

Theoretical and Experimental Study of Temperature-Dependent Spectral Properties of Multi-Layer Metal-Dielectric Nano-Film Structures

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ABSTRACT

We investigate theoretically and experimentally frequency-selective transmission and reflection characteristics of thin-film metal-dielectric multi-layer structures. The thin-film structures were deposited on glass substrates using a thermal evaporation technique, and their optical characteristics were studied in the visible and infrared frequency bands. A computational scheme based on a reiterative method for the calculation of reflection from a multi-layer stack is developed to model interference filters, polarization splitters and surface-plasmon sensors and also to study the effect of temperature change on the device characteristics. The temperature dependence is introduced in the model by taking into account the thermo-optic effect in the dielectrics and contributions from the phonon–electron and electron–electron scattering in metal layers. Detailed analysis of reflectance characteristics of thin-film stacks of various material compositions has been performed with the aim to estimate their temperature sensitivity, to achieve improved device performance and to design sensors and tunable filters.

Keywords: thin film filters, optics of metals, surface plasmon resonance, thermal effects, thermo-optic tuning.

1. INTRODUCTION

Functional optical devices based on multi-layer thin-film structures range from simple one-layer anti-reflection coatings to narrow-band interference filters to laser mirrors and surface-plasmon resonance biosensors [1, 2]. For many practical applications (e.g. for designing devices for use in adverse temperature environments or mirrors for high-power lasers) it is necessary to estimate temperature sensitivity of optical characteristics of multi-layer stacks. Temperature variations cause change of the layers permittivities and thicknesses and thus affect reflection and transmission characteristics of the structure. A combination of these effects may result in the temperature-induced instability of the performance of thin-film interference filters or sensors, which may be compensated by alternating layers of materials with positive and negative thermo-optic coefficients [3]. On the other hand, multi-layer structures composed of materials with large thermo-optic coefficients may find use in the development of thermo-optically tunable and switchable thin-film filters and temperature sensors [4].

2. THEORETICAL MODELING OF OPTICAL CHARACTERISTICS OF THIN FILM STACKS

We consider a multi-layer structure shown in Fig. 1 (a), which is illuminated by an $\exp\{-i\omega t\}$ - monochromatic plane wave with the wavevector $\vec{k}_1 = k(\vec{e}_x\sqrt{\varepsilon_1\mu_1 - h^2} + \vec{e}_y h)$ in the x - y plane. The reflection coefficient of this structure can be calculated by the repetitive application of the following equation starting at layer $N-1$ located next to the substrate [1, 2]:

$$R_n = \frac{r_{n-1,n} + R_{n-1}e^{2ik_n d_n}}{1 + r_{n-1,n}R_{n-1}e^{2ik_n d_n}}, n = N-2, \dots, 1 \quad (1)$$

where $r_{ij}^{TM} = \frac{1 - p_{ij}^{TM}}{1 + p_{ij}^{TM}}$, $p_{ij}^{TM} = \frac{\mu_i \sqrt{\varepsilon_j \mu_j - h^2}}{\mu_j \sqrt{\varepsilon_i \mu_i - h^2}}$, $r_{ij}^{TE} = \frac{1 - p_{ij}^{TE}}{1 + p_{ij}^{TE}}$, $p_{ij}^{TE} = \frac{\varepsilon_i \sqrt{\varepsilon_j \mu_j - h^2}}{\varepsilon_j \sqrt{\varepsilon_i \mu_i - h^2}}$.

Temperature and frequency dispersion of the refractive indices of dielectric layers can be described by using the modified Sellmeier equation with temperature-dependent coefficients [5]:

$$n^2(\lambda) = 1 + \sum_{i=1}^3 \frac{S_i \lambda^2}{\lambda^2 - \lambda_i^2}, \quad S_i(T) = \sum_{m=0}^M S_{i,m} T^m, \quad (2)$$

where S_i and λ_i are the strength and the wavelength location of the absorptive resonances in the material, respectively. In most cases, the Sellmeier model provides accurate description of the refractive index dispersion if only three terms in the summation (2) are taken into account: two of them (located in the ultraviolet part of the spectrum) represent electron transition absorption and the third one (in the infrared) represents the lattice vibration absorption [5]. The complex frequency-dependent permittivity of metal layers can be described by using the classical Drude model [6]:

$$\varepsilon = \varepsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i\omega_\tau)}. \quad (3)$$

Here, ε_∞ is the relative dielectric constant at high frequencies, ω_p and ω_τ are the plasma frequency and the collision frequency, respectively, ω is the angular frequency (e.g., for silver (Ag), $\omega_p/(2\pi) = 2175$ THz and $\omega_\tau/(2\pi) = 4.35$ THz) [6]. Both, plasma frequency and collision frequency vary with temperature [7]. The temperature variation of the plasma frequency owing to volumetric effects can be written as follows:

$$\omega_p(T) = \omega_{p0} \left(1 + \alpha(T - T_0)\right)^{-1/2}, \quad (4)$$

where α is the expansion coefficient of the metal and T_0 is the reference temperature (usually taken as the room temperature). The temperature dependence of the collision frequency can be attributed to a combination of two factors: phonon–electron scattering and electron–electron scattering:

$$\omega_\tau(T) = \omega_{\tau p}(T) + \omega_{\tau e}(T). \quad (5)$$

The phonon-electron scattering contribution $\omega_{\tau p}$ can be described by using the Holstein model:

$$\omega_{\tau p}(T) = \omega_0 \left(\frac{2}{5} + 4 \left(\frac{T}{T_D} \right)^5 \int_0^{T_D/T} \frac{z^4 dz}{e^z - 1} \right), \quad (6)$$

where T_D is the Debye temperature of the metal. The electron–electron scattering frequency $\omega_{\tau e}$ dispersion can be taken into account by the model proposed by Lawrence as follows:

$$\omega_{\tau e}(T) = \frac{\pi^4}{6} \frac{\Gamma \Delta}{h E_F} \left((k_B T)^2 + \left(\frac{h\omega}{4\pi^2} \right)^2 \right). \quad (7)$$

The model parameters for silver and gold used in numerical simulations were taken from Ref. 7.

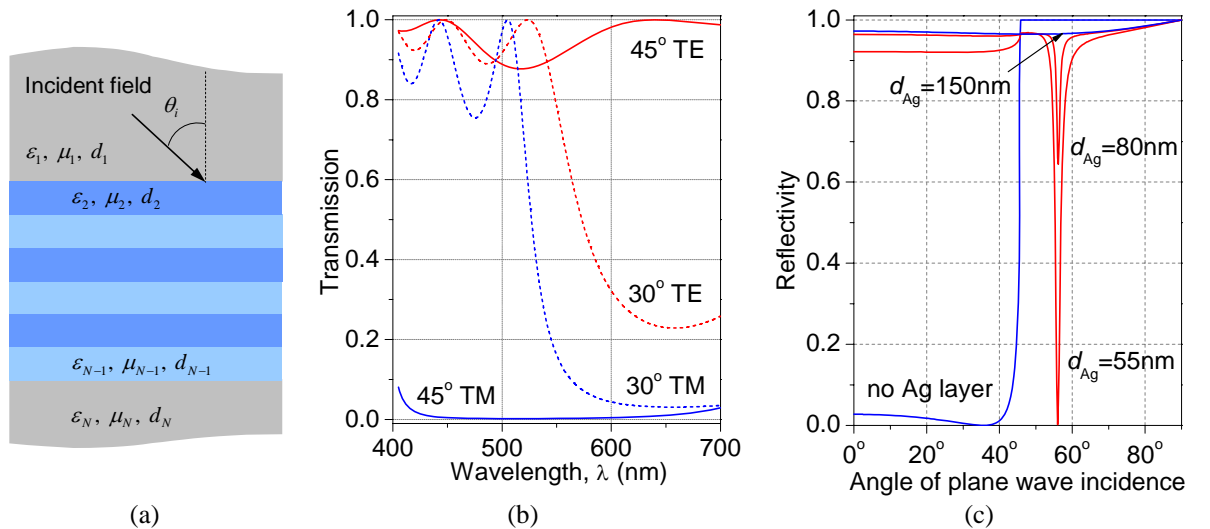


Figure 1. (a) Schematic of a multi-layer thin-film stack. (b) Transmission performance of MacNeille beam splitter for two polarizations and two incident angles: 45 and 30 degree (the structure composition: Schott SF7 glass, $d_1(\text{ZnS}) = 63$ nm, $d_2(\text{MgF}_2) = 177$ nm, $d_3(\text{ZnS}) = 63$ nm, $d_4(\text{MgF}_2) = 177$ nm, $d_5(\text{ZnS}) = 63$ nm, $d_6(\text{MgF}_2) = 177$ nm, $d_7(\text{ZnS}) = 63$ nm, Schott SF7 substrate). (c) Reflectance as a function of the angle of incidence for a surface plasmon resonance sensor based on the Kretschmann configuration: Schott SF11 glass - Ag layer - water [2].

We test the developed theoretical model and software by comparing the numerical results with those either obtained by using commercial software packages or available in the literature. As the first example, we consider a MacNeille polarizing beam splitter, which can be used for the separation of unpolarized light into two orthogonal linear polarizations (Fig. 1 (b)). As can be seen from Fig. 1 (b), polarization separation functionality can be achieved at the angle of 45 degrees. These data are in excellent agreement with the results obtained by using the TracePro® software developed by Lambda Research Corporation [8]. As the second example we consider a three-layer Kretschmann-type structure for excitation of surface plasmon waves, which is composed of a silver layer sandwiched between Schott SF11 glass and water (Fig. 1 (c)). The curves in Fig. 1 (c) show the reflectance of the structure for several thicknesses of the silver film. The sharp minimum in the reflectivity curve corresponds to the excitation of the surface plasmon wave on the metal layer. This dip disappears for the case of SF11 glass - water structure (no Ag layer) or if the Ag film is too thick, in which case the structure reduces to the SF11 glass - Ag system. These results agree well with those obtained in Ref. 2.

3. FABRICATION, CHARACTERIZATION AND NUMERICAL DESIGN OF TEMPERATURE-SENSITIVE METAL-DIELECTRIC ZnS/MgF₂/Ag STRUCTURES

The multilayer structures under investigation are composed of zinc sulfide (ZnS) layers alternated by magnesium fluoride (MgF₂) layers grown on top of a single Ag layer and a glass substrate, and are designed for use in the visible and infrared regions of the spectrum. Samples were prepared by thermal evaporation technique with in-situ ellipsometry used to control the growth process, and their reflection characteristics were measured as a function of the illumination angle for both p- and s-polarized light excitation. The source of monochromatic light was a He-Ne laser of wavelength 6328 Å.

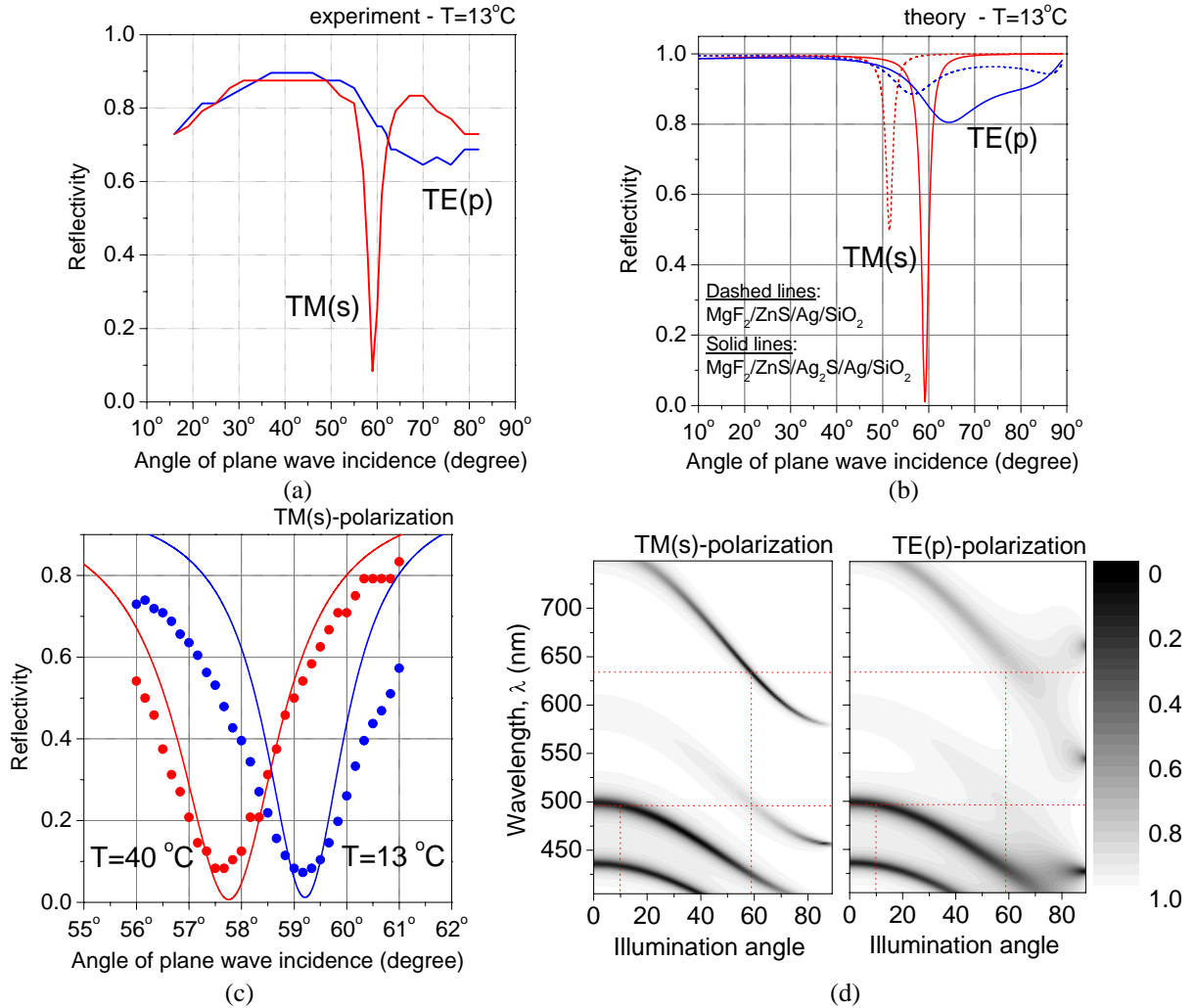


Figure 2. (a) Experimental and (b) calculated reflection coefficients for both polarizations as a function the angle of incidence (the structure composition: Air, $d_1(\text{ZnS}) = 53 \text{ nm}$, $d_2(\text{MgF}_2) = 216 \text{ nm}$, $d_3(\text{ZnS}) = 64 \text{ nm}$, $d_4(\text{MgF}_2) = 164 \text{ nm}$, $d_5(\text{ZnS}) = 33 \text{ nm}$, $d_6(\text{MgF}_2) = 263 \text{ nm}$, $d_7(\text{ZnS}) = 24 \text{ nm}$, $d_8(\text{Ag}_2\text{S}) = 3 \text{ nm}$, $d_9(\text{Ag}) = 400 \text{ nm}$, glass substrate); (c) Shift of the dip in the TM-reflectivity curve caused by the change of temperature (line-theory, dots – experiment); (d) Reflectance as a function of wavelength and illumination angle.

A measured reflectance for one of the prepared samples is shown in Fig. 2 (a). The theoretical curves presented by dashed lines in Fig. 2 (b) were calculated by using the optical constants of the materials as given in [5-7]. Clearly, experimentally observed resonance in the TM-polarization curve is shifted to a larger angle than that given by the calculated curve. We attribute this shift to the presence of a thin layer of silver sulfide (Ag_2S) that forms on top of the silver layer in the process of ZnS deposition [9]. Introducing the Ag_2S layer between Ag and ZnS into the model (Fig. 2(b), solid lines) we achieve much better agreement with the experiment (optical constants of silver sulfide have been taken from Refs. 10). Similar discrepancies between measured and calculated reflection and transmission characteristics of structures containing silver layers have previously been explained and eliminated by taking into account the presence of thin contamination layers of either silver sulfide or MgF_2/Ag composite cermet [11]. The temperature increase causes changes of the refractive indices and thicknesses of all the layers in the stack, and as a result shifts the minimum in the reflectance curve (Fig. 2 (c)). The minimum shifts to smaller angles owing to the large negative value of the thermo-optic coefficient of Ag_2S . This effect offers possibilities to create temperature-sensitive and thermally-tunable filters and sensor devices. Finally, polarization-independent device operation can be achieved if the structure geometrical parameters as well as the operational frequency are adjusted so that the dips in the reflectance curves for both polarizations at the given wavelength coincide (see Fig. 2 (d)).

4. CONCLUSIONS

In summary, a generalized theoretical approach has been developed to model reflection and transmission characteristics of metal-dielectric multi-layer thin-film structures. A comprehensive theoretical and experimental study of temperature-dependent spectral properties of ZnS/ $\text{MgF}_2/\text{Ag}_2\text{S}/\text{Ag}$ thin-film stacks has been performed. Large temperature-induced shifts of angular position of the minima in reflectivity curves of thin-film stacks have been observed. These observations pave the way for designing temperature-sensitive and thermally tunable and switchable optical elements.

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REFERENCES

- [1] P. H. Lissberger: Optical applications of dielectric thin films, *Rep. Prog. Phys.*, vol. 33, pp. 197-268, 1970.
- [2] P. Lecaruyer, E. Maillart, M. Canva, and J. Rolland: Generalization of the Rouard method to an absorbing thin-film stack and application to surface plasmon resonance, *Appl. Opt.* vol. 45, pp. 8419-8423, 2006.
- [3] H. Blifford: Factors affecting the performance of commercial interference filters, *Appl. Opt.* vol. 5, pp. 105-111, 1966; B. Li, S.Y. Zhang, J.C. Jiang, D.Q. Liu, F.S. Zhang: Recent progress in improving low-temperature stability of infrared thin-film interference filters, *Opt. Express*, vol. 13, pp. 6376-6380, 2005.
- [4] L. Domash, M. Wu, N. Nemchuk, and E. Ma: Tunable and switchable multiple-cavity thin film filters, *J. Lightwave Technol.* vol. 22, no. 1, pp. 126-135, Jan. 2004.
- [5] W. J. Tروف: Temperature-dependent refractive index models for BaF_2 , CaF_2 , MgF_2 , SrF_2 , LiF , NaF , KCl , ZnS , and ZnSe , *Opt. Eng.* vol. 34, no. 5, pp. 1369-1373, 1995; G. Hawkins and R. Hunneman: The temperature-dependent spectral properties of filter substrate materials in the far-infrared (6–40 μm), *Infrared Physics & Technology*, vol. 45, pp. 69–79, 2004.
- [6] P. B. Johnson and R. W. Christy: Optical constants of the noble metals, *Phys. Rev. B*, vol. 6, pp. 4370–4379, 1972; M. A. Ordal, L. L. Long, R. J. Bell, S. E. Bell, R. R. Bell, Jr., R. W. Alexander, and C. A. Ward: Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared, *Appl. Opt.* vol. 22, pp. 1099–1119, 1983.
- [7] A. K. Sharma and B. D. Gupta: Influence of temperature on the sensitivity and signal-to-noise ratio of a fiber-optic surface-plasmon resonance sensor, *Appl. Opt.* vol. 45, pp. 151-161, 2006.
- [8] <http://www.lambdaires.com>
- [9] *Handbook of Thin Solid Film Technology*, Eds. L.I. Massel, R. Glang, McGraw Hill Company, 1970.
- [10] J. M. Bennett, J. L. Stanford, and E. J. Ashley: Optical constants of silver sulfide tarnish films, *J. Opt. Soc. Am.* vol. 60, no. 2, pp. 224-232, 1970; G. Busch: Early history chemistry of the physics and semiconductors-from doubts to fact in a hundred years, *Eur. J. Phys.*, vol. 10, pp. 254-264, 1989; M. El-Nahass, A. A. M. Farag, E. M. Ibrahim, and S. Abd-El-Rahman: Structural, optical and electrical properties of thermally evaporated Ag_2S thin films, *Vacuum*, vol. 72, pp. 453–460, 2004.
- [11] G. J. Kovacs and G. D. Scott: Optical excitation of surface plasma waves in layered media, *Phys. Rev. B*, vol. 16, no. 4, pp. 1297-1311, 1977; P. Lalanne and J. P. Hugonin: Interaction between optical nano-objects at metallo-dielectric interfaces, *Nature Physics*, vol. 2, pp. 551-556, 2006.