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RFP-972

April 18, 1969

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VACUUM COATING OF BORON NITRIDE

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P1305

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Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information

National Bureau of Standards, U. S. Department of Commerce

Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

April 18, 1969

RFP-972

UC-25 METALS, CERAMICS,
AND MATERIALS

TID-4500

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VACUUM COATING OF BORON NITRIDE

Robert G. Kurtz and T. Van Vorous

Abstract. A method has been developed to deposit adherent metal films on boron nitride. The procedure utilizes thin (about 500 angstroms) film of beryllium deposited by ion plating techniques directly onto the boron nitride. Films of other metals may then be deposited over the beryllium film by any convenient method.

Thorough substrate cleaning and outgassing prior to the start of the deposition process are essential for good film adherence, as well as substrate heating before and during the deposition.

INTRODUCTION AND SUMMARY

Films of lanthanum, gold, silver, copper, aluminum, cerium, molybdenum, and titanium have been deposited onto disks of boron nitride. The films exhibited good adherence when deposited over a thin (500 angstroms) film of beryllium which had been applied by accelerated-ion techniques.¹ Thermal evaporation methods would not produce an adherent film.

EQUIPMENT

Vacuum:

The vacuum systems were of three different sizes, as required by the different deposition processes being used. All were oil-diffusion pumped vacuum systems using a single mechanical pump for both holding and roughing.

A 2-inch, oil-diffusion pumped system was used on a work chamber consisting of a 10-inch diameter glass sleeve mounted on a base plate and having a top plate for substrate support. The chamber jiggling is shown in Figure 1. The necessary pass-throughs were in the base plate. This system was used for depositing films by triode-sputtering methods.

The second unit was a 4-inch, oil-diffusion pumped system. The work chamber consisted of a 14-inch diameter by 24-inch high glass bell jar mounted on a 14-inch MRC² feedthrough collar. The system was used for the deposition of other films which could be evaporated from resistance-heated filaments. Jiggling for this system is shown in Figure 2.

The third unit was a 6-inch, oil-diffusion pumped system. The work chamber was a 24-inch diameter by 30-inch high metal bell jar mounted on a 24-inch NRC³ feedthrough collar and base plate. The system was equipped with a Temescal⁴ 10-kilowatt, electron-beam gun. The gun was used to deposit films of metals, such as titanium and cerium which were more readily evaporated than with the use of other methods.

Fixturing:

The fixturing arrangement shown in Figure 2 consists of two resistance-heated evaporation sources. One is for the beryllium and the other for a second evaporant metal. A wire-feed device supplied metal to the second source. This arrangement was used to deposit films up to a 0.001-inch thickness. The substrate holder is mounted on a shielded ceramic standoff and then connected to the negative high voltage lead. The holder must also be covered to prevent the film from depositing on the back side of the disks.

Power Supplies:

Several combinations of power supplies were necessary. For the electron-beam evaporation, a power supply designed and fabricated on the plant site was used.⁵ The power supply has an output of 10 kilovolts (kv) at 400 milliamperes (ma) and was designed for versatile use with several types of electron-beam guns. The beam deflection was controlled by a 5-volt, 5-ampere Kepco⁶ power supply.

¹D. M. Mattox. *Film Deposition Using Accelerated Ions*. Sandia Laboratory Report No. 1124-3. Sandia Corporation, Albuquerque, New Mexico.

²MRC Manufacturing Corporation, Orangeburg, New York.

³NRC Equipment Corporation, Newton, Massachusetts.

⁴Temescal Metallurgical Corporation, Berkeley, California.

⁵R. M. Uberecken. Internal personal communication.

June 1968.

⁶Kepco Incorporated, Flushing, New York.

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Legend

1. Substrate holder.
2. Anode.
3. Emitter and shields.
4. Cathode.

FIGURE 1. Jigging for Triode Sputtering.

Legend

11918-6

1. Evaporant wire.
2. Substrate holder.
3. Accelerated-ion high voltage lead.
4. Jig block for two-element heating.

FIGURE 2. Jigging for Two-Element Thermal Evaporation.

The triode-sputtering system used a 20-volt, 30-ampere Kinney⁷ power supply for the filament, a 6-kv, 100-ma Sorensen⁸ high voltage supply for target potential, and a 80-volt, 18-ampere Sorensen power supply for the filament bias. A concept drawing of the power-supply arrangement is shown in Figure 3.

The system used for the accelerated-ion deposition of beryllium and the resistance-heated filament evaporation used an Allen-Jones⁹ AJ-5 power supply for resistance heating and a CVC¹⁰ LC-031 5-kv, 750-ma high voltage power supply. The power supply connections are shown in Figure 4.

The power supplies shown are typical equipment for these applications. However, any other supplies with similar outputs could be used.

PROCEDURES AND DISCUSSION

The process development may be broken into two parts. One for boron nitride cleaning and preparation; and the second for film deposition.

Two grades of boron nitride were used in this study.

Grade A: Grade-A boron nitride is a hot-pressed ceramic composition first introduced by Carborundum¹¹ in 1958. It is a white solid, impervious, nontoxic, and lubricious material that closely resembles graphite. Physically, it is semisoft with an average density of 2.08 grams per cubic centimeter and a hardness of 385 (Knoop 100). Boron nitride may be used up to 5000 °F in neutral or reducing atmospheres and exhibits good resistance to thermal shock. This grade of boron nitride contains 5.0 to 8.0 percent boric oxide which has an affinity for moisture. Carborundum rates the typical Grade-A boron nitride moisture pickup as 1.1 percent weight gain in 168 hours.

Grade HP: Grade-HP boron nitride was introduced by Carborundum in 1964. It is similar to

Grade A, except that its moisture pickup is reduced to 0.16 percent in 168 hours. This can be accomplished by reducing the boric-oxide content to less than 0.10 percent. Physically the material has a density of 1.90 grams per cubic centimeter and a hardness of 205 (Knoop 100). Grade HP has an even higher resistance to thermal shock and about a 50-percent higher thermal conductivity than Grade A.

The initial work on this project involved use of Grade-A boron nitride. Results with this material indicated a serious problem of outgassing and poor film adherence that was not reproducible. These problems can both be attributed to the boric oxide (water) content of the Grade-A material. Grade HP still has an amount of absorbed water that is significant from the standpoint of good vacuum practice; however, reproducible results could be achieved. Thus the results reported, all involve use of Grade-HP boron nitride.

It was necessary to completely outgas the boron nitride up to the maximum temperature to which it would be exposed during film deposition. This was accomplished by slow bakeout in a vacuum oven for at least 24 hours at a temperature of 225 °C. As an added precaution, the boron nitride disks were kept under vacuum at this temperature until ready for placement in the vacuum system for coating. Any marks of handling or contamination were removed prior to vacuum bakeout by lightly abrading with 600-grit paper or with an air-abrasive cleaning unit containing 50-micron alumina abrasive powder. After cleaning, the boron nitride was handled with tweezers and immediately transferred into the vacuum system.

The film deposition was performed by the following method:

1. Pump-down to about 4×10^{-6} torr.
2. Heat the resistance filament containing the beryllium to just below its melting point. Leave hot for approximately one-half hour. This insures residual moisture in the boron nitride will be removed.
3. Throttle the high vacuum valve and back-fill the bell jar with argon to a pressure of 25 microns.

⁷Kinney Vacuum Division, The New York Air Brake Company, Boston, Massachusetts.

⁸Sorensen Products, South Norwalk, Connecticut.

⁹Allen-Jones Electronics, Gardena, California.

¹⁰Consolidated Vacuum Corporation, Rochester, New York.

¹¹The Carborundum Company, Latrobe, Pennsylvania.

FIGURE 3. Concept Drawing of Triode-Sputtering Film Deposition.

FIGURE 4. Concept Drawing of Accelerated-Ion Film Deposition.

4. Turn on the high voltage power supply to 3 kv (depending on substrate-holder surface area, approximately 150 ma current should be obtained).
5. Slowly increase filament temperature to evaporate the beryllium.
6. Turn off the filament power supply.
7. Connect the filament power supply to the other filament feedthroughs for evaporation of the second metal.
8. While the system is still under a partial pressure of argon and with the high voltage power supply still at 3 kv, evaporate approximately 10 percent of the metal. (It is convenient to estimate the amount of material evaporated, if a wire-feed device operates to supply evaporant metal to the filament.)
9. Turn off the high voltage power supply, the argon bleed valve, and open the high vacuum valve.
10. Continue feeding the evaporant wire into the filament in small increments until the desired amount of metal has been evaporated.
11. Turn off the filament power supply and allow at least one hour for cooling, before removing the coated boron nitride disks from the system.

This method was used for coating with metals which could be readily evaporated from evaporation boats, such as lanthanum, gold, aluminum, silver, and copper. For metals such as molybdenum, cerium, and titanium which were more easily deposited by triode-sputtering techniques or from an electron-beam gun, the process was interrupted after Step 5 and approximately one hour allowed for the boron nitride specimens to cool. After this cooling period, the substrate holder containing the boron nitride specimens was removed from the one vacuum system and immediately placed in the other system for deposition of the second metal. The specimens were cleaned by argon ion bombardment for approximately two minutes at 2 kv and at approximately 0.1 to 0.3 milliamperes per square centimeter of total cathode area, after placing in the second vacuum system and prior to depositing the final film material. Care must be taken during the sputtering and electron-beam

film deposition processes to keep the substrates from reaching a higher temperature than that developed during the beryllium deposition.

Attempts at depositing a film directly onto the boron nitride resulted in a nonadherent film. This was true whether the film was *ion-plated* or just thermally evaporated, except in the case of beryllium, which produced an adherent film when ion-plated. When beryllium was ion-plated using a gas mixture consisting of three parts argon to one part nitrogen, an adherent film was also deposited. This technique was not evaluated with metals other than beryllium.

Apparently this process is similar to that normally used to deposit metals on ceramics. A stable metal oxide, such as niobium oxide (Nb_2O_5) or tantalum oxide (Ta_2O_5), is normally deposited as an interface film to achieve good adherence. In this process, the beryllium probably exists as an oxide, or nitride, or both at the substrate interface and in the metallic form in contact with the overcoated metal film.

The metals deposited and the techniques used are given in Table I.

CONCLUSIONS

Grade-HP boron nitride can be successfully coated using vapor-deposition methods, if a thin (approximately 500 angstroms) film of beryllium is first deposited by accelerated-ion methods. A second metal film of many other metals can be deposited over the beryllium film using any convenient method of film deposition. Prior substrate cleaning and outgassing is essential to producing adherent films on the boron nitride. In addition, the boron nitride must be heated just before and during the film deposition process.

TABLE I. Summary of Metals Deposited.

Metal Deposited	Method	Remarks
Lanthanum	Accelerated Ion	Tantalum source, corroded.
Gold	Accelerated Ion	Tungsten pan.
Silver	Accelerated Ion	Tungsten pan.
Copper	Accelerated Ion	Tungsten pan.
Aluminum	Accelerated Ion	Molybdenum source, corroded.
Molybdenum	Triode Sputter	-
Cerium	Electron-Beam Gun	Some spattering at start, high gettering action at high rates.
Titanium	Electron-Beam Gun	Some spattering at start, high gettering action at high rates.