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TOPICAL REPORT
SUBLIMED EMITTER AND COLLECTOR
COATINGS

D. Ernst

R. Meyers

V. Poirier

June 1970

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Thermo Electron Corporation
85 First Avenue
Waltham, Massachusetts 02154

Prepared for
U. S. Atomic Energy Commission
Space Nuclear Systems Division
Contract No. AT(30-1)-4125
Lester K. Price, AEC Project Manager

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I. SUMMARY

In the past few years, Thermo Electron has investigated emitter and collector surfaces formed by sublimed coatings on refractory metal substrates. Considerable effort has been made to characterize these surfaces in terms of crystal structure, uniformity, stability and diode performance. To prepare the sublimed coatings, heat is applied to an "evaporator" made of the coating material, and the flux of atoms from the hot evaporator condenses onto the relatively cool emitter or collector substrate.

Our initial work in this area involved the coating of planar tungsten (W) emitters with additional layers of W, the deposition taking place in such a way that the surface of the added layer was a better cesiated emitter than the original substrate.¹ It was found that the vacuum work function of polycrystalline W (4.5 to 4.6 eV) could be increased to the level of single-crystal (110) W (5.1 to 5.2 eV). Our studies have indicated that under certain depositing conditions, the bounding planes on the new surface are predominantly (110), no matter what the orientation of the underlying substrate is; evidence suggests that it is this phenomenon that results in the improvement in work function. One such coated W emitter has been tested in a cesiated diode; its performance is presented in Section 2.5.

Related work has also been done with niobium collectors, coating them with sublimed deposits of molybdenum (Mo), nickel (Ni), niobium (Nb) and tungsten (W). Thermal cycling, metallography, X-ray diffraction, and surface contour studies have all been used to characterize these collector coatings. Actual diode performance studies are

now under way. The coated collectors have been prepared at much lower substrate temperatures than the coated emitters and would probably not be as stable to very severe annealing, but it is anticipated that they will be stable in the temperature range normally encountered by a collector.

Both the emitter and collector coating investigations indicate promising methods of achieving improved thermionic performance. Use of the coatings allows the electrode surface characteristics to be selected primarily from thermionic considerations. Selection of the substrate materials can be based on strength or other structural properties to meet the requirements of the particular diode application.

II. COATED EMITTERS

A. INTRODUCTION

The first emitters that were coated at Thermo Electron were discs of (110) "single-crystal" W. The coating experiments were an outgrowth of a new abrading-and-annealing technique which had been devised to optimize the electron emission of slightly misoriented (110) single crystals.^{2, 3} When the specially-abraded surfaces were simply annealed, they developed terraces of what were assumed to be exact (110) planes covering a significant fraction of the emitting area. It was soon found that an even greater portion of the emitting surface could be covered with the presumed (110) planes if the discs were coated with a completely new layer of W.

Practically speaking, there was little to be gained by coating (110) single crystals (aside from increased uniformity) unless they were misoriented enough that the terracing on the new surface resulted in a net improvement in the emission characteristics. There was much greater significance in the discovery that polycrystalline W emitters could also be coated so that the bounding planes on the new surface were all (110), even though the ones on the original surface were not. Coatings of this kind were successfully produced on randomly-oriented arc-cast W, and on (110) oriented and (100) oriented W "chemically vapor deposited" from the chloride and fluoride, respectively. Up until now, Thermo Electron has done emitter-coating work only on planar substrates. We are currently in the process of setting up apparatus for coating the outer surfaces of cylindrical ones.

B. SINGLE-CRYSTAL (110) TUNGSTEN SUBSTRATES

The abrading and annealing technique referred to above will be discussed here briefly, because the special type of abrasion and the theories about the terrace formation were both important to our later coating experiments.

1. Abrading, Annealing and Faceting

Single-crystal (110) emitters were ground with SiC to a 600 grit finish, and then "lapped" on a glass plate wet with an aqueous slurry of 5 μ alumina. The resulting W surfaces had a matte gray finish with no shine at all and were highly disordered to a depth of about 0.1 mil, as evidenced by Laue photography. A subsequent annealing for about 15 minutes at 2500°C, for example, helped to relieve the mechanical damage and allowed at least partial recrystallization onto the underlying single crystal. The resulting surfaces were not completely smooth; they displayed features which consisted of flat plateaus with curved boundaries, a few microns in diameter, and separated from one another by undulating hills and valleys, the overall appearance being rather worm-like (Figure 1). Longer heat treatments, such as 85 hours at 2130°C, produced a rippled pattern of overlapping waves (Figure 2).

The (110) emitters used in these experiments were all cut from a 1" diameter rod obtained from the Linde Division of the Union Carbide Corporation. The rod was nominally "single crystal", but in fact had at least four grains running along its length. The emitters were cut perpendicular to the axis of the rod and Laue photography showed that each of the four grains was within 4° of having its (110) planes parallel to the flat surfaces of the emitter discs. When these

Figure 1 (565x)

(110) Emitter W14D.
Lapped and annealed
(15 minutes at 2500°C).

Figure 2 (565x)

(110) Emitter W22A.
Lapped and annealed
(85 hours at 2130°C).

slightly misoriented emitters were abraded and annealed, the features which formed within the bounds of any one of the four grains were all oriented the same way, but were slightly tilted with respect to the features in the other grains. This effect can be seen in Figure 2, where a grain boundary separates two areas of different orientation.

The flat plateaus were thought to be exact (110) planes formed by a phenomenon known as "faceting."⁴ According to the theories of facet formation, a surface which has an orientation close to one of low surface energy may rearrange itself into a new surface, grossly parallel to the old surface but consisting of large "facets" of the low-energy plane connected by enough small facets of a higher-energy plane to maintain the gross orientation.³ In body-centered cubic materials such as W, the (110) planes have the highest atom density and the lowest surface energy, and would therefore be the ones most likely to form the bounding planes of a surface in the process of such a rearrangement.

2. Coating

Some of the emitters which were abraded as above (alumina-on-glass) were coated with an added layer of W by placing them underneath polycrystalline W covers which in turn were heated by electron bombardment from a W filament. The original intention was simply to restrict any evaporation from the emitter surface and to see what effect this might have on the nature of the surface features. The actual result, however, was evaporation from the cover and condensation onto the relatively cool emitter. In these early experiments, the covers or "evaporators" were always considerably hotter near the center than around the edge, so the coatings were always much thicker

near the center. Close to the edges of the coated emitters and in a few "background" areas near the center, the surfaces looked much like the annealed but uncoated emitters described above. (Note the background waves in Figure 3 and compare to Figure 2.) Generally, however, the parallel plateaus were larger in size and were bounded by straight lines rather than curves, being hexagonal or diamond-shaped for the most part. In places they looked like overlapping terraces or shingles (Figure 4), very nearly parallel to the overall plane of the specimen surface. As before, the surfaces of the individual terraces were tilted differently from one underlying grain to another, and it was assumed that they were exact (110) planes and that the new coating W was growing with the same bulk orientation as the substrate, the overall plane of the specimen continuing to be slightly "misoriented" with respect to the (110) direction.

In the course of this work it was soon discovered that the mechanical condition of the emitter substrate prior to coating had a profound effect on the nature of the deposited layer. It was noticed that facets or terraces formed more readily along scratches than elsewhere. Further experiments showed that terracing was also more likely to occur if the emitters were sandblasted rather than "lapped" in the usual manner (with alumina on glass). On the other hand, it was also found that if the emitter surface was electropolished, no faceting occurred at all under similar depositing conditions. In the case of the polished pre-surface, the deposited layer was of equal thickness everywhere; therefore, the new surface looked almost exactly like the underlying one. But in the case of the lapped and sandblasted pre-surfaces, the deposits were more or less faceted, were not equally thick everywhere, and looked quite different from underlying abraded surfaces.

These differences seemed to be due to the fact that abrasion or sand-blasting produced a disturbed surface layer, which stored mechanical energy available for atom rearrangement at high temperature. In contrast, the electropolished surfaces were stress-free and had no such stored energy.

The other two major parameters affecting the nature of the deposit layers were found to be the time and temperature of the coating runs. The coatings were made at evaporator temperatures of about 2500 to 3100°C and at substrate temperatures of about 2100 to 2700°C, for durations of 1 to 6 hours. (In a couple of instances, the center of the top side of the W evaporator actually melted, but the underside of the evaporator from which the vapor coating originated was considerably less than the 3400°C melting point). Generally speaking, the features on the surfaces of the coatings were largely "curvilinear" if the evaporator temperature was in the lower half of the range and the lengths of the runs were only an hour or two; features were more "rectilinear" in appearance when the runs were hotter or longer. This meant that the coatings had to be relatively thick (approximately .001 inch) before much faceting occurred. Average thicknesses were calculated by weighing the emitters before and after coating.

An excellent illustration of the above parameters is given by emitter W 18. One face of this emitter was finely ground to a 600 grit SiC finish and "lapped" with 5 μ alumina on glass, and half of this face was sandblasted. The emitter was then given three successive coatings of W; the changes in the appearance of the emitter surface were recorded after each coating run. The coating conditions and the nature of the resulting deposits are tabulated in Figure 5. The changes

Figure 3 (150x)

(110) Emitter W21E.
Lapped and W-coated.

Figure 4 (565x)

(110) Emitter W16D.
Lapped and W-coated.

Run Designation	Bombardment Power	Temperature of Evaporator	Duration of Run	Cumulative Coating Thickness	Average Facet Size	Predominant Facet Shape
W 18 E → F	3.84 KW	~ 2750°C	1 hour	4μ	10μ	Circle
W 18 F → G	6.00 KW	> 3000°C	$\frac{1}{2}$ hour	25μ	30μ	Hexagon
W 18 G → H	6.00 KW	> 3000°C	2 $\frac{1}{2}$ hours	75μ	50μ	Diamond

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Figure 5
W Coatings on a Single-Crystal (110) W Emitter

in the appearance of one particular area are illustrated in Figures 6a, b and c. In this series of coating runs, no large rectilinear features were formed on the lapped half of the emitter (to the right in Figure 6). On the sandblasted half, terraces began to form during the first coating run but they were small and distinctly curvilinear. After the second run, the terraces had grown and had taken on a more or less hexagonal appearance, and after the third run they were largely diamond-shaped. (This "circle-hexagon-diamond" sequence was observed repeatedly in our studies of terrace formation).

C. POLYCRYSTALLINE TUNGSTEN AND RHENIUM SUBSTRATES

The production of (110) bounding planes on polycrystalline W emitters seemed feasible, since faceting was routinely observed on the polycrystalline W filaments used to heat the evaporators in the above-described single-crystal experiments. Indeed, we were soon able to do this successfully on both arc-cast and CVD ("chemically vapor deposited") W emitters.

1. Vacuum Arc-Cast Tungsten

The appearance of the coated polycrystalline material was significantly different from that of the coated single crystals. More precisely, the features on the latter had all been parallel to the plane of the emitter surface, or very nearly so; however, on the coated polycrystals, many of the "facets" were tilted with respect to the emitter surface by much greater amounts. As always, within the bounds of any one grain the features all looked the same, but the shifts in orientation across grain boundaries were dramatic. This

is illustrated in Figures 7, 8, 9 and 10, which are low-power photographs of sandblasted and coated polycrystals; the first two photographs are of CVD fluoride W and the second two are of a much larger grained arc-cast W. The patches that can be seen covering the emitter surfaces correspond to the grains in the underlying substrates, and within each patch are many facets of similar orientation. Careful examination of Figure 10 reveals the textured appearance of each patch of facets, but the facets themselves can only be resolved by higher power photographs such as Figures 11, 12, and 13.

In general, the surface features on the arc-cast emitter could be described as overlapping terraces. Some of them are very nearly parallel to the surface plane (top right of Figure 11), but others are tilted to varying degrees (bottom of Figure 11). There are also some "pod-like" features (top left of Figure 11) completely unlike anything previously observed on the coated single crystals. When the focus of the microscope was altered slightly, these "pods" were seen to be optical effects between the square bases of adjacent four-sided pyramids (see Figures 13a and b). Some of the features appeared as though they could actually be described as terraces tilted so severely that one corner of each terrace had become the peak of a pyramid (see Figure 12).

2. Chemically Vapor-Deposited Tungsten

When CVD W was ground, sandblasted and coated under similar conditions, the resulting surfaces were somewhat different than when arc-cast W was used: There were more pyramids and fewer parallel

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Figure 6a (150x)

(110) Emitter W18F.
Coated with 4μ W.

Figure 6b (150x)

(110) Emitter W18G.
Coated with 25μ W.

Figure 6c (150x)

(110) Emitter W18H.
Coated with 75μ W.

Figure 7 (4x)

Emitter WF10B.
Sandblasted and
W-coated.

Figure 8 (10x)

Emitter WF10B.
Sandblasted and
W-coated.

Figure 9 (4x)

Emitter WP104B,
Sandblasted and
W-coated.

Figure 10 (10x)

Emitter WP104B,
Sandblasted and
W-coated.

Figure 11 (565x)

Emitter WP104B.
Sandblasted and
W-coated.

Figure 12 (565x)

Emitter WP104B.
Sandblasted and
W-coated.

Figure 13a (565x)

Emitter WP104B.
Sandblasted and
W-coated.
Lower (deep)
focus.

Figure 13b (565x)

Emitter WP104B.
Sandblasted and
W-coated.
Upper (shallow)
focus.

terraces on (100) oriented fluoride W, and there were more parallel terraces and fewer pyramids on (110) chloride W. These facts support the assumptions that the terraces grow parallel to the surface only on (110) grains, and that the upright pyramids are produced only on (100) grains.

There is additional support for the above scheme in crystal theory. In the body-centered cubic lattice of W, a square-based pyramid can be outlined by four triangular (110) planes which meet at a point and which intersect a square (100) plane at angles of 45° . Surface contour studies ("reflectograms") have confirmed this 45° angle on our coated fluoride W emitters; these studies will be described in Section 2. 4.

Fluoride W was investigated more thoroughly than chloride W because of its more stable grain structure and because there was more to be gained in terms of improved emission characteristics. In addition to the ground and sandblasted pre-surfaces described above, coatings were also made on a ground and electroetched surface and on several as-deposited surfaces.

As-deposited fluoride W is already covered almost entirely by pyramids, bounded by (111) planes,^{5, 6} so it was not surprising that when this type of surface was coated with more W the new surface features were still virtually all pyramids. It was not clear whether the pyramids were bound by (110) planes after coating or not. The ground and electroetched presurface displayed only partially-formed, curvilinear facets, but it was not determined whether a thicker coating would have produced better faceting or not.

The as-deposited and the etched surfaces were rough but they were presumably stress-free, unlike the highly-disturbed sandblasted ones. Therefore, if further studies were to show that facets could indeed form as readily on the former two surfaces as on the latter one, our theory that stored energy in a highly disturbed surface is necessary for facet formation would be questionable.

3. Rhenium

Theoretically it should be possible to improve the emission characteristics of thermionic emitter materials other than W. Generally speaking, other materials such as rhenium should behave in a similar way. It should be possible to coat a randomly-oriented Re substrate with more Re, in such a way that the bounding planes of the new surface would be composed of the crystal planes of lowest surface energy and highest atom density. These planes should in turn give the highest bare work function and the best cesiated diode performance. In the case of Re, this would presumably be the (0001) basal plane.

To date, only three experimental coating runs have been made using Re. No improvements in bare work function have been achieved; however, proper depositing conditions may not have been found yet. Randomly-oriented Re polycrystals were sandblasted and coated with more Re, using roughly the same evaporation rates as those used in our W work. One of them was coated with more than .010 inch of Re, using estimated temperatures of 3000°C on the evaporator and 2600°C on the substrate and requiring a power input of 5.4 kw over a period of 4 hours (compare with Figure 5). This was the thickest of the three Re coatings, and gave the best bare work function, but the

actual value was a disappointing 4.98 eV. The surface appearance of the .010 inch Re coating was very much like that of much thinner W coatings; the features were largely curvilinear but had a distinct tendency to be hexagonal. More work with Re is necessary to determine whether or not improved emission characteristics may be achieved.

D. CHARACTERIZATION

1. Photomicrographs

One of the most useful tools for characterizing metal surfaces is, of course, the microscope. Photomicrographs, taken quite frequently during the course of this work, supplied a permanent record of the appearance of the different coated surfaces. Typical emitter photographs are included in this report and have been referred to previously.

A coated fluoride W emitter (WF₆) was cut in half and prepared metallographically for examination of the coating in cross section. Figures 14 and 15 were taken after polishing with a 6 μ diamond abrasive. While some porosity is evident, the integrity of the coating-to-substrate interface is believed to be sound. No separation of the emitter coatings has ever been observed. Figures 16 and 17 were taken after etching with caustic ferricyanide; in some places it looks as though the grains in the coating are merged completely with the grains on the substrate, while in other places there is a clear demarcation between the coating and the substrate.

2. X-Ray Diffraction

The orientations of the various polycrystalline substrates were determined exactly by x-ray diffraction "pole figures"; the orientations

Figure 14 (150x)

Emitter WF1F.
Sandblasted and
W-coated.
Cross section
polished.

Figure 15 (300x)

Emitter WF1F.
Sandblasted and
W-coated.
Cross section
polished.

Figure 16 (150x)

Emitter WF1F.
Sandblasted and
W-coated.
Cross section
etched.

Figure 17 (300x)

Emitter WF1F.
Sandblasted and
W-coated.
Cross section
etched.

of a few of the sublimed coatings were also checked. It was almost definitely established that the coatings were oriented the same way as the underlying substrates; however, after coating, the grain sizes were generally too large for the sampling mechanism of the available x-ray equipment, and good "pole figures" could not be made.

3. Reflectograms

An "optical goniometer"⁵ was used to study the contours or bounding surfaces of the coated emitters and collectors. This instrument consists of a beam of light from a high pressure mercury arc, a rotating sample holder, and a photocell detector. The beam is impinged onto the rotating sample and is reflected back towards the photocell, which is fixed just above the lamp and at a very small angle to the incident beam. The sample is rotated, with respect to the beam, over a range of $\pm 70^\circ$ from the normal. The reflections from the sample within this range can be traced on a recorder, producing a "reflectogram." A shiny metal surface, for example, will give a completely flat background trace except for one strong specular peak at 0° .

In the case of as-deposited (100) oriented fluoride W, the specular peak is quite weak and there are auxiliary peaks at $\pm 55^\circ$. Since this is the angle which (100) planes make with (111) planes in the body-centered cubic lattice, such a reflectogram supports the assumption that the pyramids on the surface of as-deposited fluoride W are in fact bounded by (111) planes.^{5,6} After grinding, sandblasting and coating with more W, the surface again gives a weak specular peak, but this time the auxiliary peaks are at $\pm 45^\circ$, supporting the theory that the new surface has pyramids bounded by (110) planes.

None of the other coated W emitters gave readily-interpretable reflectograms. The only generalization that could be made about them is that they gave stronger specular peaks than the coated fluoride substrates. This fits well with the microscopic evidence that the coated fluoride showed fewer parallel terraces than any of the others.

4. Vacuum Work Function

Vacuum work function (ϕ) measurements were made to further study the emitter coatings. Van Someren has already described the field-enhancement problems associated with the rough, angular coated surfaces, and has compared some of the results with our ϕ values for other types of W substrates.⁷ To briefly summarize, the ϕ of (100) oriented fluoride W was increased by 0.65 eV (from 4.51 to 5.16), and the ϕ of (110) oriented chloride W was increased by 0.13 eV (from 5.03 to 5.16).

A more complete presentation of our ϕ data on coated emitters is given in Figures 18 and 19. All of the substrates included had been ground flat and sandblasted prior to deposition. The graph (Figure 19) suggests a slight trend: the higher the evaporation rate during the coating process, the higher the resulting work function. (In the course of this work, it was found to be extremely difficult to get reliable temperature measurements: evaporation or coating rates calculated from the amount of weight gained by the emitter substrates are expressed as the weight gained per unit of substrate area per unit of time).

It can be seen from the table (Figure 18) that an evaporation or coating rate of about 150 mg/cm²/hour resulted in a ϕ that was significantly

Sample Designation	Substrate Type	Substrate Source	Coating Rate (mg/cm ² /hour)	Vacuum Work Function (eV)
WF6a-10B WF6a-10D WF6a-20B	Fluoride W	Gulf General Atomic (via NASA-Lewis Research Center)	62 260 155	4.74 5.16 5.16
WF1D WF2D WF3D WF3F WF11N	Fluoride W	San Fernando Laboratories	87 80 44 188 105	5.01 4.80 4.86 5.11 4.91
WC0D	Chloride W	San Fernando Laboratories	113	5.16
W15M W28B	(110) Single Crystal W	Linde Division of Union Carbide Corporation	79 72	5.06 4.97
Re64B Re64D Re65B	Sheet Re	Cleveland Refractories	145 158 158	4.88 4.98 4.94

Figure 18
Vacuum Work Function Data

Figure 19. Vacuum Work Function ϕ versus Coating Rate
(on Fluoride W Emitters).

less for Re than for W. Re may simply require a higher evaporation rate to achieve the same degree of atom rearrangement on the surface.

5. Thermal Stability

In the course of taking bare work function data, many of the coated emitters had been routinely exposed to temperatures more severe than those typical of a converter: emitter WP104B was exposed to about 50 hours at 1875°C, emitter WF6a-10D to 2 hours at 2075°C, and emitter Re65B to 16 hours at 2125°C. None of the three showed any change other than slight rounding of the sharp edges.

One side of (110) emitter W18 had been coated and had shown partially formed facets on the sandblasted portions (coating run D→E). The other side of this emitter had then been coated as itemized previously (Figure 5), and in the process the features on the first side were given a pretty severe annealing (estimated to be 1 hour at 2275°C and 3 hours at 2600°C). Figures 20a and 20b show the exact same area before and after: it can be seen that some rounding occurred. Again, this was at a much higher temperature than would be encountered in a diode.

E. DIODE PERFORMANCE

A fixed-spacing planar diode was fabricated and tested to evaluate the thermionic performance of a coated W emitter. This emitter (WF10B) had been ground, sandblasted and then coated with 875 mg of new W. The actual parameters used in the coating operation were 1-1/2 hours at about 6.5 kw. The average coating thickness was .006 inch, with a variance of ±.001 inch. (Variances in thickness and flatness are a result of nonuniform temperature distribution on the evaporator.)

The overall appearance of the coated surface is shown in Figures 7 and 8, and the detail of the surface structure was similar to that shown in Figures 11, 12 and 13.

The diode design is shown in Figure 21. It required a Mo(50) Re emitter heat choke welded directly to the emitter substrate. Initial trial welds of this type resulted in contamination of the emitter surfaces by spray from the welding. Welding parameters were modified to eliminate this effect. The collector assembly consisted of a niobium collector, a .020 inch thick niobium-alumina cermet insulator and an outer collector guard ring. This assembly was fabricated using pressure bonding techniques, which resulted in a completely bonded structure. The surface of the collector was mechanically polished to lower its emissivity. The interelectrode spacing was set at .010 inch hot. The actual collector area was 1.26 cm^2 . To compensate for possible current pickup from the emitter area over the cermet insulator, half of the insulator thickness was assigned to the collector area and half to the guard ring area. Accordingly, the effective area of the collector was taken as 1.36 cm^2 to calibrate the test data.

Emitter temperatures were obtained optically by observation into a black-body cavity. Collector and cesium reservoir temperatures were monitored with chromel-alumel thermocouples. Voltage taps were located at the emitter and the collector to eliminate voltage losses through the lead structures. Initial diode testing was performed to assure the absence of oxygen from the diode. Collector optimizations were performed at the expected testing temperatures. Figures 22, 23 and 24 illustrate the cesium family performance data at 1700°K , 1800°K , and 1900°K . Electrode power densities were computed from

Figure 20a (300x)

(110) Emitter W18E.
Sandblasted and
W-coated.

Figure 20b (300x)

(110) Emitter W18E.
Sandblasted and
W-coated. Annealed
1 hour 2275°C and
3 hours 2600°C.

Figure 21. Schematic of Planar Thermionic Diode.

Figure 22. Coated Emitter Performance Data (1700°K).

Figure 23. Coated Emitter Performance Data (1800°K).

Figure 24. Coated Emitter Performance Data (1900°K).

the I-V curves at each emitter temperature and are presented in Figure 25 for current densities of 4, 6, 8, and 10 amps/cm². Within the accuracy of the test parameters, the performance is believed to be at least as good as that of nominal single-crystal W. Since the observed cesium reservoir temperatures for the coated emitter were slightly lower than those required for single-crystal W diodes, it is believed that the coated emitter surface may actually be superior to the single-crystal surface. After the initial evaluation of the diode, all the data obtained were rechecked to determine whether degradation had occurred. The data were very repeatable; it was concluded that the diode performance was stable throughout the testing period.

At the completion of the diode testing, the diode was removed from its test station and dismantled for examination of the emitter surface. Figure 26 illustrates the condition of the coated surface after diode operation. Minor changes in the surface structure were evident: the features had become slightly rounded, surface pitting of the pyramids and terraces had occurred, and the pyramid-shaped features had become somewhat truncated. As indicated in the previous section, several coated emitters had been vacuum-annealed at temperatures much more severe than those produced in this diode and had shown only mild rounding off, so the pitted and truncated appearance of WF10B were unexplained. The fact remains, however, that the diode was stable during testing and these minor changes did not affect the performance.

F. COATING APPARATUS

The emitter substrates were typically 0.2" thick and 0.5" or 0.75" in diameter. They were coated in a water-cooled furnace by

Figure 25. Coated Emitter Performance Data
(Power Density versus T_E).

Figure 26a (565x)

Emitter WF10B.
Sandblasted and
W-coated. Operated
in a diode. Lower
(deep) focus.

Figure 26b (565x)

Emitter WF10B.
Sandblasted and
W-coated. Operated
in a diode. Upper
(shallow) focus.

heating an evaporator by electron bombardment from W filaments. The design of the coating furnace is illustrated in Figure 27 and the furnace components are shown in Figure 28. The substrate temperature could be adjusted by varying the number of W insulation foils placed between the substrate and the pedestal. Temperature measurements on both the evaporator and substrate were made using an optical pyrometer.

Thin W foil was usually wrapped around the evaporator, and free-standing cylindrical shields were used to minimize radial heat losses. The better the radial shielding, the more uniform the temperature of the evaporator and the less convex the coatings on the emitter substrates. For coating thicknesses up to .005 inch, emitters were out of flat by approximately .001 inch. This was compensated for by making the emitter slightly concave prior to coating.

Most of the early runs were made in a chamber evacuated with a titanium sputter-ion pump, but later in the program this vacuum system was replaced by a diffusion pump system with a much larger pumping capacity, drastically reducing the time required to reach coating temperatures.

In many cases the W foil insulation was coated with thoria to prevent adhesion between the layers. This raises the question as to whether or not any thoria could have gotten into the emitter coatings and resulted in artificially low bare work function data. In the case of emitter WF10B, which was used in the diode performance study (see previous section), thoria was not present in the coating system.

Figure 27. Emitter Coating Apparatus.

Figure 28

Exploded view of emitter-coating apparatus
diagrammed in Figure 27.

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III. COATED COLLECTORS

A. INTRODUCTION

In addition to the coated emitter studies described above, similar work was performed with Nb collectors, coating them with layers of Mo, Ni, Nb and W. Both planar and cylindrical collectors were successfully coated and characterized by microscopy, x-ray diffraction, surface contour studies, and thermal cycling. Diode performance studies on Mo-coated collectors are now under way.

The planar samples used in this work were cross sections of Nb rod stock, coated using flat evaporators heated by electron bombardment, much as the planar emitters were done. The inside surfaces of the cylindrical collectors were coated by using solid rods of the coating materials positioned along the axes of the cylinders and heated by electrical resistance, or by using hollow cylinders of the coating material heated by electron bombardment from filaments inside.

As in the coated-emitter work, the mechanical condition of the Nb pre-surface had a decided effect on the nature of the coating. The microscopic appearance and the crystallographic orientation of the coatings depended a great deal on the way the Nb surface was prepared before coating. Contrary to expectations, the coatings generally adhered just as well to smooth pre-surfaces as to rough ones.

Figure 29 is a summary of most of the planar coating experiments, including information on the coating parameters, the surface preparations, and the character of the deposits. More detailed discussions of the tabulated data will be found below.

	Coating Parameters			Pre-Surface		Nature of Coatings			
	Duration of Run (hours)	Collector Temp. (°C)	Evaporator Temp. (°C)	Preparation	Orientation	Rectilinear Features ?	Orientation	Angle of Glints	Bounding Planes
PNb-1	24	900	2200	SB	Random	Yes?	111	50°	100
PNb-2	24	800	2250	E-Pol.	110	Yes?	111	55°	100
PNi-1	1-1/2	500	1325	SB	Random	No	Random	--	---
PNi-2	1-3/4	500	1325	E-Pol.	110	No	Random	--	---
PNi-3	2	800	1325	SB	Random	Yes	Random	--	---
PNi-4	2	800	1325	E-Pol.	110	Yes	Random	--	---
PMo-2	3	675	2100	SB	Random	No	Random	--	---
PMo-3	4	840	2125	15μ Pol.	110	Yes	111	35°	110
PMo-4	2	860	2150	SB	Random	Yes	Random	--	---
PMo-5	2-1/4	770	2150	SB	Random	Some	Random	--	---
PMo-6a	4	900	2150	SB	Random	Yes	Random	--	---
PMo-6c	4	900	2150	15μ Pol.	110	Yes	111	35°	110
PMo-7	1-1/2	900	2175	E-Pol.	110	Yes	111	35°	110
Collector for parametric diode	3	880	2150	E-Pol.	110	Yes	110	--	110

Figure 29

Coatings on Planar Nb Collectors

B. COATING MATERIALS

The four different coating materials used were Mo, Ni, Nb, and W. The first of these (Mo) was the one evaluated most extensively. The Mo-coated Nb collectors included many experimental runs used for evaluating the coating parameters, both planar and cylindrical. In addition, one planar and five cylindrical Mo-coated collectors were fabricated for actual diode performance studies (one parametric diode and five heat-pipe diodes), and are currently being tested. A few Ni coatings were also evaluated in both planar and cylindrical configurations, but Nb was coated only onto planar surfaces and W only onto cylinders.

1. Molybdenum (Mo)

The coating parameters and the importance of the Nb surface preparation were most thoroughly examined on Mo-coated collectors. As in the case of the coated emitters, the two major coating parameters were time and temperature. This is well illustrated by Figures 30a, b, and c, which are photomicrographs of three sandblasted planar collectors coated with Mo under increasingly severe conditions of time and temperature. The surface features can be seen to be increasingly rectilinear, much like the series of coated emitters illustrated in Figure 6, except that here the rectilinear features are primarily three-sided pyramids rather than parallel terraces. The data accompanying the figures refer to the duration of the coating run, the evaporator temperature, and the collector temperature; it is not clear which of these parameters was most significant. Actually, it is not even clear whether the rectilinear features are particularly desirable, since the advantages of having a preferred type of bounding plane have only been demonstrated for emitters, not for collectors.

The effects of time and temperature have been studied on cylindrical collectors as well as planar ones. In the case of the cylindrical configuration, the studies have been largely concentrated on the uniformity and the adhesion of the coatings, rather than on their crystallographic properties. Early experiments⁸ were made using a filament to heat a cylindrical Mo evaporator. The inside surfaces of the Nb collectors were left in their machined condition prior to coating. Deposit thicknesses of up to 1 mil were obtained using an evaporator temperature of about 2100°C, collector temperatures of 520 to 680°C, and coating durations of 15 minutes to 2 hours. Samples prepared this way showed excellent adhesion even after being cycled 10 times to 1000°C.

More recent experiments were made using a resistance-heated rod of Mo as the source of evaporation. The new configuration resulted in coatings that were of uniform thickness over greater distances (1.5 mils thick $\pm 5\%$ over a collector length of 1.2", and $\pm 10\%$ over 1.7", for example). Somewhat higher temperatures were employed than those in the early work. With 2150°C on the evaporator and 600 to 800°C on the collector, adhesion was again excellent.

Several different surface preparations were investigated: sand-blasting, rough machining, fine grinding, mechanical polishing, and either chemical or electrochemical polishing. Taken in that order, the list represents a decreasing degree of roughness and mechanical surface damage.

Unlike the case of W-coated W emitters, polishing the Nb pre-surface did not result in a Mo coating that was of equal thickness everywhere and, therefore, was as featureless as the underlying substrate. On the contrary, the coated collectors shown in Figures 31,

Figure 30a (1400x)

Planar collector PMo-2.
Sandblasted and Mo-
coated. (3 hours,
2100°C, 675°C.)

Figure 30b (1400x)

Planar collector PMo-5.
Sandblasted and Mo-
coated. (2-1/4 hours,
2150°C, 770°C.)

Figure 30c (1400x)

Planar collector PMo-6a.
Sandblasted and Mo-
coated. (4 hours, 2150°C,
900°C.)

32, and 33 all show angular features quite unlike the underlying polished surfaces. The three-sided pyramids in Figure 31 are smaller and more uniform, but are otherwise quite similar to those on the sand-blasted pre-surface shown in Figure 30c. Actually, the effects of the substrate preparation on the surface contours of the coating were less significant than the effects on the crystallographic orientation of the coating, as will be seen in Section C below. As mentioned in the introduction, all indications throughout this work were that the adhesion of the coatings to the Nb substrates was largely independent of the surface preparation.

2. Nickel (Ni)

Work with planar Mo coatings had suggested that the formation of rectilinear features was a function of the time, the evaporator temperature, the collector temperature, or all three. Work with planar Ni coatings indicated that a threshold collector temperature was the important factor. Four different coating runs were made, all using an evaporator temperature of 1325°C. When the collector temperature was 500°C, rectilinear features did not form on either a sandblasted pre-surface or on a polished one, but when the collector was at 800°C, rectilinear features formed on both.

Several cylindrical experiments with Ni were made at the same time as early cylindrical work with Mo, using an EB-heated Ni evaporator.⁸ Deposit thicknesses again ranged up to 1 mil, the evaporator temperature was about 1240°C, the collector temperatures were 400 to 600°C, and the coating times were 20 minutes to 1 hour. Again, the Ni coatings adhered well to the machined Nb substrates, even after cycling 10 times to 1000°C.

Figure 31 (1400x)

Planar collector
PMo-6c. Polished
and Mo-coated.
(111) Mo on (110) Nb.

Figure 32 (1400x)

Planar collector for
parametric diode.
Polished and Mo-coated.
(110) Mo on (110) Nb.

Figure 33a

Oblique view along
the axis of the
cylinder.

Figure 33b

Oblique view at
right angles to the
axis of the cylinder.

Figures 33a and 33b (6900x)⁹

Cylindrical prototype collector for heat
pipe diodes. Polished and Mo-coated.
(111) Mo on random Nb.

3. Niobium (Nb)

Niobium was evaluated only in the planar configuration. Two runs were made, one on a sandblasted surface and one on a polished surface. The features on both surfaces could barely be resolved by our light microscope, but if anything they looked like three-sided pyramids, producing symmetrical "reflectograms" with distinct peaks 50 to 55° from the normal. Such peaks presumably could result only from a uniform and repeating pattern of surface features; see Section C for a discussion of this.

4. Tungsten (W)

Tungsten was investigated only in the cylindrical configuration. All of the W coatings were made using a resistance heated evaporator. As in the case of either the Mo or Ni cylindrical coatings, good adhesion and uniformity were obtained for deposit thicknesses of up to 1 mil. The collector temperatures ranged from 600 to 950°C, and the evaporator temperatures were about 2750°C, but the evaporation rates were much lower than in the Mo or Ni runs, so the coating times were considerably longer (5 to 8 hours).

C. CHARACTERIZATION

1. Orientation and Surface Studies

The crystallographic orientations of both the Nb pre-surfaces and the various coatings were studied quite thoroughly on the planar samples, using conventional x-ray diffraction techniques. In each of the experimental runs, the "planar" Nb substrate was actually the flat cross section of a cylindrical piece of stock. When the cross

section was sandblasted, the surface layer was, of course, randomly oriented, and Mo coatings deposited on such a surface were also randomly oriented. When the damaged layer of the machined Nb cross section was systematically removed by fine grinding (to a 600 grit SiC finish), mechanical polishing (to a 15 μ diamond finish), and electrolytic polishing (in 90/10 sulfuric acid/hydrofluoric acid) the surface became increasingly representative of the bulk material, which proved to be (110) oriented. When the different pre-surfaces were coated with Mo, the degree of orientation of the coatings was a function of the degree to which the substrate had been polished, but the crystal plane that exhibited a preferred orientation in the Mo coating was the (111) plane, and not the (110) plane exhibited by the underlying Nb.

In the case of the planar Nb collector fabricated for diode testing, the planar Nb surface was also (110) oriented and the coating conditions were presumably the same, but the collector configuration and the coating apparatus were different, and the Mo coating turned out to be (110) oriented like the Nb substrate. This collector was the only planar one showing "patches" on the coated surface which corresponded to the grains in the underlying Nb substrate. The patches were apparently due to differently-tilted bounding planes from one Nb grain to the next and were thought to be analogous to the patches observed on W-coated W emitters (see Figures 7, 8, 9, and 10).

Still another result was obtained on the cylindrical prototype for the five heat-pipe diodes. In this case, the inside wall of the polished Nb collector was too large grained to be defined well but it appeared to be more or less random. The Mo coating was much finer-grained and was easily defined as being (111) oriented.

The three observed variations - (111) Mo on (110) Nb, (110) Mo on (110) Nb, and (111) Mo on random Nb - had different surface characteristics as well as different bulk orientations. Photographs of the two planar samples were taken on a light microscope (Figures 31 and 32), but the features on the surface of the cylindrical sample were not resolvable even at 1400 X, and were, therefore, photographed in a scanning electron microscope (Figure 33).⁹ The small size of the features should be noted in reference to the much larger ones typical of the coated W emitters; the difference is presumably due to the huge difference in substrate temperature during coating (700 to 900°C for the Nb collectors and 2100 to 2700°C for the W emitters).

These same three samples were also examined with the optical goniometer already described in Section II-D. The information supplied by the microscopes and the goniometer can be considered together. The surface features of the "(110) on (110)" collector were predominantly diamond-shaped and nearly parallel to the surface plane (see Figure 32), and the "reflectogram" of this surface gave a strong narrow specular peak and no auxiliary peaks, much like the polished Nb pre-surface. This evidence suggests that the bounding planes of the surface of the Mo coating were also (110).

The surface features on the other two samples under consideration were quite different: they were pyramids rather than parallel terraces. The surface of the "(111) on (110)" collector was composed entirely of three-sided pyramids (see Figure 31) and produced a reflectogram with no specular peak, but with peaks at $\pm 35^\circ$. This again suggests that the bounding planes were (110), since a three-sided pyramid can be outlined by three triangular (110) planes which meet at a point and which intersect

a triangular (111) base at angles of 35° . The surface of the "(111) on random" cylindrical collector was composed of four-sided pyramids (see Figure 33) and produced a reflectogram with peaks at ± 40 to 45° . The pyramids appeared to be unsymmetrical: diamond-based rather than square-based (compare Figures 33a and 33b), and the peaks on the reflectograms were much weaker when the segment of the cylinder was rotated in a plane perpendicular to its own axis than when it was rotated in a plane parallel to its axis. A satisfactory scheme has not yet been devised to explain this particular Mo coating, and the interpretation may be complicated by the fact that the coating is on a curved surface rather than a flat one.

Planar collectors had been coated with Ni and Nb as well as with Mo, and these coatings were also studied in terms of their crystal structure. The orientations of both the Ni and Nb proved to be independent of whether the Nb substrate was sandblasted (and therefore random) or whether it was polished (and therefore (110) oriented). The Ni coatings were randomly oriented in either case, and the Nb coatings were (111) oriented in either case (see Figure 29). The Nb-coated surfaces had reflectograms with peaks at ± 50 to 55° , indicating preferred (100) bounding planes.

2. Cross Sections

The cylindrical collectors were sectioned routinely to check the adhesion, the thickness, and the uniformity of the deposits. As indicated already in Section III-8, excellent adhesion was achieved with Mo, Ni, and W deposits as thick as 1 mil. Uniformities of 1 mil $\pm 10\%$, over lengths of 1.3", were achieved with both Mo and W. Figure 34 shows a polished cross section of a typical Mo-coated cylinder.

Figure 34 (565x)

Typical cylindrical collector. Machined and Mo-coated. Cross section polished.

Figure 35 (565x)

Planar collector PMo-7. Polished and Mo-coated. Cross section etched.

Two of the planar Mo coatings were also sectioned, one which had a sandblasted Nb pre-surface (PMo-4) and another which had an electro-polished one (PMo-7). The adhesion of both of them appeared to be excellent. The grain structure of both was markedly "columnar" in appearance. The sandblasted one showed considerable porosity, within the coating itself, but the polished one did not. Figure 35 shows the columnar grains in the etched cross section of sample PMo-7; the Nb substrate is out of focus in this photograph because the Nb was attacked by the etchant much more rapidly than the Mo coating was.

3. Thermal and Mechanical Stability

The adherence of the cylindrical coatings was checked thermally and mechanically as well as metallographically. As described already, Mo and Ni coatings were thermally cycled 10 times to 1000°C without any noticeable effect. Segments of many of the coated cylinders were also tested by vigorous mechanical twisting and bending, again without any effect.

Two of the planar samples (PMo-3 and PMo-6) were heated for 1 hour at 1150°C and were cooled without peeling. The planar Mo-coated collector for the parametric diode was heated while a Cu braze was being made, also without effect.

4. Diode Performance

As indicated already, diode performance studies are currently under way on several Mo-coated Nb collectors. All of them had polished pre-surfaces: the planar one was electrolytically polished and the five cylindrical ones were chemically polished. Details of

the polishing procedures are given in the next section. The surface appearance of the actual planar collector is shown in Figure 32, and the surface of the cylindrical prototype is shown in Figure 33.

The planar collector is being put in a parametric diode with an electropolished CVD "duplex W" emitter having an emitting surface of "chloride W" on top of a base of "fluoride W". The five cylindrical collectors are going into heat-pipe diodes with electropolished "chloride W" emitters.

D. POLISHING OF NIOBIUM SUBSTRATES

When preparing planar Nb surfaces for deposition, the metal was mechanically ground with 240, 320, 400 and 600 grit SiC discs, more finely ground with a loose water slurry of 600 grit SiC on canvas cloth, and then polished with 15 μ and 6 μ diamond on nylon cloth. A good mechanical polish was relatively easy to achieve and could be successfully followed by an electrolytic polish of 10 to 15 minutes in 450 ml concentrated sulfuric acid and 50 ml 48% hydrofluoric acid.

When trying to duplicate this procedure on the inside surfaces of cylindrical Nb collectors, it was difficult to achieve a good enough mechanical "pre-polish" to have this particular electropolish work very well. Different electropolishing conditions and different electrolytes were tried, but to no avail. Much better results were obtained with a modified mechanical pre-polish and hot chemical polish, as described below.

The inside surfaces of the five collectors for the heat-pipe diodes were cut on a precision lathe with a very slow feed, honed with a Sunnin K20-CO5 cork-bound stone, and polished with Buehler

"microcloth" wrapped around the hone and wet with 1μ , 0.5μ , and 0.1μ alumina slurries. They were then chemically polished by immersing them for about 5 seconds in a hot (60° to 70°C) solution of 250 ml concentrated sulfuric acid, 100 ml concentrated nitric acid and 100 ml 48% hydrofluoric acid.

E. COATING APPARATUS

The early cylindrical work with Mo and Ni was done using a hollow evaporator heated from the inside by a coiled filament. The apparatus had a space between the collector holder and the water-cooling tubes, and the temperature of the collector could be regulated by evacuating the space or pressurizing it with inert gas. A schematic of that apparatus was presented in an earlier report.⁸ The more recent cylindrical work was done using resistance-heated evaporator rods. Figure 36 is a schematic of the apparatus used to coat the collectors for the heat-pipe diodes. All of the experimental work was done on Nb cylinders with an inside diameter of 0.94". The collectors for the diodes had inside diameters of 0.78", and were coated over a length of 1.3".

The planar coatings were all made by EB-heating of suitable evaporator discs. Figure 37 shows the apparatus used in all the experimental runs. In these cases the substrate was a 0.63" diameter cross section of a Nb rod 3" to 4" long; this rod was water-cooled at the non-coating end.

In all of the coating work, whether planar or cylindrical, the collector temperatures were measured using thermocouples and the evaporator temperatures using optical pyrometers. The coating chambers were evacuated using diffusion pump systems.

Figure 36. Cylindrical Collector-Coating Apparatus.

Figure 37. Planar Collector-Coating Apparatus.

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