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PREPARATION AND DEGRADATION
OF REACTIVELY EVAPORATED
BLACK CHROME

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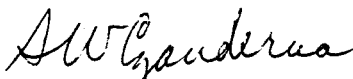
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FOREWORD

This report was prepared in compliance with the provisions of Contract No. EG-77-C-01-4042. The work has been carried out in support of the Surface and Interfaces Task (FY79 AOP-3122.70) in the Materials Branch, Research Division, of the Solar Energy Research Institute.

This work has been carried out as a small part of a subcontract to Clarkson College (AD-8-0908-1) with H. F. Helbig as the principal investigator and A. W. Czanderna as the cognizant SERI collaborator. This document is a report of progress of the first few months of effort and is not intended to present a completed piece of work. The report is to be included in the Proceedings of the Absorber Coatings Conference held in Boulder, Colo., in January 1979. The initial results document encouraging progress for incorporating an oxygen-18 isotopic label on black chrome. Further reaction in oxygen-16 and analysis of the samples should provide the information needed to understand the mechanism of degradation of black chrome.

The authors are pleased to acknowledge the contributions of two SERI scientists: Pat Call, who suggested study of the problem, and Keith Masterson. Both have offered suggestions, provided thoughtful comments, and furnished valuable information as progress has been made.



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SERIO 

PREPARATION AND DEGRADATION OF REACTIVELY EVAPORATED BLACK CHROME

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ABSTRACT

Preliminary results are described for the preparation of black chrome films by reactive evaporation of chromium in oxygen-18. Chromium coated tungsten rods and an oxygen diffuser are used in a conventional bell jar system to form films up to 110 nm thick. Chromium, black chrome, or Cr_2O_3 films are deposited depending on the chromium flux and steady state oxygen pressure. The films are topographically smooth, but are porous since they range up to 2.5 times the thickness expected for the bulk density. An ISS spectrum is shown of a successfully labelled film with 73% oxygen-18. The valence states of Cr^{+3} and Cr^0 , deduced from ESCA at various ion etched depths below the surface, are consistent with Cr in a Cr_2O_3 matrix.

INTRODUCTION

Electrodeposited black chrome films have desirable optical properties for use as selective solar absorber coatings in applications up to ca. 300°C [1-4]. It has been observed that degradation of the optical properties occurs between 250-400°C [3, 4], but the mechanism of this process is not understood [4]. The purpose of this work is to prepare isotopically labelled reactively evaporated black chrome films and to establish that the films have optical properties similar to those of electrodeposited films. If successful, study of the degradation of the films in oxygen-16 could then be made using gravimetric, optical, SEM, and surface analysis techniques to elucidate the degradation mechanism. Previous work on reactively evaporated black chrome [5] and

rf sputtered films [6] showed the optical properties are comparable to those of the electrodeposited material. Reactive evaporation was chosen as the preparation method because it can be easily adapted to an apparatus that permits the simultaneous measurement of mass change, optical transmittance, and reflectance [7]. Since this project began a few months prior to this conference, only the initial progress of preparing and characterizing the films can be reported.

EXPERIMENTAL

For the preparation of isotopically labelled reactively evaporated black chrome, a standard bell jar vacuum station (Fig. 1), was equipped with feed-throughs for evaporation of chromium from coated rods. To control the uniformity and extent of the oxygen reaction of the chromium flux [5], a circular diffuser tube with holes through the outer wall was erected between the substrate and evaporation source. Oxygen-18 was backfilled into the chamber through a leak valve attached to the $^{18}\text{O}_2$ supply flask. Steady state ion gauge readings ranging between 10^{-3} to 5×10^{-2} Pa [5] were easily obtained by using the leak valve and partially opening the main valve to the diffusion pump. The mass of deposited material, chromium oxide and chromium, was measured with a crystal oscillator centered in the substrate holder. The initial films were non-uniform in their depth distribution of chromium oxide and chromium, so a rate controller operating with feed-back from the thickness monitor was added. Deposition rates were typically 0.2nm/s. The substrates are located 46 cm (18 in) above the source to provide a thickness uniformity of about 1% in the films.

Composition in depth profiles were obtained using ISS, SIMS, AES and ESCA surface analysis techniques with continuous or incremental ion etching. The ISS data were obtained with a 3-M Model 520 ion scattering spectrometer. Physical Electronics units were used for the ESCA, AES, and SIMS profiles.

The topographical features of the films were determined from SEM photographs made at the Denver Research Institute. The thickness of the films was estimated with an alpha-step profilometer.

RESULTS AND DISCUSSION

Five sets of films ranging in thickness from 20 to 110 nm were prepared at ion gauge readings of 10^{-3} to 5×10^{-2} Pa in a steady state flow of oxygen-18. At the lowest gauge reading, almost pure chromium is deposited and at the highest gauge reading, almost pure Cr_2O_3 is deposited. Thus, control of the gauge reading during reactive evaporation provides the possibility of varying the mixture of Cr in Cr_2O_3 , and confirms the results of Hahn [5].

Using SEM photographs, all films were found to be topographically smooth ranging from chromium to chromic oxide. This is in contrast

with electrodeposited black chrome which exhibits varying degrees of topographical roughness. Films containing the oxide had varying degrees of porosity, as deduced by comparing measured thicknesses with those calculated from the mass deposited and bulk densities. Depending on the $\text{Cr}_2\text{O}_3/\text{Cr}$ ratio prepared, the increase in thickness ranged up to about 2.5 times that expected for the bulk density. No assessment of the chromium particle size in the films has been attempted, but to achieve those typically reported by Ignatiev, et. al. [8], preparation by reactive evaporation in argon and oxygen [9] could be adapted to the present scheme as well as to the apparatus described [7].

From composition in depth profiles, the films were generally found to consist only of chromium and oxygen (AES, ESCA, and ISS), although traces of Na, Mg, Al, Fe and Si were detectable using SIMS. The indicated impurity concentration would be less than 0.1%. The initial films were not uniform in the oxide/metal mixture from the surface to the substrate interface. Oxide concentrations were higher at the surface and interface. The surface oxide probably results from room temperature oxidation during transfer in air. The increased oxide content at the interface most likely is a kinetic effect as the deposition process is building up to the steady state rate of reactive evaporation. Neither of these effects are expected to be of importance when films are prepared in situ on a substrate suspended from a microbalance [7] for studying the reaction of black chrome in degrading gases.

Analysis with ESCA showed that only Cr^{+3} and Cr^0 oxidation states were present, in agreement with a recent analysis of electrochemically deposited black chrome [8]. Furthermore, the ESCA spectra showed that the $\text{Cr}^{+3}/\text{Cr}^0$ ratios were larger where the oxygen content of the films was greatest. Some care must be exercised in drawing conclusions about the quantitative ratios of $\text{Cr}_2\text{O}_3/\text{Cr}$ present in the films [8] because of the action of bombarding ion beams on the valence of exposed chromium [10]. The model of chromium particles in a chromium oxide matrix, proposed by several previous investigators, is qualitatively supported from our composition in depth profiles and the analyses of ESCA, AES, SIMS and ISS spectra.

A most important goal of this project was to prepare black chrome with an oxygen-18 labelled oxide. This has been achieved as shown by the ISS spectrum in Fig. 2. The $^{18}\text{O}/^{16}\text{O}$ peak height ratios [11] indicate that 73% of the oxygen content is oxygen-18, which is greater than that achieved for copper films thermally oxidized by heating in oxygen-18. The tungsten peak in Fig. 2 resulted from continued heating of the chromium coated tungsten rods after the chromium was exhausted. The volatility of tungsten oxides is a well established phenomenon in high temperature-high vacuum technology. The tungsten contamination can be (and has been) eliminated from other film preparations by terminating the reactive evaporation before the chromium coating on the rods is exhausted.

In conclusion, the initial goals of this project have been achieved. Black chrome films, labelled with an oxygen-18 isotope, have been prepared up to "thicknesses" of 110 nm. The films consist of $\text{Cr}_2\text{O}_3/\text{Cr}$ mixtures, contain less than 0.1% impurities, are topographically

smooth, but are porous. The desired ratios of Cr_2O_3 to Cr can be obtained by varying the oxygen partial pressure during reactive evaporation, a technique applicable for depositing black chrome films in situ on substrates suspended from a microbalance.

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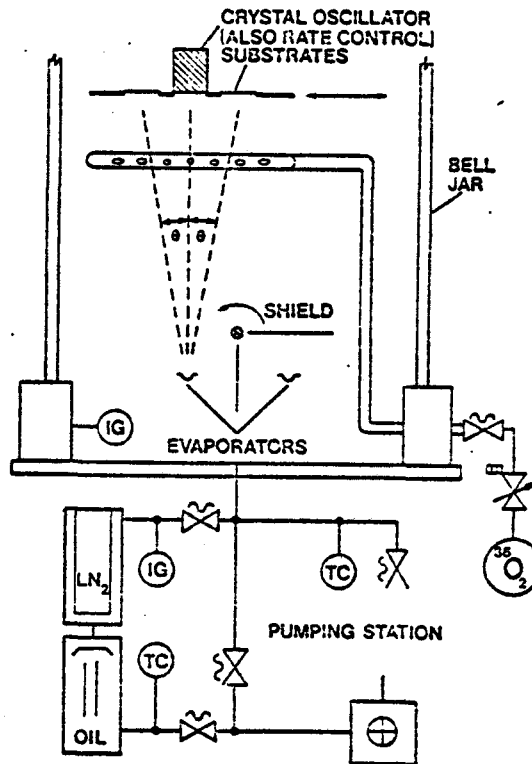
REFERENCES

1. G. E. McDonald, "Spectral Reflectance Properties of Black Chrome for Use as a Solar Selective Coating," *Solar Energy*, 17 (1975) 119.
2. D. Mattox, "Application of Thin Films to Solar Energy Utilization," *J. Vac. Sci. Technol.*, 13 (1976) 127.
3. R. B. Pettit and R. R. Sowell, "Solar Absorptance and Emittance Properties of Several Solar Coatings," *J. Vac. Sci. Technol.*, 13 (1976) 596.
4. R. R. Sowell and R. B. Pettit, "Thermal Aging of Electrodeposited Black Chrome," *Proc. DOE/DST Thermal Power Sys. Workshop*, 6-8 Dec. 1977, SERI, Golden, CO.
5. R. E. Hahn, "Optical Properties of Chromium Oxide Films and the High Temperature Stabilization of Silver Films for Photothermal Solar Energy Conversion," Ph.D. Thesis, U. Arizona (1976) pp. 84 ff.
6. J. C. C. Fan and S. A. Spura, "Selective Black Absorbers Using rf-Sputtered $\text{Cr}_2\text{O}_3/\text{Cr}$ Cermet Films," *Appl. Phys. Lett.*, 30 (1977) 511.
7. E. T. Prince, H. F. Helbig and A. W. Czanderna, "Apparatus for the Simultaneous Measurement of Mass Change, Optical Transmittance and Reflectance of Thin Films," *J. Vac. Sci. Technol.*, 16 (1979) 244.
8. A. Ignatiev, P. O'Neill and G. Zajac, "The Surface Microstructure Optical Properties Relationship in Solar Absorbers: Black Chrome," *Solar Energy Materials*, 1 (1979) 69.
9. C. G. Grangvist and R. A. Buhrman, "Ultrafine Metal Particles," *J. Appl. Phys.*, 47 (1976) 2200.
10. N. S. McIntyre, D. G. Zetaruk and D. Owen, "X-ray Photoelectron Studies of the Aqueous Oxidation of Inconel-600 Alloy," *Appl. Surface Sci.* (In Press).

11. A. W. Czanderna, et al., "Ion Scattering Analysis of Copper Films Oxidized in ^{18}O ," J. Vac. Sci. Technol., 14 (1977) 227.

FIGURE 1

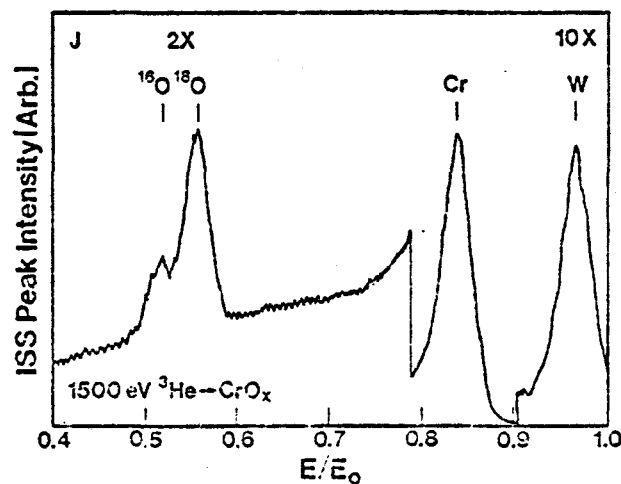
Schematic of a High Vacuum Bell Jar System with Components for the Reactive Deposition of Black Chrome Films.



Deposition System and Pumping Station

FIGURE 2

ISS Spectrum of a Black Chrome Film Prepared in Oxygen- ^{18}O at an Ion Gauge Reading of $7 \pm 2 \times 10^{-3}$ Pa.





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