Preparation of High Efficient Solar Absorbers by Low Pressure Sputtering

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Abstract

Multilayer solar power absorber was implemented by a novel DC sputtering method for metal deposition at low pressures. A Mo-Zn-Mo multilayer system was deposited in argon atmosphere using pressure of 0.1-1 mTorr and sputtering voltage of 1,500-2,000 V. A lower Mo sub-layer represents a high reflective film, providing high adhesion with substrate, glass or metal. A thick Zn interlayer, deposited by flash sputtering, creates a high porous absorbing layer. An upper Mo coating protects the system and stabilizes it. This black multilayer system uses as an absorbing coating and may be applied for solar absorbers fabrication. High deposition rate and reproducible process due to the sheet plasma sputtering technology was obtained. Preliminary measurements showed high thermal stability of the novel multilayer solar absorbers in vacuum conditions.

1. Introduction

Widespread utilization of thermo-solar converters to convert solar radiation into electricity using concentrating systems, requires an increase in the working temperature. To meet these requirements, new efficient coatings for solar absorbers must be made, coatings for heat generation. This class of coatings is characterized by high absorption capabilities of solar energy and low emittance at longer wavelengths. Thus theses coatings generate high temperatures. Solar heat concentrators, water heaters, and surface temperature control are common applications for them. One way to increase the operating temperature of a solar collector is to apply an effective selective coating which has both high solar absorbance and low thermal emission at high temperatures of up to 500 ^{0}C. For this goal, the solar absorber surface must have low reflectance at wavelengths lower than 3 μm and high reflectance at wavelengths higher than 3 μm. There are various types of such solar absorbing structures.

The most efficient absorbers at high temperatures are multilayer absorbers consisting of a sequence of metal and dielectric layers and metal-ceramics (cermet) absorbers, made of metal-ceramic composites on a metal substrate [1]. These coatings consist of a cermet layer, which contains absorbing species in a dielectric matrix, or single or multiple layer designs. An example to the cermet approach is a nickel-silicon oxide black material that can be easily evaporated. Another example is the Cr / Cr_2O_3. One design consists of a thin layer of Ti immersed between two TiO_2 layers. Multi-layer structures such as Al_2O_3 / Mo /Al_2O_3 have been developed for stability in high temperatures. Intrinsically selective absorbing materials such as ZrB_2, exist as well. Ge and Si layers in aluminum absorb short wavelengths and reflect above 2000 nm and 1000 nm respectively [2]. Also, the heat absorbing multilayer structures of HfO_x / Mo / HfO_2 were made for solar absorbing applications due to the attractive properties of the hafnium oxide [3]. The function of absorbing layer may be realized using semiconductor materials coated with correcting and protecting layers. If this semiconductor layer is porous or textured, the absorption will increase. Thus, a thick porous conductive layer may successfully play a role in a solar absorber. For this reason, it is necessary to provide such a thick absorptive porous layer, with a reflecting sublayer and then to seal the porous layer by a transparent conductive layer. For this role, a multilayer metal system may be applied.

In this present work, we have designed a Mo / Zn / Mo multilayer metal, high temperature, absorbing system for solar selective applications. The most suitable method to manufacture effective high-temperature absorber is by sputtering, due to the high energy of the deposited particles. The pressure of the sputtering gas plays an important role in the transport of sputtered material to the substrate. The most pure and stoichiometric films may be obtained at low pressures since only at such low pressures the ballistic type of the mass transfer may be realized. In our work we used a home-made DC sputtering setup, which is able to deposit thin metal films at very low pressures, 0.1-1 mTorr. Thus, the main goal of our work is to make high effective thermal absorbers using low pressure DC sputtering system.

2. Experimental details

Experiments with low-pressure plasma sputtering were done using a laboratory triode sputtering setup equipped with a standard two-stage vacuum system, providing residual vacuum of $2\text{-}3\times10^{-5}$ Torr [4]. This setup enables deposition of thin films using a sheet shaped plasma discharge. A specific form of plasma discharge is achieved by using a concentrating magnetic field of ~ 80 Oe and a linear grounded cathode deflector creating the plane shape of the plasma discharge. Pure metal sputtering targets of various metals, 2 inch in diameter and of 0.125 inch thick, were used. The distance between the sputtering target and substrate was about 50 mm. Sputtering voltage in all experiments was ~1.8 kV. All metal thin films were deposited at pure argon atmosphere at 0.1-1.0 mTorr. Zn coatings were deposited using the so called “flash” sputtering process. At a certain concentration, the sputtered Zn atoms excite in plasma and grow on the substrate a grey coloured porous conductive layer, in high rate of 1 μm per minute. An upper semi-transparent Mo coating changes this colour into black.

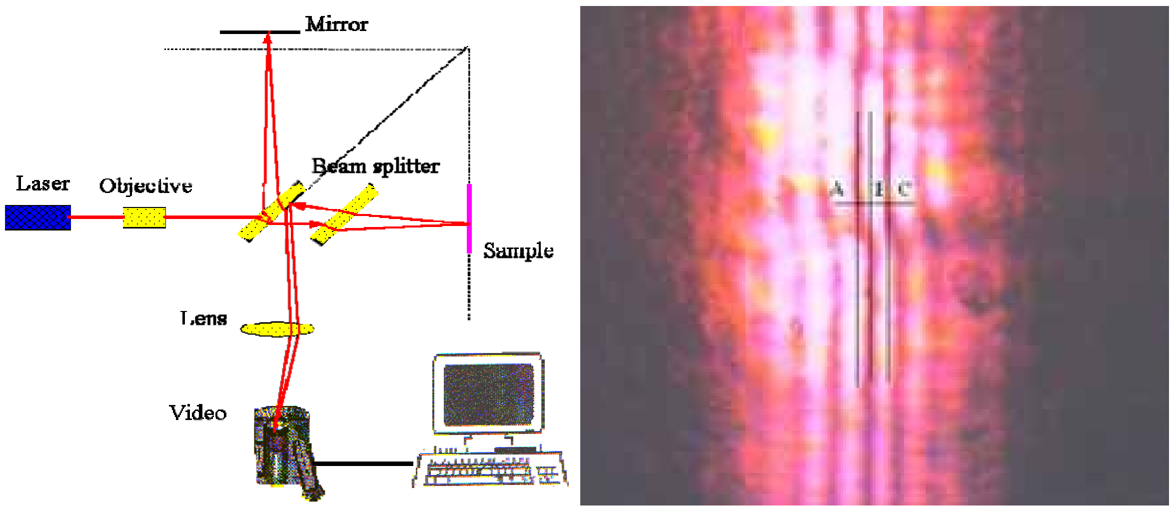
Typical parameters of the triode sputtering process are presented in tables 1.

Table 1. Typical parameters of sputtering processes

Number	Parameter	Symbol	Units	Value
1	Argon (work) pressure	P_{Ar}	Torr	$(0.1\text{-}1)\times10^{-4}$
2	Electromagnet current	I_H	A	4
3	Cathode current	I_C	A	15.0-15.8
4	Discharge current	I_A	A	3
5	Voltage drop on plasma	V_A	V	30-35
6	Sputtering voltage	V_T	V	~1800
7	Ions current	I_T	mA	18-28

All the parameters in this table, except the anode voltage and the target current are kept independently of each other. The anode voltage is the voltage drop along the plasma discharge between the thermo-cathode and the anode. The target current represents the ion flux of the ionized argon atoms impinging the sputtering target. The substrate temperature was measured while sputtering and found to be less than 100 ^{0}C.

Glass slides and pieces of p-type [100] single-crystalline silicon were used as substrates in our experiments. A standard four-point probe method was applied to measure the sheet resistance of the deposited thin films. The surface structure was studied using a computerized metallurgical microscope “Nicon-Optiphot 100“ with optical magnification of up to ×1600. Measurement of the Mo films thickness was provided using a home-made computerized Michelson micro-interferometer [5]. Figure 1 illustrates the measurement system and estimation of the thickness:



(b)

Fig.1. Mo thin films thickness measurements: (a) Thickness contactless measurement scheme, (b) Interferential picture of the measured Mo film deposited in 30 minutes.

Interferential images were obtained using a red laser of "ThorLabs Inc." with 670 nm wavelength. Measurements were provided for a thick enough Mo film, deposited on a polished surface of single-crystalline silicon slice, to provide high reflection and good interference picture. The thickness of the film was calculated as follows:

$$d = \lambda/2 \cdot (B - A)/(C - A) = 335 \cdot 12/33 \approx 122 \text{ nm} \quad (1)$$

here λ is the laser wavelength, (C – A) is the wavelength measured in pixels on the picture, and (B – A) is the displacement of the interference fringes on the step, created by the molybdenum film, on the reflecting silicon substrate. The thickness of the thin Mo film was calculated from the micro-interferometer measurements, in relation to the sputtering duration. Optical transmittance and absorbance were measured at wavelengths of 200-1100 nm using the UV-2800 UV/VIS spectrophotometer of UNICO. Reflectance of the coatings was calculated using the conservation energy principle:

$$R + A + T = 1 \tag{2}$$

Where R, A, and T represent reflectance, absorbance and transmittance, respectively.

Reflectance of Mo layers and absorbance of multilayer systems were measured using FTIR spectrophotometer Tensor 27 equipped by the module PMA50 of Bruker.

3. Results and discussions

The main goal of the presented work was to create a multilayer thin film system that can provide both high solar energy absorbance and low thermal emittance at high temperatures. For this goal, various metal thin films were deposited on glass to compare their optical behaviour. Part of the metal thin films was obtained by vacuum evaporation. These metal films were: Al, Ag, Ti, Sn, Cu, Zn. Moreover, the Zn thin films, with the bright surface, were deposited only by thermal evaporation. Our goal was to select the most suitable metal coating for the system. Measurements were done using the reflectance characteristics. Typical reflectance characteristics calculated according to relation (2) for various metal films, are presented in figure 2.

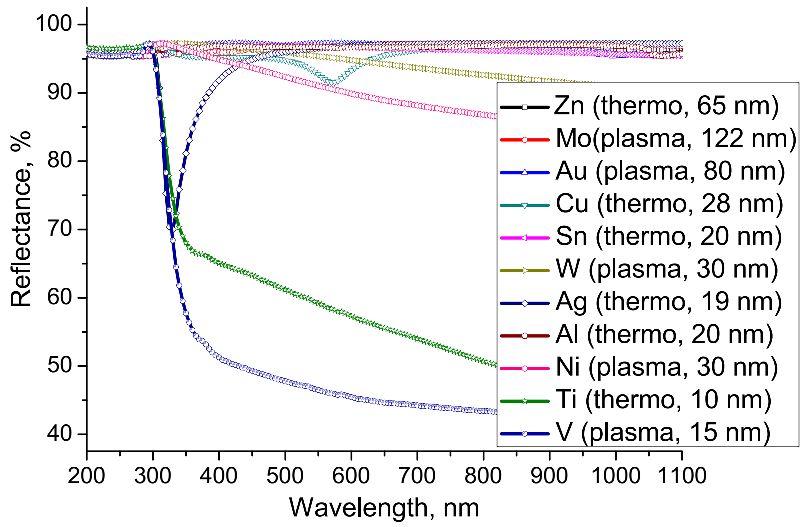


Fig. 2. Typical reflectance characteristics of thin metal films

As shown in Fig. 2, the obtained characteristics enable choosing the type and material of the first reflective coating deposited directly on the substrate. Analysis of this figure shows that only two metals have maximum reflectance in the visible range: these metals are Zn and Mo. One of the requirements to the first layer deposited on substrate is high adhesion. Mo, as a transition and refractive metal makes good adhesion to the substrate. On the other hand, all films deposited by thermal evaporation had lower adherence than the metal films deposited by sputtering.

Figure 3 presents reflectance characteristics of thin Mo films of different thicknesses. As shown, the molybdenum films deposited for 30 min with thickness of approximately 120 nm provide high reflectance in the measuring range and high adhesion to the glass substrate. At the same time, a thin

Mo coating of ~ 4-10 nm enables to introduce solar irradiation into the absorbing multilayer system and transfers it into heat. Application of the Mo film as an upper coating is preferred due to resistance of molybdenum to the oxidation at room temperature [6].

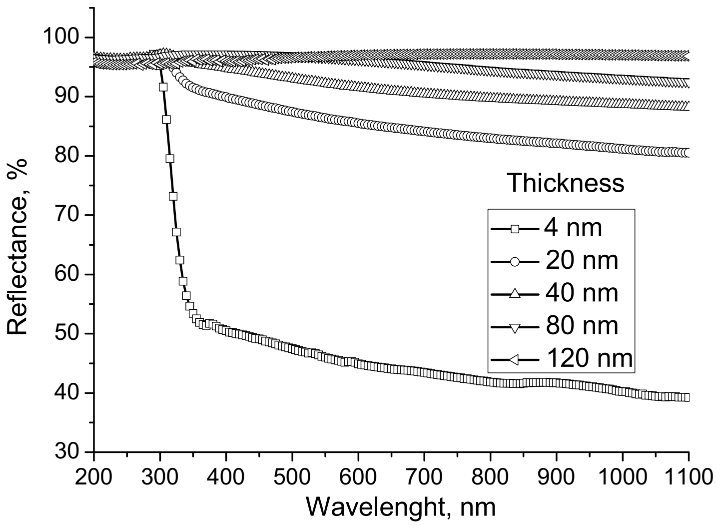


Fig. 3. Reflectance of Mo thin films versus thickness

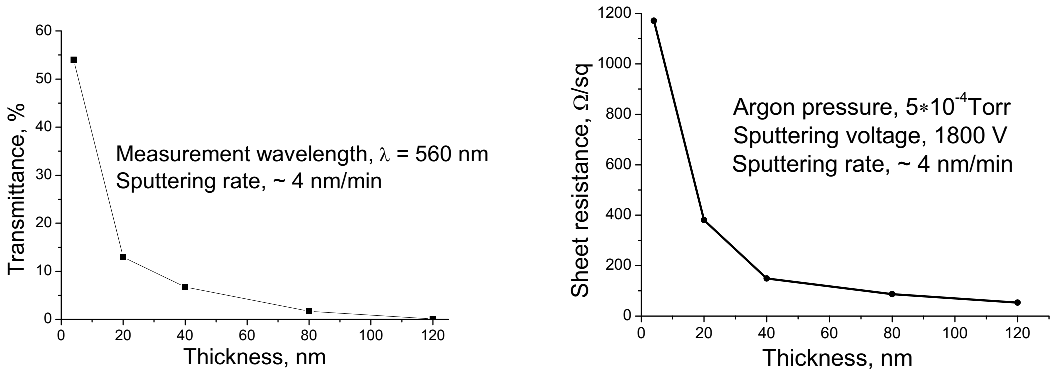
The second layer in our multilayer system was Zn which was deposited by a novel combined, flash-sputtering method. While sputtering, Zn particles were ionised and excited in the plasma, a fact which changed the plasma's colour from violet, in pure argon, to bright blue due to recombination and relaxation of the Zn ions and exited atoms. Growth of Zn films occurs in high rate and the deposited film looks like fully opaque with grey colour. Figure 4 represents an external view of various deposited thin films.

(a) (b) (c)

Fig. 4. External view of deposited thin films (×1600) : (a) the Mo high reflective sub-layer; (b) the high-absorbing porous Zn inter-layer; (c) the selective absorbing multi-layer system Mo/Zn/Mo.

The images presented in fig. 4, show the bright metal character of the pure Mo film and a developed porous surface on the pure Zn film. The Zn surface coated by very thin Mo coating changes the colour. It transmits light into the Zn absorptive layer without letting it go back. The light reflected from the lower Mo surface returns to the Zn layer and absorbs as well. Thus, all the absorbed light transforms into heat. The upper thin Mo film ensures a black colour and stable properties of the multilayer system due to the high resistance of the Mo coating to environmental conditions. Moreover, the developed surface of the upper Mo film repeats the Zn interlayer and provides surface texturing. Such texturing decreases the reflection from the upper surface of the system. As known, in such cases the irradiated surface may be considered as a collection of lots of individual black bodies which exhibit an emissivity of around 0.85 [7]. Preliminary measurements showed high thermal stability in vacuum conditions.

Figure 5 represents the dependence of the optical and electrical properties of the Mo films on thickness.



(a) (b)

Fig. 5. Dependence of Mo thin films properties on thickness: (a) Transmittance, (b) Sheet resistance.

Both characteristics, transmittance dependence and sheet resistance dependence on thickness, look very similar. Such behaviour of optical and electrical properties of thin metal films may be explained by the films' structure. Very thin films of molybdenum are the islet, i.e. the film is a random system of isolated islands of metal on the glass surface. The shape of these islands represents disks with diameters and heights defined by the substrate temperature while sputtering [8] and by the relation between the internal binding energy of the molybdenum and the binding energy of Mo with glass. More thin film has a higher resistance and higher transparency due to an increase of the distance between islands. Increasing the thickness of the films leads to a complete opaque. On the other hand, thickness increase leads to a sheet resistance decrease. However, resistivity of non transparent films can not reach the resistivity levels of bulk metal due to amorphous or nano-crystalline structures of the films which defined by high energy of sputtered metal particles. These particles can reach the substrate without collisions due to the high vacuum conditions in the sputtering chamber. Working pressure of 5×10^{-4} Torr provides a mean free path to the sputtered particles significantly more than the distance between target and substrate. Mean free path of particles may be calculated using the following approximation [9]:

$$L = 5\times10^{-3}/p = 10 \text{ cm} \quad (3)$$

Were L is the mean free path measured in cm and p is the working pressure measured in Torr. Comparing between the obtained L with the distance between target and substrate (see table 1) shows that a ballistic type of mass transfer is realized at our system while sputtering.

Figure 6 represents qualitatively the behaviour of a multilayer system: Mo /Zn /Mo designed for collection of solar irradiation for elevated temperatures. As shown, the deposited system has a low reflectance at wavelengths lower then 3 µm and a high reflectance at wavelengths higher than 3 µm. Reflectance characteristic of the multilayer collecting system shown in figure 6 was measured at room temperature and at 100^0C. Evidently, the cut-off may be higher or lower as it is dependent on the temperature. Operational temperature for the designed system is designed to be higher than 400^0C.

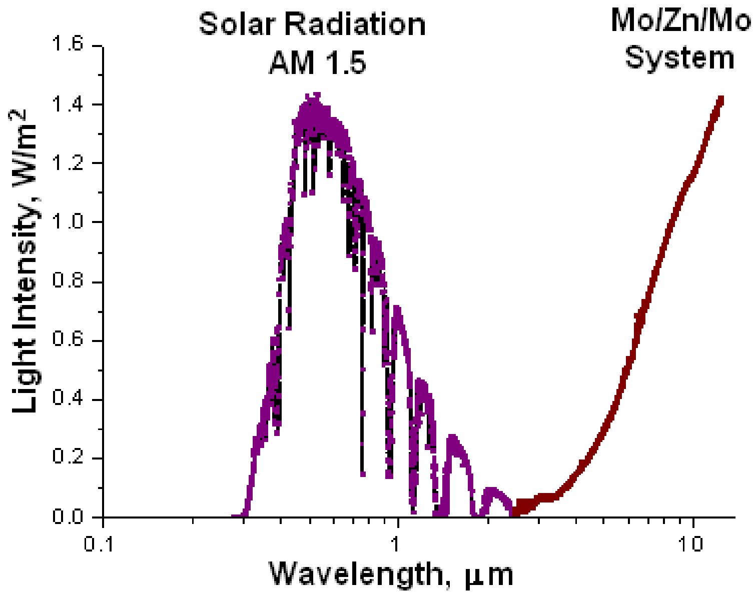


Fig. 6. Behaviour of Solar irradiation collecting system at low temperatures.

4. Conclusion

Feasibility proof of a multilayer thermal absorber consisting of: Mo-Zn-Mo thin layers built by a novel technology, was presented. Thickness of the layer was of ~120-150 nm, 1.5-2 µm, and ~5-10 nm, respectively. All layers constituting the collecting system were prepared by a novel sputtering method, enabling the deposition of various metal films in a reliable and reproducible process at a low sputtering pressure. This method provides ballistic type of mass transfer from a metal target to the substrate. This investigation shows that the low-pressure triode sputtering method enables deposition with high sputtering rate. Method enables deposit pure metal films and to build solar absorbers from these films.

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