

AD

TECHNICAL REPORT ARCCB-TR-01022

**ORIGINS OF BETA TANTALUM
IN SPUTTERED COATINGS**

C. P. MULLIGAN

NOVEMBER 2001

	<p>US ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER CLOSE COMBAT ARMAMENTS CENTER BENÉT LABORATORIES WATERVLIET, N.Y. 12189-4050</p>	
-------------------------------------------------------------------------------------	--------------------------------------------------------------------------------------------------------------------------------------------------------------------------	---------------------------------------------------------------------------------------

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

20011130 070

DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

The use of trade name(s) and/or manufacturer(s) does not constitute an official endorsement or approval.

DESTRUCTION NOTICE

For classified documents, follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19, or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

For unclassified, limited documents, destroy by any method that will prevent disclosure of contents or reconstruction of the document.

For unclassified, unlimited documents, destroy when the report is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE November 2001	3. REPORT TYPE AND DATES COVERED Final	
4. TITLE AND SUBTITLE ORIGINS OF BETA TANTALUM IN SPUTTERED COATINGS			5. FUNDING NUMBERS AMCMS No. 6226.24.H191.1	
6. AUTHOR(S) C.P. Mulligan				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Benet Laboratories, AMSTA-AR-CCB-O Watervliet, NY 12189-4050			8. PERFORMING ORGANIZATION REPORT NUMBER ARCCB-TR-01022	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Close Combat Armaments Center Picatinny Arsenal, NJ 07806-5000			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The source of beta tantalum formation in sputtered coatings has been a subject of controversy going back over thirty years. For every research paper in which the cause is seemingly identified, there are others, which seem to disprove it. It has been very difficult to find a unifying theory that explains the contradictory results found in these papers. The purpose of this report is to compile the vast amount of information gathered from the literature so that connections can be made between the many parameters involved. Some of the most recent work has attempted to relate the energetics (i.e., atom/ion energy) of the plasma to the alpha →beta transition. It has been shown that the energetics of the plasma can relate to the most crucial sputtering parameters. The most significant feature of the use of plasma energy to explain the alpha →beta transition is that it relates the formation of beta-tantalum to a quantifiable measure.				
14. SUBJECT TERMS Sputtering, Beta-Tantalum, Plasma Energy, Tantalum, Protective Coatings			15. NUMBER OF PAGES 10	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

TABLE OF CONTENTS

	<u>Page</u>
RESEARCH.....	1
Substrate Temperature.....	2
Substrate Crystal Structure.....	2
Impurities	3
Sputtering Rate.....	3
Compressive Stresses	3
Role of Plasma Energy	3
CONCLUSIONS.....	5
REFERENCES.....	8

TABLES

1. Summary of Crucial Parameters and Proposed Effects on Tantalum Phase Formation.....	6
-------------------------------------------------------------------------------------------	---

LIST OF ILLUSTRATIONS

1. Schematic representation of the effect of excessive bombardment on the lattice structure of sputtered coatings.....	1
2. Schematic representation of the effects of ion/target ratios in sputtering	5

RESEARCH

Beta (β) tantalum was discovered in the 1960s through the use of physical vapor deposition, and there were many theories as to its source. Initial studies examined the effects of impurity levels on the formation of the β -phase. Early results indicated that β -tantalum was formed only in *clean* atmospheres and impurities such as nitrogen and oxygen acted to *stabilize* the growth of body-centered cubic (bcc) alpha (α) tantalum (refs 1,2). However, several subsequent studies were conducted indicating the exact opposite. Most notably, Westwood and Livermore (ref 3) postulated that the β -phase was stabilized by impurities. Then Westwood et al. (ref 4) reported a transition from α to β with increasing oxygen content. Taking into account the contradictory results obtained from different systems, the formation of β must not be simply impurity based. There has been ample evidence acquired that shows both the α and β -phases can accommodate impurities (refs 1-11).

β -tantalum exhibits a metastable tetragonal lattice structure. The fact that it is metastable illustrates that the atoms making up the lattice are not in their lowest energy positions. The question of why these atoms are not in their equilibrium positions is what needs to be answered. It has been shown that impurities play a role in the $\alpha \rightarrow \beta$ transition, but impurities are clearly *not* the dominating factor in all systems. In very pure deposited β -tantalum, the only explanation for its formation is the role of plasma energy. Either, the deposited atoms do not have enough energy to overcome the obstacles to reach their lowest energy positions (e.g., settling of atoms in high-energy sites due to surface energy variations), *or* the energy of the atom/ion bombardment acts to knock the tantalum atoms out of their lowest energy positions (e.g., atom implantation and lattice recoil mechanisms). A schematic of atomic implantation is shown in Figure 1.

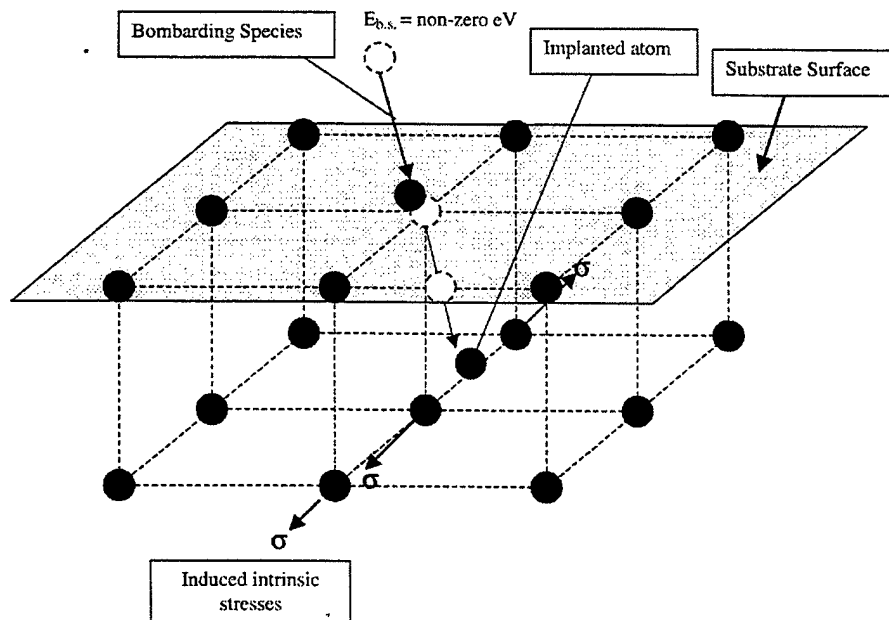


Figure 1. Schematic representation of the effect of excessive bombardment on the lattice structure of sputtered coatings.

Putting aside the specific role of plasma energy for the moment, it should be stated that there are many potential barriers to the surface mobility of the depositing atoms. Many of the contradictory results are most likely based on variations in these barriers from system-to-system. Some of the more important factors to consider include:

- Substrate temperature
- Substrate material
- Impurities
- Sputtering rate
- Role of compressive stresses

Substrate Temperature

An increase in substrate temperature results in an increase in surface mobility, thus, intuitively, it should be understood that increasing temperature would increase the probability of forming the equilibrium phase α -tantalum. Studies have shown that the growth of sputtered β -tantalum is indeed less stable at higher substrate temperatures (ref 12), and temperatures in excess of 600°C ensure the deposition of 100% α -tantalum (ref 13). It should also be noted that when heated to ~750°C, sputtered β -tantalum spontaneously transforms to α -tantalum (ref 1).

The importance of substrate temperature is further exemplified by the fact that the relationship between temperature and diffusion is exponential in nature. According to the Arrhenius equation governing diffusion, relatively small increases in substrate temperature may lead to greatly increased α -tantalum production. A simulation of adatom diffusion versus temperature is illustrated in Reference 14. Here, greatly increased diffusion is apparent over the modest changes in temperature.

Substrate Crystal Structure

Another very important factor to consider is the role of substrate material in sputtering. It has been cited in numerous reports that with all other parameters being equal, α -tantalum is preferentially formed on substrates of similar crystal structure with comparable lattice parameters (refs 13, 15-17). This stands to reason since a depositing atom will need less energy to arrive at its equilibrium position. For instance, niobium, which has a lattice mismatch with tantalum of less than 0.5%, has been successfully used as a sputtered interlayer to produce 100% α -tantalum coatings (refs 13, 15). Kondo et al. (ref 16) have also shown that amorphizing a silicon carbide substrate (taking away any lattice match) or inserting a thin amorphous interlayer greatly stabilized the formation of (002) oriented β -tantalum. Formation of α -tantalum has also been reported on pure α -tantalum substrates under conditions that otherwise formed β -tantalum (ref 17).

Impurities

Impurities on the surface will tend to decrease the mobility of depositing atoms and in the case of oxide layers, may form a lattice mismatch between coating and substrate (ref 18). Experiments performed by Matson et al. (ref 13) showed a loss of α formation if a deposited niobium interlayer was exposed to atmosphere prior to tantalum deposition. It should also be noted that Face and Prober (ref 15) took special care not to contaminate the niobium interlayer used in their study by immediately rotating it (within one second) under the tantalum target after niobium deposition. This illustrates how sensitive the use of an interlayer may be. Even slight contamination may completely nullify the positive effects.

Sputtering Rate

The role of sputtering rate in the formation of β -tantalum has not been as rigorously studied as other factors, and much of the information is conflicting. From the point of view of kinetics, it is intuitive that a lower sputtering rate would allow more time for surface diffusion to take place, but it must be stated that a very low sputtering rate may lead to increased impurity adsorption in the depositing film so this trade-off must be taken into account. It should also be noted that exceedingly high sputtering rates might introduce compressive stresses (ref 19), which will be discussed subsequently.

Compressive Stresses

The fact that considerable intrinsic stresses (1-2 GPa) can be present in thin films has been known for years and the mechanisms that bring about these stresses have been thoroughly studied (ref 19). Known sources of compressive stress in coatings are excessive atom/ion bombardment and high sputtering rate (ref 19). The role of compressive stresses in the formation of β -tantalum has also been among the topics of several studies (refs 20-22). It was found in these studies that β -tantalum preferentially forms under compressive stresses. In addition, it was found that the intrinsic stresses in β -tantalum decreased linearly with heating up to the $\beta \rightarrow \alpha$ transformation temperature of 600°C, but from 600 to 800°C, a rapid stress relaxation of ~40% accompanied the formation of α -tantalum (ref 21). These trends seem to follow the notion that β -tantalum is formed by the implantation of atoms in high-energy sites resulting in an over-dense structure.

Role of Plasma Energy

With the advent of more advanced sputtering systems with more precise controls, studies within the last decade or so have focused on the role of plasma energy in the $\alpha \rightarrow \beta$ phase transition (refs 20-24). The results obtained in these investigations give compelling evidence that the formation of β -tantalum in sputtering systems is primarily due to implantation of tantalum atoms in interstitial and grain boundary sites leading to the development of compressive stresses and the unstable tetragonal crystal structure. This can occur by two mechanisms. First,

excessive high-energy atom/ion bombardment results in direct or recoil implantation of the tantalum atoms into unstable lattice positions. Second, if the total energy supplied to the plasma and growing film is insufficient to overcome barriers on the surface (e.g., lattice mismatch, impurities, surface mobility, etc.), the tantalum atoms cannot arrange themselves in their lowest energy positions (i.e., bcc α -tantalum). These competing mechanisms then leave a *window of total plasma energy* where either excessive or deficient total energy can lead to β formation.

There is substantial evidence in the aforementioned literature that supports these claims. Catania et al. (ref 22) carried out magnetron sputtering of tantalum at a very low pressure of 0.04 Pa (0.3 mT), while varying the negative substrate bias in an attempt to isolate the effects of plasma bombardment. Only α -tantalum was detected in the sputtered coating in the absence of a bias and a rapid transition to β -tantalum was recorded, as the bias was increased (ref 22). The complete transition to β occurred at ~ -100 V. Findings that seem contrary to this have been reported by Matson et al. (ref 13) and Mattox and Kominiak (ref 25), where increasing the substrate bias resulted in increased α formation. This can be explained by the different deposition conditions in these operations. First it must be stated that in a low-pressure magnetron sputtered film there are several sources of bombardment. In the absence of a bias, the depositing target atoms and the reflected neutrals of the sputtering gas control the bombardment. When a bias is added, the bombardment of the sputtering gas ions adds to the total energy. In the work done at IBM by Catania et al. (ref 22), the very low sputtering pressure left the reflected argon neutrals and the depositing tantalum atoms with sufficient energy to promote α , and with the addition of the bias, the upper bound of the energy window was crossed and β was formed. On the contrary, in the other works, the sputtering pressure is higher and the energy of the depositing atoms and neutrals is attenuated by increased collisions within the plasma, leaving the plasma energy below the lower bound of the energy window. Increasing the bias in these cases makes up for the loss in energy of the plasma and also acts as a healing mechanism by preferentially resputtering the unstable atoms (ref 25).

Further evidence of the presence of this energy window is shown in supplementary work done by Catania et al. (ref 22) and Roy et al. (ref 23), as well as by Ino et al. (ref 24). In the latter, it was shown that heavier gases require more energy input to promote α . The reason for this is that heavier sputtering gases such as xenon and krypton more effectively dissipate energy from depositing tantalum atoms and reflected neutrals during collisions. This phenomenon was observed by Matson et al. (ref 26). In sputtering with xenon, it was noted that a greater bias was needed to produce α -tantalum. A schematic illustrating this phenomenon is given in Figure 2.

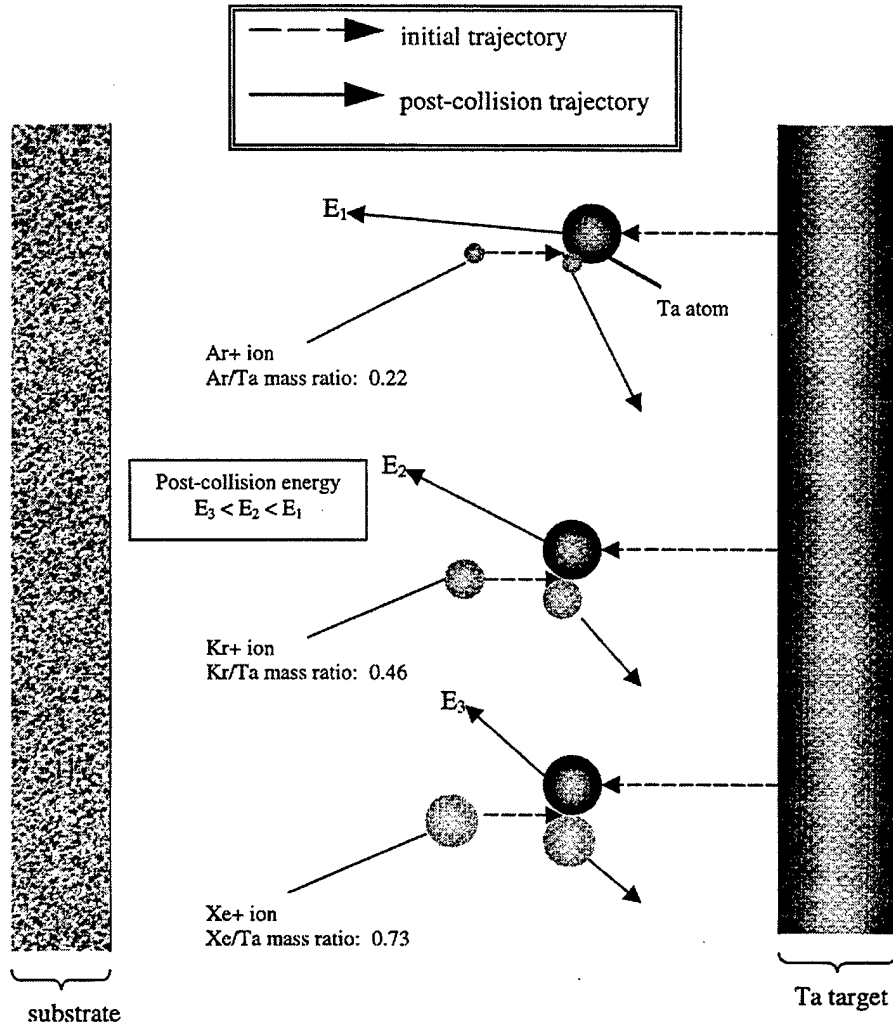


Figure 2. Schematic representation of the effects of ion/target mass ratios in sputtering.

CONCLUSIONS

Although the mechanisms of β -tantalum formation are fairly well understood at this point in time, an atomistic model quantifying the $\beta \rightarrow \alpha$ transition in sputtering is, to the author's knowledge, currently unavailable. In the work done by Roy et al. (ref 23), the total energy of the plasma was estimated by calculations of the momentum of each bombarding species and subsequently summing the values to obtain the total momentum input per depositing atom. Several different sputtering systems were compared using the same semi-empirical method. The results are listed in total momentum input per tantalum atom, and a regime of ~ 70 to 100 $(\text{amu} \cdot \text{eV})^{1/2}$ per tantalum atom was calculated to promote α -tantalum. Roy et al. (ref 23) go on to state, "This level of energetic bombardment is not generally seen in high pressure (>15 mT) sputtering, where the energy of sputtered atoms and reflected neutrals is attenuated by collisions with background gas, helping to explain why pure bcc phase is difficult to synthesize in the latter [high pressure sputtering]."

While this approach to determine the total momentum needed to promote α -tantalum may be sufficient for the specific geometries and system properties dealt with in this research, it does not take into account crucial parameters that would undeniably affect the total energy requirement (shifting the energy window or making it wider/narrower). Substrate temperature, impurity level, lattice parameter ratio, and sputtering rate are just a few of the variables that may alter the total energy needed to deposit α -tantalum. In addition, target-to-substrate distance and sputtering voltage are parameters that directly control total atomic energy based on collision frequency and average energy and must also be taken into account. Table 1 gives a summary of the crucial parameters and their proposed effects on tantalum phase formation. Since each of these parameters may summarily increase or decrease the total plasma energy window needed to form α -tantalum, it may explain the often-contradictory results obtained in outwardly similar studies.

Table 1. Summary of Crucial Parameters and Proposed Effects on Tantalum Phase Formation

Parameter	Relation to Plasma Energy	Relation to β formation
1. Substrate Temperature	Increasing T decreases the total plasma energy required to deposit α -Ta	Increasing T decreases β -Ta formation
2. Substrate Material	Increasing lattice mismatch increases total plasma energy required to deposit α -Ta	Increasing lattice mismatch increases β -Ta Formation
3. Impurity Level	Surface impurities tend to increase total plasma energy required to deposit α -Ta	While surface impurities have been shown to promote β -Ta formation, work with reactively sputtered Ta has shown that interstitial impurities may stabilize the α -Ta phase
4. Sputtering Rate	---	No conclusive studies available but results observed at Benet indicate β -Ta may preferentially form with high sputtering rates
5. Sputtering Gas	Increasing atomic weight decreases total plasma energy in system	Dependent on plasma energy
6. Compressive Stress	Excessive plasma energies tend to promote compressive stresses	Compressive stresses are favorable towards β -Ta
7. Target/Substrate Gap	Increasing gap distance decreases total plasma energy in system	Dependent on plasma energy
8. Sputtering Voltage	The sputtering voltage dictates the <i>maximum</i> (i.e., release energy) and average energies of each bombarding species (ref 27)	Directly related to plasma energy
9. Sputtering Pressure	The sputtering pressure dictates the average arrival energy of each bombarding species	Directly related to plasma energy
10. Plasma Energy	---	At both deficient and excessive plasma energy levels, β -Ta may form

Considering the importance of sputtered tantalum in the electronics industry and possibly as a protective coating material in gun tubes, it would be of great benefit for Benet Laboratories to focus part of the modeling effort on an atomistic model quantifying the $\beta \rightarrow \alpha$ transition. Ideally, the model would include the effects of all the aforementioned sputtering parameters. The inclusion of these parameters would ensure a robust model that would be scalable to other dissimilar systems. If this approach is not a feasible option, at the very least, a semi-empirical formula similar to Roy et al. (ref 23) should be further developed to increase control of the sputtering systems here at Benet.

REFERENCES

1. Read, M.H., and Altman, C., *Applied Physics Letters*, Vol. 7, 1965, p. 51.
2. Nakamura, M., Fujimori, M., and Nishimura, Y., *Japanese Journal of Applied Physics*, Vol. 9, 1969, p. 557.
3. Westwood, W.D., and Livermore, F.C., *Thin Solid Films*, Vol. 5, 1970, p. 407.
4. Westwood, W.D., Willmott, D.J., and Wilcox, P.S., *Journal of Vacuum Science and Technology*, Vol. 9, 1972, p. 444.
5. Moseley, P.T., and Seabrook, C.J., *Acta Crystallographica*, Vol. B29, 1973, p. 1170.
6. Gerstenberg, D., and Calbick, C.J., *Journal of Applied Physics*, Vol. 35, 1964, p. 402.
7. Krikorian, E., and Sneed, R.J., *Journal of Applied Physics*, Vol. 37, 1966, p. 3674.
8. Huttermann, R.D., Morabito, J.M., Steidel, C.A., and Gerstenberg, D., *Proceedings of 6th International Vacuum Congress 1974, Japanese Journal of Applied Physics*, Supplement 2, Part 1, 1974, p. 513.
9. Rottersman, M.H., and Bill, M.J., *Thin Solid Films*, Vol. 61, 1979, p. 281.
10. Sato, S., *Thin Solid Films*, Vol. 86, 1981, p. 21.
11. Sato, S., *Thin Solid Films*, Vol. 94, 1982, p. 321.
12. Hieber K., and Mayer, N.M., *Thin Solid Films*, Vol. 90, 1982, p. 43.
13. D.W. Matson, Merz, M.D., and McClanahan, E.D., *Journal of Vacuum Science and Technology A*, Vol. 10, 1992, p. 1791.
14. Müller, K.H., *Journal of Applied Physics*, Vol. 58, 1985, p. 2573.
15. Face, D.W., and Prober, D.E., *Journal of Vacuum Science and Technology A*, Vol. 5, 1987, p. 3408.
16. Kondo K., et al., *Journal of Vacuum Science and Technology A*, Vol. 11, 1993, p. 3067.
17. Baker, P.N., *Thin Solid Films*, Vol. 14, 1972, p. 3.
18. Thornton, J.A., *Journal of Vacuum Science and Technology A*, Vol. 4, 1986, p. 3059.
19. Hoffman, D.W., *Journal of Vacuum Science and Technology A*, Vol. 12, 1994, p. 953.

20. Window, B., Sharples, F., and Savvides, N., *Journal of Vacuum Science and Technology A*, Vol. 6, 1988, p. 2333.
21. Clevenger, L.A., Mutscheller, A., Harper, J.M.E., Cabral, C., Jr., and Barmak, K., *Journal of Applied Physics*, Vol. 72, 1992, p. 4918.
22. Catania, P., Roy, R.A., and Cuomo, J.J., *Journal of Applied Physics*, Vol. 74, 1993, p. 1008.
23. Roy, R.A., Catania, P., Saenger, K.L., Cuomo, J.J., and Lossy, R.L., *Journal of Vacuum Science and Technology B*, Vol. 11, 1993, p. 1921.
24. Ino, K., Shinohara, T., Ushiki, T., and Ohmi, T., *Journal of Vacuum Science and Technology A*, Vol. 15, 1997, p. 2627.
25. Mattox, D.M., and Kominiak, G.J., *Journal of Vacuum Science and Technology*, Vol. 9 1971, p. 528.
26. Matson, D.W., McClanahan, E.D., Lee, S.L., and Windover, Donald,, *Proceedings of the International Conference on Metallurgical Thin Films*, San Diego, CA, April 2001, to be published.
27. Schuetze, H.G., Ehlbeck, H.W., and Doerbeck, G.G., *Transactions of 10th National Vacuum Symposium 1963*, MacMillan Co., NY, 1964, p. 434.

TECHNICAL REPORT INTERNAL DISTRIBUTION LIST

	<u>NO. OF COPIES</u>
TECHNICAL LIBRARY ATTN: AMSTA-AR-CCB-O	5
TECHNICAL PUBLICATIONS & EDITING SECTION ATTN: AMSTA-AR-CCB-O	3
OPERATIONS DIRECTORATE ATTN: SIOVV-ODP-P	1
DIRECTOR, PROCUREMENT & CONTRACTING DIRECTORATE ATTN: SIOVV-PP	1
DIRECTOR, PRODUCT ASSURANCE & TEST DIRECTORATE ATTN: SIOVV-QA	1

NOTE: PLEASE NOTIFY DIRECTOR, BENÉT LABORATORIES, ATTN: AMSTA-AR-CCB-O OF ADDRESS CHANGES.

TECHNICAL REPORT EXTERNAL DISTRIBUTION LIST

	<u>NO. OF COPIES</u>		<u>NO. OF COPIES</u>
DEFENSE TECHNICAL INFO CENTER ATTN: DTIC-OCA (ACQUISITIONS) 8725 JOHN J. KINGMAN ROAD STE 0944 FT. BELVOIR, VA 22060-6218	2	COMMANDER ROCK ISLAND ARSENAL ATTN: SIORI-SEM-L ROCK ISLAND, IL 61299-5001	1
COMMANDER U.S. ARMY ARDEC ATTN: AMSTA-AR-WEE, BLDG. 3022 AMSTA-AR-AET-O, BLDG. 183 AMSTA-AR-FSA, BLDG. 61 AMSTA-AR-FSX AMSTA-AR-FSA-M, BLDG. 61 SO AMSTA-AR-WEL-TL, BLDG. 59 PICATINNY ARSENAL, NJ 07806-5000	1 1 1 1 1 2	COMMANDER U.S. ARMY TANK-AUTMV R&D COMMAND ATTN: AMSTA-DDL (TECH LIBRARY) WARREN, MI 48397-5000 COMMANDER U.S. MILITARY ACADEMY ATTN: DEPT OF CIVIL & MECH ENGR WEST POINT, NY 10966-1792	1
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-DD-T, BLDG. 305 ABERDEEN PROVING GROUND, MD 21005-5066	1	U.S. ARMY AVIATION AND MISSILE COM REDSTONE SCIENTIFIC INFO CENTER ATTN: AMSAM-RD-OB-R (DOCUMENTS) REDSTONE ARSENAL, AL 35898-5000	2
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-WM-MB (DR. B. BURNS) ABERDEEN PROVING GROUND, MD 21005-5066	1	COMMANDER U.S. ARMY FOREIGN SCI & TECH CENTER ATTN: DRXST-SD 220 7TH STREET, N.E. CHARLOTTESVILLE, VA 22901	1
COMMANDER U.S. ARMY RESEARCH OFFICE ATTN: TECHNICAL LIBRARIAN P.O. BOX 12211 4300 S. MIAMI BOULEVARD RESEARCH TRIANGLE PARK, NC 27709-2211	1		

NOTE: PLEASE NOTIFY COMMANDER, ARMAMENT RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER,
BENÉT LABORATORIES, CCAC, U.S. ARMY TANK-AUTOMOTIVE AND ARMAMENTS COMMAND,
AMSTA-AR-CCB-O, WATERVLIET, NY 12189-4050 OF ADDRESS CHANGES.
