MASTER

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COMPOSITION PROFILING OF SOLAR COATING MATERIALS.

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Table of Contents

	<u>Page</u>
Abstract	1
Background	3
A. Analysis Service to Other ERDA-DOE Grantees	4
B. Cr_2O_3 -Diffusion Barrier	5
a) Mo on SS 304	5
b) Mo on SS 316, SS 321 and on Ferritic Steel 430	10
c) Al_2O_3 on Mo on Cr_2O_3 on SS 304	12
d) W on SS 304	13
e) Ag and Au on SS 304	13
C. Optical Properties of Sputter Deposited Mo	15
D. Optical Properties of Various Other Surfaces	16
E. Sputter Deposition by a Torus Ring Gap Magnetron Discharge	16
F. Black Cobalt	19
G. Cones on Metal Surfaces	20
H. Publications	20
I. Personnel	21
K. References	22
L. Figures 1 to 14	23
M. Attachments	38

Abstract

This grant was split into two parts: own studies and cost-free analysis service to other solar thermal NSF-ERDA-DOE grantees. The service amounted to roughly 50% of our efforts and discussion of results was left to the individual users.

Our own studies were the subject of progress reports COO-1-2-3 and a number of publications, ~~of which reprints are~~
~~attached~~

Auger electron composition vs. depth and optical analysis revealed that a very inexpensive-to-produce [15 min. 900°C heat treatment in air] Cr_2O_3 layer on stainless steels provides an excellent diffusion barrier for preventing stainless steel constituents from entering into an IR reflective Mo coating. With this diffusion barrier the operating temperature of a solar thermal absorber stack such as an AMA coating can be raised by at least 250°C. Alumina coated Mo on Cr_2O_3 on SS showed no damage after 400 hours at 725°C.

This Cr_2O_3 coating on SS provides as well an excellent barrier for preventing noble metal atoms from diffusing into stainless steel. Au, for instance, diffuses readily into untreated SS at > 300°C but with the Cr_2O_3 barrier heat treatments at 600°C in air retained fully the Au coating on the surface.

It was shown that with sputter deposition of Mo at high rate in a clean noble gas plasma, one can obtain Mo coatings of excellent IR reflectance [> 96% between 2.5 and 25 μm wavelength]. The potentialities of a torus ring-gap magnetron discharge for economic production-type sputter deposition of Mo on SS tubing are being discussed.

The optical properties [α and ϵ] of various other absorber surfaces such as stacked razor blades, cone or whisker-covered metal surfaces, plasma-sprayed chromic oxide coatings etc. were measured and explored. A very simple, not very selective, solar thermal absorber coating [$\alpha = 91\%$, $\epsilon = 80\%$] can be obtained simply by heating SS 304 for 45 min. at 900°C in air.

The potentialities of an electrolytically deposited black cobalt coating, as described in a German patent, were explored. Initial results showed that this coating is probably not suited for operation at temperatures exceeding 300°C .

An unscheduled interesting fallout during these studies was the fact that different isotopes of a metal are sputtered at low bombarding ion energy [$< 200\text{ eV}$] with different angular distribution. This work is described in the attached reprints from Applied Physics Letters and Journal of Applied Physics.

Background

This grant was initiated as a follow-on of studies which we performed as part of a University of Minnesota and Honeywell team, whose efforts in "Research Applied to Solar Thermal Power Systems" were sponsored by NSF-RANN from 1972 - 1975. In that time we received NSF-RANN funds for acquiring an Auger Thin Film Analyzer and Scanning Auger Microprobe apparatus. This analysis tool has played a dominant role in most of our studies. During information exchange at various workshops it became evident that many other NSF-RANN-ERDA-DOE solar thermal grantees could benefit enormously from Auger thin film composition analysis but they lacked easy access to this sophisticated and expensive [> 130K\$] equipment. As a result our grant was split into two parts: own studies and cost-free analysis service to other solar thermal NSF-ERDA-DOE grantees. This service, performed by experienced postdoctoral research associates, has amounted to roughly 50% of our efforts. Reporting of results obtained from this service was left to the individual users.

Our own studies under this grant were reported in many workshops, in our yearly renewal proposals, in reports COO-1-2-3 and in a number of publications of which reprints are attached. This final report is intentionally kept concise, with a minimum number of representative Auger composition vs. depth profiles selected from many thousands which we recorded and evaluated under this three-year grant.

We have been informed that SERI intends to fund the continuation of our studies for another year retroactively beginning May 1, 1979.

A. Analysis Service to other ERDA-DOE Grantees.

Our main customers in Auger thin film composition vs. depth analysis service to other DOE grantees were: Honeywell Corporate Research (Vankatasetty, D. Zook), Honeywell Systems and Research (H. Mar, R. Lin), SERI (Czanderna), Argonne National Laboratory (R. Griffith), the University of Chicago (H. Fritzsche) and in particular the University of Arizona (G. Carver, B. Karlson and R. Shimshock of Prof. Seraphin's group).

Details about results were reported by those who made use of this service.

In some cases it became necessary to supplement the Auger with ESCA analysis for obtaining information about chemical bonds such as in black Cr and black Ni coatings. This service was performed in the Analytical Lab of Physical Electronics Ind., a local company which manufactured our Auger equipment and with which we maintain a very close working relationship [many of our graduate students became employees of this company]. In the course of this work for outsiders we ran sometimes into challenging problems such as the following:

Some of the film stacks from the University of Arizona had a fairly thick Si coating on top. With our sputtering rate in the Auger system limited to $100 \text{ \AA}/\text{min}$, the depth profiling became very time consuming. This problem was solved with a new "sputter angle lapping" technique. For this the samples were presputtered, before transfer into the Auger system, in a Hg plasma [ion current densities of several mA/cm^2]. Near the edge of the samples where the ion sheath curves around the [negative] target, the bombarding ions become focused and cause much more intense sputtering than in

the flat areas of the sample. With the resulting depth gradient, one can spread out the layered stack laterally and switch to point or to lateral line analysis without the need for sputter profiling and one can collect in this manner useful composition data as a function of depth without the need of in situ sputter microsectioning.

For Czanderna [SERI] we studied the differences between corroded and uncorroded areas of Ag mirror samples. These latter samples came covered with a protective polymer coating which needed to be removed in order to collect valid depth profiles. By rubbing the samples with a cork (which has high friction but no abrasive properties) soaked in methanol the polymer coating can be readily removed without damage to the underlying films.

During studies in which quantitative composition analysis was required we became aware [as others must have noticed] of an artifact which arises from the ion beam. The ion space charge reduces the intensity of low energy Auger signals [< 100 eV] by as much as 50% because many of these Auger electrons are deflected and are not reaching the analyzer. This effect is, of course, much less pronounced for higher energy Auger electrons. It is, therefore, advisable to either switch off temporarily the ion beam and interrupt the profiling for collection of quantitative data or to use if possible higher energy Auger electrons for analysis.

B. Cr₂O₃-Diffusion Barrier.

a) Mo on SS 304.

Solar-thermal power systems often require high-temperature ($> 400^{\circ}\text{C}$) solar absorber coatings [1] on stainless steel (SS)

substrates. However, the SS substrate can cause detrimental effects -- for example, consider the AMA interference coating (Al_2O_3 on MoO_x on Al_2O_3) [2]. On a Mo substrate, this coating performs well in vacuum for operating temperatures up to about 900°C ; but, on a SS substrate, it fails when the temperature exceeds 500°C . We [3] have demonstrated that such failures result from the diffusion of SS constituents from the substrate into the coating. This diffusion can be inhibited if an effective diffusion barrier is inserted between coating and substrate.

Our objective here was to study the effectiveness of a Cr-oxide diffusion barrier between a Mo coating and a SS 304 substrate.

For each experiment, two samples -- one with a Cr-oxide diffusion barrier and the other without -- were prepared as follows: The two samples were cut from the same sheet of SS 304. One sample was heated in air for 15 min at 900°C . This heating formed a Cr_2O_3 surface layer having a thickness of about $2000 \text{ \AA}$. Heating at such high temperatures is essential because air heating at lower temperatures (such as 700°C) causes the formation of a Fe-oxide instead of a Cr-oxide layer at the surface [4]. The two samples were then placed side-by-side in a sputter deposition system and sputter-coated simultaneously with a $\sim 5000 \text{ \AA}$ thick Mo coating. Subsequently these samples were heated in vacuum ($\sim 0.13 \text{ Pa}$) for given temperatures (500°C to 1000°C) and time intervals.

After the vacuum heat treatment, each sample was analyzed using our Auger Thin Film Analyzer, operated with an electron beam energy of 5 keV; electron current, $2 \mu\text{A}$; beam diameter,

20 μm ; and angle of incidence of 60° with respect to the surface normal. For the Auger spectra, the background pressure was less than 10^{-7} Pa. For the composition vs. depth profiles an Ar-ion beam was used for in situ microsectioning. At an Ar pressure of about 7×10^{-3} Pa the approximate Ar⁺-ion beam characteristics were: beam energy: 2 keV; ion current: 5 μA ; beam diameter: 2 mm; and angle of incidence of 30° with respect to the surface normal.

Composition vs. depth profiles for four typical sample pairs are shown in Figs. (1) through (4). For each figure, the bottom profile corresponds to a sample with the Cr_2O_3 diffusion barrier; the top profile, to one without.

The two profiles shown in Fig. 1 are representative of all sample pairs just prior to the heat treatment. The Auger profiles show that the sputter deposited Mo coatings contain few impurity atoms.

Figure 2 shows that a heat treatment of 1 hr at 800°C causes the movement of C from the SS 304 substrate into the Mo coating, while the Cr-oxide layer prevents this C diffusion. The shape of the C Auger peak in the Mo film indicates that the C has been combined with Mo to form Mo-carbide, which is by far not as good an IR reflector as pure Mo. Experiments on other un-oxidized samples demonstrated that such Mo-carbide layers are formed for 1-hr heat treatments at temperatures that exceed 500°C while the Cr-oxide diffusion barrier remains effective for such treatments at temperatures up to 900°C .

The atomic percentage of C in SS 304 is about 0.06 percent. The diffusion rate of C is much greater than the diffusion rate of any of the other SS 304 constituents.

Figure 3 (17 hr. at 800°C in vacuum) shows more dramatically the effectiveness of the Cr-oxide diffusion barrier. The un-oxidized sample shows that not only C but also the other SS constituents have now diffused into the Mo-film. The surface region is an approximately 1000 Å thick layer which consists of Mo and the four SS constituents -- C, Fe, Cr, and Ni. These constituents have diffused from the SS 304 substrate through the Mo coating into the surface region. The next region is a ~ 1000 Å Mo layer which is relatively free of SS constituents, followed by a ~ 2000 Å Mo-carbide layer. The final region is a ~ 3000 Å thick layer which seems to be a solid phase consisting of Mo-C, Fe, Cr, and Ni. The Cr-oxide covered SS shows no sign of such diffusion.

Figure 4 shows that the Cr-oxide diffusion barrier finally failed for a heat treatment of 1/2 hr at 990°C. Note that the various SS constituents have diffused from the SS 304 substrate through the Cr-oxide layer through the Mo coating into the surface region. For the sample without a diffusion barrier, the original Mo coating has been completely transformed into a new (solid solution) coating which is about 7000 Å thick, as compared to the original coating which was about 5000 Å thick. This coating contains five primary constituents having the following atomic percentages: (1) Mo, 40%; (2) C, 20%; (3) Fe, 26%; (4) Cr, 9% and (5) Ni, 2%. Scratching tests showed that this coating is much harder than the underlying SS and does well adhere even when made rather thick (~ 1 μm). This coating may have interesting properties for other applications (hardness, corrosion resistance, inertness, etc.). The C Auger signal has the typical shape of a carbide and

not of an atomic C peak (See Handbook of Auger Electron Spectroscopy, Physical Electronics Inc., Eden Prairie, MN 55343).

Some exploratory studies were performed on the same coating pairs for longer duration, vacuum exposures. At 725°C for 165 hours the Cr_2O_3 covered SS 304 holds up as well as under a one-hour treatment as shown in Fig. 5. However, after 100 hours at 825°C the SS components have penetrated the barrier and reached the sample surface.

Longer duration heat treatments created an unexpected problem insofar as a layer of Mo-carbide was formed at the Mo surface. By heating simultaneously with the samples a piece of pure Mo, the same carbide layer was found confirming the suspicion that carbon containing gases in the vacuum system must have been the source of this carbon. This problem needed no further attention because our next goal was, and still is, to study in detail the Al_2O_3 coated Mo on SS 304 and the Alumina coating eliminates this surface interaction problem.

An interesting artifact was discovered in the course of these Auger profiling studies: the profiles in Figs. 1 - 4 have a common feature insofar as a pronounced Mo tail extends into the Cr_2O_3 layer and even fairly deep into the SS substrate. This must have resulted from Mo being driven deeper inside by the ion bombardment during profiling.

Confirmation of such a knock-in effect was obtained from the following experiment: after sputter profiling somewhat into the SS substrate such that the Mo tail has not yet gone to zero, the Ar-ion beam energy was changed during profiling from 2 keV to .5 keV and after a new steady state condition

was reached back to 2 keV. Points A and B in Fig. 6 indicate the times when the ion energy was changed. At point A the Mo signal begins to increase towards a new higher equilibrium value. At point B the Mo signal decreases rapidly to the original 2 keV value. A similar behavior has previously been observed by Wehner [5] for the case of a small amount of Ag in Al.

The explanation for this phenomenon is the following: at an ion beam energy of 2 keV part of the Mo atoms are driven or knocked into the SS substrate beyond the Auger analysis depth. This causes a lower Mo Auger signal than under the .5 keV ion bombardment in which the knock-in effect is less pronounced. Changing from 2 keV to .5 keV reduces the sputtering rate such that it takes a noticeable delay before the profiling has proceeded to the new .5 keV steady state near-surface Mo content. Changing from .5 keV back to 2 keV leads to an instantaneous response to the enhanced knock-in. The Mo content in the region studied in Fig. 6 was so small [notice enhancement factor X10] that the Ni, Cr, Fe signals show only negligible complementary opposite intensity changes during this experiment.

b) Mo on SS 316, SS 321, and on Ferritic Steel 430.

The diffusion studies into a Mo coating were expanded to other steels such as SS 316, SS 321, and 430. A one-hour heat treatment at 800°C of Mo on bare SS 316, which contains 3% Mo, creates a very similar situation as observed with SS 304, namely, a pronounced diffusion of the SS constituents into the Mo with the formation of a [hard] Mo-C-Fe-Cr-Ni solid solution layer. The Cr_2O_3 diffusion barrier, however, is by far not as effective on 316 as on 304. For one hour at 900°C the Cr_2O_3 barrier became absolutely useless.

Quite a different situation arises with SS 321, which contains about .4% of Ti. Figure 7 demonstrates that after a one-hour 800°C heat treatment the small amount of Ti in the 321 has prevented any C movement, even without the diffusion barrier. Although in this case Fe and Cr and to a lesser amount Ni have penetrated into the Mo, the Cr_2O_3 seems to be even more effective as on SS 304 because a 900°C one-hour heat treatment showed no diffusion effects whatsoever.

Finally, we studied the ferritic steel 430, which contains 14% - 18% Cr and .2%C but no Ni. It was found that the Cr_2O_3 layer fails to show any diffusion barrier properties when the samples are heated for one hour at 800°C.

One can conclude from these experiments that among SS 304, SS 316, SS 321, and ferritic steel 430 the [900°C, 15 min.] air-oxidized SS 321 would be the best substrate choice if one intends to coat it with a high IR reflective Mo layer as a base for a thermal absorber stack, which is able to stand the highest possible operating or run-away-condition temperature.

In summary, it can be stated that a very inexpensive to produce [15 min., 900°C in air] Cr_2O_3 layer on stainless steels provides an excellent diffusion barrier for preventing stainless steel constituents from entering into the IR reflective Mo coating. The operating temperature of this stack can be raised by at least 250°C with this diffusion barrier. Even in low solar concentration in which the operating temperature is normally below any damage limit, one may encounter runaway conditions during failure of the working fluid pumps. In such a case the Cr_2O_3 diffusion barrier will substantially reduce the possibility of coating damage.

c) Al_2O_3 on Mo on Cr_2O_3 on SS 304.

Since our original goal was to prevent the diffusion of SS components into the AMA coating, the next logical step was to cover the Mo/ Cr_2O_3 /SS 304 with Al_2O_3 . The inert alumina layer over Mo should furthermore prevent carbon [from the vacuum environment or the atmosphere] to form Mo-carbide at the Mo surface during heating of these stacks and make it possible to operate the coating stack at high temperature in poor or no vacuum.

Alumina was deposited on Mo/ Cr_2O_3 /SS 304 substrates by rf sputtering in a triode mercury plasma discharge [6]. An alumina crucible was used as the target. Before mounting the target in the sputtering chamber, it was heated for a few hours in order to drive out the absorbed moisture. This is important as otherwise the alumina target starts outgassing as soon as the rf is switched on and this results in poor alumina deposits. The Mo surface was first sputter cleaned by biasing the substrate negatively for a few minutes.

Figure 8 shows a depth profile of such a coating stack. In this case the Al_2O_3 layer is about 2500 Å thick. For obtaining a well-defined stack profile, the Mo layer should be sufficiently thick [> 2000 Å] such that during profiling the O signal from the Al_2O_3 has disappeared before the O signal from the Cr_2O_3 appears. This coating held up extremely well after heating at 725°C in a 10^{-4} Pa vacuum for 400 hours. Heating of such stacks in air instead of vacuum is in progress. Preliminary results show that the stack suffers no damage when heated at 700°C in air for one hour as shown in Fig. 9.

d) W on SS 304

Some exploratory studies were performed for investigating the diffusion barrier performance of the Cr_2O_3 layer on SS 304 when covered with a W instead of a Mo layer. Sputter deposition in a clean vacuum system can produce W films of similar good quality as Mo films, as the Auger spectra indicate.

A one-hour heat treatment at 800°C shows two marked differences to Mo: a.) No W-carbide is formed at the interface to the bare SS 304 but some of the SS constituents, Fe and Cr, have diffused completely through the W coating and have appeared at the surface. b.) The Cr_2O_3 coating provides hardly any improvement over the uncoated SS. In fact, at 900°C for 1 hr., the Cr_2O_3 coated SS has even enhanced the diffusion of the SS constituents into the W coating, although still no sign of W-carbide formation is noticeable.

Although no plausible explanation for the pronounced differences between Mo and W exists, one can conclude that W may have an advantage on SS 304 insofar as it does not attract the C from the SS 304 even when the SS is not Cr_2O_3 coated. At temperatures above 800°C , however, the W is much more prone to SS constituent through-diffusion than Mo.

e) Ag and Au on SS 304

The objective was to gain as much information on the barrier properties of Cr_2O_3 coating on SS as possible. Of interest in a number of proposed solar absorber coatings is the diffusion behavior between a noble metal such as gold or silver and SS.

We prepared by sputter deposition similar sets of samples as with Mo. Figure 10 shows the composition vs. depth profiles of a Ag layer on untreated and on air-oxidized [15 min., 900°C] SS 304 after a one-hour heat treatment at 780°C. Neither the untreated nor the Cr-oxide-covered SS shows any changes at the interface with Ag. No Ag agglomeration has become noticeable. This situation, however, is quite different with Au. Figure 11 shows the profiles of the Au coated set of SS samples before any heating. Similarly as was the case with Mo, the Au has, under the ion beam bombardment during profiling, been driven deeper into the SS or into the Cr_2O_3 coated SS as indicated by the pronounced Au tail. Figure 12 shows that one hour at 500°C causes the Au to diffuse into the untreated SS but not into the Cr_2O_3 covered SS. In fact, one can repeat this heat treatment even at 600°C in air [Fig. 13] and find that the Au color has been fully retained at the Cr_2O_3 covered but not at the untreated sample which begins to lose its Au color already at 300°C. In vacuum even at 700°C the diffusion barrier still performs well. Only at 800°C does it finally break down.

Thus, the Cr_2O_3 layer on SS provides an excellent diffusion barrier for preventing not only the outward movement of stainless steel components but also the inward movement of constituents from other surface coatings. The pronounced difference in diffusion behavior between Ag and Au on untreated SS came [at least to us] as a surprise. The fact that diffusion of Au into SS can be stopped at temperatures of up to 600°C in air or 700°C in vacuum by providing a simple-to-produce Cr_2O_3 barrier on the SS surface may have practical implications in non-solar-related areas.

C. Optical Properties of Sputter Deposited Mo

The major part of the work for the University of Arizona concerns the quantitative analysis of CVD deposited Mo films with respect to their C and O content. This, in turn, stimulated some efforts of our own: we wanted to compare the composition and the optical properties of our sputter deposited Mo films with those deposited by CVD in Arizona. Arizona supplied us with four quartz blanks onto which we sputter deposited Mo under as clean vacuum conditions as we could possibly achieve. Three of those coated samples were sent back to Arizona for their optical evaluation. On the other sample we first checked with Auger the C and O content and found both to be barely detectable. We then forwarded the sample to Honeywell for optical evaluation. The average reflectivity as shown in Fig. 14 amounted to at least 96% in the range between 2.5 and 25 μm wavelength. This result certainly disproves the validity of published graphs in which sputter deposited Mo films, when compared to various other film deposition methods, were depicted as poor IR reflectors.

Beyond doubt, the secret is that the films need to be deposited at a high rate in a clean noble gas plasma. We anticipate that the films could be even further improved with negative biasing of the substrate during the sputter deposition. This biasing is known to preferentially resputter oxygen and thus creating coatings which may be more pure than the target from where the material was sputtered.

D. Optical Properties of Various Other Surfaces

In order to get an idea of what typical values of α and ϵ are achievable, the optical properties of various absorbing surfaces were measured for us at Honeywell. The edge-on surface of stacked razor blades, for instance, gave $\alpha = 98\%$, $\epsilon = 53\%$.

Three samples which METCO had prepared for us by plasma spraying with chromic oxide powder, showed for coatings of various thicknesses the following values: 25 μm : $\alpha = 90\%$, $\epsilon = 85\%$; 50 μm : $\alpha = 89\%$, $\epsilon = 82\%$; 100 μm : $\alpha = 90\%$, $\epsilon = 82\%$.

Copper samples on which we had created densely-spaced cones which were formed by seeding with a small flux of Mo during sputtering gave an average of $\alpha = 95\%$ and $\epsilon = 52\%$. Such coney surfaces are most likely tolerating fairly high operating temperatures because only surface topography is involved.

We found that the possibly simplest and most economical way of producing a fairly high solar absorbtivity coating [not very selective] consists of heating SS 304 for 45 min. at 900°C in air. Such samples showed $\alpha = 91\%$ and $\epsilon = 80\%$. It is interesting that subsequent heating of this coating in vacuum improved the selectivity such as 4 hrs. at 725°C in vacuum gave $\alpha = 90\%$, $\epsilon = 64\%$.

E. Sputter Deposition by a Torus Ring Gap Magnetron Discharge

Finding a cheap tubular substrate material like SS 304 and a cheap method for covering it with an effective diffusion barrier solves only part of the problem, because for the AMA on Mo coating, one still has to coat the tubing with a rather pure, oxygen-free, Mo film and the $\text{Al}_2\text{O}_3\text{-MoO}_x\text{-Al}_2\text{O}_3$ stack.

The principal investigator's main expertise acquired over a span of forty years has been the subject of "sputtering". It was only natural for us to investigate if one could find an economical scheme for coating SS tubing with this four-layer stack by sputtering. High rate sputter deposition of films has in recent years made some remarkable progress with the so-called magnetron approach. With magnetic and electrostatic focusing of the electrons in a ring-gap plasmatron discharge, one can achieve in cathode vicinity on a given closed directrix [such as a ring or racetrack] a very high plasma density and thereby achieve sputter deposition rates of the order of microns per minute. The same principle as used in the planar ring-gap discharge can be applied to a torus configuration. One can sputter towards the major axis and coat tubing uniformly from all sides without the necessity for rotating the tubing. We set out to explore the performance of such a torus ring-gap discharge. The experiments were performed in our Hg vapor triode discharge apparatus by sputtering Mo from a 6 cm diameter cylindrical target concentrically onto a SS tubing of 1 cm diameter. Two ring magnets were mounted surrounding the Mo cylinder for creating a ~ 0.5 cm wide magnetic ring tunnel on the inside of the Mo target for plasma confinement. The sputtering was performed with 750 eV Hg ions of 12 ma/cm^2 ion current density at 0.1 Pa Hg gas pressure. Although this setup is far from being optimized, the tubing became coated over about 3 cm length with a film of ~ 600 Å thick Mo in about 1 minute. Schiller and his coworkers in East Germany [7] have demonstrated that such magnetron discharges are ideally suited for deposition of

oxide insulator films by sputtering the metal with dc in an argon-oxygen mixture. By sputtering Ta in this mixture Ta_2O_5 deposition rates of 10,000 Å/min. were reported.

It should become a rather straightforward engineering task to build a coater in which sections of SS tubing move successively through concentric dc sputtering chambers arranged and operated such that the desired stack of 2,000 Å Mo, 600 Å of Al_2O_3 , 300 Å of MoO_x and 600 Å of Al_2O_3 is achieved. Based on own experience and published data, it should be possible to deposit in such a coater several kilometers of tubing with the desired solar thermal absorber stack in a period of one month.

At the major Japanese vacuum equipment manufacturer of Ulvac in Chigasaki, I saw personally such equipment in operation for coating steel tubing with a one-layer solar thermal absorber coating consisting of ZrC.

In view of the fact that industry is much better suited to pursue this coating scheme, our efforts in this direction were shelved in agreement with the sponsor. Should the necessity arise to demonstrate the feasibility and economy of this scheme in the form of a preproduction plant, I am convinced that the best suited place for such a task would exist at Battelle Northwest in Richland, Washington where a highly competent group of sputterers [McClannahan etc.] has pursued high rate sputter deposition of metallurgical coatings for many years.

F. Black Cobalt

A remarkable selective solar absorber coating is described in a German patent application "Offenlegungsschrift 256716" of June 30, 1977. The high selectivity is achieved by choosing a material which has such a high absorption in the solar spectrum that one can make this coating so thin [$1000 \text{ \AA}$] that the reflectivity of the metal underneath remains the dominating factor in the IR. The values reported for this coating on a Cu substrate covered with an electrolytically deposited $1000 \text{ \AA}$ cobalt sulphide layer are $\alpha = 97\%$ and $\epsilon [90^\circ\text{C}] = 6\%$. The same coating on a Ag covered glass substrate gave values of $\alpha = 96\%$ and $\epsilon = 4\%$.

Using the recipe furnished in the patent, we prepared such coatings on Cu substrates and achieved with a current density of 5 mA/cm^2 in 90 sec. values of $\alpha = 91\%$ and $\epsilon = 5\%$. Auger analysis showed that the composition close to the surface was: S = 7%, O = 26%, Co = 53%, Ni = 12%, Cu = 2%. Deeper inside, the oxygen content decreases. The α and ϵ remained unchanged when this coating was heated to about 200°C in air; however, heating to 240°C showed that the coating deteriorated significantly.

From the very fragmentary and preliminary results so far, one can conclude that black cobalt seems to resemble the black nickel and is probably inferior to black chromium with respect to its temperature tolerance. One should, furthermore, not overlook the fact that cobalt becomes a scarce and expensive metal. Closer studies and attempts to optimize this coating are supposed to be part of our efforts in the continuation of this work under SERI sponsorship.

G. Cones on Metal Surfaces

The subject of another grant under NASA Lewis Research Center sponsorship concerns the study of formation of cones on metal targets during sputtering. Considerable progress was made when we recognized and proved experimentally that such cones are not, as was widely believed so far, a "left standing" phenomenon only but that actual growth of metal whiskers is involved. We have now to a certain degree learned how to grow cones of desired steepness [including cylindrical whiskers] and density on any target metal. In view of the potential usefulness of such coney or whiskery surfaces for thermal or photovoltaic solar coatings, we attach here a recent status report NASA Cr-159549 "Whiskers, Cones and Pyramids Created in Sputtering by Ion Bombardment" in which some partial support from our DOE-Solar Program is acknowledged. This NASA grant has been extended for another year. The attached abstract of a paper to be presented at the American Vacuum Society Meeting in New York City October 4, 1979 indicates that we are making rapid progress in this area. By seeding a hot Mo target during sputtering with a very small flux of W atoms, we can now grow forests of cones or whiskers on Mo. Such surfaces with whisker length and density optimized are likely to provide solar thermal absorber surfaces for extremely high temperature operation. The monitoring of the optical properties of such surfaces has become an ongoing by-product program to this NASA grant.

H. Publications

Attached are reprints of two publications "Interdiffusion in Mo-covered Stainless Steels studied by Auger Electron

Spectroscopy" and "Characterization of Selective Absorber Coatings", both published in Proceedings 7th International Vacuum Congress and 3rd International Conference on Solid Surfaces, Vienna, 1977.

The basis for substantially improving the temperature tolerance of solar thermal absorber stacks on SS with the economically-to-produce [900°C, 15 min. in air] Cr_2O_3 diffusion barrier had been established with reference 4 before this grant was initiated. For completeness and convenience, we attach a reprint of this earlier paper.

Some unscheduled fallout resulted from our studies. Probably the most interesting was the discovery that different isotopes are sputtered at low bombarding ion energy [< 200 eV] from a metal target with different angular distribution. This work in which we acknowledged the partial ERDA support resulted in the two attached publications: "Isotope Enrichment in Sputter Deposits", Applied Physics Letters, 30, 185, 1977 and "Mass Effects on Angular Distribution of Sputtered Atoms", Journal of Applied Physics, 50, 3677, 1979. In another attached paper "Sputter Yields of Bi-Metal Mixtures", we acknowledged the equipment support by ERDA and DOE.

I. Personnel

Under guidance by the principal investigator, G. K. Wehner, the following personnel were involved in various phases of this work: research fellows: Dr. P. Braun, Dr. G. Betz, Dr. W. Faerber, Dr. B. Grung, Dr. P. Lindfors, Dr. T. Raj; the graduate students: W. Durand, R. Olson, M. King and Paul Yurista and the undergraduate lab technicians: Susan Kempf, Kathleen Peterson, Tom Kulenkamp and Ravi Sinha.

K. References

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L. Figures 1 to 14

Fig. 1. Composition vs. depth profiles which are representative of all sample pairs Mo/SS 304 and Mo/Cr₂O₃/SS 304 just prior to the vacuum heat treatment.

Fig. 2. Composition vs. depth profiles for a sample pair after vacuum heat treatment of 1 hr at 800°C.

Fig. 3. Composition vs. depth profiles for a sample pair after vacuum heat treatment of 17 hrs at 800°C.

Fig. 4. Composition vs. depth profiles for a sample pair after vacuum heat treatment of 1/2 hr at 990°C.

Fig. 5. Composition vs. depth profile for a sample of Mo/Cr₂O₃/SS 304 after a vacuum heat treatment of 1 hour at 725°C.

Fig. 6. Knock-in of Mo into the SS 304 substrates.

Fig. 7. Composition vs. depth profiles for a sample pair
Mo/SS 321 and Mo/Cr₂O₃/SS 321 after a vacuum heat
treatment of 1 hour at 800°C.

Fig. 8. Composition vs. depth profile for a stack $\text{Al}_2\text{O}_3/\text{Mo}/\text{Cr}_2\text{O}_3/\text{SS 304}$.

Fig. 9. Composition vs. depth profile for a stack $\text{Al}_2\text{O}_3/\text{Mo}/\text{Cr}_2\text{O}_3/\text{SS 304}$ after heating in air for one hour at 700°C.

Fig. 10. Composition vs. depth profiles for a sample pair Ag/SS 304 and Ag/Cr₂O₃/SS 304 after a vacuum heat treatment of 1 hour at 780°C.

Fig. 11. Composition vs. depth profiles for a sample pair
Au/SS 304 and Au/Cr₂O₃/SS 304 before heating.

Fig. 12. Composition vs. depth profiles for the sample pair in Fig. 11 after a vacuum heat treatment of 1 hour at 500°C.

Fig. 13. Composition vs. depth profiles for a sample pair Au/SS 304 and Au/Cr₂O₃/SS 304 after an air heat treatment of 1 hour at 600°C.

Fig. 14. Reflectance of sputter deposited Mo on quartz in the wavelength range 2.5 μ to 40 μ as measured with Beckman IR-4240 at Honeywell.