19/86
JB

1

17

DR-1542-3

UCID--20601

DE86 006656

AN ASSESSMENT OF THE APPLICATION OF THE SPUTTERING
PROCESS TO BERYLLIUM FOR
FOR HARDENING OPTICAL COATINGS

C. W. Chen
C. S. Alford

November 11, 1985

MASTER

Lawrence
Livermore
National
Laboratory

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.
Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

An Assessment of the Application of the Sputtering
Process to Beryllium for Hardening Optical Coatings

C. W. Chen and C. S. Alford
Lawrence Livermore National Laboratory
Livermore, CA 94550

Abstract

Two principal deposition processes are compared for the case of depositing 1-2 μm beryllium on fused-silica substrates. While the evaporation-deposition process offers advantages such as higher deposition rate, purification of the evaporant and efficient use of masks, the sputter-deposition is more versatile, and therefore more effective, in varying and controlling the microstructure of the deposits. *The versatility comes about because the latter process has five major operational parameters to be selected or adjusted.* Consequently sputter-deposited beryllium films are expected to display more desirable microstructures and better surface finish than evaporation-deposited films.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

90
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The thermal damage caused by nuclear weapon radiation to aluminum coatings of optical mirrors can be alleviated¹ when a thin layer of beryllium is inserted between the optical coating and the fused-silica substrate. Properly deposited beryllium coatings effect this "hardening" by serving as an effective heat sink, protecting the aluminum coating from melting and other thermal deterioration in a nuclear environment. By properly deposited it is meant that the beryllium layer must adhere to the substrate and be porosity-free, and that its grain structure must be refined and have no pronounced columnar growth and texture. The present contract work deals with further development of the technology for hardening optical coatings with emphasis on qualities of the beryllium layers and optical properties of the hardened coatings.

The beryllium films used in the previous study¹ were prepared by the evaporation-deposition process at Rocky Flats. Since 1979, the Fusion Target Fabrication (FTF) laboratory of LLNL has built excellent facilities and developed considerable expertise for beryllium coating and film preparation by the sputtering process. It would be more convenient, and perhaps technically more desirable, if our beryllium coating could be done by the sputtering process in the FTF laboratory. The change in locality from Rocky Flats to LLNL is secondary to the change in process from evaporation-deposition to sputter-deposition. This means that the sputter-deposited beryllium films must display qualities as good as, or preferably better than, those of the evaporation-deposited films.

The purpose of this report is to compare these two processes when they are applied to depositing beryllium onto quartz substrates for hardening optical coatings. It is shown that even though the evaporation-deposition process offers advantages such as purification of the evaporant and higher deposition rates, the sputter-deposition process is more versatile, and therefore more effective, in varying and controlling the microstructure of the deposits. Consequently sputter-deposited beryllium films are expected to exhibit superior qualities to evaporation-deposited films.

Before comparing the two processes, however, it is worthwhile to mention that beryllium shows strong affinity for oxygen and that it has an electrode potential higher than that of hydrogen. Hence such deposition processes as electroplating² and chemical vapor deposition (CVD)³ are neither effective nor convenient for the metal. This leaves evaporation deposition and sputter-deposition as the two major processes for preparing beryllium films.

Our recent literature survey on beryllium coating has confirmed the limited choice of deposition processes for beryllium. The survey also revealed that various aspects of the evaporation-deposition process have been studied by many workers, notably Smonenko et al.⁴ and Palatnik and Fedorenko⁵ in the USSR (1961-9), Verderber⁶ at Burroughs (1964), Mah and Nordin⁷ at Rocky Flats (1972), Bunshah and Juntz⁸ at LLNL (1973), Wheeler et al.⁹ (1981) and Nieh et al.¹⁰ (1982) at Lockheed, and Taylor¹¹ at ONRL (1982). The application of the sputtering process to beryllium was not known until Patten and McClanahan's report¹² on their work at Battelle-Northwest (1973). Paulson and Lorigan¹³ at Motorola (1976) examined rf-sputtered thin films of beryllium. Work on magnetron sputtering of beryllium at LLNL was described by Burke et al.¹⁴ (1980) and by Chen and Alford (1982-84).

As is well known, evaporation and sputtering constitute the bases of two principal physical vapor deposition (PVD) processes. They share the same principle that the deposits are produced by attaching atoms to the substrate - exclusively, in the case of evaporation-deposition, and predominantly, in the case of sputter-deposition. Films prepared by either process usually show columnar growth and preferred orientation in the grain structure. This tendency becomes more prominent for beryllium, whose hexagonal crystal structure tends to promote preferred growth of grains along the c-axis normal to the basal plane.

Similarities notwithstanding, the two processes differ vastly in several aspects.¹⁵ First, the depositing atoms are generated by two separate mechanisms: They are produced collectively into the vapor phase by thermal energy through vaporization or sublimation in the evaporation process, but individually by inert-gas ions through momentum transfer in the sputtering process. Second and third, the energy and the transport mode of the depositing atoms differ significantly, as is described in Table 1.

Impacts of these differences on the outcome of the deposition processes are listed in the last column of Table 1. The production of vapor from liquid or solid through thermal energy is a spontaneous reaction, which leads to higher (5 to 50 times) deposition rates for evaporation-deposition than those for sputter-deposition. The difference in deposition rate is enhanced for beryllium, because this metal exhibits one of the lowest sputtering yields.¹⁶ For instance, Bunshah and Juntz⁸ attained a rate of 25 $\mu\text{m}/\text{min}$ (equivalent to 1.5 $\text{mm}/\text{hr.}$), whereas Chen and Alford, in an effort to increase the rate of sputter-deposition for beryllium, switched the sputtergun from the Sloan Research model to a "fast" model of Sputtered Films, Inc. and used relatively high (1800 W) dc power, yet the increased rates were still lower than 0.35 $\mu\text{m}/\text{min}$.

The evaporation process involves no external gas and is therefore capable of purifying the evaporant by eliminating three groups of impurities: gaseous elements (H, N, and O), volatile elements (Na, Mg, Cl, Ca, and Zn), and insoluble compounds (BeO , Be_2C , etc.). Bunshah and Juntz¹⁷ demonstrated the capability of purifying beryllium by reducing contents of C, N, O, Na, and Cl from 28, 2, 60, 1.8, 10, and 24 ppm atomic (appm) to 7, 0.2, 15, 0.3, 1, and 0.15 appm, respectively, in the evaporation-deposition process. The sputtering process lacks such purifying capability. In fact, even though we were using argon produced from high-purity liquid argon, the sputter-deposited beryllium still showed a slight increase in oxygen content.

The collisionless, line-of-sight transport mode of depositing atoms in the evaporation process allows masks to be used to control the size and scope of deposits more closely than in the sputtering process, in which the transport mode is not of the line-of-sight form and in which collisions take place. These differences account for the widespread application of the evaporation-deposition process to fabrication of integrated circuits in the computer industry and in other high-technology fields.

At first glance, the higher energies carried by sputtered atoms would seem to cause more intense heating of the substrate. Actually the heating effect is a combination of energy of the depositing atoms and the rate of deposition. Combining both factors considerably reduces the difference in substrate heating to less than a factor of 2 to 3, instead of 10 to 100. Moreover, the heating effect can be minimized in the sputtering process by adopting such measures as increasing the distance between the target and substrate, using dc power, and precooling the substrate.

Thus the evaporation process offers three advantages over the sputtering process for beryllium: (1) higher deposition rates, (2) capability of purifying the starting material, and (3) better control of the shape and size of deposits by masking. As far as our future work on beryllium deposition for hardening optical coatings is concerned, however, none of these advantages would play a significant role for the following reasons. Because the thickness of the beryllium films chosen for the hardening function is limited to 1 to 2 μm , the relatively low rates of deposition in the sputtering process would not pose any problem in practice. We estimate that even using the "slow" sputtergun of Sloan Inc. for superior surface finish, depositing 1 μm of beryllium on quartz substrate at 4" distance from the target under 600-W rf power would only take 40 to 70 min, depending on whether or not a bias voltage is applied to the substrate. Even at 70 min, the time is still short enough for the run to be made without excessive delay. Unless our work on beryllium later demands ultrahigh purity, the present beryllium target should be sufficiently pure (about 99.8%) for

application to the hardening of optical coatings. Masks will not be used here, so the third advantage of the evaporation-deposition process is of consequence.

The sputtering process, on the other hand, has many operational parameters to be adjusted so as to yield the desired microstructure and other qualities; it is thus much more versatile than the evaporation process. The more important parameters include the design of the sputtergun, the sputtering mode (rf or dc), the sputtering power, the voltage of a negative bias applied to the substrate, and the pressure of the sputtering gas. None of these parameters exists in the evaporation process. Taking advantage of these parameters, Chen and Alford were able to gain the following benefits in sputter-deposition of beryllium:

- (1) Changing the sputtergun from the Sloan Research model to the Sputtered Films Research S-gun increased the rate of deposition by a factor of 2 to 5.
- (2) Other conditions being equal, switching the sputtering mode from rf to dc lowered the induced temperature of the glass substrate from 185 to 95°C and suppressed columnar growth in the deposits.
- (3) The rate of deposition increased with sputtering power linearly up to 1800 W, irrespective of the sputtering mode.
- (4) In the dc mode, the application of a negative bias voltage of up to -80 V tended to change the surface morphology drastically, from coarse grains with pronounced columnar growth to randomly oriented, fine grains. Similar benefits of substrate bias were observed in the rf mode.
- (5) The pressure of the sputtering gas (argon) was found to be critical. Too low pressure would not allow the plasma to be ignited or sustained; too high pressure tended to reduce the deposition rate and to cause arcing and excessive erosion of the

target. Proper pressures in the mid-range together with other optimal conditions would yield fine microstructure. To assist ignite the plasma while a beryllium target is covered by a thin film of BeO, higher gas pressure are used at the outset of the run.

Knowing the effects of the parameters, Chen and Alford established two combinations of sputtering conditions (specified in Table 2) for the production of porosity-free, fine-grained microstructures of 1- μ m thick beryllium deposits on optically polished quartz substrates, which were characterized by 65- $\text{\AA}$ peak-to-valley height surface finish.¹⁸ Figure 1 shows such a surface finish obtained from a typical beryllium film sputter-deposited on a glass slide. We believe that beryllium films prepared by the evaporation process would show inferior surface finish.

In conclusion, we have shown that the sputter-deposition process is superior to the evaporation-deposition process for preparing beryllium films in hardening the aluminum coatings of optical mirrors. Sputter-deposition offers operational versatility for improving qualities of the deposits which is not available in evaporation-deposition.

References

1. W. P. Barnes and G. R. Wirtenson, "Hardened Coatings for Glass Mirrors", Itek Corporation Report ISM75(S)2 (January 21, 1975).
2. S. Jayakrishnan, M. Pushpavanam and B. A. Shenoi, "Electrodeposition from Organic Solutions of Metals that are Difficult to Deposit from Aqueous Solutions", *Surface Technol.*, 13, 225 (1981).
3. R. O. Adams and J. T. Hurd, "The Properties of Beryllium Surfaces and Films", *J. Less-Common Metals*, 18, 406 (1969).
4. V. M. Amonenko, I. I. Papinov, G. F. Tikhinski and V. Finkel, *Fiz. Metal. Metalloved.*, 12, 73 (1961).
5. L. S. Palatnik and A. I. Fedorenko, *Fiz. Metal. Metalloved.*, 17, 866 (1964); 18, 69 (1964) and 22, 637 (1966).
6. R. R. Verderber, "Orientation of Vacuum-Deposited Be Thin Films", *J. Appl. Phys.*, 35, 1643 (1964).
7. G. Mah and C. W. Nordin, "Characterization Studies of Physical Vapor-Deposited Beryllium", Report RFP-1814, Rocky Flats Div., Dow Chemical Co., Golden Colo. (1972).
8. R. F. Bunshah and R. S. Juntz, "Fabrication of Framed Beryllium Windows by High Rate Physical Vapor Deposition Process", *J. Vac. Sci. Technol.*, 10, 83 (1973).
9. W. Wheeler, R. F. Karlak, T. G. Nieh and A. E. Vidoz, "Beryllium Optical Mirrors by Vapor Deposition", SPIE Vol. 306 on Contemporary Methods of Optical Fabrication (1981), p. 71.
10. T. G. Nieh, R. F. Karlak and A. E. Vidoz, "The Effect of the Atomic Incident Angle upon the Microstructure of Thick Beryllium Deposits Produced by Physical Vapor Deposition", *J. Vac. Sci. Technol.*, 21, 980 (1982).
11. R. D. Taylor, "Preparation of High Purity Beryllium Foils", *Nuclear Instruments and Methods*, 200, 135 (1982).
12. J. W. Patten and E. D. McClanahan, "Effects of Deposition Temperature and Substrate Bias on Orientation and Hardness of Thick Sputter-Deposited Beryllium Foils", *J. Less-Common Metals*, 30, 351 (1973).
13. W. M. Paulson and R. P. Lorigan, "Properties of RF-Sputtered Beryllium Thin Films", *J. Vac. Sci. Technol.*, 14, 210 (1977).

Table 1. Comparison between sputtering and evaporation

	Sputtering	Evaporation	Impact on the outcome of the deposition process
1. Production mechanism	Momentum transfer from gas ions to target atoms	Thermal energy	Higher deposition rate for evaporation
2. Transport of depositing atoms from source to substrate	Collisions expected, not line-of-sight	Collisionless, line-of-sight	More effective use of masks for evaporation
3. Energy of depositing atoms	1-100 eV	0.1-0.5 eV	Less substrate heating in evaporation

Table 2. Two sets of optimized sputtering conditions for producing fine-grained Be films

	Set I	Set II
Design of sputtergun	Sloan research gun	Sloan research gun
Sputtering mode	rf	dc
Sputtering power	600 W	600 w
Bias voltage applied to substrate	-800 V	-40 V
Pressure of sputtering gas	3.2 mtorr	12.9 mtorr
Deposition rate at indicated target-substrate distance	253 Å/min at 4" distance	283 Å/min at 2" distance

Figure 1. Scanning electron micrographs showing fine grains and smooth surface finish of a typical 1-um thick beryllium film deposited on glass slide by the sputtering process at 600 W rf without substrate bias.

14. R. J. Burt, S. F. Meyer and E. J. Hsieh, "RF Magnetron Sputtering of Thick Film Amorphous Beryllium", J. Vac. Sci. Technol., 17, 407 (1980); E. J. Hsieh, "Advances in Beryllium Coatings", 1980 Laser Program Annual Report, LLNL, Vol. 2, 4-28.
15. R. F. Bunshah, "Evaporation" in Deposition Technologies for Films and Coatings (Noyes Publications, New Jersey; 1982), p. 85.
16. N. Laegreid and G. K. Wehner, "Sputtering Yields of Metals for Ar^+ and Ne^+ Ions with Energies from 50 to 600 eV", J. Appl. Phys., 32, 365 (1961).
17. R. F. Bunshah and R. S. Juntz, "The Purification of Beryllium by Vacuum Melting Followed by Distillation and Simultaneous Deposition to Sheet in an Electron Beam Furnace", Trans. Vac. Metallurgy Conf. (Am. Vac. Soc., New York, 1965), p. 200.
18. W. E. Alston, private communication.