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CHEMICAL VAPOR DEPOSITED MOLYBDENUM FILMS FOR USE IN PHOTOTHERMAL CONVERSION*

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Abstract

High infrared reflectance, coupled with high solar absorptance, is required for efficient photothermal conversion. Converters can be fabricated by depositing an absorber on a highly reflecting metal. The absorber functions in the visible, yet becomes transparent in the near infrared, allowing the metal to suppress the thermal emittance. Economic considerations demand the use of thin films, rather than bulk materials. The thin film reflector must be capable of withstanding high temperatures of operation. Compatibility of the reflector with the substrate below, and the absorber above, is required for long-time service. Highly reflective silver films suffer reflectance losses by agglomeration, and require stabilization layers. Refractory materials such as molybdenum avoid agglomeration at temperatures of operation of photothermal converters. Unlike other deposition methods, chemical vapor deposition (CVD) can produce molybdenum films with an infrared reflectance rivaling that of bulk molybdenum. CVD is a non-vacuum based technology with potential for sequential through-put fabrication. Studies are being undertaken to determine how sensitively the reflectance reacts to inclusions of impurities into the molybdenum. Thin film passivators deposited on the molybdenum prevent reflectance losses induced by oxidation, and insure high temperature survival of optimal reflectance. Complete converter stacks have been annealed at 550°C for over 1000 hours in air.

Introduction

Surfaces designed to intercept incident radiation in photothermal converters should satisfy several requirements. They must first possess a spectral profile that is properly matched to the solar emission and thermal reradiation properties by providing a high solar absorptance (a) and a low thermal emittance (e). Second, because large areas must be intercepted, the surfaces should consist of thin films that avoid the expense of bulk materials. Third, they must withstand elevated temperatures without deterioration of their optoelectronic characteristics.

Absorber-reflector tandem stacks previously produced at the Optical Sciences Center[1] consisted of thin silver layers overcoated with silicon. The combination of the high infrared reflectance of silver with the high infrared transparency of silicon gives the stacks a low infrared emittance. However, thin silver films tend to agglomerate and thereby lose their high reflectance at temperatures above 250°C. This problem can be solved by using complex stabilization layers,[1] and can be completely avoided if silver is replaced with a refractory metal such as molybdenum.

The high temperature stability of molybdenum can be utilized only if the thin films also have the following properties. The films must have a sufficient reflectance, if possible approximating that of bulk molybdenum. (The difference between the reflectance of bulk molybdenum and silver is only two percent at 10 microns). Without excessive preparatory effort, films deposited by evaporation and sputtering fall short of this requirement.[2] In contrast, chemical vapor deposition (CVD) is capable of producing films of high reflectance, even with one atmosphere pressure in the reaction chamber.[3] A comparison of the reflectances of molybdenum films produced by different deposition systems is shown in Fig. 1.

CVD techniques are well established for specific applications in the semiconductor devices and atomic energy fields. In all of these areas, little or no attention has been paid to the optical properties of the resulting layers and their dependence on CVD process parameters.[4,5] Once the technology of producing CVD films of high optical quality is developed, new high temperature applications for them will appear in the thin film industry. The following two sections of this paper discuss the production and characterization of these CVD molybdenum thin films. The final sections discuss additional properties required of the films, specifically the passivation of molybdenum thin films against oxidation and their incorporation as a component of photothermal converter stacks.

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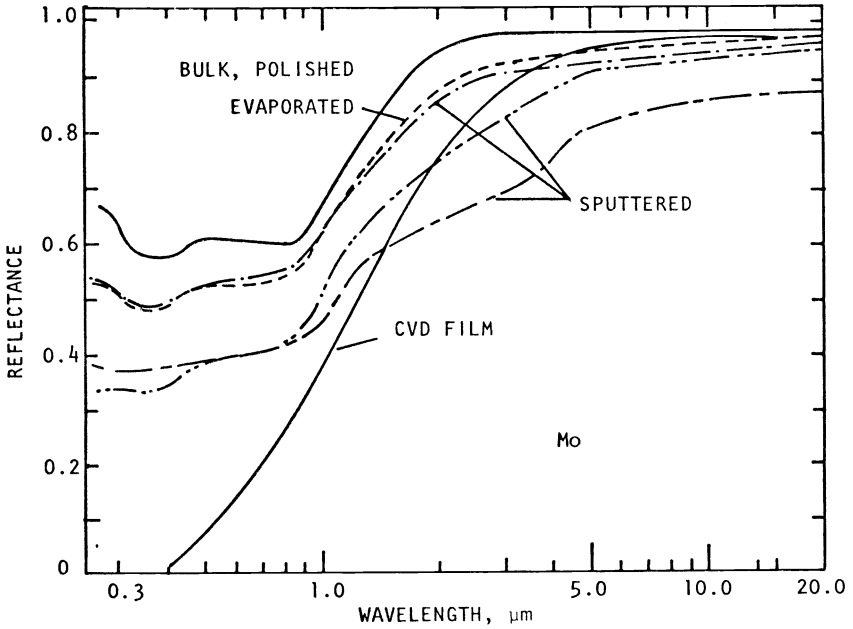


Fig. 1. Reflectance of evaporated,[2] sputtered,[2] chemical vapor deposited,[3] and bulk molybdenum.

Deposition of CVD Molybdenum

In this study, the following two reactions were selected for the CVD of molybdenum: the thermal decomposition of $Mo(CO)_6$ (the carbonyl process[6,7]) and the hydrogen reduction of $MoCl_5$ (the chloride process[8,9]). Table 1 summarizes the deposition parameters used for each reaction.

Table 1: Comparison of the process parameters for the two Mo deposition systems.

Reactant	Temperature	Pressure	Secondary Reactants
$Mo(CO)_6$	250°C - 600°C	0.1 Torr - 1 atm	H_2, H_2O, O_2 or CO_2
$MoCl_5$	500°C - 900°C	1 atm	O_2 or H_2O

The idealized reaction for the deposition of molybdenum from molybdenum carbonyl is:

$$Mo(CO)_6 \rightarrow Mo + 6CO\uparrow \quad (1)$$

There are two competing reactions which could cause the resulting film to be contaminated with oxides, carbides, or oxycarbides.[10] The first is the incomplete decomposition of the carbonyl molecule, which is a kinetically controlled process. The second involves the reaction of the growing film with some of the carbon monoxide generated by reaction 1. This is shown below as equation 2.

$$2CO \rightleftarrows C \text{ (in the film)} + CO_2\uparrow \quad (2)$$

The incomplete decomposition process, however, is reported to dominate at 1 atmosphere pressure and at temperatures below 800°C.[10] It is possible to remove carbon from the film by adding gases such as CO_2 to the reaction chamber. Additions of CO_2 decarburize the film following equation 2, from right to left. In order to produce films of various oxygen and carbon content, depositions are being carried out as a function of temperature, pressure, and in the presence of secondary reactants.

Deposition from molybdenum chloride involves the following primary reaction:

$$2MoCl_5 + 5H_2 \rightarrow 2Mo + 10HCl\uparrow \quad (3)$$

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Molybdenum chloride is a hygroscopic and highly air sensitive compound which is usually contaminated with MoO_2Cl_2, $MoOCl_4$, and $MoOCl_3$. These oxychlorides also decompose and produce oxides within the growing film according to:

$$xMoO_2Cl_2 + xH_2 \rightarrow 2MoO_x + (x-2)Mo + 2xHCl\uparrow \quad (4)$$

Depositions using $MoCl_5$ of the highest available purity produce films with the lowest levels of oxygen contamination. If this same high purity $MoCl_5$ is used in the presence of controlled amounts of oxygen, films of various oxygen compositions are produced.

Variations of carbon and oxygen levels in the carbonyl films, and variations of the oxygen level in the chloride films affect the optical properties. Some of these effects are discussed in the next section.

Film Characterization

Characterization of CVD molybdenum films can be based on optical, compositional, structural, and electrical measurements. Optical measurements include the infrared, near-normal, specular reflectance from 3-15 μm, and the determination of the optical constants, n and k. The following three paragraphs discuss correlations between the optical measurements, and the other three parameters used in the characterization. Two such correlations have been established.

Film composition is determined by Auger spectroscopy.[11] The relative atomic percents of the three major constituents, molybdenum, carbon and oxygen, is determined irrespective of their chemical state. Fig. 2 shows the correlation between the reflectance and composition of the films. The figure plots the molybdenum-carbon-oxygen ternary phase diagram as independent variables. An axis perpendicular to the paper plane representing reflectance has been projected onto the triangular base plane.

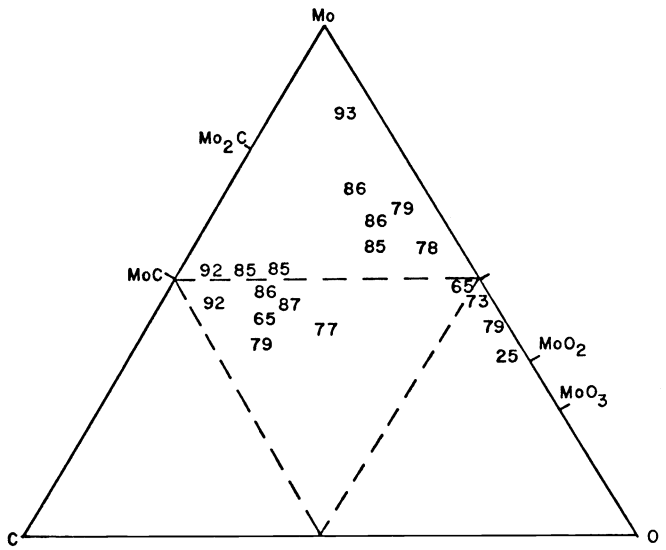


Fig. 2. Reflectance at 10 microns plotted within the molybdenum-carbon-oxygen ternary phase diagram.

Points within the triangle represent atomic percents. The $Mo(CO)_6$ process produces films whose compositions lie within the triangle's interior, while the $MoCl_5$ process locates films along the Mo-O axis. Films containing only 47 atomic percent molybdenum still reflect 87% of 10 μm radiation. This suggests that reflectance maxima at the metal rich corner of the phase diagram may not be the only maxima within the diagram. More points, generated by both molybdenum CVD systems, will be required to prove this hypothesis. These extra maxima would make the production of highly reflective molybdenum films by CVD more economical, since certain levels of contamination would not only be tolerable, but desirable. These speculations are substantiated by the fact that pure metals do not always reflect better than their compounds. Titanium nitride's reflectance increase over that of bulk titanium[12] is a case in point.

The structure of the films is determined by X-ray diffraction and transmission electron microscopy. X-ray diffraction complements the Auger measurement by distinguishing between the presence of contaminants as inter-

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stitials or compounds.

Figure 3 presents the second correlation between reflectance values and film composition. The horizontal axis represents a cut across the middle of Fig. 2. Points with higher reflectance values have been related with strong X-ray diffraction lines. This demonstrates that reflectance curves within the phase diagram are not only related to composition, but also to structure. Electron microscopy will determine the spatial distribution of these compounds.

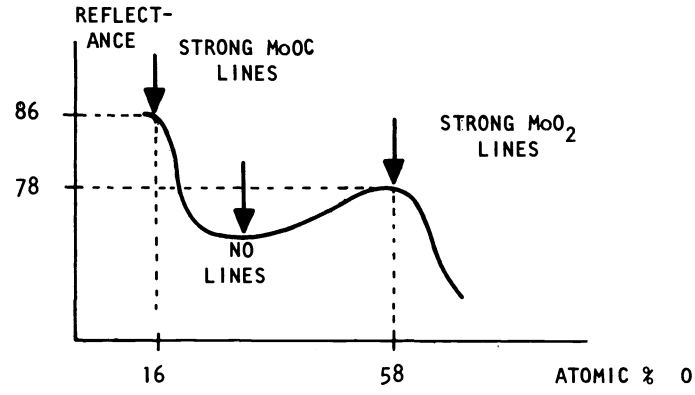


Fig. 3. Reflectance at 10 microns plotted as a function of oxygen composition. The arrows indicate oxygen percents for films with strong X-ray responses.

Electrical measurements include use of a four-point probe for determining conductivity, and a Hall effect apparatus for determining carrier concentrations. Combining these results will determine the mobility of the carriers. Making these measurements as a function of temperature may determine those effects responsible for reflectance maxima and minima. Combined with a measurement of the optical constants, these electrical measurements allow for a comparison of the optical and electronic conductivities, and the scattering mechanisms involved.

Passivation of CVD Molybdenum Thin Films

The ease with which molybdenum oxidizes in air at 500°C is well known. A CVD thin molybdenum film is completely converted to the oxide within 10 minutes of heating at 500°C in air. The infrared reflectance is destroyed as a result. Recent studies at the Optical Sciences Center[13] have established that CVD thin films of molybdenum can be passivated with Al_2O_3 (50 nm) or Si_3N_4 (38 nm). These thin overcoats allow the metal films to withstand temperatures of 500°C for 160 minutes in air without loss of infrared reflectance.

Stack Fabrication and Testing

The molybdenum reflector, silicon nitride passivator, and silicon absorber are easily integrated to form a photothermal converter fabricated by chemical vapor deposition. A schematic diagram of the complete converter is shown in Fig. 4.

The CVD sequence allows for an economically large flow-through production system, operating at 1 atmosphere. However, the process relies on the molybdenum film's survival during the subsequent Si_3N_4 and silicon depositions. By producing a large sample set of complete converters, etching the silicon away, remeasuring reflectance values, and then comparing to original values, it can be stated that the molybdenum does indeed survive all production steps. In addition, stacks have been annealed for over 1000 hours at 550°C in air. These rigorous tests have determined one encouraging fact, besides identifying two failure modes. First, the molybdenum reflector survives annealing if the overall stack retains its integrity. This is evidenced by its high reflectance after post anneal etching of the silicon.

Two failure modes are prominent: cracking caused by the crystallization of the original amorphous silicon layer, and the occurrence of raised areas in the top surface of the converter. These areas have tentatively been related to pinholes in the silicon layer which allow oxygen to diffuse to the molybdenum surface and form oxides.

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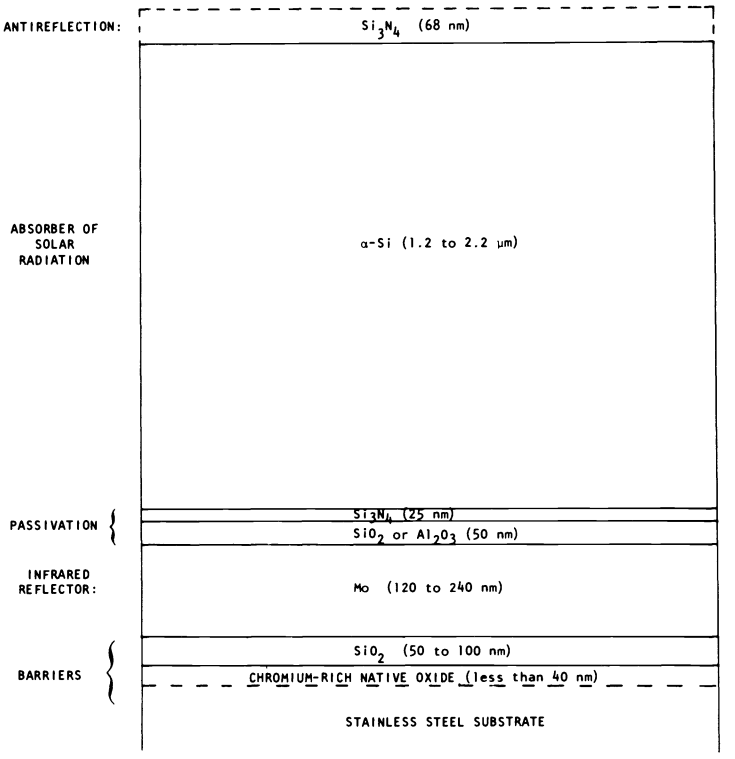


Fig. 4. Schematic diagram of a complete photothermal converter.

Conclusions

1. The infrared reflectance of CVD molybdenum thin films is affected by the incorporation of various amounts of carbon and oxygen.

2. Reflectance extrema exist within the Mo-C-O phase diagram.

3. Occurrence of the carbon and oxygen contamination in the form of molybdenum compounds, as evidenced by X-ray diffraction, has been correlated with reflectance maxima.

4. CVD molybdenum films can be passivated, with thin overcoats of Al_2O_3 or Si_3N_4, against infrared reflection losses caused by oxidation. These passivators are effective for over 160 minutes exposure to air at 500°C.

5. Molybdenum reflectors fabricated by CVD as part of the manufacture of an entire selective stack survive the process without deterioration of their infrared reflectance.

6. Anneals of the entire stack for over 1000 hours at 550°C in air demonstrate that the molybdenum reflector is compatible with the other components of the converter, if two failure modes are avoided.

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