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APPLICATION OF VITREOUS As-S-Se CHALCOGENIDES AS ACTIVE LAYER IN SURFACE PLASMON RESONANCE CONFIGURATION

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Surface Plasmon Resonance (SPR) in four layer configuration was analyzed in this paper. Thin film, less the 400 nm thickness, of chalcogenide glass was used as 4-th layer in such SPR interaction. Software for numerical simulations was developed. Calculations are performed for the film refractive index of 2.47 and GaP coupling prism. Some chalcogenide materials, like As-S-Se or GaLaS, which exhibit photoinduced changes of the refractive index can be used as active media. Many reflectivity dips exist in such configuration as for p-polarization as for s-polarization. The later are more sensitive to the film refractive index changes that can be on the order of 10^{-4} – 10^{-5}. SPR configuration opens new possibilities for the development of optical memory devices based on chalcogenide glasses.

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Keywords: *chalcogenides, plasmon, thin-film*

1. Introduction

Today, the chalcogenide glasses (ChG) have extensive commercial applications in CD memory largely on the effect of crystal-amorphous phase changes [1] that occur at the time scale of nanosecond. In the nearest future the re-writable CD with data transfers up to 200 Mbit/s [2, 3] are predicted. The registration of the informational signal may be or on the reflectivity change up to 100 %, or on the refractive index change that may be up to 0.1. The systems based on surface plasmon resonance may achieve considerable improvement as they are sensitive to small, on the order of 10^{-4}–10^{-5} changes of the refractive index. Many optical sensors are based on the principle of SPR, among them biosensors are especially important.

Among the several SPR sensing structures, the most prominent is the Krestschmann attenuated total reflection configuration [9] in which a thin metallic layer is deposited directly on the base of a prism. In general, silica substrates are used for SPR sensing applications. SPR measurements with silica-based glass do not allow the detection in infrared (IR) wavelength region.

Chalcogenide materials are characterized by high transparency in IR region and also have high refractive index [10]. In paper [11] SPR biosensor has been set up by using chalcogenide compound $Ge_{20}Ga_5Sb_{10}S_{65}$ (called 2S2G) as coupling prism. Sensor detection limit for refractive index was $5x10^{-5}$. Another SPR experiments can be find in paper [12] were the photoinduced modifications in As_2Se_3 [13] was enhanced in SPR resonance configuration. The transmission change of planar structure was measured during the illumination with He-Ne laser. In a recent investigation of chalcogenide materials as active media in paper [14] the light-by-light modulation was demonstrated in SPR configuration. A rutile coupling prism was used in experiments. As the authors mention, the “reflectivity dip associated with SPP coupling is only observed for p-polarized light, in SPR”. As we expect, more complex resonance phenomena occur when a thin

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chalcogenide film, characterized by a high refractive index, is used as sensing media in multilayer's SRP configuration.

The aim of this article is to investigate particularities of SPR in four layer configuration with a high refractive index chalcogenide thin film. The results may be used for experimental set up with chalcogenide glasses like As-S, As-Se or Ga-La-S characterized by a high value of refractive index n_s=2.45 [15]. The results of investigation will consist in the appreciation of the possibilities of application of chalcogenide glasses as high sensitive media for optical modulators or optical storage devices.

2. Three Layer Surface Plasmon Resonance configuration – Basic theory

A SPR system set up in the conventional three layers Kretschmann arrangement is done in Fig. 1a). Four-layer configuration (Fig. 1b) was used for numerical simulations. The lower medium may be a semi-infinite ChG glass. Chalcogenide glasses are characterized by high refractive index. The GaLaS compound have the refractive index n_s=2.45 [15], As_2S_3 or other ternary compounds As-S-Se may have nearest refractive indexes.

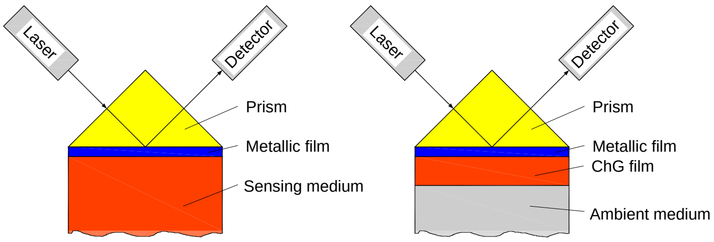

Fig. 1. 3-layer SPR configuration (left) and 4-layer SPR configuration (right). Chalcogenide glasses with finite thickness serves as active media.

In the configuration employed an incident beam undergoes total internal reflection at the prism base, generating an evanescent field that extends through the thin metal film to couple to the plasmon mode on its lower surface. The resonance corresponds to the condition when the phase velocity of light parallel to surface equalizes the velocity of density of charge excitations, named plasmon:

$$k_0 n_{pr} \cdot \sin\theta = k_0 \sqrt{\frac{\varepsilon_{mr} \cdot n_s^2}{\varepsilon_{mr} + n_s^2}} \qquad (1)$$

where n_{pr} - is the prism refractive index, n_s - is the refractive index of sensing media, that may be air, water, or above mentioned chalcogenide glasses, ε_{mr} – is the real part of metal dielectric constant. The glass medium is considered semi-infinite for the moment.

According to Drude-Lorenz model, many metals possess negative dielectric constant, but only some of them like Ag, Au, and Cu satisfy this condition in the VIS wavelength region. The calculations will be done for silver film.

At the resonance a sharp dip appear in the reflected signal due to strong light absorption by plasmon. By using the Maxwell's theory the analytical formulae for the reflection of light was obtained [9] for three layer configuration, the lower medium being considered as semi-infinite. From this formula it can be sawn that a) only p-polarized light excites plasmons and b) the coupling prism refractive index must be higher than the lower cover medium (chalcogenide glass in our case).

3. Four-layer plasmonic structure - Matrices method for numerical simulation

The physical model for optical configuration with a lower finite thickness film (Fig. 1b) corresponds to a four-layer optical system. For this configuration is impossible to obtain explicit formula for the reflectance calculation.

Explicit formulas are derived for the mean-square electric fields induced by plane electromagnetic radiation in a two-phase, three-phase, and *N*-phase stratified medium. The first (incident) and last phases are semi-infinite in extent. Boundaries separating phases are plane and parallel. Phases are isotropic with arbitrary optical constants.

However, simple relationships can be obtained by deriving the equations for the *N*-layer case in terms of characteristic matrices which can be readily programmed for a computer [16, 17]. In this formalism the tangential fields at the first boundary are related to those at the last boundary by

$$\begin{bmatrix} U_1 \\ V_1 \end{bmatrix} = M_2 \cdot M_3 \cdots M_{N-1} \cdot \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} = M \cdot \begin{bmatrix} U_{N-1} \\ V_{N-1} \end{bmatrix} \tag{2}$$

The matrices M_k have the form

$$M_k = \begin{bmatrix} \cos\beta_k & (-i\sin\beta_k)/q_k \\ (-i\sin\beta_k)q_k & \cos\beta_k \end{bmatrix} \tag{3}$$

where β_k and q_k can be computed as:

$$q_k = \sqrt{\varepsilon_k - (n_1 \sin\theta_k)^2} \tag{4}$$

$$\beta_k = \frac{2\pi}{\lambda} d_k \sqrt{\varepsilon_k - (n_1 \sin\theta_k)^2} \tag{5}$$

Here ε_k denotes the complex refractive index.

The calculated reflectivity R_p for the p-polarized has the form

$$R_p = \left| \frac{(M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N)}{(M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N)} \right|^2 \tag{6}$$

with $M_{i,j} = \left(\prod_{k=2}^{N-1} M_k \right)_{i,j} \quad i, j = 1,2$.

Similar equations may be written for the reflectivity Rs in the case of s-polarized wave. Surface Plasmon computation was accomplished in Maple and comprises two programs: the first calculates the reflectivity for different incidence angles and for several values of the thickness of the ChG layer. All results are stored in an Excel worksheet. This worksheet acts both as data storage and as pipeline for the second program that processes these data.

Software for numerical Surface Plasmon Resonance calculations of four layer structure is presented in APPENDIX.

4. Results

Calculations of the reflectivity R_p and R_s for p-polarization and respectively s-polarization were performed for a four-layer system made up of a GaP prism, a 50 nm silver layer, a ChG layer with variable thickness and air. Two different thicknesses for the ChG layer were considered: d_{ChG} = 50 nm and d_{ChG} = 250 nm. Gallium phosphate is an optically isotropic material has the refractive index n_{pr} = 3, 31 and it is transparent for the wavelength of 633 nm. It was used before for the characterization of planar chalcogenide waveguides [18, 19]. An average refractive index value for this class of ChG films was taken to be 2.47.

A remark must be done about the silver dispersion curve ε(ω).

There are many tabulated data in the literature that contains the refractive index dispersion for silver. In some cases they differ very much. The reason is in different measurements and preparation methods that are used: some of them are deduced from the electron reflectance of the bulk material surface; other are obtained from thin film transmission of electromagnetic wave. The film is usually obtained by thermal vacuum evaporation on NaCl substrate and later it is detached. The properties of Ag films that are used in SPR experiments strongly depend on the preparation technology. This is because the needed film thickness is approximately 50 nm and 25-30 nm is many the limit of film discontinuity. We used the refractive index data presented in E.D.Palik's Handbook [20]: n = 0.0575 + 4.27i. In some cases the silver optical parameters are obtained even from SPR data [21]. In paper [22] a method for the preparation of ultra-smooth Ag film is presented.

The relation between the reflectivity spectra and the incidence angle θ was studied for the 632.8 nm wavelength (HeNe laser). Reflectivity was computed for a large range of incidence angles (from 10° to 80°) with a very small step (0.005°) in order to sense the narrowest peaks and to determine accurately the peak value of the reflectivity. For each case the reflectivity was re-calculated using 1 % increased value of the ChG refractive index, also re-calculated were performed using 1 % increased value of the film thickness. The results are presented in Fig. 2 - Fig. 4.

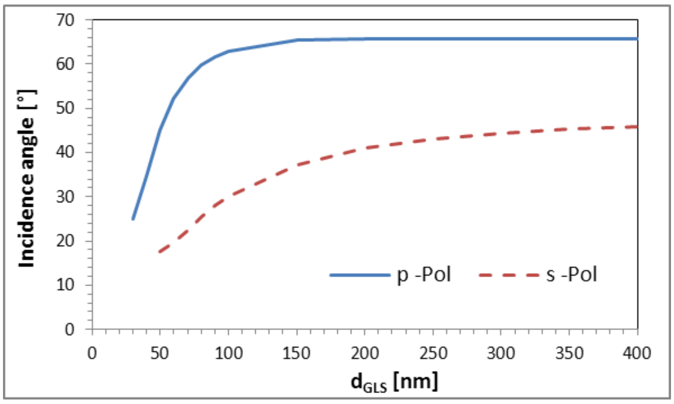

Fig. 2. Simulations of SPR angle as function of GLS film thickness. Results are for higher p-polarization (p-Pol) and higher s-polarization (s-Pol)

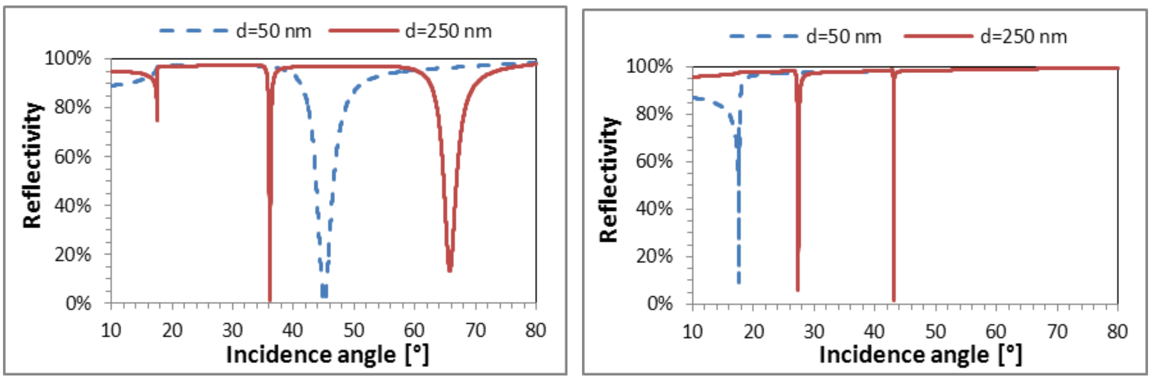

Fig. 3. SPR spectra R(θ) for all the curve of p-polarization (left) and s-polarization (right). Two GLS film thicknesses (50 nm and 250 nm) were taken into consideration. The prism was made of GaP and the considered wavelength was 632.8 nm

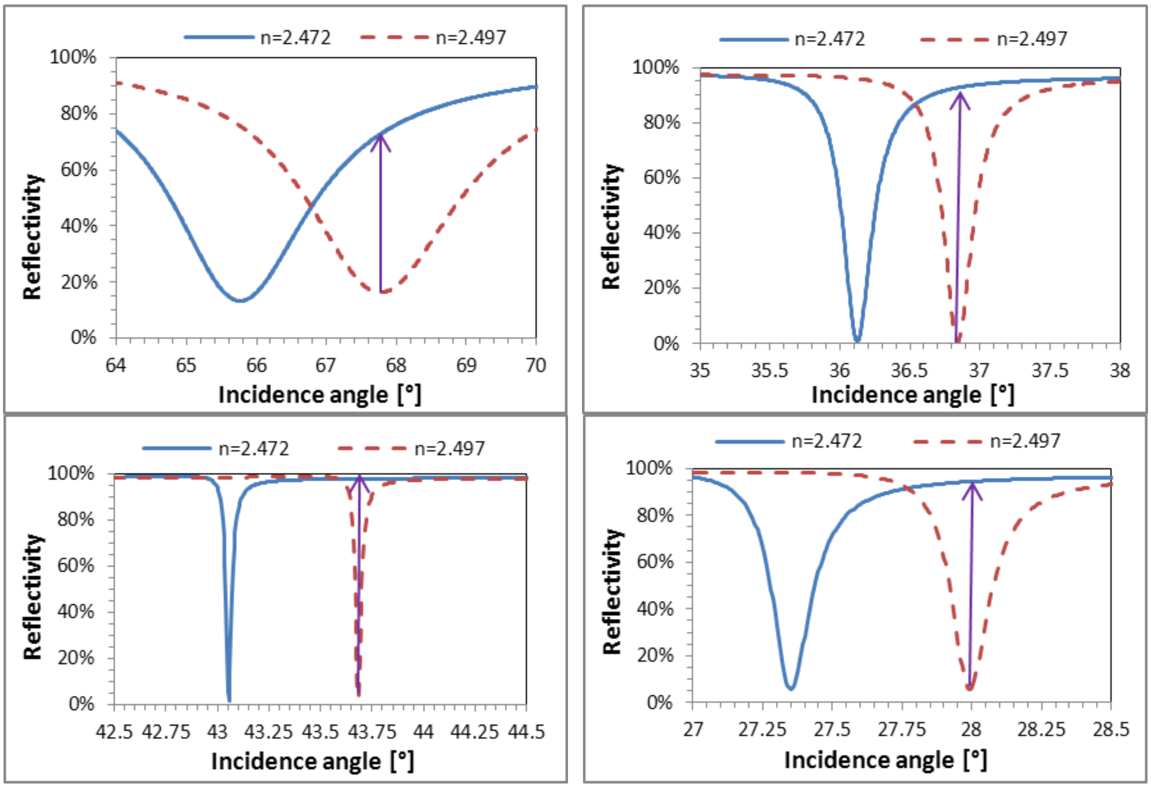

Fig. 4. Reflectivity changes for two values of ChG film refractive indices which have 1% difference. Simulations are for higher p-mode (up-left), lower p-mode (up-right), higher s-mode (down-left), lower s-mode (down-right). The prism was made of GaP and the wavelength was 632.8 nm

SPR simulations give us important information regarding experiments by use of the high refractive index films like ChG in a four layer configuration. The first one (Fig. 2) is that besides p-polarization mode, s-polarization modes are exited. For low thicknesses values the resonance angle lowers also up to 20-30°. It means that silica glasses (n = 1.5) may be used as prism material for film thicknesses on the order of 50 nm.

As SPR spectra denote (Fig. 3) two or more resonance peaks appear besides the main plasmonic mode that corresponds to p-polarization wave and the incident angle of 65.8°. The new resonances have sharp dips that correspond to coupled plasmon-waveguide modes. One of the first theoretical predictions of hybrid mode was done in papers [23, 24, 25].

In order to compare the SPR sensing capacities for the changes of the ChG refractive index, an intrinsic quality factor $Q_s = \Delta\theta/\delta$ has to be defined. Here $\Delta\theta$ is the resonance angle change for a 1% refractive index change of ChG film and δ is FWHM of the reflectance dip. The simulations results are presented in Fig. 4. The most significant shift is for the higher angle s-mode (Fig. 4, down-left). The full sensitivity depends generally on registration schematic and usually 0.1% is achieved in the differential set up measurements. With these admittance, we estimate the sensitivity for registration of ChG film refractive index modifications on the order of 10^{-4} – 10^{-5}, that is 1/1000 smaller than the refractive changes of 0.1 as it is required in the actual CD technology.

5. Conclusions

In this paper, a software use matrices method for finding the surface plasmon modes in a four-layer thin-film structure was developed. Numerical simulations concerning SPR spectra with a ChG film as active media were performed. Besides the basic plasmonic resonance that appears at 65 deg., new resonance exists at lower angle as for p-polarization and for s-polarization. The s-polarization and lower angle p-polarization resonances correspond to bound plasmon-planar waveguide modes that may be of TE or TM type. The shape of resonance dip for s-polarization is in general sharper that improve sensibility to refractive index changes. The expected sensitivity of SPR configuration for the ChG film refractive index changes is on the order of $10^{-4} – 10^{-5}$, opening the possibilities of use new low energy mechanisms for optical memory devices based on chalcogenide glasses.

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References

[1] M. Popescu, J. Optoelectron. Adv. Mater. **7**, 2189 (2005)
[2] M. Wuttig and N. Yamada, Nature Mater. **6**, 824 (2007)
[3] S.R. Ovshinsky, D.Strand, D.Tsu, U.S. Patent no. 7292521, (2006)
[4] T.J. Wang, C.W. Tu, F.K. Liu, H.L. Chen, IEEE Photon. Technol. Lett., **16,** 1715 (2004)
[5] R. Jha, S. Chand, B.D. Gupta, Sens. Actuator B-Chem., **123**, 661 (2007)
[6] Abbas A., Linman M.J., Cheng Q., Sens. Actuator B-Chem., **156,** no.1, 169 (2011)
[7] Z. Salamon, H.A. Macleod, G. Tollin, Biochim. Biophys. Acta, **1331**, no.2, 117 (1997)
[8] E. Matveeva, J. Malicka, I. Gryczynski, Z. Gryczynski, J.R. Lakowicz, Biochem. Biophys. Res. Commun., **313,** 721 (2004)
[9] Erwin Kretschman, Z.Physik, **241**, 313 (1971)
[10] M.A. Popescu, Non-crystalline chalcogenides, Kluver Academic Publicher, Durdrecht, (2000)
[11] J. Le Person, F. Colas, C. Compère, M. Lehaitre, M.-L. Anne, C. Boussard-Plédel, B. Bureau, J.-L. Adam, S. Deputier, M. Guilloux-Viry, Sens. Actuator B-Chem., **130**(2), 771 (2008)
[12] S. Charnovych, S. Kokenyesi, Gy. Glodán, A. Csik, Thin Solid Films, (2011), doi:10.1016/j.tsf.2011.02.023
[13] A.M. Andries, M.S.Iovu, Moldavian J. Phys. Sci., **2**, 246 (2003)
[14] Zsolt L. Sámson, Shih-Chiang Yen, Kevin F. MacDonald, Kenton Knight, Shufeng Li, Daniel W. Hewak, Din-Ping Tsai, Nikolay I. Zheludev, P hys. Status Solidi RRL, **4**(10), 274 (2010)
[15] A.A. Popescu, D.Savastru, S.Miclos, V.Braic, M.Popescu, A.Manea, A.Kiss Dig. J. Nanomater. Biostruct., **6**, no. 2, 341 (2011)
[16] W. N. Hansen, J. Opt. Soc. Amer., **58**, no.3, 380 (1968)
[17] H.A. Macleod, Thin-film Optical Filters, McGrow Hill, New York, 1988
[18] A.A. Popescu, D. Savastru, S. Miclos, J. Optoelectron. Adv. Mater. **13(**3), 213 (2011)
[19] A.A.Popescu, D. Savastru, S. Miclos, J. Optoelectron. Adv. Mater. **12**(5), 1012 (2010)
[20] Edward D. Palik, Handbook of Optical Constant of Solids, Academic Press (1998)
[21] J.H. Gu, Z.Q. Cao, Q.S. Shen and G. Chen, J. Phys. D: Appl. Phys., **41**, 155309 (2008)
[22] W. Chen, K.P. Chen, M.D. Thoreson, A.V. Kildishev and V.M. Shalaev, Appl. Phys. Lett., **97**, 211107 (2010)
[23] Mihalache D., Baboiu D.M., Ciumac M., Opt. Quantum Electron., **26**, no. 8, 857 (1994)
[24] Ciumac M., Mihalache D., J. Opt. Soc. Am. A-Opt. Image Sci. Vis., **12,** no. 8, 1695 (1995)
[25] Zdzislaw Salamon, H. Angus Macleod, and Gordon Tollin, Biophys. J., **73**, 2791 (1997)

APPENDIX

Surface Plasmon

Input data: ns - number of surfaces, λ - wavelength

$> with(LinearAlgebra) : Digits := 16 : ns := 4 : \lambda := 632.8e{-9} : \omega := evalf\left(\frac{2\cdot\pi}{\lambda}\right);$

$with(ExcelTools) : \varphi 0 := 10.0 : \varphi 1 := 80.0 : imax := \mathrm{round}(200\cdot(\varphi 1 - \varphi 0));$

$kmax := 1 : d30 := 350e{-9} : d31 := 400e{-9} : dk := \frac{d31 - d30}{kmax} :$

$MP := Matrix(imax+2, kmax+2) : MS := Matrix(imax+2, kmax+2) :$

$with(plots) :$

$$\omega := 9.929180321080254\ 10^{6}$$

$$imax := 14000 \qquad (1)$$

$>$

Layers: 1- GaP, 2- Silver, 3- GLS 4- Air

$$> n := \begin{bmatrix} 3.3125 \\ 0.0575 \\ 2.472 \\ 1.00 \end{bmatrix} : k := \begin{bmatrix} 0.0 \\ 4.276 \\ 0.0 \\ 0.0 \end{bmatrix} : d := \begin{bmatrix} 0.0 \\ 50e{-9} \\ d30 \\ 0.0 \end{bmatrix} : e := Vector(ns) :$$

$>$ **for** j **from** 1 **to** ns **do**

$e_j := Complex\left(n_j^2 - k_j^2, 2\cdot n_j\cdot k_j\right)$

end do

$$e_1 := 10.97265625 + 0.\ I$$

$$e_2 := -18.28086975 + 0.4917400\ I$$

$$e_3 := 6.110784 + 0.\ I$$

$$e_4 := 1.0000 + 0.\ I \qquad (2)$$

$>$ $Reflect :=$ **proc**(s) **description** "Reflectivities p and s"

local $Mp, Ms, j, qs, qp, qs1, qp1, qsn, qpn, \beta, a, b, bp, bs, cp, cs, Ap, Bp, As, Bs, rp, rerp, rs, rers;$

global $e, d, ns, \omega, Rp, Rs;$

$Mp := \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} : Ms := Mp :$

for j **from** 1 **to** $ns - 1$ **do**

$qs := \sqrt{e_j - s} : qp := \frac{qs}{e_j}$: **if** $j = 1$ **then** $qs1 := qs : qp1 := qp$: **end if**:

$\beta := \omega\cdot d_j\cdot qs : a := \cos(\beta) : b := Complex(0.0, -1.0)\cdot\sin(\beta) :$

$bp := \frac{b}{qp} : bs := \frac{b}{qs} : cp := b\cdot qp : cs := b\cdot qs :$

$Mp := evalf\left(Multiply\left(Mp, \begin{bmatrix} a & bp \\ cp & a \end{bmatrix}\right)\right) : Ms := evalf\left(Multiply\left(Ms, \begin{bmatrix} a & bs \\ cs & a \end{bmatrix}\right)\right) :$

end do:

```
qsn := sqrt(e_ns - s) : qpn := qsn/e_ns :
Ap := (Mp[1,1] + Mp[1,2]·qpn)·qp1 : Bp := Mp[2,1] + Mp[2,2]·qpn : As := (Ms[1,1] + Ms[1,2]·qsn)
    ·qs1 : Bs := Ms[2,1] + Ms[2,2]·qsn :
rp := (Ap - Bp)/(Ap + Bp) : rerp := evalf(rp·conjugate(rp)) : Rp := Re(rerp) :
rs := (As - Bs)/(As + Bs) : rers := evalf(rs·conjugate(rs)) : Rs := Re(rers) :
end proc:

> φ := Vector(imax + 1) : refp := Vector(imax + 1) : refs := Vector(imax + 1) : S
     := Vector(imax + 1) :
> for i from 1 to imax + 1 do
  φ[i] := φ0 + (φ1 - φ0)·(i - 1)/imax : S[i] := (n[1]·sin(φ[i]·π/180))^2 : MP[i+1,1] := φ[i] : MS[i+1,1] := φ[i] :
  end do:
> for kk from 1 to kmax + 1 do MP[1,kk+1] := sprintf("d=%5.2f nm", (d30 + (kk - 1)·dk)·1e9) :
     MS[1,kk+1] := MP[1,kk+1] : end do:
> for kk from 1 to kmax + 1 do
  d[3] := d30 + (kk - 1)·dk :
  for i from 1 to imax + 1 do
  s := S[i] : Reflect(s) : refp[i] := Rp : refs[i] := Rs : MP[i+1,kk+1] := Rp : MS[i+1,kk+1] := Rs :
  end do:
  end do:
> XLf := "GaP_633_7.xls" : MD := Matrix(ns + 4, 3) : MD[1,1] := λ : MD[1,2] := ns : MD[2,1] := φ0 :
     MD[2,2] := φ1 :
  MD[3,1] := imax : MD[3,2] := kmax : MD[4,1] := d30 : MD[4,2] := d31 :
  for j from 1 to ns do MD[j+4,1] := n[j] : MD[j+4,2] := k[j] : MD[j+4,3] := d[j] : end do: Export(MD, XLf,
     "Data", "A1") :
  Export(MP, XLf, "p Pol", "A1") : Export(MS, XLf, "s Pol", "A1") :
>
```

Plasmon - prelucrare date

```
> with(LinearAlgebra) : with(ExcelTools) : with(plots) : Digits := 16 :
> MP := Import("Ref.xls", "p Pol", "A1") : MS := Import("Ref.xls", "s Pol", "A1") :
> rngx := ArrayDims(MP); irng := rngx[1]; krng := rngx[2];
                         rngx := 1 ..14002, 1 ..12
                            irng := 1 ..14002
                             krng := 1 ..12                                  (1)
> imax := rhs(irng) - 2; kmax := rhs(krng) - 2
                             imax := 14000
                              kmax := 10                                     (2)
> Solp := Matrix(20, kmax + 1) : Sols := Matrix(20, kmax + 1) :
> with(ArrayTools) :
> Rp := Vector(imax + 1) : Rs := Vector(imax + 1) :
> mp := convert(MP, Matrix) : ms := convert(MS, Matrix) : vp := Vector(imax + 1) : vd
       := Vector(imax + 1) :
> vd := mp[2 .. imax + 2, 1] : vs := Vector(imax + 1) :
> for k from 1 to kmax + 1 do
   vp := mp[2 .. imax + 2, k + 1] : vs := ms[2 .. imax + 2, k + 1] :
   jp := 0 : js := 0 :
   for i from 2 to imax do
   if (vp[i] < vp[i-1]) and (vp[i] < vp[i+1]) then jp := jp + 1 : ja := 2·jp - 1 : jb := 2·jp : Solp[ja,k]
       := vd[i] : Solp[jb,k] := vp[i] : end if:
   if (vs[i] < vs[i-1]) and (vs[i] < vs[i+1]) then js := js + 1 : ja := 2·js - 1 : jb := 2·js : Sols[ja,k]
       := vd[i] : Sols[jb,k] := vs[i] : end if:
   end do: end do:
> Export(Solp, "Ref.xls", "Sol p", "A1") : Export(Sols, "Ref.xls", "Sol s", "A1") :
>
```