that shown in Fig. 25. In this spectrum, which was obtained from a Nujol mull of the sample, the absorptions in the vicinity of 3 microns are probably attributable to NH and perhaps OH stretching modes. The peak predominating at 4.5-5.0 microns most probably arises from an Si-H vibration.²⁶

The absorptions at lower energies, from 8-13 microns, probably are attributable to Si-O and Si-N modes. Although it is felt that the concentration of reactive oxygen species in the closed reaction tube is fairly low, the Si-O and Si-OH groupings in the gas phase deposits probably arise, at least in part, from that source and also from reaction occurring when the material is exposed to air and during the mulling procedure.

Regardless of the actual chemical composition of this solid phase by-product, it is apparent that the production of high quality films of silicon nitride would be best served by the elimination of the gas phase reaction product. This would result in reduction of solid contamination and prevent depletion of reagents necessary for deposition on the substrate. To accomplish this objective the reactor was constructed with a cooling water jacket and the reaction was carried out at reduced pressure to increase the mean-free path of the gases. It was felt that these steps would allow reasonable deposition rates to be achieved without the production of significant quantities of gas phase reaction products. The characterization of nitride films obtained in this manner are described in Section 2.3.1.9.

2.3.1.8 Mechanism of the Reaction

The nature of the solid phase by-product, combined with the known properties of silane and ammonia, aids in suggesting a mechanism for the reaction. Silane is known to undergo pyrolysis at temperatures as low as 400°C with the onset of appreciable reaction (that occurring at a measurable rate) at 600°C.²³ In contrast, ammonia is relatively inert and does not undergo decomposition unless it is exposed to temperatures of 800-900°C.²⁷ If, as is the case in many of these reactions, the substrate is held at 700-800°C, the temperature in the flowing gases

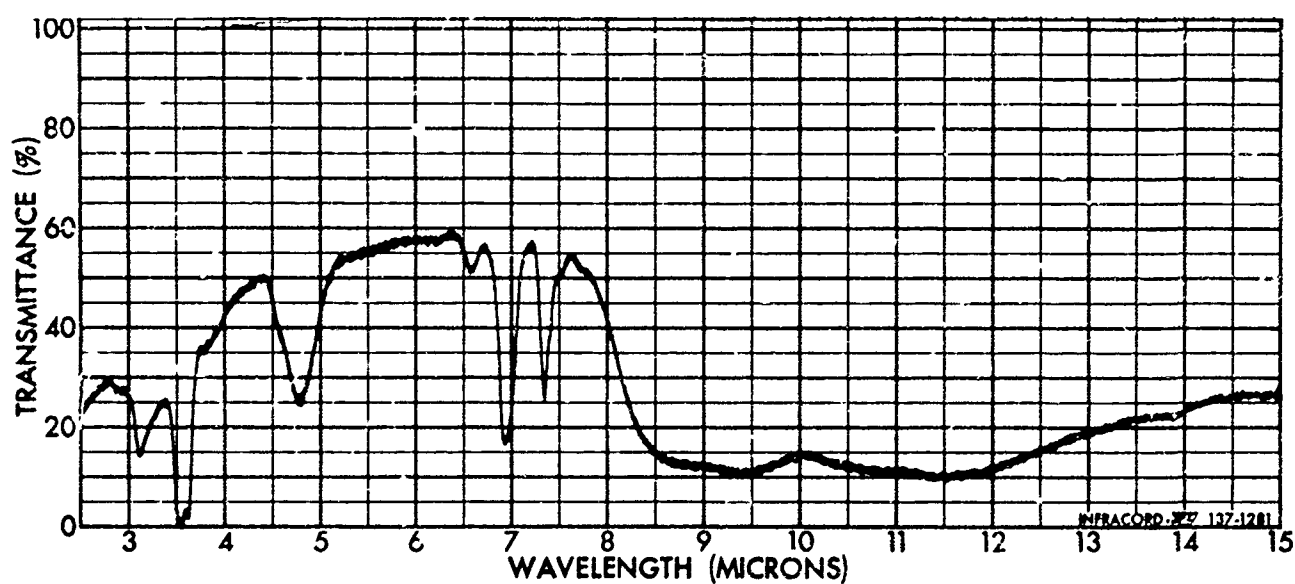
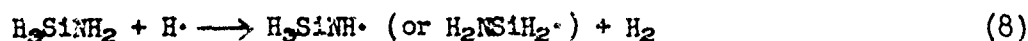


Fig. 25 Infrared Spectrum (Nujol) of the Solid Phase By-Product from the Pyrolysis of Silane and Ammonia

must be lower. Therefore the formation of a gas phase product must be initiated by the pyrolysis of silane. Since thermal activation is known to be a ready source of radical species in both organic and inorganic chemistry,²⁸⁻³⁰ it seems reasonable to postulate that the pyrolysis of silane, by a free radical mechanism, initiates the reaction. Accordingly a reaction sequence similar to that below is suggested.



The reaction proceeds yielding increasingly complex products, which, when they are of sufficient molecular weight and in a sufficiently cool temperature zone, nucleate and form a solid condensing from the gas phase.

Termination of the reaction can be accomplished in a variety of ways, the most obvious of which is simple radical combination as shown in Equations 7 and 9. If the reaction is to be terminated by this mechanism, it is assumed that the product is not in a zone where pyrolysis or radical abstraction can occur. Of course hydrogen and higher silanes can also arise from a mechanism like that proposed here as shown in Equations 10 and 11.



Although no attempts have been made to gather data to verify this mechanism, some additional experimental data seems to bear on this problem. On several occasions attempts were made to deposit silicon nitride on a thin mirror of platinum which had been sputtered onto a fused silica slide. Initially the platinum formed a bright continuous film but after deposition of silicon nitride had occurred and the substrate was again examined it was observed that much of the platinum had been removed destroying the mirror. This observation may be related to the experiment of Paneth in which metal

mirrors were removed and redeposited by the action of organic radical species.³¹ It seems likely that further investigations of this mechanism could benefit from the use of radical scavengers, electron spin resonance, and analysis of the gaseous reaction products by infrared and mass spectroscopic techniques.

2.3.1.9 Deposition at $\sim 1000^\circ\text{C}$

Typically, substrate temperatures of 1000°C with flow rates of 1-20 cc/min of silane and 25-35 cc/min of ammonia at a pressure of 5-10 torr give silicon nitride coatings which seem to possess favorable high temperature properties. Some details of the synthesis of these films regarding general operating conditions and substrate preparation appear in Section 2.3.1.4 while other aspects of the synthesis and characterization are covered in the subsequent paragraphs. The electrical properties are reported in Section 2.4.

2.3.1.9.1 Structural Characteristics

Investigations into the crystalline structure of the compounds have been pursued using x-ray techniques. Debye-Scherrer diffraction patterns (Cu K α radiation) and tracings from a Norelco diffractometer (Cr K α radiation) indicate that the coatings obtained on crystalline molybdenum substrates, at these temperatures, are generally amorphous. In some instances, however, areas of crystalline silicon nitride, probably arising from surface impurities or other conditions which could lead to nucleation of the crystalline material, are observed. Such factors could include for example, small particles carried in the reactant gases, localized high temperature or an initially greater temperature than that desired for deposition of the amorphous material.

Infrared spectral analysis lends support not only to the designation of the coatings as amorphous but indicates the presence of Si-N bonds. Actual infrared spectra that illustrate the significant differences in absorption between the amorphous and the crystalline materials are shown in Figs. 26 and 27. The broad, relatively featureless, spectrum shown in Fig. 26 would be expected from the amorphous material while a large number

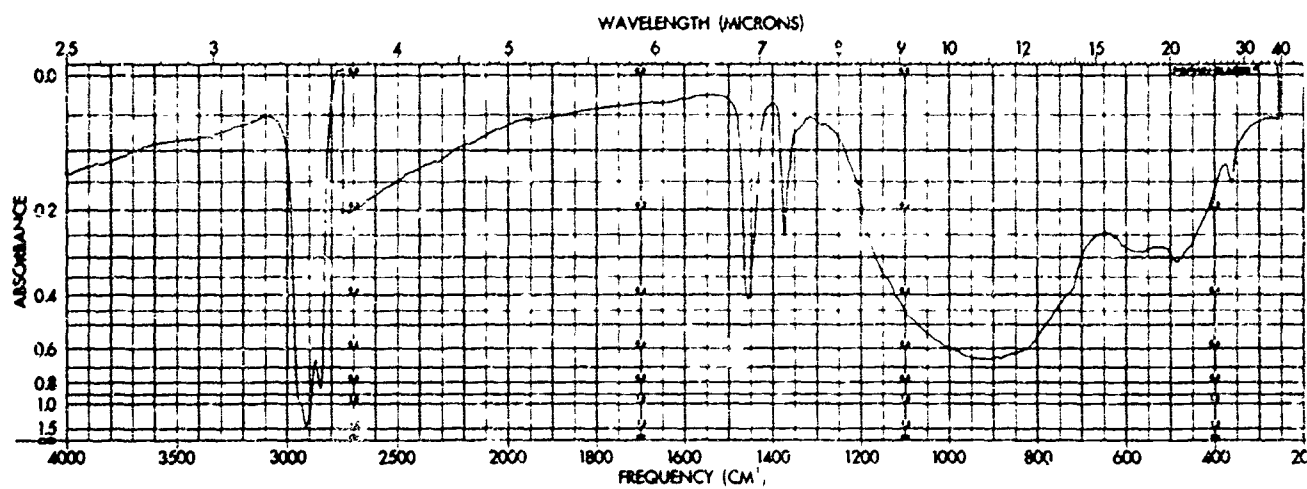


Fig. 26 Infrared Spectrum (Nujol) of Amorphous Silicon Nitride Formed at $\sim 1000^{\circ}\text{C}$

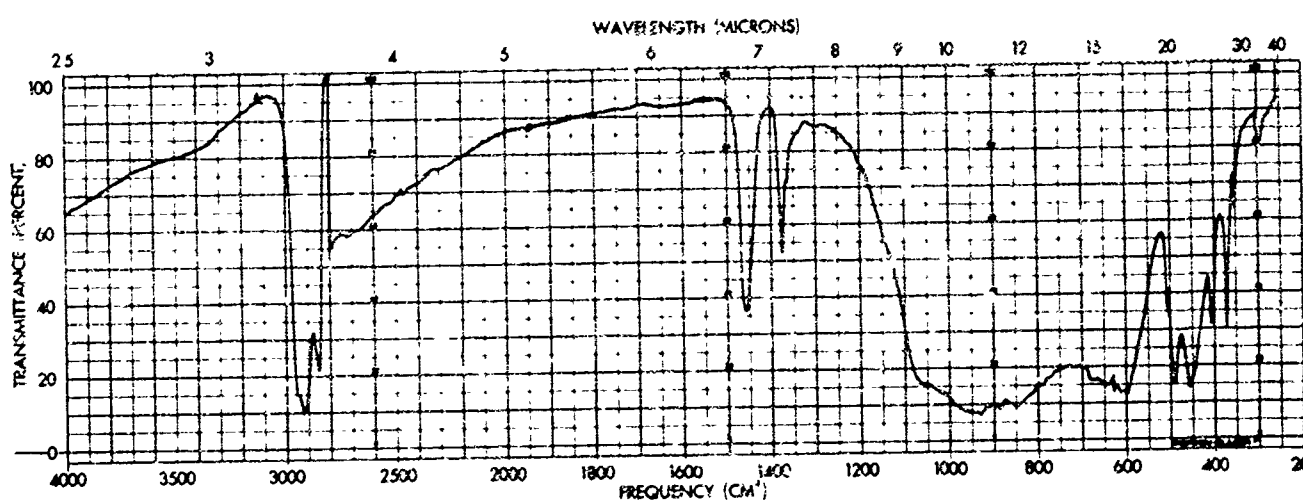


Fig. 27 Infrared Spectrum (Nujol) of Crystalline Film of Si_3N_4

of relatively sharp bands, as shown in Fig. 27, are expected from a crystalline material. The sample yielding the spectrum shown in Fig. 27 was confirmed to be $\alpha\text{-Si}_3\text{N}_4$ by x-ray powder work.³²

2.3.1.9.2 Elemental Composition

Efforts to obtain elemental analytical data on samples of silicon nitride film were carried out by an alkali fusion method which consisted of mixing a weighed amount of the sample with 5g of sodium hydroxide in a platinum boat and heating the mixture in a tube furnace at $\sim 700^\circ\text{C}$ for two hours. The ammonia produced in the fusion was carried by nitrogen into a saturated solution of boric acid and then titrated with 0.1 N hydrochloric acid. Determination of silicon was carried out by fusion of a mixture of the sample, potassium nitrate and sodium carbonate contained in a platinum crucible. The resultant fused mass was subsequently treated with sulfuric acid, the precipitated silica being washed and then ignited at 1000°C for one hour. The weight of silica was used to determine the silicon content of the film.

Analysis of several samples by this method seemed to indicate non-reproducibility of results. A limited amount (27 mg) of coating was analyzed for nitrogen by the above technique with only 29.8% being found. Analysis of another sample yielded values of 35.3% and 31.7% for nitrogen. This, coupled with a 72.8% analysis for silicon on the same sample preparation, suggested that either the sample was not completely homogeneous or the analytical techniques did not allow complete decomposition of the sample. Since the original sample had been crushed and mixed thoroughly prior to analysis it seems that the latter explanation is more reasonable. (It should also be mentioned, however, that only small quantities of samples were available at that time and this undoubtedly added to the uncertainty of the analytical result.) The analytical technique was therefore modified by using lithium hydroxide rather than sodium hydroxide for the decomposition of the nitride sample. The temperature remained at 700°C and the apparatus was modified to minimize possible loss of ammonia. In order to eliminate the carry over of contaminating base, the ammonia was first trapped in

dilute sulfuric acid and then regenerated and dissolved in boric acid for a final determination by titration with 0.1 N hydrochloric acid.

The results yielded by this technique for the analysis of silicon nitride gave good reproducibility on analysis of commercial samples of silicon nitride as indicated in Table 5.

Table 5
Elemental Analysis of Silicon Nitride

<u>Sample</u>	<u>% Si</u>	<u>% N</u>
Pyrolytic Silicon Nitride Film	58.5	38.9
A.D. McKay Si_3N_4 Powder	58.3	37.0
Union Carbide Si_3N_4 Powder		37.4
		37.2
		36.7
		37.4
Si_3N_4 , Theoretical Values	60.05	39.94

Since the modified technique incorporates a distillation of the evolved ammonia, the possibility of erroneous high nitrogen values is virtually eliminated. The values quoted for nitrogen content are therefore taken as representing the minimum nitrogen values; the possibility of incomplete decomposition or loss of ammonia from other factors still being a possibility.

2.3.1.9.3 Oxidation Protection

Relatively thin molybdenum substrates were chosen for this oxidation study in order to reduce the overall mass of the substrate and give the highest surface area to weight ratio possible. Since previous experience with 5 mil foils had indicated that these were difficult to heat uniformly, 10 mil foil was used in this series of experiments. Substrate preparation and deposition conditions were, in general, the same as those previously described and the sample received two coatings on each side for a total of

88.7 mg of silicon nitride deposited over an area of $\sim 43.6 \text{ cm}^2$. Assuming a density of 3.18 g/cc^{32} for the deposited coating, the calculated thickness is $\sim 6.4 \mu$. The original weight of the uncoated foil was 5.4700 g.

For the oxidation test on this foil the sample was placed on a piece of platinum foil and inserted into a furnace maintained at 1000°C . The sample was continuously exposed to air during the heating period and was shock-heated and air-quenched in the sense that it was inserted and removed from the furnace without preheating or slow cooling of the sample. After 32 minutes at 1000°C the sample was removed from the furnace and allowed to cool to room temperature. A weight loss of 2.1 mg had occurred (0.04% of the coated specimen) but no pits or other flaws were obvious. The sample was returned to the furnace for heating at 1000°C for an additional 32 minutes and was again removed for observation. The sample had suffered a total weight loss of 14.3 mg (0.26%) and had obvious failures at two locations (Fig. 28). One of these was at a corner (Fig. 29) and the other was a pinhole near the center of the foil (Fig. 30). A number of cracks were observed in the coating prior to this oxidation protection study and these were periodically observed during the test (Fig. 31). No signs of oxidation were visible in the vicinity of these cracks, indicating that they either do not extend to the molybdenum surface or are compression cracks that are still closed and air tight at 1000°C . Since the coatings are deposited in a two stage process it is not unreasonable to postulate the former of these two conditions as a reason for the absence of oxidation at a surface crack.

Of interest, and visible in both Figs. 29 and 31, are the deformed edges of the molybdenum foil. These edges, which are very rough and show the effect of being sheared from a large piece of foil, are remarkably well coated with the nitride film and show no pronounced tendency to break down by cracking or spalling from the substrate. Although this specimen has failed in the vicinity of a corner, the coating has shown good oxidation protection along the distorted edges and at the three remaining corners of the foil.

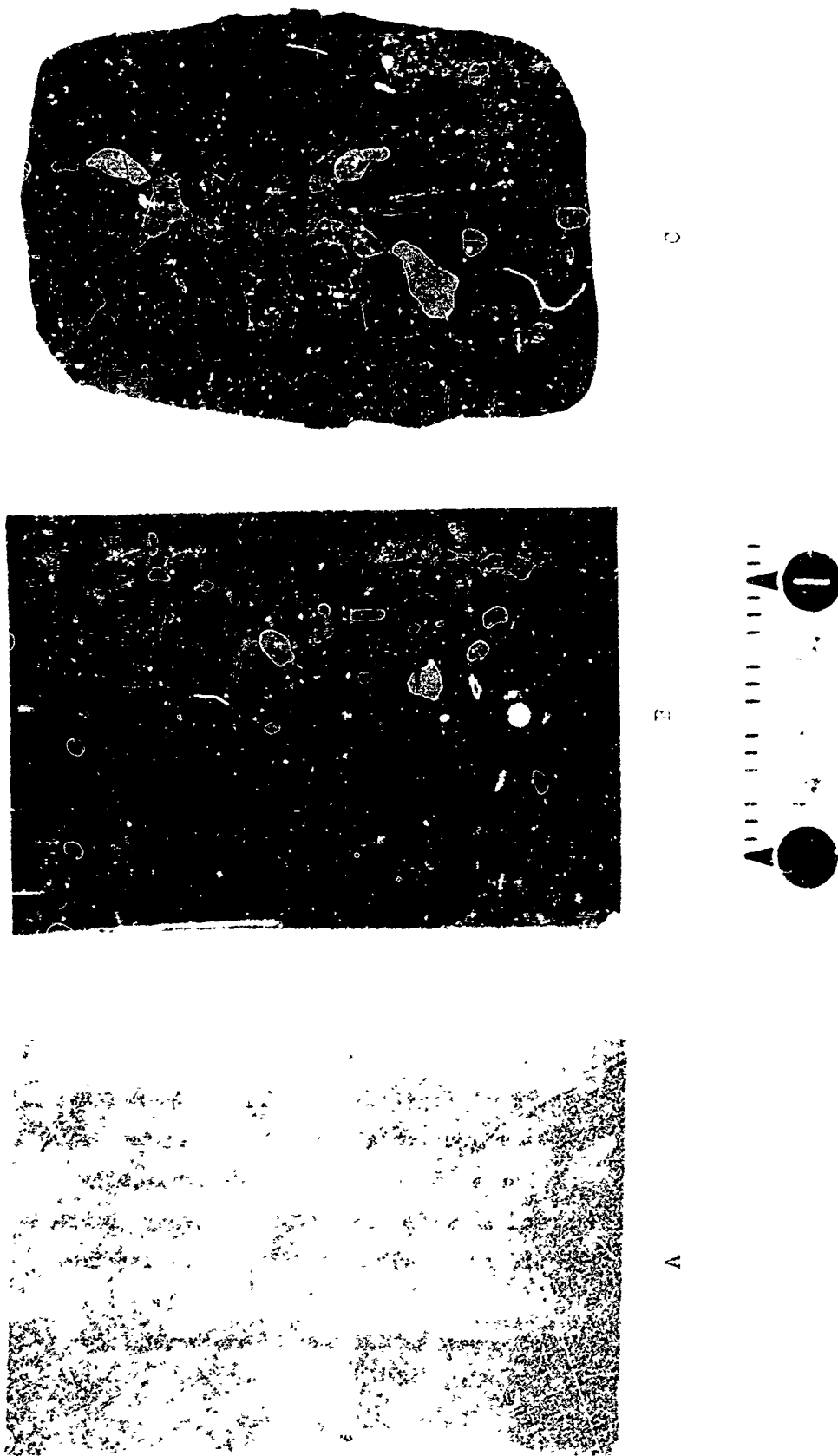
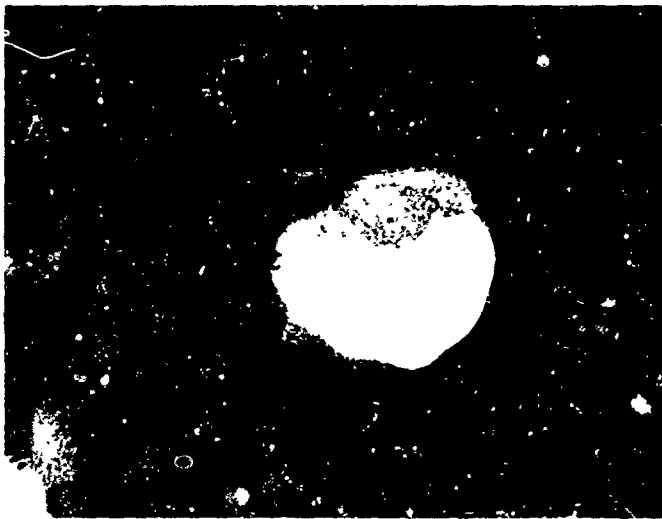


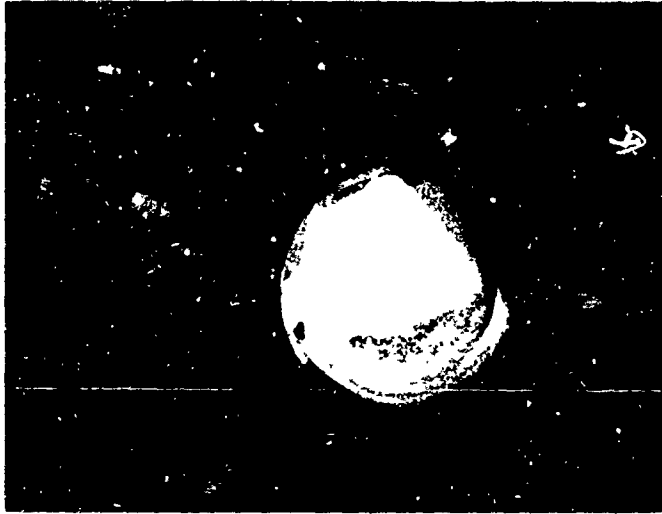
Fig. 28 A Comparison of Samples of Molybdenum Foil Before and After Oxidation. The pieces of foil are shown (a) prior to deposition of a film of silicon nitride; (b) after deposition of silicon nitride and heat treatment in air at 1000°C for 64 minutes; and (c) after the heating in air at 1000°C for 15 minutes of a similar but uncoated sample. The silicon nitride coated foil suffered a weight loss of 0.26% while the uncoated sample underwent a weight loss of ~ 65%.



Fig. 29 Oxidized Corner of Silicon Nitride Coated Molybdenum Foil.
The sample, Fig. 28, was heated at 1000°C for 64 minutes and
showed a total of two pinholes over 43.6 cm² of surface area
(12.5X).

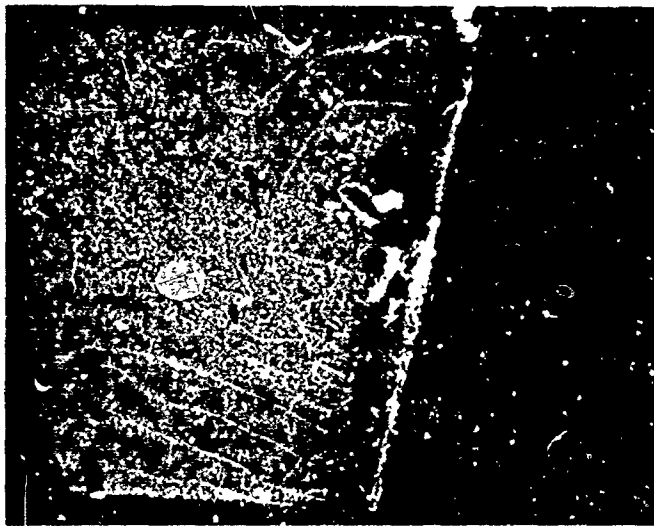


A

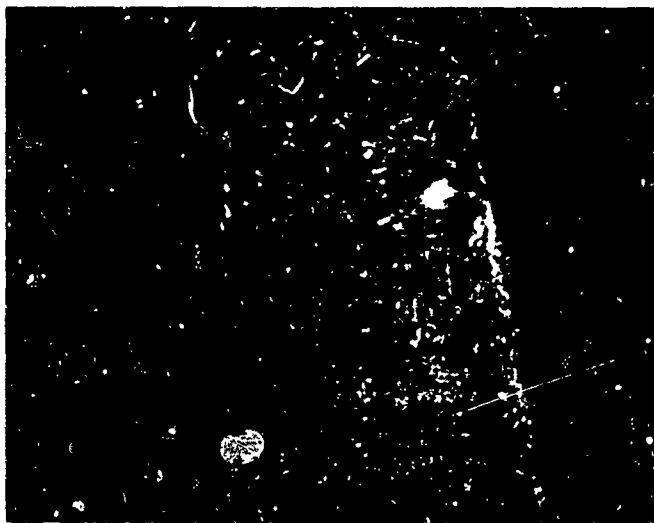


B

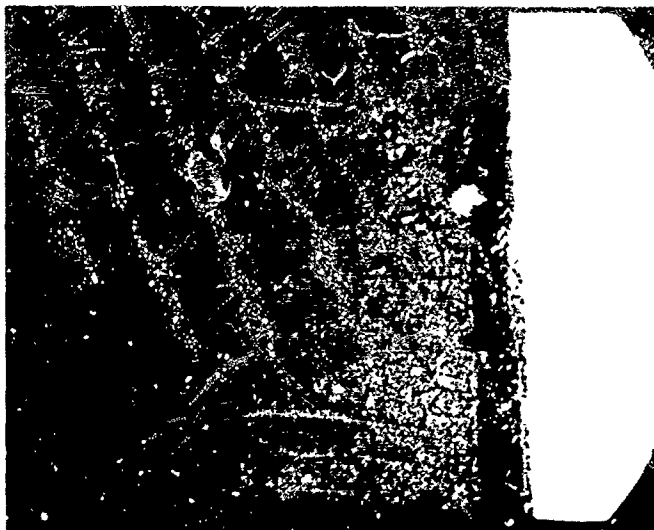
Fig. 30 Pinhole in Silicon Nitride Coated Molybdenum Foil. Top (a) and bottom (b) views of the oxidation hole in the silicon nitride coated molybdenum foil depicted in Fig. 28. The hole diameter is approximately 0.21 cm with the original defect being evidenced by a smaller pinhole in the coating. In (b) the coating, which appears to be pinhole free, has fallen into the oxidation hole as indicated by the shadowing (12.5X).



A



B



C

Fig. 31 Cracks in Silicon Nitride Coating. These micrographs, of the sample shown in Fig. 28, were taken (a) immediately after deposition of the coating; (b) after heat treatment at 1000°C in air for 32 minutes; and (c) after heat treatment at 1000°C in air for a total of 64 minutes. No oxidation of molybdenum is evident at or around any of the cracks. The blurred white particles (two in (a)) near the deformed edge of the molybdenum plate are a mass of crystalline silicon nitride needles (12.5X).

A similar molybdenum substrate was prepared in a slightly different manner by rounding the edges and corners before film formation. This sample received a total of 94.2 mg of coating over essentially the same area; yielding a calculated thickness of $\sim 6.8 \mu$. This specimen was tested for oxidation protection in a similar manner at 1000°C , but was removed from the furnace and examined after 17 minutes and, again, after 38 minutes of heating. No flaws were obvious at these times but after 60 minutes of heating, the sample had again failed at one corner. This was the only visible flaw in the coating and was responsible for a weight loss of 20.9 mg (0.37%).

For comparative purposes, an uncoated sample of the same molybdenum foil was heated at 1000°C for 15 minutes and was observed to have undergone a weight loss of $\sim 65\%$ (see Fig. 28).

The coverage of the substrate, which gives rise to the oxidation protection, was determined by sectioning and polishing a sample and microscopically observing the coverage obtained. Micrographs taken during this investigation are shown in Figs. 32 to 36. These, in general, indicate that the films obtained are, on the upper surface, uniform and continuous. The large number of voids apparent in several of the micrographs probably arose from damage and pullouts during the cutting and polishing of the sample or during voltage breakdown testing of the sample.

2.3.1.9.4 Density

The density of a sample of amorphous silicon nitride film, which had been removed from the molybdenum substrate, was determined by the buoyancy method using a mixture of bromoform (sp. gr. 2.89) and methylene iodide (sp. gr. 3.33). A value of 3.08 g/cc, which compares favorably with the x-ray density of 3.18 g/cc for $\alpha\text{-Si}_3\text{N}_4$, was obtained.³³

2.3.1.9.5 Flexibility

The flexibility of silicon nitride films on 10 mil molybdenum foil was investigated by bending strips of the coated foil around successively smaller mandrels. Since the thermal coefficient of expansion of molybdenum is greater than that of silicon nitride (see Table 4) these coatings, which

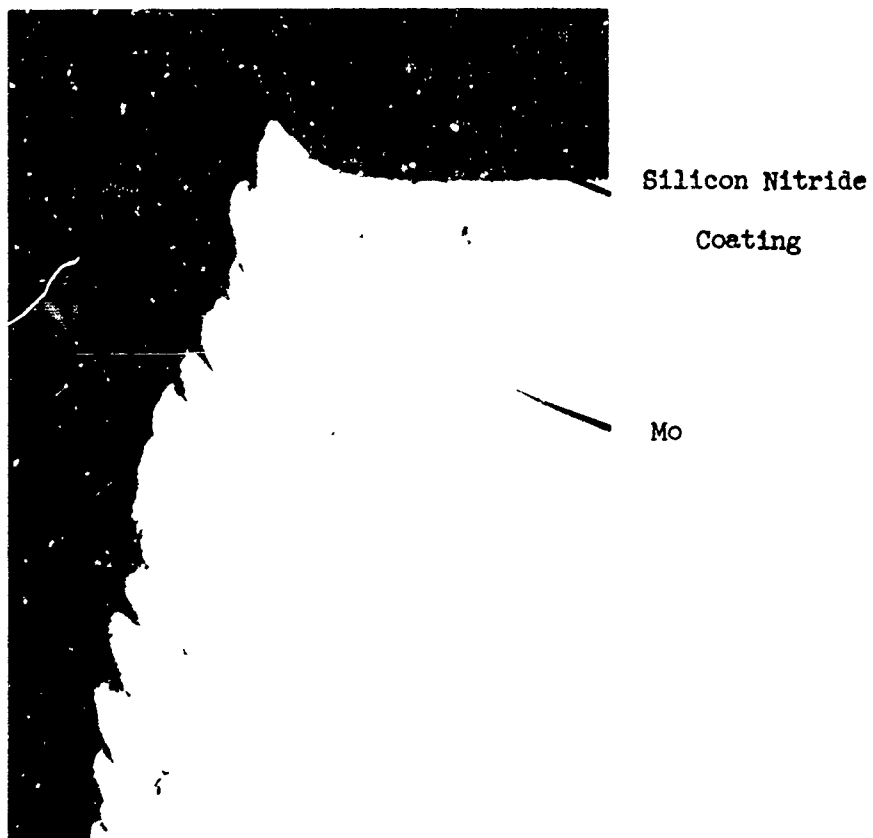


Fig. 32 Cross Section of Silicon Nitride Coated Molybdenum
Showing Coverage over a Sharp Edge (200x)

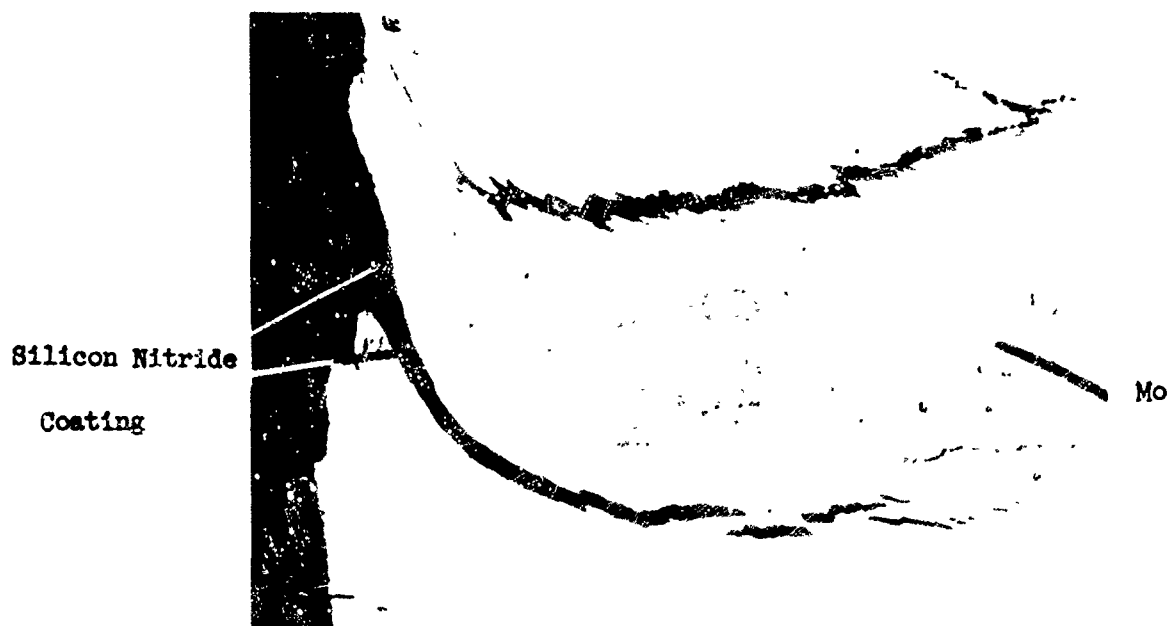


Fig. 33 Penetration of Silicon Nitride into a Local Flaw (200X)

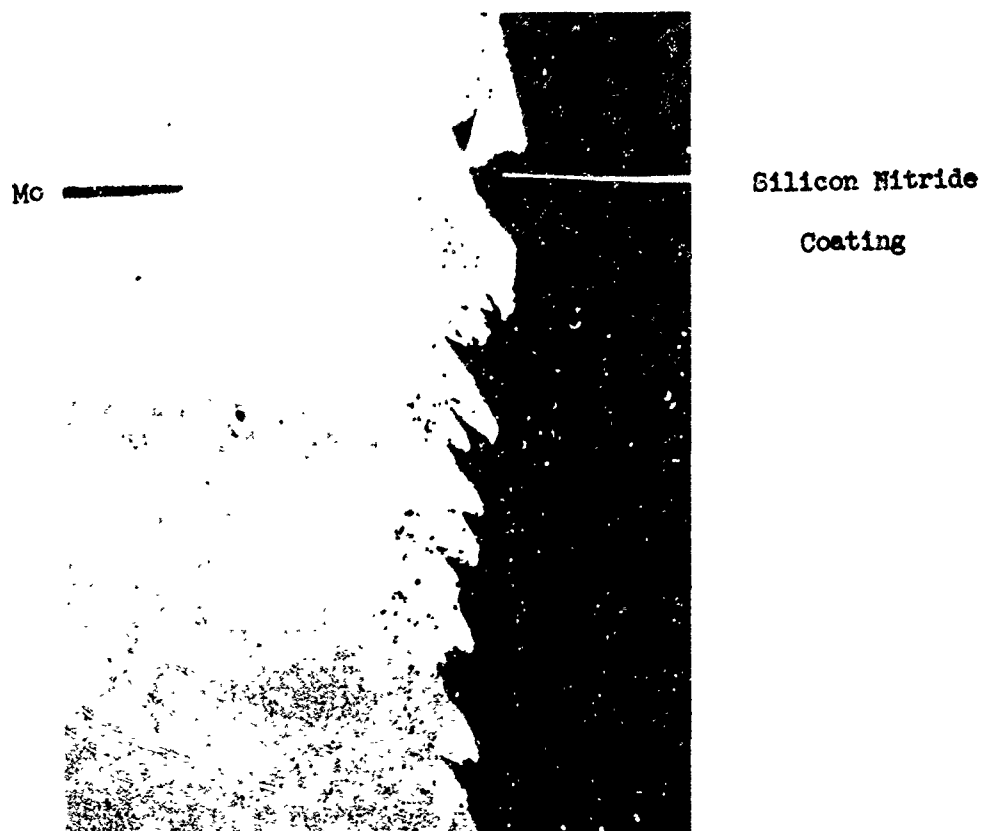


Fig. 34 Cross Section of Substrate Showing In-Depth Coverage of Silicon Nitride on the Side of a Molybdenum Plate (200X)

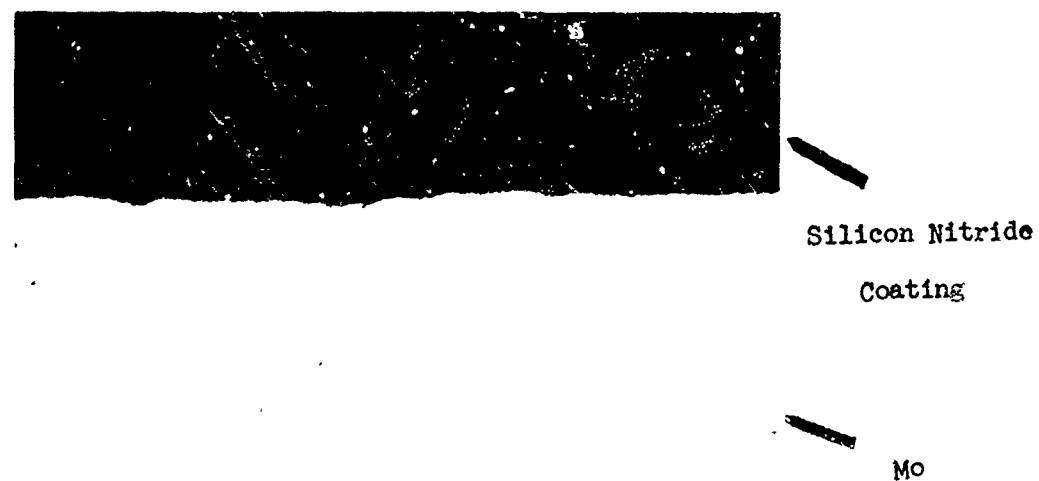


Fig. 35 Cross Section of the Substrate at the Electrode Area (200X)

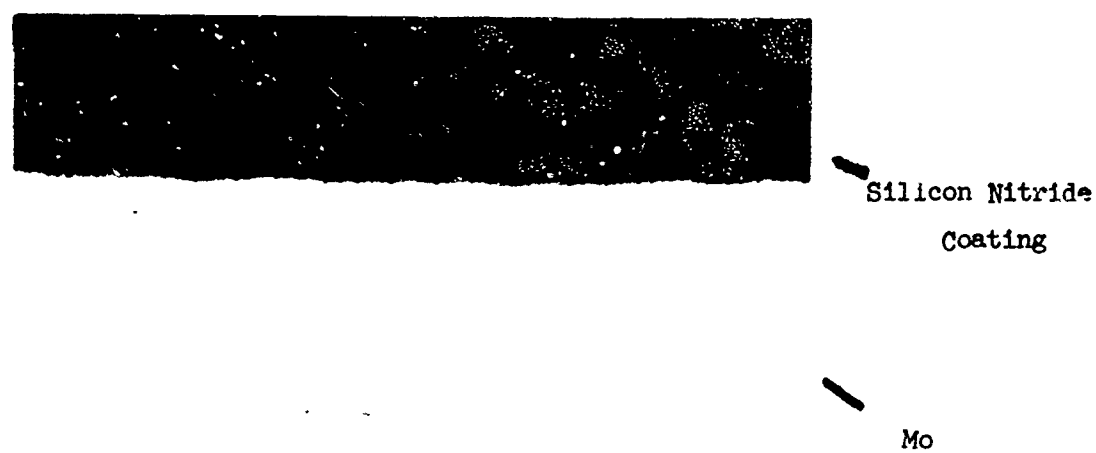


Fig. 36 Cross Section in a More Uniformly Coated Area of the Sample (200X)

Silicon Nitride

Coating

Interface

Mo

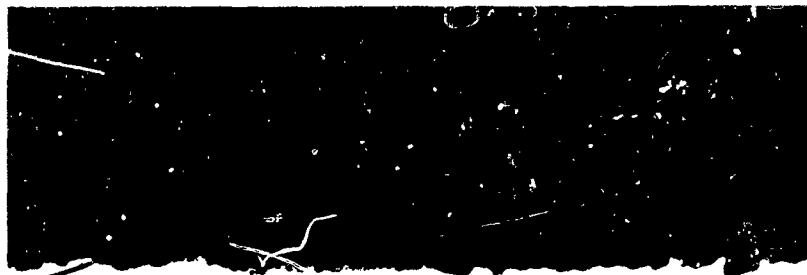


Fig. 37 The Interface Between the Silicon Nitride Coating and the Molybdenum Substrate (1000X)

are deposited at 1000°C, would be expected to be in compression at room temperature. It is anticipated then that bending the foils, which are coated on only one side, with the uncoated molybdenum surface against the mandrel would relieve the compression or put the coating under tension. Bending the samples with the coated surface against the mandrel would put the coating under greater compression. It would be expected, therefore, that flexing the samples to relieve compression would give a lesser chance of failure than flexing to put the coating under greater compression.

This is borne out by the data presented in Table 6 which indicate that flexing to relieve compression can be carried out successfully. Bending in the opposite direction results in early failure.

Table 6
Flexibility Tests on Coated 10 Mil Molybdenum Foil

<u>Coating Thickness(μ) *</u>	<u>Bending Direction</u>	<u>Mandrel Size (diameter=inches)</u>	<u>Observation**</u>
2.4	increase compression	0.512	flaking of coating
3.5	relieve compression	0.050	no cracking or flaking
6.9	relieve compression	0.212	no cracking or flaking

* Thickness determined by angle lapping at 3° and measuring microscopically

** Examined microscopically at 100X after each bend.

2.3.1.9.6 Deposit-Substrate Interface

It has been experimentally observed (Fig. 37) that a dark interface is often formed between the molybdenum substrate and silicon nitride coating and that upon removal of the coating, when this is possible, the interface can either remain with the substrate or adhere to the coating. Some preliminary investigations, primarily using x-ray techniques, have been conducted into the nature of this interface material.

Upon removal of a portion of the silicon nitride film of one sample the interface material adhered to the substrate in certain areas but, in others, remained with the removed silicon nitride coating. This interface was very dark and adhered quite well to the substrate and coating, respectively. X-ray diffractometer tracings of the interfacial material remaining with the molybdenum substrate revealed the presence of α - Si_3N_4 and γ - MoN_2 as recorded on ASTM card 3-907. A portion of the interface was then scraped free of the molybdenum and examined by normal powder methods. Once again γ - MoN_2 was identified, with the possible presence of MoSi_2 (ASTM card 5-749). A weak phase of α - Si_3N_4 was also found in this powder work.

2.4 Dielectric Measurements

2.4.1 Measurement Techniques

The measurement techniques used throughout this work were essentially as described in the technical report⁸ covering the first year of work on this project.

During this second year, dielectric measurements were made almost exclusively with sputtered platinum electrodes on the specimens, which were thin coatings of aluminum nitride or silicon nitride on molybdenum substrates. Thus the specimen had a molybdenum electrode base and a platinum electrode on the other side. A few tests were made toward the end of the program of AlN specimens which had been removed from the substrate, and platinum electrodes applied to both sides.

Earlier measurements, particularly of AlN, were made with coatings on round rods (1/2 inch diameter). Many later tests were made with coatings on flat plates of molybdenum.

Dielectric measurements were frequently made with both increasing temperature and with decreasing temperature from the maximum test temperature. In all cases the tests were made at a few torr pressure, or 1 atm of dry N_2 , the latter being preferred. Tests were always made using a guarded electrode, so placed that any conduction current, except that which passed through the measuring electrode area, was intercepted by the guard electrode and did not influence the measurements. This was done with both a-c and d-c tests. Usually d-c measurements were tried with both

polarities. The values with polarity reversed usually agreed within 10%, except as noted in several instances. Except as noted, the d-c values were reported for the case with the substrate negative.

In most cases the applied voltage for the dielectric measurements was less than 10 volts.

2.4.2 Dielectric Tests on Aluminum Nitride

The conductivity of the aluminum nitride coatings varied appreciably from specimen to specimen, depending on the method of preparation. The lowest conductivity values were obtained on specimens LH79-1 and LH90-3, as shown in Figs. 38 and 39.

Often conductivity, $\tan \delta$ and capacitance values were lower after having been heated to the highest test temperature at 800° or 900°C. Since the heating during this measurement was usually at a reduced pressure or in dry, slowly circulating N_2 , it is presumed that the heating removed some volatile conductive material, possibly water. Since the specimen had usually already been, during preparation, at a temperature higher than the highest measurement temperature it is presumed that the agent, which was being evolved, had been absorbed while the specimen was kept under atmospheric conditions prior to measurement. Whatever was changing to reduce the conductivity occurred quite slowly, since quite a few hours, sometimes days, elapsed during the measurements with increasing temperature. Several samples were held at 200°C for 75 hours, and the capacitance and conductivity were observed to decline slowly over this period.

Continuity of the thin sputtered platinum electrode continued to be a problem, particularly with some of the rougher coatings. This factor, together with the variability and uncertainty of the coating thickness over the measured area of the specimen usually prevented very accurate dielectric constant measurements. Dielectric constant values in the vicinity of 6 to 11 were obtained at low temperatures, increasing with temperature, faster at low frequency.

Curve 581727-A

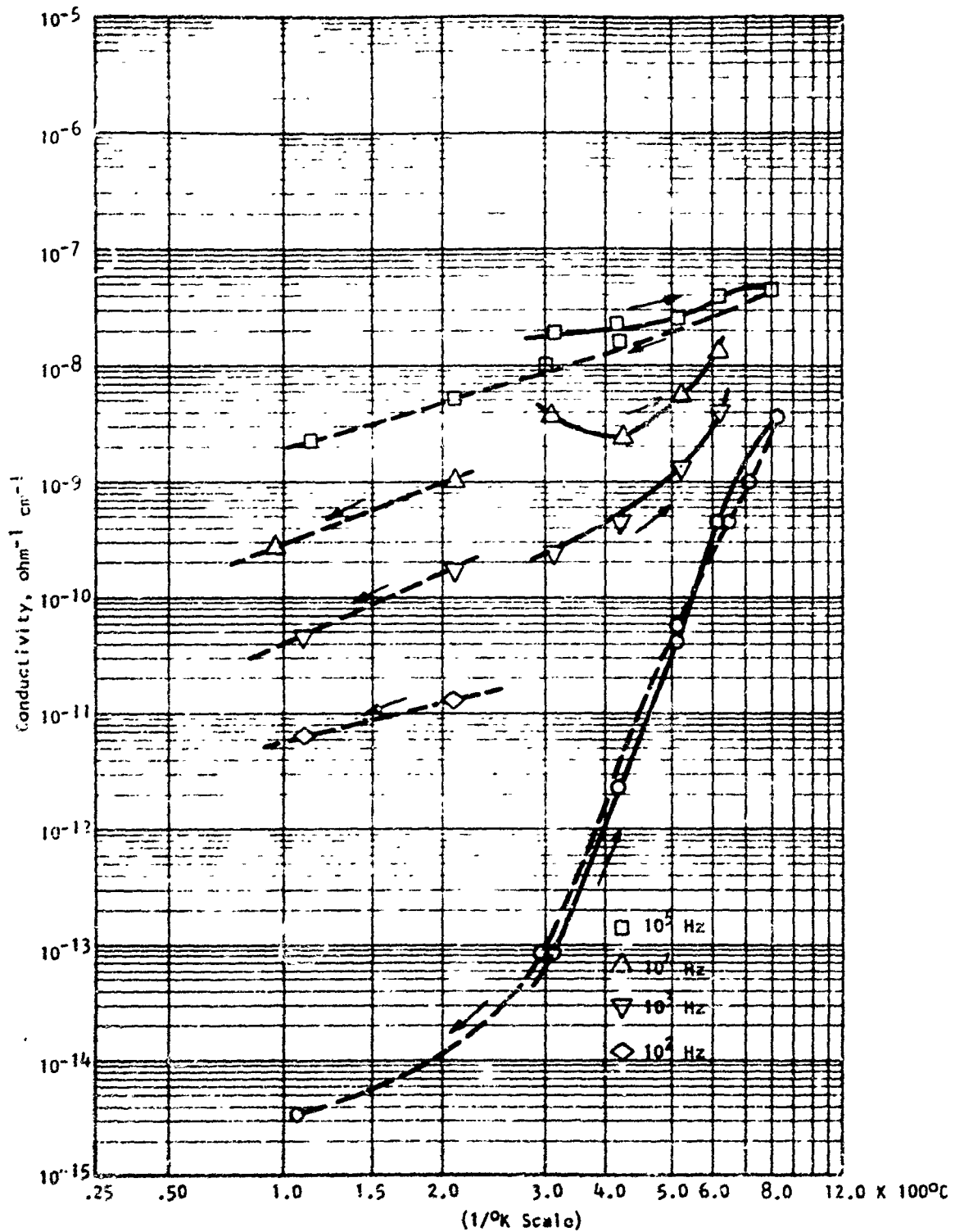


Fig. 38—Conductivity of 0.0025" AlN Coating on Molybdenum Rod;
Sample LH79-1

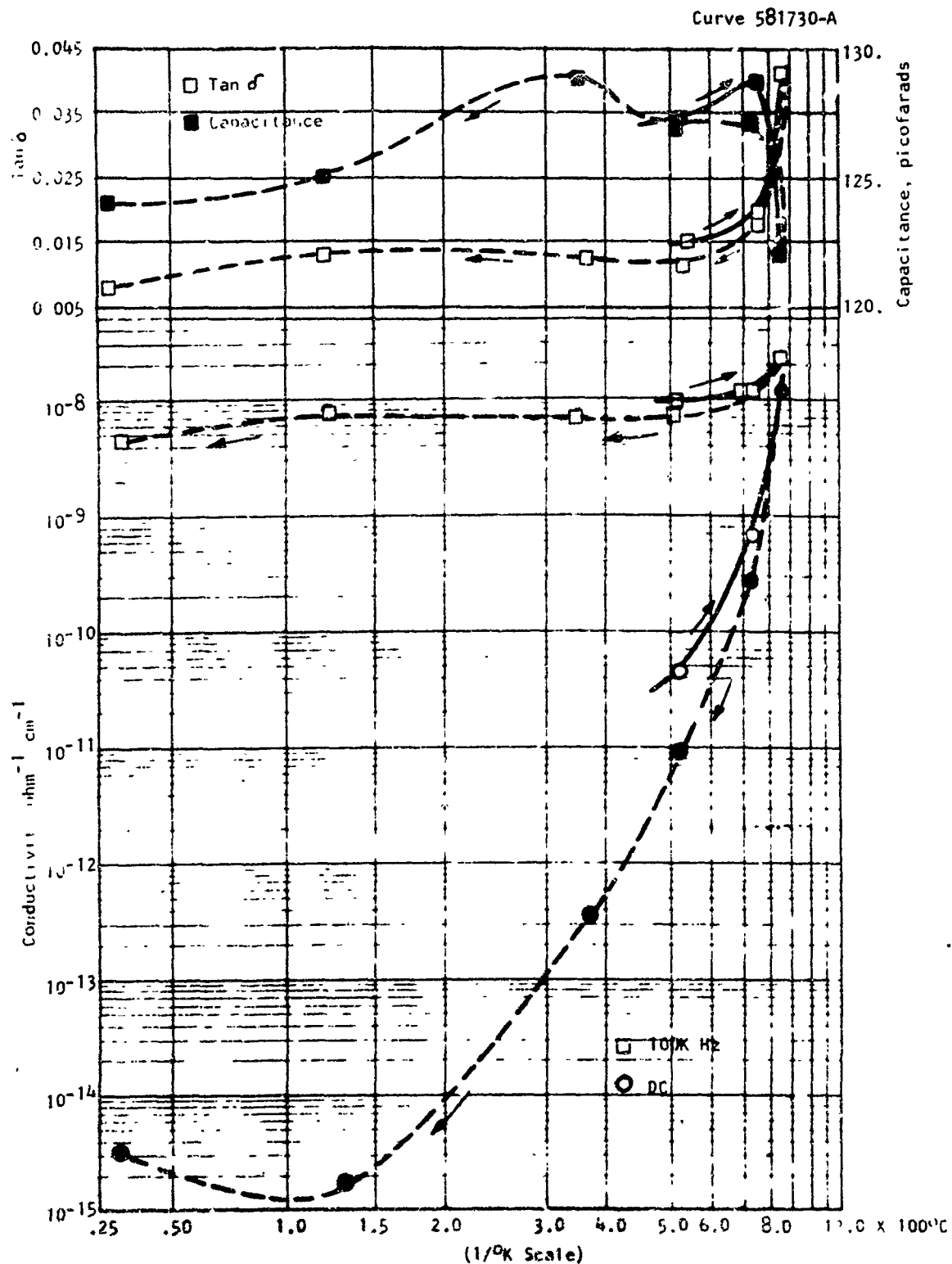


Fig. 39—Dielectric Properties of AlN Coating on Molybdenum Rod;
Sample LH90-3

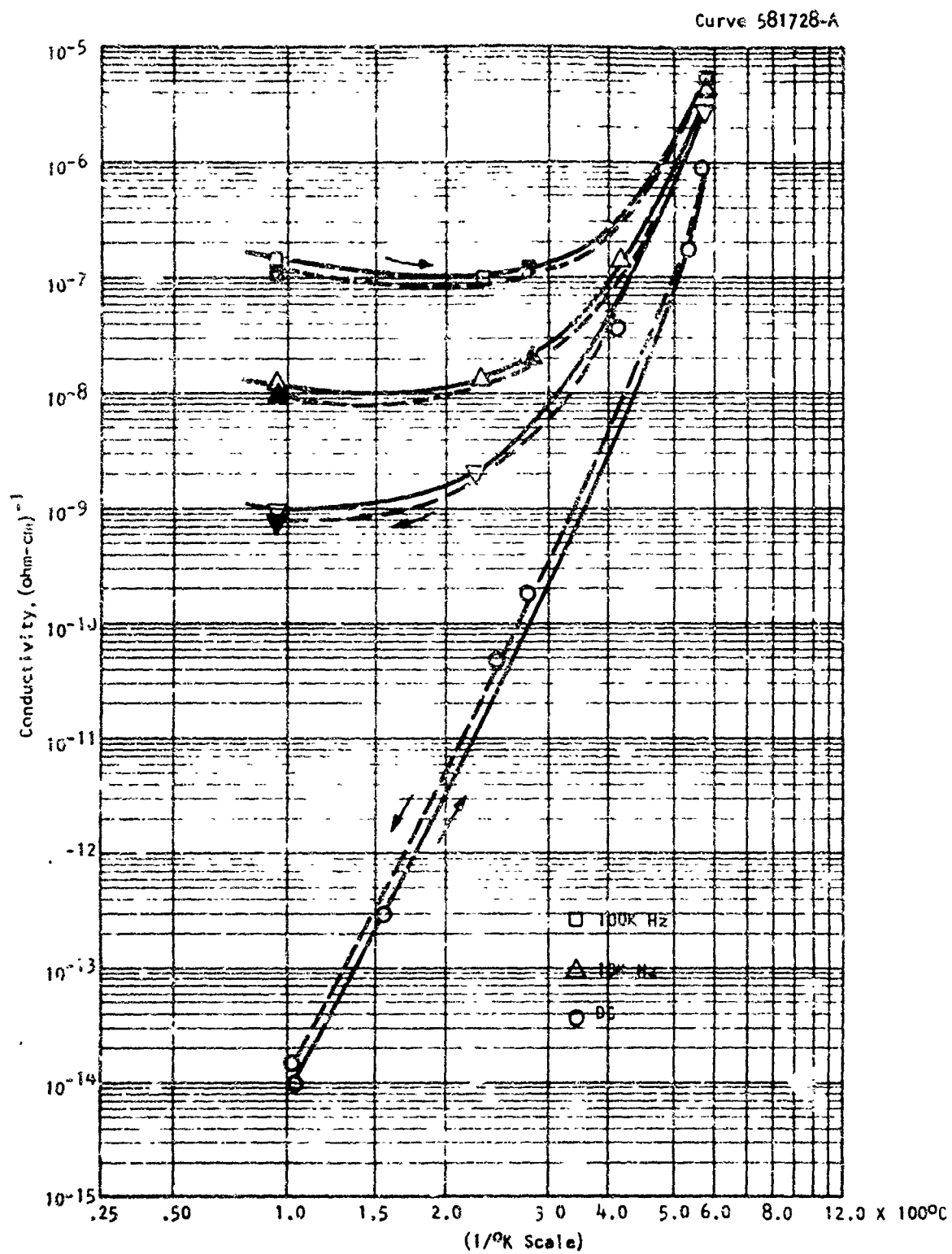


Fig. 40—Conductivity of 0.0025" AlN Coating on Molybdenum Plate;
Sample LH101-2

Curve 581726-A

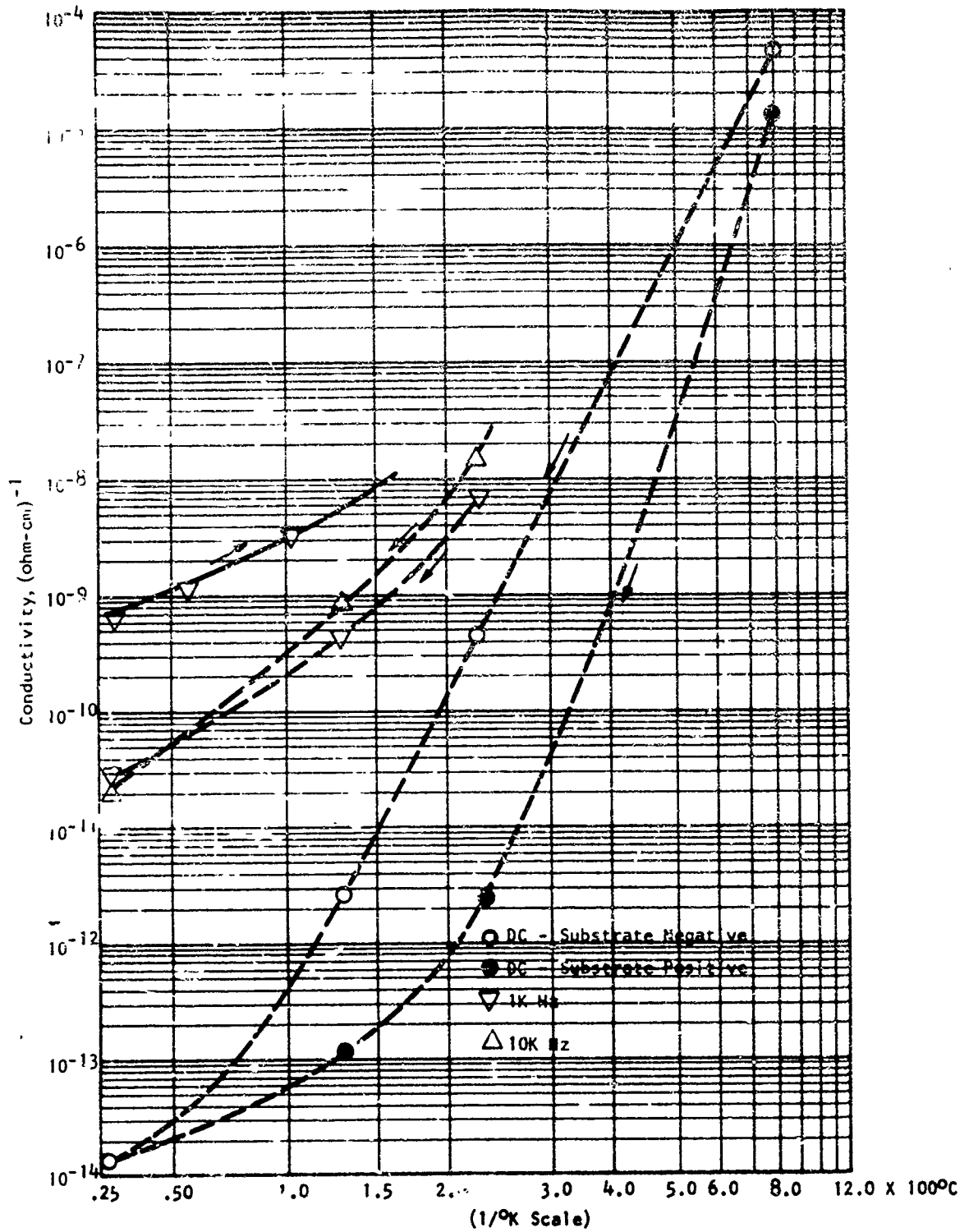


Fig. 41—Conductivity of 0.0044" AlN Coating on Molybdenum Plate:
Sample LH107-1

Curve 581722-A

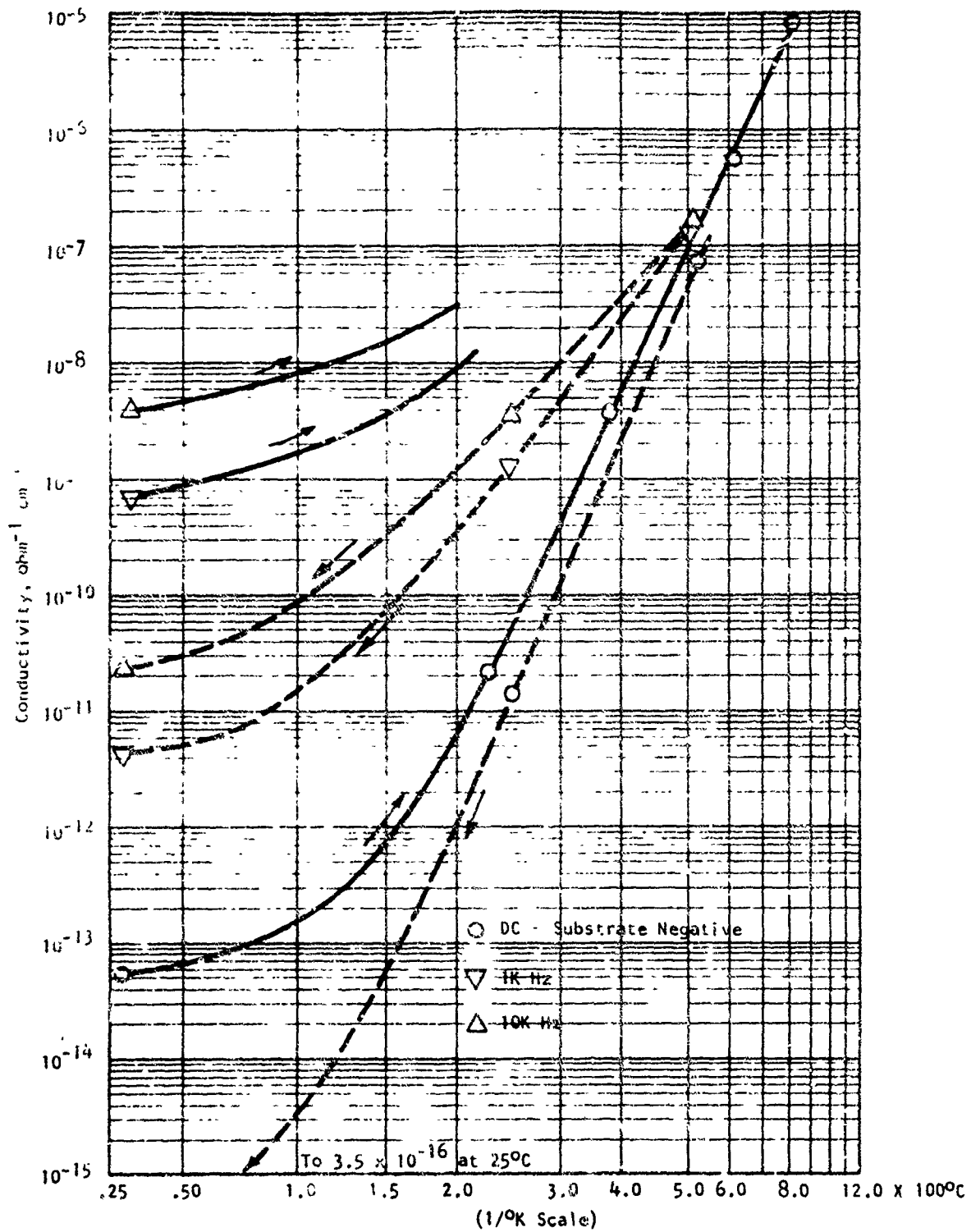


Fig. 42—Conductivity of 0.0047" AIN Coating; Sample LH110-1

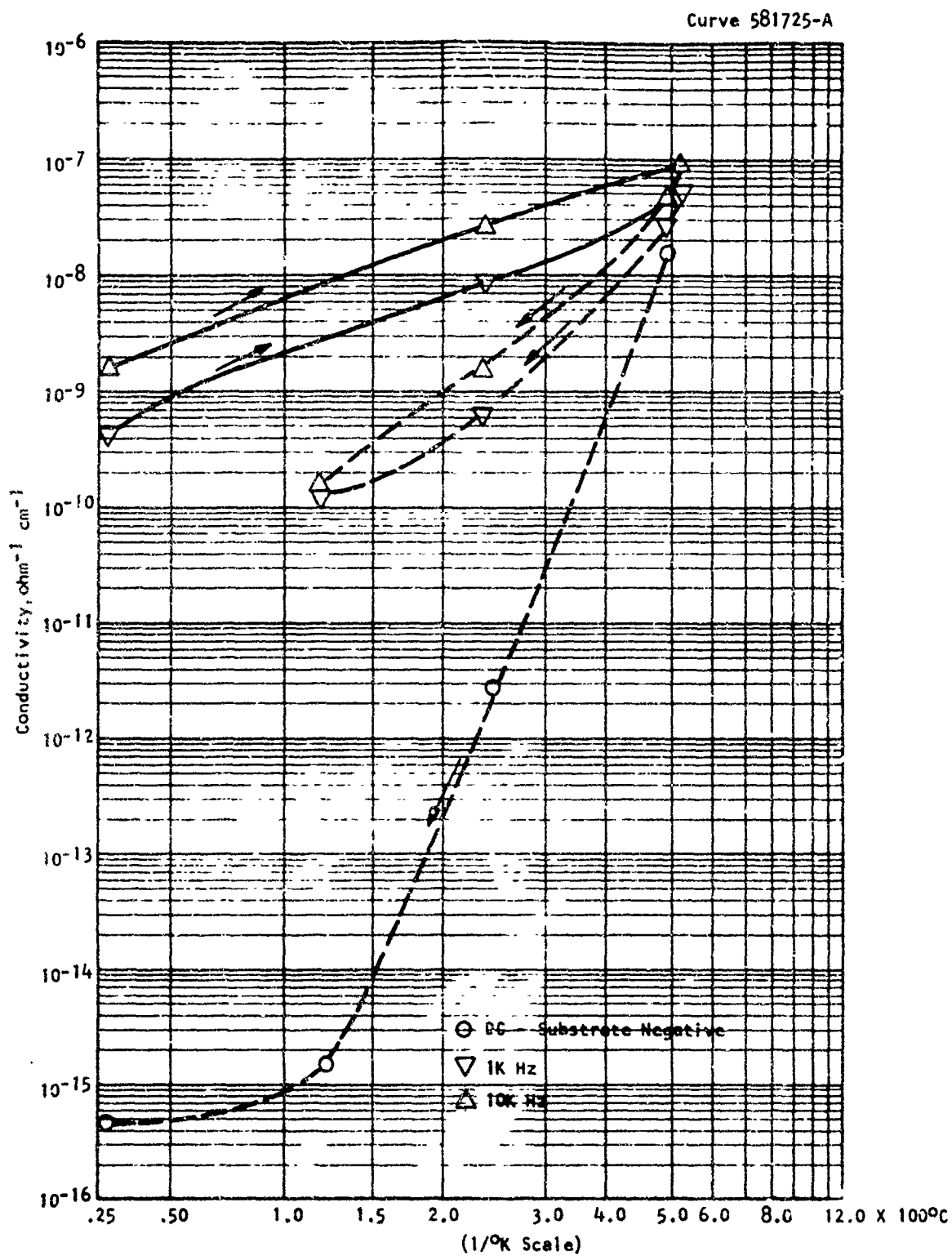


Fig. 43—Conductivity of 0.015" AIN Coating Removed from Substrate;
Sample LH111-2

Curve 581723-A

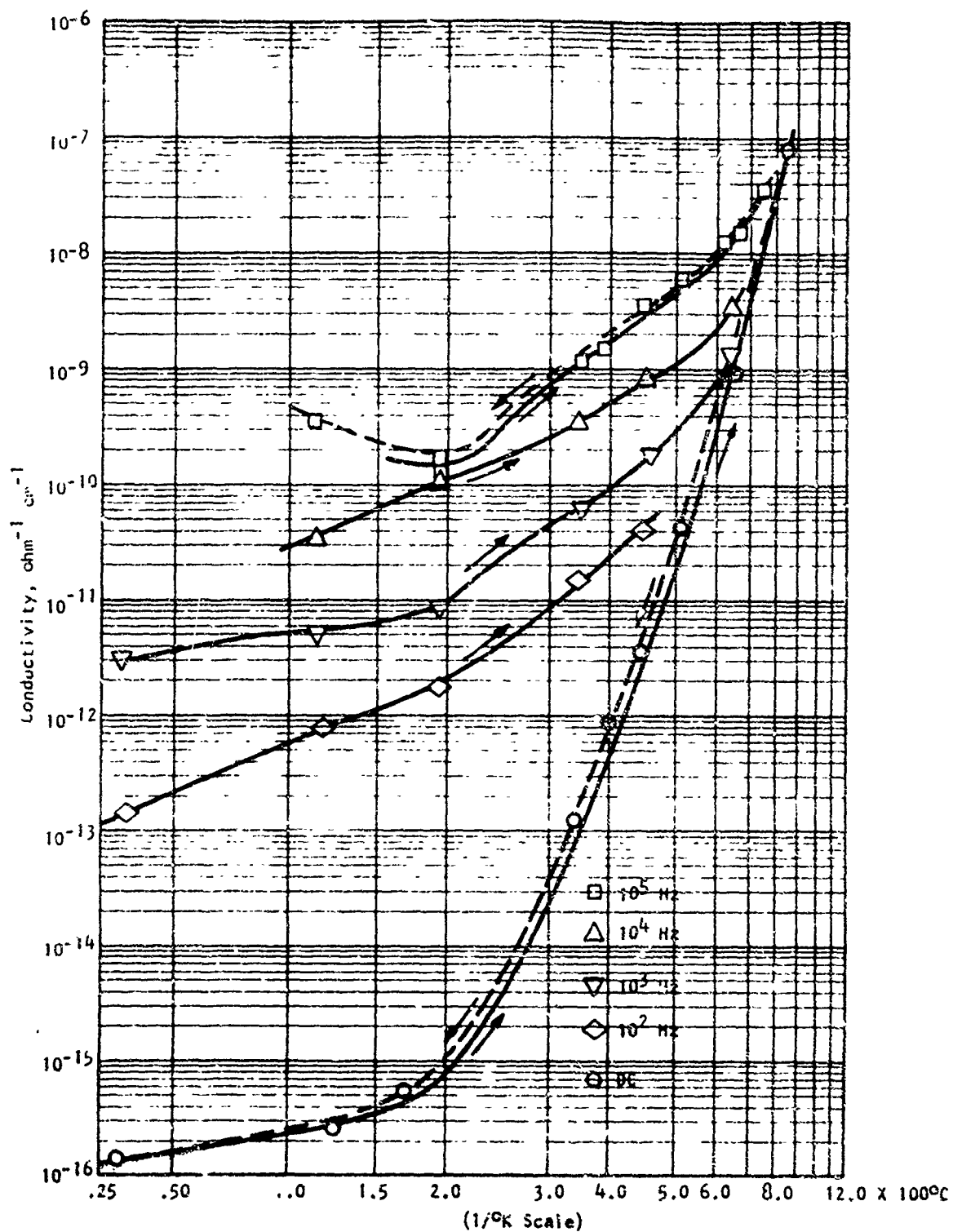


Fig. 44—Conductivity of 0.0015" Si_3N_4 Film on Molybdenum Plate;
Sample 104-113

It is of interest to note that the activation energy for conduction is of the order of 1.1 electron volt. This is obtained from the slopes of the d-c conductivity curves, Figs. 38, 42, and 43, which have the most reliable linearity of slope at the higher temperature end. Even though sample LH79-1 (Fig. 38) has nearly a 3 decade lower level of conductivity than samples LH110-1 and 111-2 (Figs. 42 and 43) the activation energies for conduction in the high temperature region are nearly identical, indicating a similar conduction mechanism. Activation energies on the other specimens were not calculated because of insufficient data or curvature of the $\log \sigma$ vs $1/T$ plot. This activation energy for conduction is much lower than the optical energy band gap of 3.8 eV reported for this material,³³ which indicates the conductivity is probably not electronic. It is probably due to impurity ions, possibly chloride.

The conductivity level for these specimens of AlN is at least 3 orders of magnitude lower than reported recently for their preparations of AlN by Cox, Cummins et. al.,⁵ who must have been testing more impure materials. Their activation energy is similar, however. Their tests were limited to low temperatures (130°C maximum).

2.4.3 Dielectric Tests on Silicon Nitride

The silicon nitride coatings demonstrated a more consistently lower level of conductivity than the aluminum nitride. However, the best silicon nitride specimen (149-174, Fig. 47) was not better than the best aluminum nitride specimen at high temperatures.

Silicon nitride coatings showed less decline in conductivity, $\tan \delta$ and capacitance after being heated to high temperatures, which indicated a lesser amount of impurities or water absorption. All three specimens reported here in Figs. 44, 46 and 47 demonstrated conductivity levels close to 10^{-16} at room temperature, which was lower than any aluminum nitride specimen tested. A comparison of the conductivity curves for these pyrolytic silicon nitride coatings with those for bulk pyrolytic Si_3N_4 as reported by Westphal³⁴ indicates somewhat higher values for the coatings, but on the whole somewhat comparable. He reported no d-c measurements.

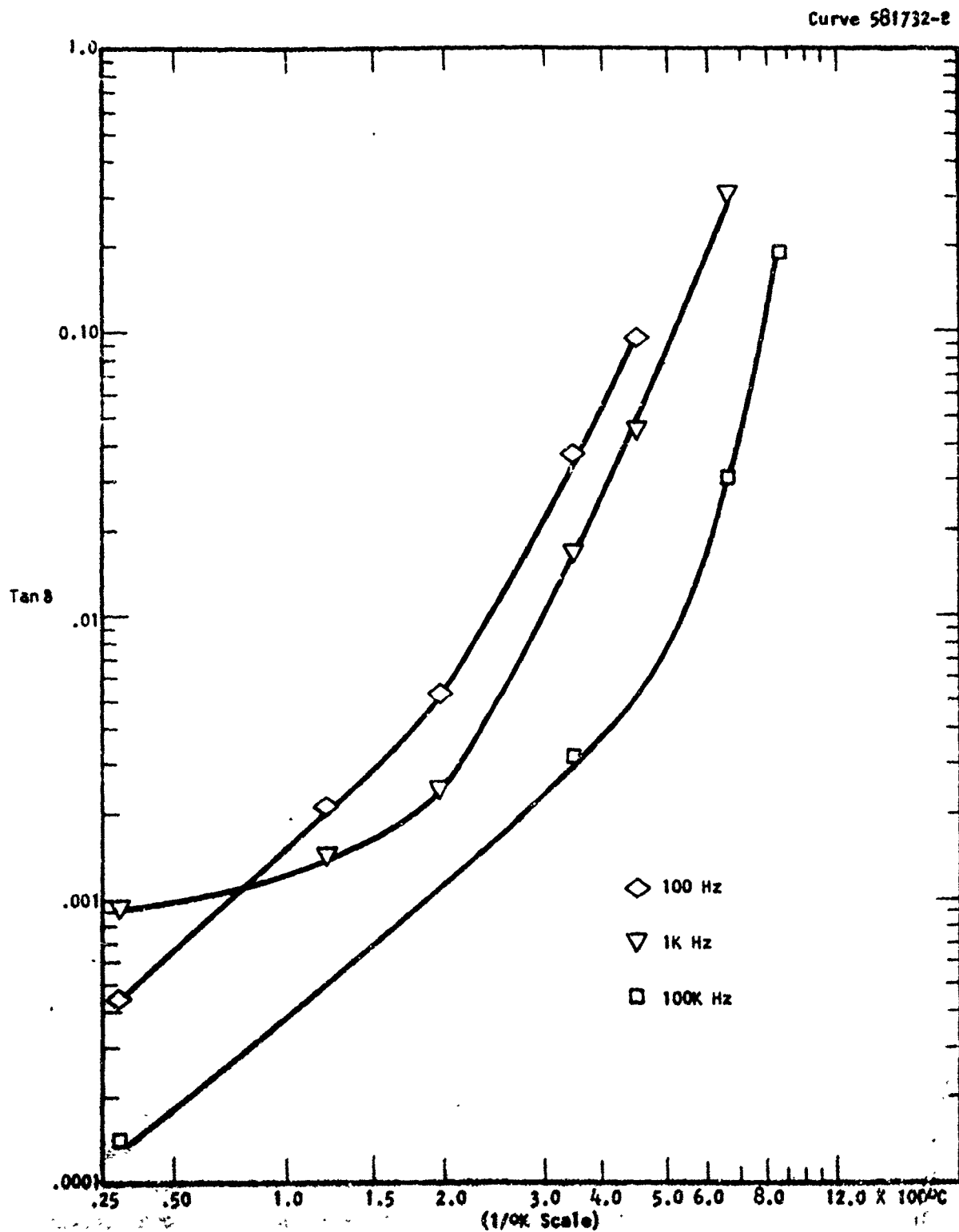


Fig. 45--Dissipation Factor of Si_3N_4 ; Sample 104-113

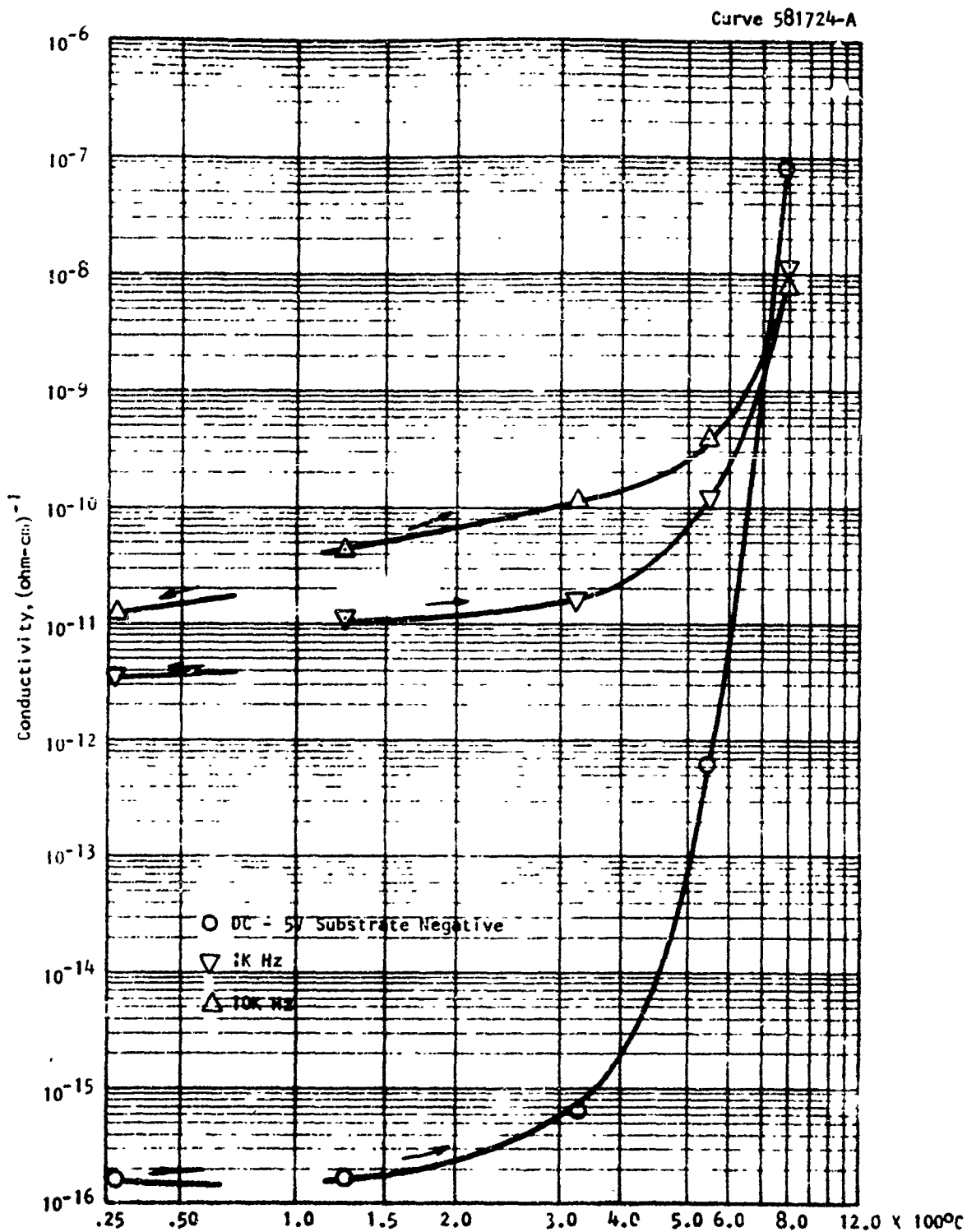


Fig. 46-Conductivity of 0.0013" Si₃N₄ Film on Molybdenum Plate;
 Sample 146-168

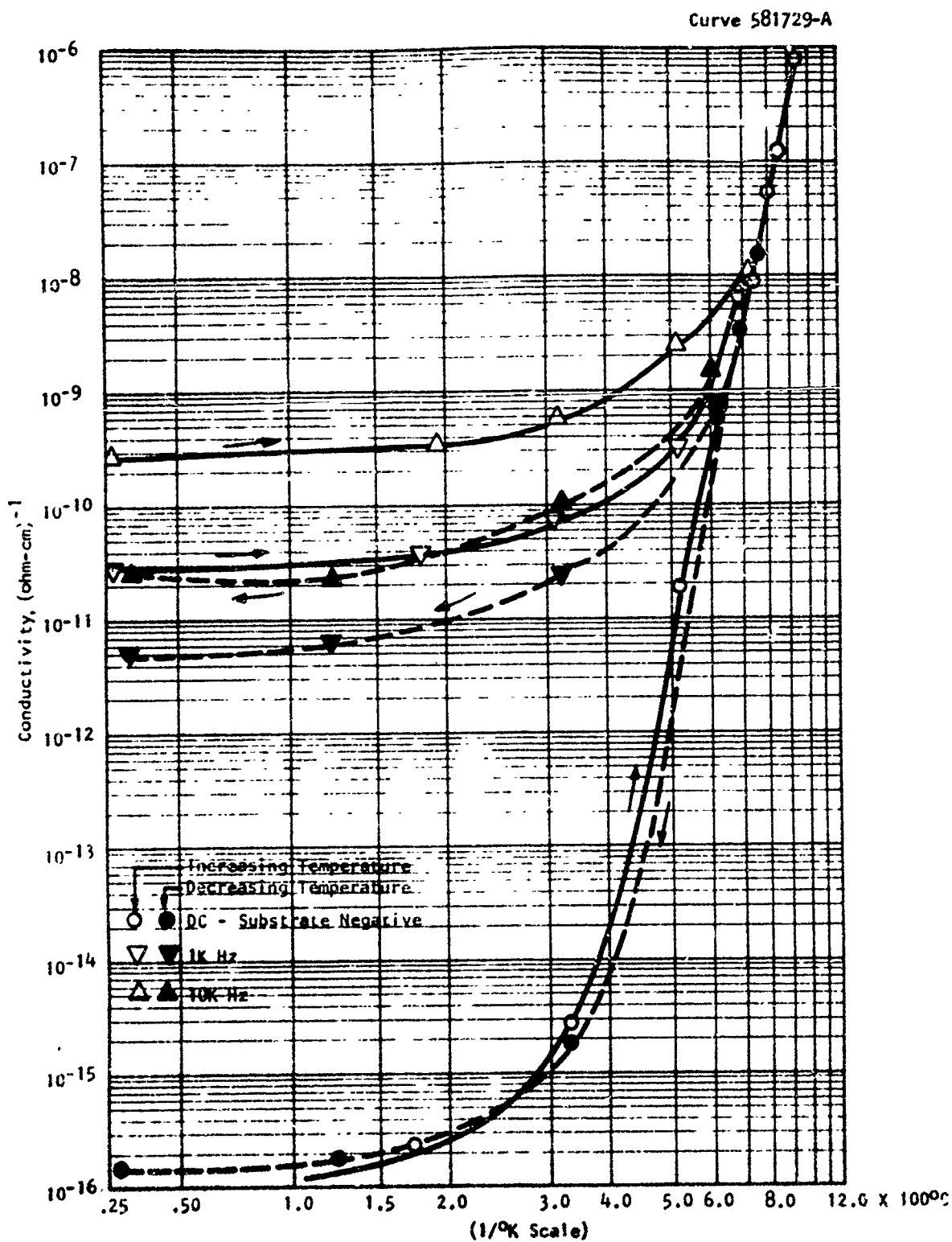


Fig. 47—Conductivity of 0.0034" Si₃N₄ Coating on Molybdenum Plate;
Sample 149-174

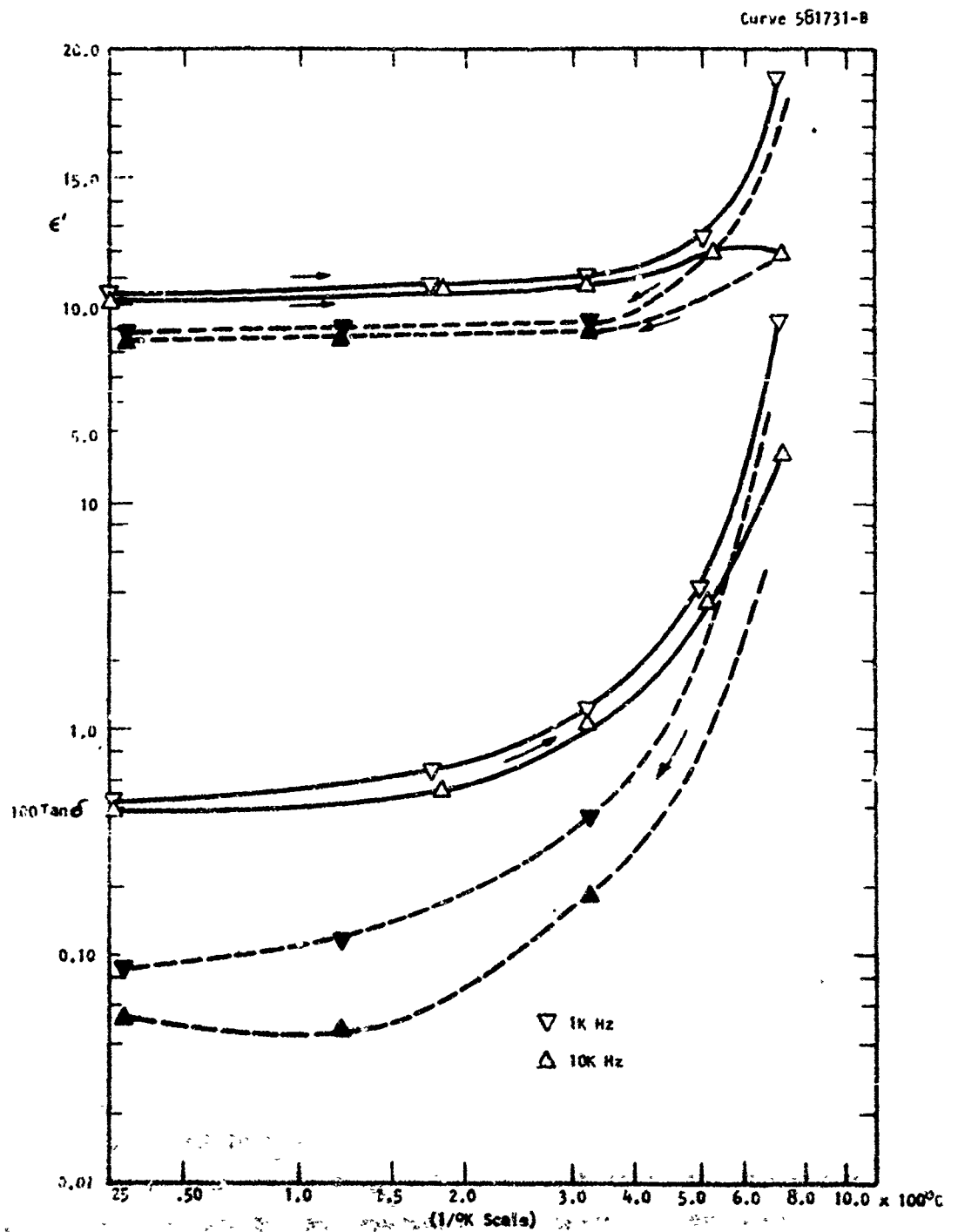


Fig. 48—Dielectric Properties of Si_3N_4 ; Sample 149-174

The activation energy for conduction as indicated by the slopes of the high temperature conductivity curves, Figs. 44 and 47, for two specimens were 1.8 and 2.3 electron volts respectively. This is significantly higher than for aluminum nitride.

A-C dissipation factor curves for silicon nitride specimens showed consistently smoother curves than for aluminum nitride, with no evidence of $\tan \delta$ maxima and Maxwell-Wagner type polarization. The levels of $\tan \delta$ are rather low.

Dielectric constant values for the silicon nitride specimen 149-174 shifted downward during heating to 800°C. It is not known whether this was a material change or possibly a loss in effective area of the sputtered platinum. The lower values, after heating, are very close to those reported by Westphal³⁴ for bulk Si_3N_4 .

2.4.4 Dielectric Strength Measurements

The areas of specimens available for these dielectric strength tests were very limited and the tests had to be made with non-standard 1/16" diameter cylinder end, platinum foil covered, electrodes. The results are an indication of the strength and particularly the continuity of the coatings. Values are listed in Table 7.

In the d-c tests the current was measured up to the breakdown level in a number of cases. The current appeared in exploratory tests to increase steadily up to breakdown, where a discontinuous high level of current occurred. It was noted at the high temperatures that the current increased approximately exponentially with the applied voltage. Approximate values for the slope of these lines for silicon nitride are 1200 v/mil per decade increase in current at 500°C and 730 v/mil per decade increase at 700°C. The slope of the log current vs voltage curves for different spots and different specimens was similar for the same temperature but the level differed. The slope of the log current versus voltage or stress curve increased with temperature and was greater for the AlN.

With the silicon nitride, at 500°C, the current reached, with increasing voltage, a stable level of about 0.01 milliamp (for about 0.02 cm²) just prior to breakdown, and at 700°C about 1.0 milliamp

just prior to breakdown. With the aluminum nitride the stable current prior to breakdown was about 10 times higher than with the silicon nitride, reaching about 0.2 milliamp at 500° and 10 m at 700°C. This interesting phenomena should be analyzed further with more precise measurements.

At high temperature the breakdown mechanism is very certainly thermal and depends on the electrical conduction level as well as the heat transfer rate to the electrodes and environment. In addition, the exponential increase in current with voltage prior to breakdown is indicative of electric field emission of electrons into the specimen from the electrodes, which would enhance the conduction.

Table 7
Dielectric Strength of Si₃N₄ and AlN

Si₃N₄

Specimen	Thickness (mils)	Temperature °C	KV Breakdown, d-c
146-168	1.3	25	2.4, 3.2, 3.8, 2.6
149-174	1.3-1.7	25	2.2, 2.2, 2.4, 2.1
146-168	1.3	510	< 0.3, 2.6, 0.65, < 0.3
149-174	1.3-1.7	510	1.9, 1.1, 1.6, 2.6
149-174	1.3-1.7	707	1.9, 2.1, 2.2

RMS KV Breakdown, 400 cycles

148-173	0.9	25	3.5, 2.9, > 3.6, > 3.2
148-173	0.9	390	1.2, 1.6

AlN

KV Breakdown, d-c

1H115-3	5.6-6.4	25	> 6.0, 6.5, > 5.9
1H115-3	5.6-6.4	508	< 0.4, 1.0, 1.6
1H115-3	5.6-6.4	702	0.65, 0.72, 0.76

RMS KV Breakdown, 400 cycles

1H114-1	2.0-2.3	390	0.75, 0.92
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2.4.5 Thermionic Emission in Relation to the Behavior of Insulators at High Temperature

The phenomenon of conduction across gas spaces at high temperatures was explored and discussed at length in the first annual report⁸ on this project. It was shown that this is undoubtedly due to thermionic emission, and that the levels of current could be comparable to currents through solid insulating barriers. This effect was explored somewhat further to demonstrate that thermionic emission also occurs from insulator surfaces. The consequence of this is that solid insulating barriers are only partially or negligibly effective in preventing current flow between conductors separated by a gas space at high temperatures.

Exploratory studies of this effect were carried one step further by tests with a relatively thick insulating barrier. In these tests a (0.125") quartz plate sample was used, (General Electric Type 101). Tests of the d-c conduction current were made with a platinum foil electrode directly on the sample on both sides and, also, with a gap above the sample, between the uncoated quartz surface and a disc electrode covered with platinum foil. In the latter case, current necessarily flowed in series through the gas or vacuum gap from, or to, the quartz surface and then through the quartz. A good guard-shield electrode prevented fringing currents. The results are summarized in Fig. 49. With the gap present, the current is lower but still significant. With the gap at low pressure the current was higher than at atmospheric pressure. It had a higher activation energy than conduction through the quartz alone. At 300°C, the current with the low pressure gap equaled that with the electrode in contact with the sample, indicating that the effective resistance of the low pressure gap was negligible compared to that of the quartz at this temperature.

In the presence of the gap, the currents were more difficult to reproduce on repeated tests after going to higher or lower temperature and returning. Thus the data are graphed as a band. A polarity effect was observed which has not been explained. If it is assumed that the current is conducted across the gap by electrons, the results indicate that the quartz surface was a better emitter at low pressure, but a poorer emitter at atmospheric pressure.

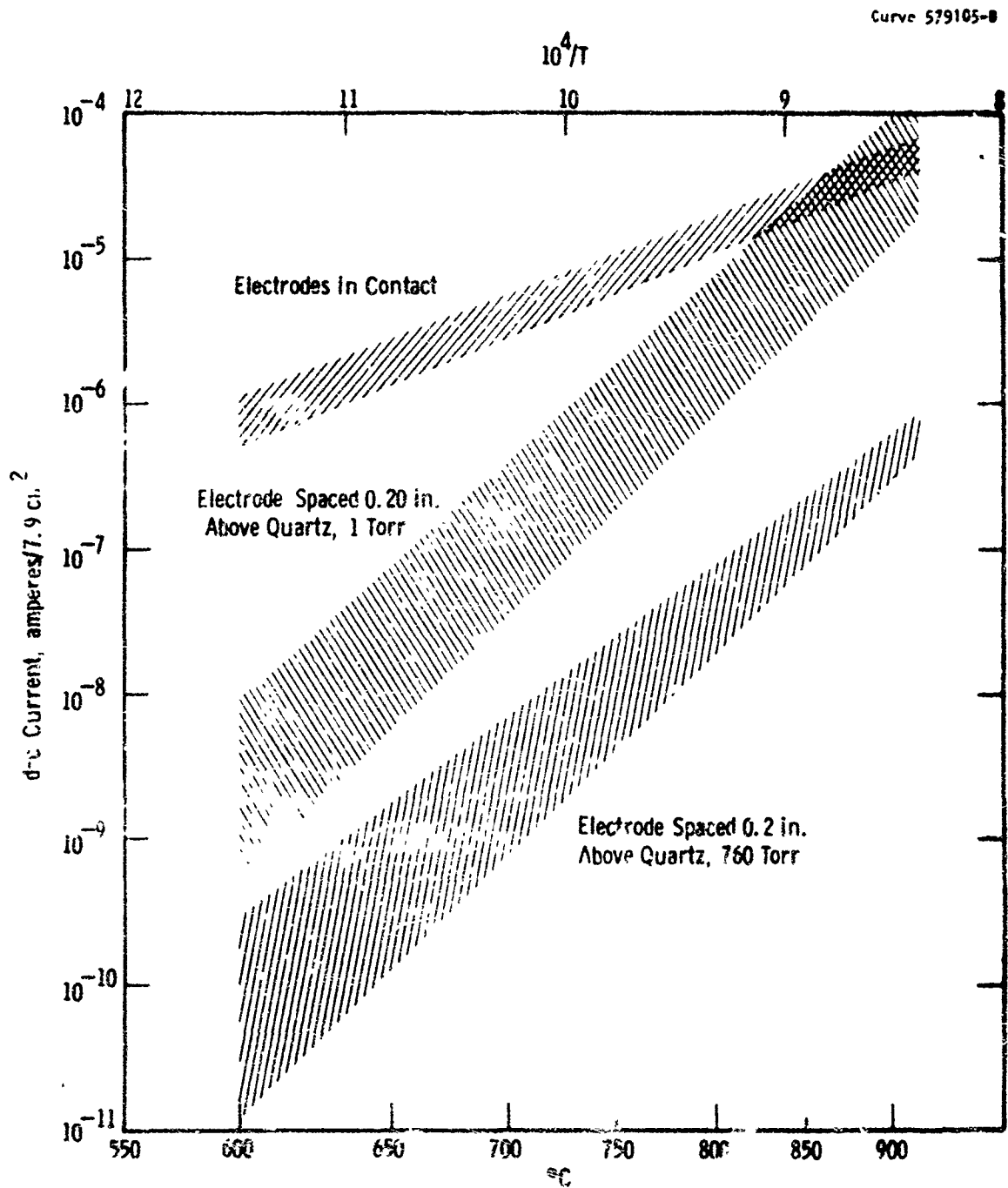


Fig. 49—High Temperature Conduction Through 0.125" Thick Quartz
with and without a Gas Gap; 180 V d-c

The results of these tests demonstrate that a gas gap can be considered at high temperature as a high resistance conductor with a high temperature coefficient of resistance. Conduction occurs by thermionic emission even when solid insulating barriers occur in series with the gap. The magnitude of the thermionic emission current increases with decreasing pressure and increasing voltage. It should be more widely recognized that this factor is important when designing insulation system for temperatures above 500°C.

3. SUMMARY AND CONCLUSIONS

Pyrolytic aluminum nitride has been deposited on the refractory electrical conductors, molybdenum, tungsten and graphite, using $\text{AlCl}_3 \cdot \text{NH}_3$ as the source material. The presence of AlN has been confirmed by elemental analysis, x-ray diffraction and infrared spectra. Changes in properties of deposited films resulting from variations in deposition parameters were examined. The main deposition variables studied were temperature, pressure, and rate of deposition. The temperature at which deposition takes place has a very significant effect on the structure, composition, electrical properties and hydrolytic stability of the deposit. The pressure and more especially the rate of deposition affect such properties as uniformity of coating thickness, the occurrence of nodules and the smoothness of the coating surface. Coatings deposited at 700° to 800°C were softer, more susceptible to hydrolysis and had a lower order of crystallinity than those deposited at 1000° to 1350°C . The hydrolytic instability of the low temperature deposits is believed to be due to the presence of incompletely condensed intermediates still containing hydrolyzable chlorine and possibly amino groups. As the deposition temperature is increased to 1350°C , the deposited material is stable enough to be heated at 1000°C in ordinary air atmosphere for weeks with no change in physical structure and very little change in weight. But even at the highest deposition temperature the product still contains some chlorine contamination.

It has not been found possible to deposit AlN films under our experimental conditions, at temperatures greater than 1350° to 1400°C . At 1400° the deposit consists of relatively large individual beads making only very small area of contact with the substrate surface. At 1500° to 1600°C nothing deposits on the substrate. Possibly this failure to deposit at higher temperatures is related to a phenomenon described by Langmuir³⁵ in the deposition of Cd, Hg and Zn films. Langmuir showed that there was a critical temperature above which deposition would not take place at any set vapor intensity. He pointed out that the temperature at which condensation would take place could be increased by increasing the source material temperature, that is, by increasing the intensity of vapor striking the substrate

surface. According to Langmuir a vapor atom has an average life on a surface which it strikes before it evaporates. The average life will be longer, and condensation more likely, the lower the substrate temperature and the greater are the forces which bind the atom to the substrate. If the average life of the condensed atom is long enough for a second atom to condense on it, then the energy required to evaporate either atom is increased and deposition begins.

Aluminum nitride deposited on molybdenum rods and wire coils was found to offer considerable protection to these substrates when heated in air up to 900°C. A limitation of this process is the inability of the coating to penetrate deep pits or crevices.

Coatings of aluminum nitride on molybdenum foil are quite brittle. However, they could find use in capacitor construction where sharp bends are not encountered. They might also be used to insulate preformed coils.

Pyrolysis of gaseous mixture of silane, ammonia and occasionally nitrogen has resulted in the deposition of films of α - Si_3N_4 on molybdenum substrates heated to high temperatures. It has been observed that the coatings prepared in this manner are crystalline, hard, have high spectral emissivities and provide some degree of oxidation protection to a molybdenum substrate. If the films are deposited at low temperature (700-800°C), they are observed to have quite different characteristics. Prominent among these are a lack of crystallinity, relative softness and instability above 1000°C to yield crystalline silicon. At temperatures of $\sim$ 1000°C and reduced pressures the films obtained are found to be adherent and amorphous materials. These coatings, which have been more thoroughly investigated than those deposited at lower or higher temperatures, are hard (>9 on Mohs' scale) and characteristically yield an infrared spectrum like that expected from amorphous silicon nitride. The elemental constitution of material synthesized under these conditions, as determined by an alkali fusion method, is consistent with the designation of these films as silicon nitride. Silicon nitride prepared in this manner is dense, having an experimental density of 3.08 g/cc compared to the x-ray density of 3.18 g/cc for α - Si_3N_4 , and affords oxidation protection to a molybdenum substrate.

Projection onto a substrate is excellent with deposition occurring rather uniformly over smooth surfaces, sharp edges and rough sides of molybdenum substrates.

Consideration of the nature of the reactants and examination of the solid phase by-product sometimes obtained in the pyrolysis of silane and ammonia allows a mechanism for the reaction to be suggested. This mechanism postulates that the reaction is initiated by the pyrolysis of silane to a radical species with propagation and termination proceeding by radical abstraction and combinations respectively.

Continued dielectric tests on aluminum nitride coatings have indicated some preparations which have lower conductivities than previously found for this material - levels as low as 4×10^{-16} (ohm-cm) $^{-1}$ at 25°C and 3×10^{-9} at 800°C. However, many preparations of this material show much higher conductivities and the level appears to be not very reproducible upon heating and cooling.

Silicon nitride coatings appear to have more stable and reproducible dielectric properties than AlN coatings as prepared in this project. Conductivities of silicon nitride coatings have been made repeatedly close to 10^{-16} (ohm-cm) $^{-1}$ at 25°C and about 10^{-6} at 1000°C. It should be a usable dielectric at lower voltages up to that temperature. D-C dielectric strengths of about 1300 volts/mil have been obtained at 700°C, on Si_3N_4 coatings. Further investigation of the dielectric strength of silicon nitride coatings for larger areas should be made over wide temperature ranges and for practical conditions.

Further exploratory tests of conduction across gas spaces at high temperature by thermionic emission reveal that insulator surfaces also are emitters and that conduction occurs across gas spaces in series with solid insulating barriers. Such thermionic emission conduction should be considered in designs of future high temperature insulation systems. A further systematic investigation of this phenomenon and the practical limitations it places on high temperature electrical systems is recommended.

There are several areas in which interesting basic research programs are suggested by this project. These areas are: the study of thermionic emission from insulator surfaces and practical types of high temperature conductors (i.e. with oxidized surfaces); and in the study of high electric field conduction at high temperature in solid insulators up to breakdown stresses.

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DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Westinghouse Research Laboratories Pittsburgh, Pennsylvania 15235		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE Development on High Temperature Insulation Materials Part II Deposition and Properties of Pyrolytic Aluminum and Silicon Nitrides		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Scientific Report, Final Technical Report, June 1965 to June 1967		
5. AUTHOR(S) (Last name, first name, initial) Lewis, D. W., Sestrich, D. E., Esposito, J. N., Dakin, T. W., Berg, D. "(PI)"		
6. REPORT DATE August 1967	7a. TOTAL NO. OF PAGES 90	7b. NO. OF REFS 35
8a. CONTRACT OR GRANT NO. AF 33(615)-2782	8b. ORIGINATOR'S REPORT NUMBER(S)	
a. PROJECT NO. 7371		
c. Task No. 737101	8c. OTHER REPORT NUMBER(S) (Any other numbers that may be assigned this report) AFML-TR-66-320, Part II	
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11. SUPPLEMENTARY NOTES 49 Figures	12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory (MAYT) Wright-Patterson AFB, Ohio 45433	
13. ABSTRACT (UNLIMITED)--Pyrolytic aluminum nitride has been deposited on refractory electrical conductors using $AlCl_3 \cdot NH_3$ as the source material. Effects which pressure, temperature and rate of deposition have on electrical and other properties of deposits have been determined. Density of deposited coatings approach that of the calculated value. However, they still contain residual chlorine, causing electrical properties to fall short of what is expected of dense high purity AlN. (U) Pyrolytic silicon nitride has been prepared from gaseous mixtures of silane and ammonia under varying conditions of temperature and pressure. Adherent, relatively soft, amorphous films have been deposited on substrates heated in the 700° to $800^\circ C$ range while hard crystalline coatings of $\alpha-Si_3N_4$ have been obtained in the vicinity of $1250^\circ C$. Coatings, which are both hard and amorphous, have been deposited at $\sim 1000^\circ C$ and have been characterized by a number of techniques. (U) High temperature dielectric property tests of aluminum and silicon nitrides have indicated good high temperature resistivities with some samples, but considerable variability existed among samples. Measurements on aluminum nitride in particular, have indicated the presence of impurity conduction. Silicon nitride coatings seem to demonstrate more consistently high resistivities which make this material a potentially useful dielectric at 800° to $1000^\circ C$ at low voltages. (U) Studies of the conduction across gas spaces, due to thermionic emission at high temperature, indicate this effect is very important in high temperature insulation systems. Solid insulating barriers do not prevent, but only modify such conduction, since the insulation surface is also a thermionic emitter.		

DD FORM 1473
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Silicon Nitride	Tungsten						
Pyrolytic	Graphite						
Films	Emissivity						
High Temperature							
Electrical Insulation							
Dielectric Properties							
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