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Plasmonic modes in molybdenum ultra-thin films suitable for hydrogenated amorphous silicon thin film solar cells

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Abstract

We have recently demonstrated that molybdenum ultra-thin films interposed between hydrogenated amorphous silicon (a-Si:H) and SnO₂:F transparent conductive oxide (TCO) in thin film a-Si:H solar cells show light trapping effects which enhance the solar cells performances. The effect of this improvement may be attributed to surface plasmon polariton (SPP) modes excited at the molybdenum interface by the solar radiation. In this paper we show direct evidence of such SPP modes in the case of the molybdenum/air interface by using the attenuated total reflection (ATR) technique, pioneered by Kretschmann, and we evaluate the dielectric constant of molybdenum at 660 nm.

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1. Introduction

Light trapping is a crucial issue of thin film photovoltaics (PV) [1], in particular for silicon based materials, given the very low absorption coefficient of silicon, which requires relatively thick layers to achieve sufficient absorption of the solar spectrum. Among the various approaches in recent years it has been put in evidence the potential offered by plasmonics [2-5]. Plasmonics [3] is based on the circumstance that many metals present a negative real part of the dielectric constant in the visible range of the electromagnetic spectrum. This, especially when the imaginary part of the dielectric constant is small, gives rise to a resonant scattering from metallic

nanoparticles embedded in a dielectric or a semiconductor (approximately when $\epsilon_m \approx -2\epsilon_s$, where ϵ_m and ϵ_s are the dielectric constants of the metal and of the semiconductor, respectively) or to surface plasmon polariton (SPP) modes in the case of planar metal / semiconductor interfaces, (when both $\epsilon_m\epsilon_s$ and $\epsilon_m + \epsilon_s$ are negative). In particular the SPP modes are longitudinal polarization waves of the metal free electrons at the interface which can propagate laterally along the metal/semiconductor interface for relatively long distances (also tens of microns in the visible range for suitable metals). They can therefore be considered similar to guided modes in a waveguide, i.e. essentially a light trapping effect for a thin film PV cells.

We have focused our attention to the use of SPP modes at the interface between a-Si:H and an ultra-thin film of molybdenum deposited on glass covered with a textured TCO layer of SnO₂:F to enhance light trapping. Molybdenum appears a good choice also because it provides a lower Schottky barrier height compared SnO₂:F [6] and improved (lower) recombination current in dark conditions [7]. In a previous paper we have shown that under suitable conditions of molybdenum deposition, a-Si:H solar cells show enhanced short circuit current, fill factor, reduced series resistance, and increased power conversion efficiency [8]. Such positive effects have been attributed to light trapping effects due to SPP modes at the Mo / a-Si:H interface.

The values of the Mo dielectric constant $\epsilon_{Mo} = \text{Re}(\epsilon_{Mo}) + i \text{Im}(\epsilon_{Mo})$ in the visible range are quite unclear. The value of $\text{Re}(\epsilon_{Mo})$ reported in [9] in one approach, from REELS measurements is very large and negative. Still in [9] but with another approach, from DFT calculations, it is concluded that $\text{Re}(\epsilon_{Mo})$ is positive. Another reference [10] also reports positive values of the real part of the Mo dielectric constant. Other experimental results [11] report negative values in the visible range, but with values in module that vary from 1 to 5. Clearly, since the occurrence of SPP modes requires negative $\text{Re}(\epsilon_{Mo})$, it is quite important in the present context to establish the value of ϵ_{Mo} .

In this paper we investigate the optical properties of the Mo thin film focusing on the SPP modes at 660 nm, i.e. at ≈ 1.85 eV, very close to the a-Si:H band-edge, the most relevant range of wavelengths for light trapping in a-Si:H solar cells.

Nomenclature

SPP	surface plasmon polariton
a-Si:H	hydrogenated amorphous silicon
TCO	transparent conductive oxide
ϵ_{Mo}	dielectric constant of molybdenum
θ_i	incidence angle at prism/glass interface
t_{Mo}	thickness of the molybdenum layer
$R_{Meas}^{\theta_i, t_{Mo}}$	measured reflectivity
$R_{Model}^{\theta_i, t_{Mo}}$	model reflectivity

2. Results and Discussion

Molybdenum thin films of nominal thickness of 50 nm, 20 nm, and 10 nm were deposited on glass by magnetron sputtering at 200 °C. SEM micrographs show that such layers are continuous and homogeneous with a roughness of a few nanometer. Sheet resistance shows a strong superlinear dependence on metal thickness, as reported in Table 1.

Table 1. Sheet resistance of ultra-thin Mo films on glass.

Mo thickness (nm)	Sheet Resistance (Ω / square)
10	116
20	29.4
50	6.93

Reflectivity of Transverse Magnetic (TM) or Transverse Electric (TE) modes from the glass side as a function of incidence angle was measured by using the ATR method [12] through a glass prism on which the Mo covered glass was attached, as sketched in Fig. 1. Light source was a solid state CW laser at 660 nm coupled with a linear polarizer. An index matching oil was used at the glass / prism interface to reduce interference fringes. Depending on the incidence angle and the polarization of light beam, the SPP mode at the molybdenum/air interface changes its intensity, and such dependence is monitored by measuring with a photodetector the intensity of the reflected light.

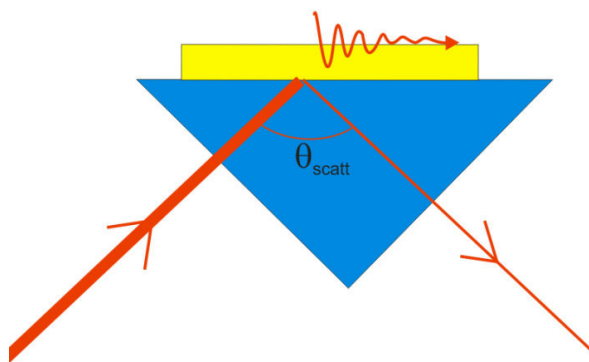


Fig. 1. Sketch of the used method to detect SPP modes: as proposed by Kretschmann [12], the reflectivity of TM and TE modes from the glass side as a function of incidence angle is measured through a glass prism on which the Mo covered glass is attached.

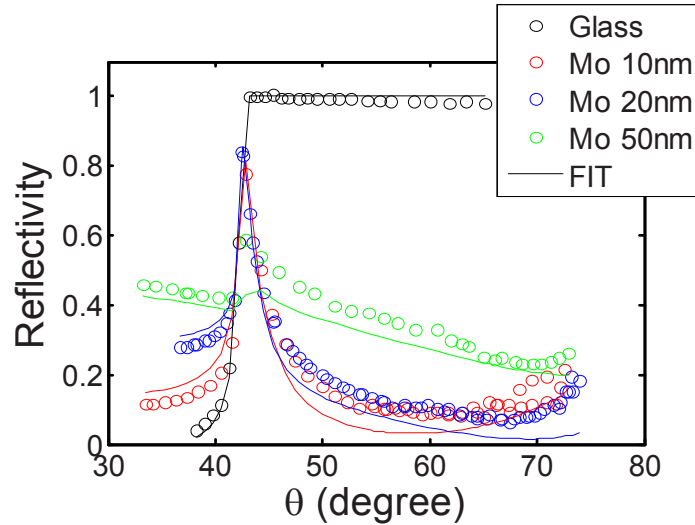


Fig. 2. Experimental data of reflectivity (open circles) for a reference glass sample and for three samples with various Mo metal film thicknesses, for TM polarized exciting beam. Best fit curve to the experimental data (continuous lines) are also reported.

Figure 2 reports the reflectivity experimental data (open circles) for the reference glass sample and for the three samples with various Mo metal film thicknesses, when the excitation is TM polarized. For the reference sample it is evident the onset of total internal reflection at the glass / air interface at an incidence angle of about 43° (i.e. the critical angle). In the case of TE modes (not shown), the reflectivity is higher than that of the TM mode and increases monotonically with the incidence angle. Best fit curve to the experimental data (continuous lines) are also reported. Calculation of the reflectivity curves is based on the Fresnel's equations for multi-layer system (see e.g. [15]). Such reflectivity depends on ϵ_{Mo} and on the glass refractive index n_{glass} , so we have performed a best fit to the experimental data to determine the values of both ϵ_{Mo} and n_{glass} . To visualize the domain of the best fit values one can plot the sum of the squares

$$\chi^2 = \sum_{\theta_i, t_{Mo}} (R_{Meas}^{\theta_i, t_{Mo}} - R_{Model}^{\theta_i, t_{Mo}})^2$$

where $R_{Meas}^{\theta_i, t_{Mo}}$, $R_{Model}^{\theta_i, t_{Mo}}$ are, respectively, the measured and calculated reflectivity for the Mo thickness t_{Mo} and incidence angle θ_i . One can visualize χ^2 as a function of the $\text{Re}(\epsilon_{Mo})$ and $\text{Im}(\epsilon_{Mo})$ parameters (Fig. 3, left), or as a function of n_{glass} (Fig. 3, right).

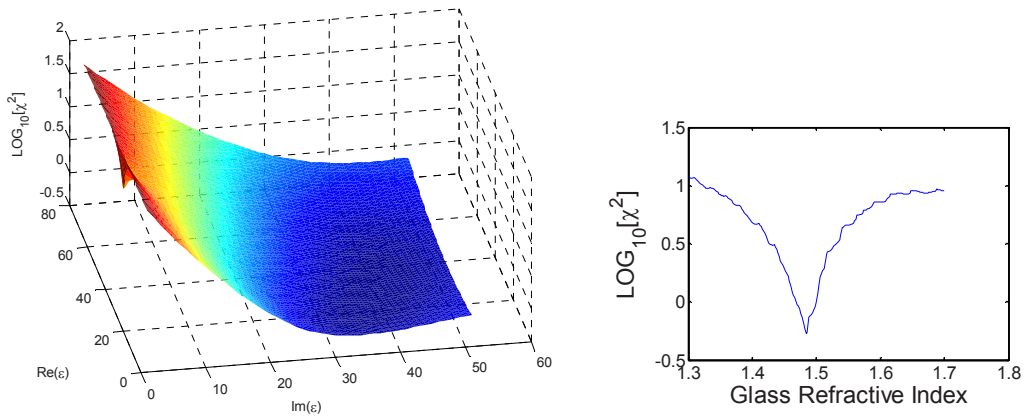


Fig. 3. (a) χ^2 as a function of the $\text{Re}(\epsilon_{Mo})$ and $\text{Im}(\epsilon_{Mo})$ parameters; $\text{Re}(\epsilon_{Mo})$ is varied in 70 steps from -10 to +10 (in units of the vacuum dielectric constant) while $\text{Im}(\epsilon_{Mo})$ is varied in 50 steps from 0 to +30. It is evident that the sensitivity of χ^2 to $\text{Im}(\epsilon_{Mo})$ is stronger, but nevertheless a clear minimum is present in the range of negative $\text{Re}(\epsilon_{Mo})$. (b) χ^2 as a function of n_{glass} .

From such plots it is evident that well defined minima are present (note the logarithmic scale for χ^2), and this gives us confidence about the reliability of the found values. The actual fit procedure has been performed by varying $\text{Re}(\epsilon_{Mo})$, $\text{Im}(\epsilon_{Mo})$, and n_{glass} and the best fit values corresponding to the minimum χ^2 are $\text{Re}(\epsilon_{Mo}) = -4.8 \pm 0.2$, $\text{Im}(\epsilon_{Mo}) = 22.2 \pm 0.1$ and $n_{glass} = 1.485 \pm 0.0025$ at 660 nm. The corresponding best fit reflectivity curves are reported in Fig. 2 (continuous line). The analytical curves reproduce quite well the experimental data.

The found $\epsilon_{Mo} = -4.8 + 22.2i$ at 660 nm is substantially different from the REELS and DFT values of ϵ_{Mo} , respectively equal to $\approx -80 + 15i$ and to $\approx +4 + 30i$, reported in [9]. Another reference [10] also reports a positive value of $\text{Re}(\epsilon_{Mo}) \approx +1.2$. Our measurement, on the contrary, gives a value of ϵ_{Mo} relatively close to the value $-1.22 + 25i$ reported in [11].

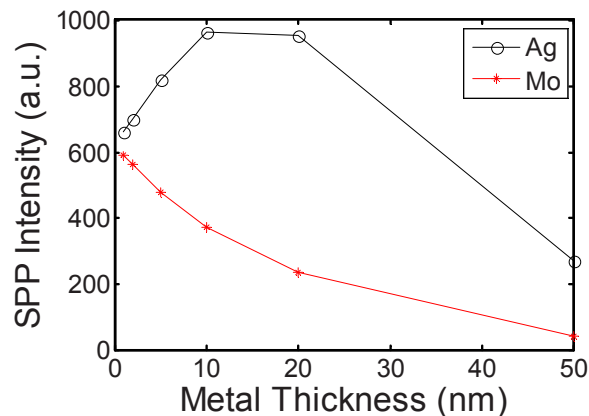


Fig. 4. Intensity of the SPP mode at the metal / air interface as a function of the metal thickness in the case of silver and molybdenum, calculated at $\lambda = 660$ nm. For each thickness the intensity is calculated by adding the contribution for θ_i varying from 40° to 70°

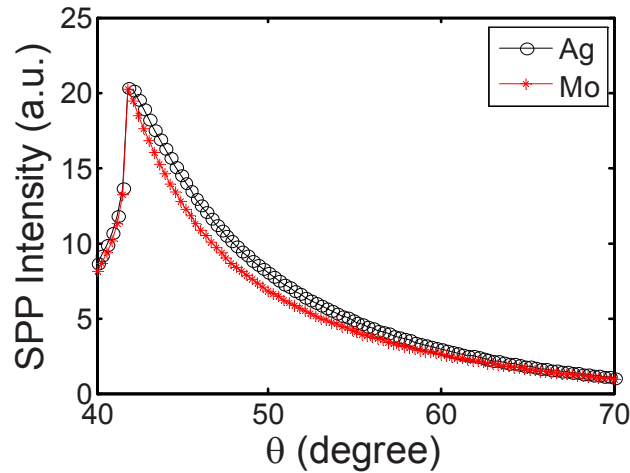


Fig. 5. Intensity of the SPP mode at the metal / air interface as a function of incidence angle θ_i in the case of silver and molybdenum, calculated at $\lambda=660$ nm and for 1 nm thick metals.

So from our measurements we conclude that ϵ_{Mo} is negative, i.e. consistent with the presence of SPP modes at the Mo / silicon interface in the regime relevant for light trapping in silicon cells, though the imaginary part of ϵ_{Mo} is quite large, i.e. the dissipative component is important compared, for example, to the case of silver ($\text{Im}(\epsilon_{Ag})=2.62$ at 660 nm [9]).

We have used the model with the corrected value of ϵ_{Mo} to evaluate the intensity of the SPP mode at the metal / air interface as a function of the metal thickness and of the incidence angle, in the case of silver and molybdenum. For the silver layer we used the value $\epsilon_{Ag} = -18.78 + 2.62i$ at 660 nm, as reported in fair agreement in [9] and [13]. The results are reported in Fig. 4, which shows the SPP intensity as a function the metal thickness. The SPP intensity is evaluated by calculating the integral of the SPP intensity for θ_i varying from 40° to 70°. Silver shows a maximum, while molybdenum shows a monotonic increase as the metal thickness decreases. The difference between the two metals is due to the much larger imaginary part of molybdenum: for silver the losses are much lower so for "intermediate" metal thicknesses there is a destructive interference between the leakage radiation into the prism of the SSP mode and the reflected part of the excitation, which enhances the observed metal / air SPP mode [14]. However, for ultra-thin metals one expects to have very similar values of SPP intensities for Ag and Mo. Fig. 5 in particular reports the SPP intensity as a function of θ_i in the case of 1 nm thick metals. Negligible difference is found by comparing Mo and Ag.

In [8] we have studied the effect of the deposition by sputtering of ultra-thin Mo films of different thickness on $\text{SnO}_2:\text{F}$ TCO layers of AGC VU-Type glass substrates on the photovoltaic characteristics of p-i-n a-Si:H solar cells, deposited on these substrates in superstrate configuration. We find that exists an optimum value of the Mo thickness for which the internal quantum efficiency of the solar cell improves by about 10%. A significant improvement was also noted in the short circuit current, fill factor, series resistance, and power conversion efficiency. The optimum Mo thickness value was of about a few nanometer, i.e. in the range in which we find a significant intensity of SSP modes, as shown in Fig. 5.

3. Conclusions

We have presented in this study the results of the attenuated total reflection experiment for prism-molybdenum-air configuration, at an excitation wavelength of 660 nm (≈ 1.85 eV), i.e., in a regime very relevant for light trapping in a-Si:H solar cells. The reflectivity curves as a function of the angle of incidence show a cut-off for angles greater than the critical angle, due to the excitation of SPP modes at the molybdenum / air interface. The reflectivity minimum is not characterized by a sharp dip as in the case of Silver and Gold metal, due to their smaller damping as compared to molybdenum.

By fitting the reflectivity curves with analytical model we determine the value of the molybdenum dielectric constant at 660 nm, i.e. $\text{Re}(\epsilon_{Mo}) = -4.8 \pm 0.2$ and $\text{Im}(\epsilon_{Mo}) = 22.2 \pm 0.1$, which are consistent with the conditions which allows interface waves that propagate along the interface.

Based on these values of the dielectric constant we estimate that ultra-thin films of Molybdenum should provide SPP modes of comparable intensity to Silver.

Acknowledgements

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References

- [1] M. Zeman, R. A. C. M. M. van Swaaij, J. W. Metselaar, and R. E. I. Schropp, *J. Appl. Phys.* 88, 6436 (2000).
- [2] S. A. Maier, M. L. Brongersma, P. G. Kik, S. Meltzer, A. A. G. Requicha, and H. A. Atwater, *Adv. Mater.* 13, No. 19, 1501 (2001).
- [3] S. A. Maier and H. A. Atwater *J. Appl. Phys.* 98, 011101 (2005).
- [4] E. Ozbay, *Science* 311, 189 (2006).
- [5] H. A. Atwater and A. Polman, *Nature Materials* 9, 205 (2010).
- [6] G. Cannella, F. Principato, M. Foti, S. Di Marco, A. Grasso, S. Lombardo, *J. Appl. Phys.* 110, 024502 (2011).
- [7] M. Foti, G. Cannella, C. Gerardi, S. Di Marco, S. Ravesi, N. Sparta, S. Lo Verso, F. Principato, S. Coffa and S. Lombardo, *Proc. ECS Trans.* 41 (4), 15 (2011).
- [8] S. Lombardo, C. Tringali, G. Cannella, A. Battaglia, M. Foti, N. Costa, F. Principato, and C. Gerardi, *Appl. Phys. Lett.* 101, 123902 (2012); doi: 10.1063/1.4753936
- [9] Werner W.S.M., Glantschnig K. and Ambrosch-Draxl C. *Optical Constants and Inelastic Electron-Scattering Data for 17 Elemental Metals* *J. Phys. Chem. Ref. Data*, Vol. 38, No. 4, 2009
- [10] Palik, E. D. *Handbook of Optical Constants of Solids*. Elsevier. 1998.
- [11] Kirillova M.M., Nomerovannaya L.V. and Noskov M.M. *Optical properties of molybdenum single crystals*. *Soviet Physics JETP* 33, 1210–1214, 1971.
- [12] Kretschmann, E. and Raether, H. Radiative decay of non-radiative surface plasmons excited by light. *Z. Naturforschung*, 23A:2135–2136, 1968.
- [13] S. A. Maier, *Plasmonics: Fundamentals and Applications*, 2007 Springer Science, ISBN 0-387-33150-6 e-ISBN 0-387-37825-1
- [14] H. Reather, *Surface Plasmon*. Springer-Verlag. 1988.
- [15] I. Gryczynski, J. Malicka, Z. Gryczynski and J.R. Lakowicz, *Anal. Biochem.* 2004 15; 324(2): 170–182.