Indian Journal of Pure & Applied Physics
Vol. 60, March 2022, pp. 204-208

Effect of Temperature on the Surface Plasmon Resonance (SPR) Mode along a Metal - Liquid Crystal Interface

Navina Mehan

Department of Physics, Dyal Singh College (University of Delhi), Lodi Road, New Delhi -110 003, India

Received 8 October 2021; accepted 24 February 2022

The effect of temperature on the surface plasmon mode parameters for surface plasmons (SPs) excited by prism coupling along the interface of a thin silver film and homeotropically aligned liquid crystals (LCs), 5CB and UCF2[5] are theoretically studied. The change in the SPR angle of dip with temperature is found to be almost linear below the clearing temperature of the LCs. The temperature sensitivity is found to be high in the temperature range where the LC behaves as an anisotropic material. The sensitivity is found to be higher when SPR reflectance at a fixed incident angle is used as the variable parameter. The shift in SPR angle of dip is found to be linear with the change in birefringence of the LC due to the change in temperature. The change in SPR parameters with temperature is found to be much lesser in the temperature range where the LC behaves as an isotropic material.

Keywords: Surface plasmon resonance, Thin film, Prism coupling, Liquid crystal, Sensor

1 Introduction

Surface plasmon Resonance (SPR) is a sensitive technique for the development of many types of devices including sensors due to the sensitivity of the SPR characteristics to the dielectric environment in the vicinity of the interface along which the surface plasmon wave (SPW) travels. Many types of gas sensors, corrosion sensors, biosensors *etc*. based on SPR using different types of coupling techniques viz. prism coupling, coupling via optical fibers *etc*. have been developed[1-4].

Liquid crystals are an interesting class of materials due to their various interesting and different properties like an intermediate behavior between solids and liquids, orientational orders that can be manipulated by electric field, temperature *etc*.[5-7]. Jun Li *et al*.[5,6] reported changes in ordinary refractive index, n_o and extraordinary refractive index, n_e with temperature in the case of several liquid crystals and liquid crystal mixtures prepared by them. Juan Carlos Torres *et al*.[7] fabricated a temperature sensor utilizing the temperature dependence of the dielectric permittivity of a liquid crystal for different initial alignments of the optic axis of the liquid crystal (director axis) that was set during the fabrication process. Several techniques have been used to fabricate liquid crystal layers of a desired orientation on substrates[8-10].

*Corresponding author: (E-mail: navinamehan@dsc.du.ac.in)

Recently, there is a growing interest in SPR devices based on Liquid crystals (LC)[11-13]. A surface plasmon resonance (SPR) temperature sensor has been reported using hollow optical fibers internally coated with Ag and filled with liquid crystal[11]. A liquid crystal-based surface plasmon resonance (LC-SPR) biosensor *via* prism-coupling has also been theoretically proposed[12]. An optical sensor based on SPR, using LC layer for chemical and biosensors has been proposed[13].

This paper presents a theoretical study of the effect of temperature on the SPR parameters for surface plasmon waves (SPWs) excited along a metal-LC interface when the LC molecules are in homeotropic orientation *i.e*. the optic axis (OA) is perpendicular to the silver film - LC interface. The paper discusses the scope of application of a prism-coupling based SPR temperature sensor employing a thin silver film and liquid crystal mixture UCF2 reported by Jun Li *et al*.[5] and commercial LC 4-cyano-4'-pentylbiphenyl (5CB)[5]. The sensitivity of the sensor with different variable parameters, using refractive index data reported in the literature[5] is evaluated and compared.

2 Theory

The structure in Fig. 1 consists of a thin Ag film of thickness *d* on one face of a rutile prism. A liquid crystal layer can be homeotropically aligned on top of

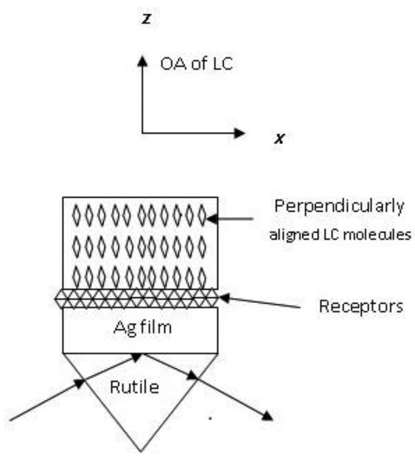

Fig. 1 — Schematic diagram of the rutile prism – Ag film – LC (semi-infinte medium) structure for homeotropic alignment of LC molecules, and incident *p*-polarized light.

the Ag film using receptors[8-10]. One of the reported techniques is to treat the substrate with copper perchlorate (Cu(ClO4)2) layer (a receptor) to homeotropically align 5CB molecules[10].

Consider a LC layer that is thick enough so that it acts as a *semi-infinite* medium. A *p*-polarized, monochromatic laser beam is incident on the one face of the prism and is internally incident on the silver film, as shown in Fig. 1. Depending on the refractive indices of the liquid crystal and the *metallic film* and the thickness of the metallic film, when the tangential component of the incident wavevector matches the surface plasmon wavevector along the silver-LC interface, a dip may be observed in the reflected intensity at the corresponding angle of incidence (θ_{SPR}) according to the equation,

$$\frac{2\pi}{\lambda} n_0 \sin\theta_{SPR} = \mathrm{Re}(k_{sp}) \quad \ldots (1)$$

where λ is the wavelength of the incident TM-polarized light, n_0 is the refractive index of the prism, θ_{SPR} is the SPR angle of dip, and Re(k_{sp}) is the real part of the surface plasmon wavevector, k_{sp}, given by :

$$\mathrm{Re}(k_{sp}) = \left(\frac{2\pi}{\lambda}\right)\left(\frac{\varepsilon_1'\varepsilon_3}{\varepsilon_1'+\varepsilon_3}\right)^{1/2} \quad \ldots (2)$$

where ε_1' is the real part of the dielectric constant of the silver film and ε_3 is the dielectric constant of the LC layer. As the temperature rises, the resulting change in the refractive indices of the LC causes a shift in the angle at which the reflection minimum occurs due to the excitation of the surface plasmon mode.

The amplitude of reflected light from the structure is derived using Fresnel's relations for the reflection coefficient at the interface of two media. Fresnel's relation for the reflection coefficient for TM polarized light at the interface of two media *l* and *m* is given by[14,15]:

$$r_{lm} = \left(\frac{k_{l,z}}{\varepsilon_l} - \frac{k_{m,z}}{\varepsilon_m}\right) \Bigg/ \left(\frac{k_{l,z}}{\varepsilon_l} + \frac{k_{m,z}}{\varepsilon_m}\right) \quad \ldots (3)$$

where ε is the dielectric constant of the corresponding layer ('*l*' or '*m*') and k_z is the normal component of the wave vector of light in that layer. In case the medium is an anisotropic medium, as is the case with the LC film, ε is replaced by ε_x, which is the dielectric constant in the *x*-direction of that layer Fig. 1. The optic axis of the rutile prism is parallel to the edge which defines its thickness, and hence perpendicular to the plane of incidence. Therefore, in case of TM light, the electric field vector is perpendicular to the optic axis of the prism. Hence, although the rutile prism is an anisotropic medium, for all practical purposes, the TM light travels as an *o*-ray in the prism.

For a uniaxial, nematic homeotropic liquid crystal i.e. for a LC with its pass axis (director) perpendicular to the surface of the LC, the normal component of the wave vector for TM waves is given by[15,16]

$$k_{za} = \frac{2\pi}{\lambda}\left(\frac{\varepsilon_o}{\varepsilon_e}\left(\varepsilon_e - n_0^2 \sin^2\theta\right)\right)^{1/2} \quad \ldots (4)$$

where ε_o and ε_e are respectively the ordinary and extraordinary dielectric constants of the anisotropic layer, θ is the angle of incidence, λ is the wavelength of incident light and n_0 is the refractive index of the medium from where the light is incident on the layered structure. In an isotropic medium of dielectric constant ε (which is metal film in this case), it is given by

$$k_z = \frac{2\pi}{\lambda}\left(\varepsilon - n_0^2 \sin^2\theta\right)^{1/2} \quad \ldots (5)$$

For a single film of thickness d_l between two media *k* and *m*, the reflection amplitude is given by[14]

$$r_{klm} = \frac{r_{kl} + r_{lm}\exp(2ik_{l,z}d_l)}{1 + r_{kl}r_{lm}\exp(2ik_{l,z}d_l)} \quad \ldots (6)$$

For a uniaxially symmetric LC, the molecular order in the direction of the director axis decreases with increase in temperature[5]. As a result, the extraordinary refractive index, n_e decreases as the temperature increases, and the ordinary refractive index n_o of the LC mildly increases with temperature[5] in the case of the two LCs under consideration[5]. At the clearing temperature, T_c, the LC becomes completely isotropic as n_o becomes equal to n_e, and hence, birefringence becomes zero. The changes in refractive index with temperature are reversible due to the unique properties of the LCs.

The effect of the receptors on the SPR parameters have been neglected in this study.

3 Results and discussion

A *p*-polarized laser of wavelength λ = 5890 Å is considered to be incident on one face of the rutile prism, which acts as the coupling prism for exciting the surface plasmons (SPs) along the silver film – homeotropic liquid crystal interface Fig. 1. The refractive index of rutile was taken as n_0 = 2.6142 and dielectric constant of silver for this wavelength was taken as n_{Ag}= (0.052 + i3.92) for calculations[17,18]. The values of the ordinary refractive index, n_o and extraordinary refractive index, n_e of the LCs at different temperatures for monochromatic light of λ = 5890 Å reported by Jun Li *et. al*[5] have been used for calculations. The sharpness and depth of the mode reflectance dip are affected by the thickness of the silver film, which was theoretically optimized to 500Å at a fixed temperature.

Theoretical SPR curves at different temperatures were obtained for SPWs excited along the silver film - LC interface in Fig. 1 *via* evanescent coupling through the Ag film, with two LC mixtures, UCF 2 and 5CB. These curves are obtained using Eqs. (3), (4), (5) and (6) with the numerical values[5] of n_o and n_e. Fig. 2 shows the reflectance v/s angle of incidence curves for the SPR modes for the liquid crystal UCF 2, at different temperatures. It is noted that the SPR curves shift steadily towards lower incident angles with increase in temperature from 291.5 K to 303.5 K. Just above the LC *clearing temperature* 305.3 K[5] for UCF 2, as n_o and n_e become equal, a sudden large angular shift in the SPR curve is observed due to the phase change of the LC to the isotropic phase. Fig. 3

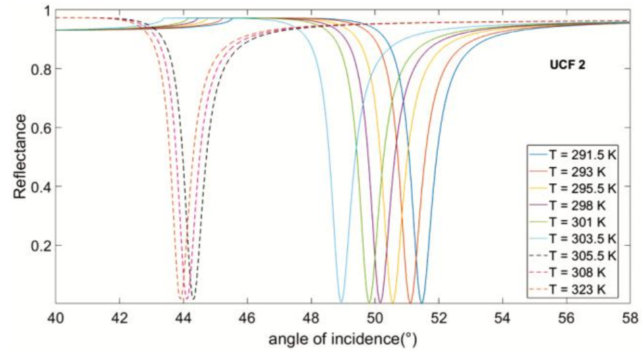

Fig. 2 — Calculated SPR reflectance curves for SPWs excited along silver film - UCF 2 interface for homeotropic alignment of LC molecules, at different temperatures.

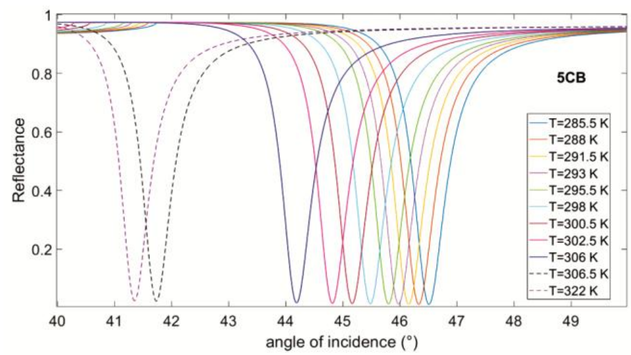

Fig. 3 — Calculated SPR reflectance curves for SPWs excited along silver film-5CB interface for homeotropic alignment of LC molecules, at different temperatures.

shows the reflectance v/s angle of incidence for the SPR modes for the LC 5CB, at varying temperatures. A similar trend is observed in this case, as for UCF 2, except for that the jump in the SPR parameters is observed above the clearing temperature 306.4 K[5] in this case. Dip reflectance, R_{min} changes very slowly with temperature in the anisotropic temperature range of the LCs and jumps to a somewhat higher value close to T_c and thereafter doesn't change much with temperature.

Changes in the *SPR angle of dip*, θ_{SPR} at different temperatures are shown in Fig. 4 for UCF 2 and 5CB. It is seen that a significant and good linear change in θ_{SPR} is observed over the whole range of temperature in which the behaviour of the liquid crystals is anisotropic. The shift in the SPR angle is by 2.531° for an increase in temperature of 12 K from 291.5 K to 303.5 K for UCF 2. The shift in the SPR angle is by 2.318° for an increase in temperature by 20.5 K from 285.5 K to 305.5 K in the case of 5CB. This also clearly shows the dependence of the SPR angle of dip θ_{SPR} on the degree of order of the molecules along the optic axis. As temperature increases, the degree of

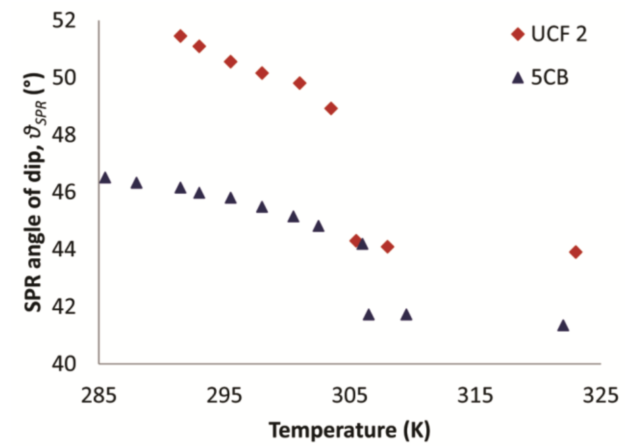

Fig. 4 — Calculated changes in the *SPR angle of dip*, θ_{SPR} with temperature for the liquid crystals UCF 2 and 5CB.

alignment of molecules aligned along the optic axis decreases and θ_{SPR} changes as observed. For a change in temperature by 2 K above 303.5 K, there is a sudden large shift in θ_{SPR} by 4.624° in the case of UCF 2. Similarly, for 5CB, as the temperature rises by 0.5 K from 306 K to 306.5 K, θ_{SPR} undergoes a sudden change by 2.469° Fig. 4. Thereafter, above the *clearing temperature* T_c of the LC, the response gradually becomes flat for both the liquid crystals, as n_e becomes equal to n_o because the changes in refractive indices with temperature for the LC are minimal above this temperature.

It is possible to calibrate the shifts in the SPR angle of dip in terms of the corresponding changes in temperature in the temperature range in which the LC behaves as an anisotropic material, thus making temperature sensing possible. The operational range of the temperature sensor using SPR angle of dip, θ_{SPR} as the varying parameter is therefore below T_c *i.e.* below 305.3 K for UCF 2 and below 306.4 K for 5CB. For an instrumental angular detection limit of 0.001^{o}, the sensitivity of the sensor calculated from Fig. 4 is of the order of 0.006 K for UCF 2. In comparison, for the same angular detection limit, the sensitivity in case of 5CB is of the order of 0.01 K, and is hence lower in comparison. This is also evident from the slope of variation of the SPR angle of dip with temperature for the two materials.

It is also possible to fix the angle of incidence, θ of the *p*-polarized laser light close to the angle of dip for a SPR curve corresponding to a particular temperature, and note the reflected intensity at different temperatures at that fixed angle. The fixed incident angle was chosen as 51.396° close to θ_{SPR} for the SPR reflectance curve at temperature 291.5 K for UCF 2, and changes in the reflectance with temperature were noted. Similarly, for a fixed incident angle 46.471° close to θ_{SPR} for the SPR reflectance curve at temperature 285.5 K in case of 5CB, reflectance v/s temperature was noted. These are shown in Fig. 5 (a,b) respectively.

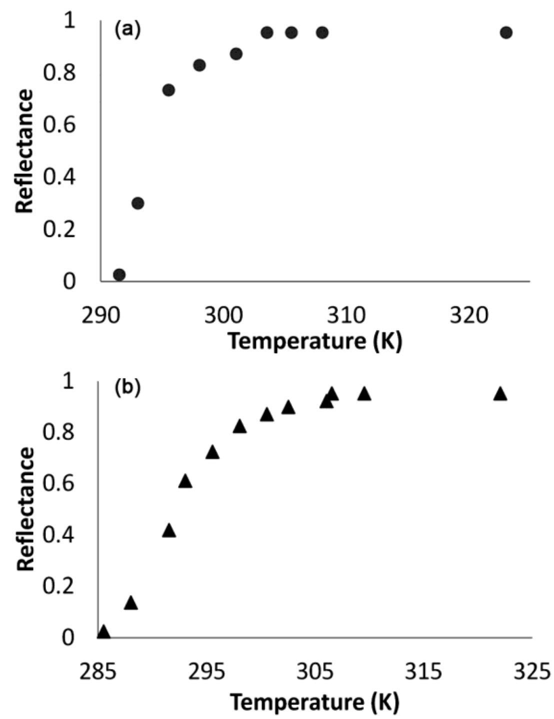

Fig. 5 — Calculated change in reflectance as a function of temperature (a) at a fixed incident angle = 51.396° close to θ_{SPR} for the SPR reflectance curve at temperature 291.5 K for UCF 2 and (b) at a fixed incident angle = 46.471° close to θ_{SPR} for the SPR reflectance curve at temperature 285.5 K for 5CB, as a function of temperature.

It can be seen from the curves in Fig. 5 that the change in reflectance at a fixed incident angle close to θ_{SPR} is almost linear over a small range of temperature, for both the materials. The reflectance at the fixed angle changes significantly and more or less linearly from 0.028 at 291.5 K to 0.83 at 298 K in the case of UCF 2 and from 0.026 at 285.5 K to 0.83 at 298 K for 5CB. Beyond this temperature range, the curves tend to become flat for a particular fixed angle. For a least count of 0.001 mW of the Laser power detector, and with an incident Laser power of 5 mW, the temperature sensitivity in this small range, as calculated from Fig. 5 is found to be of the order of 0.0016 K in the case of UCF 2 and 0.0030 K in the case of 5CB. Therefore, temperature may be measured with a higher sensitivity in this case, as

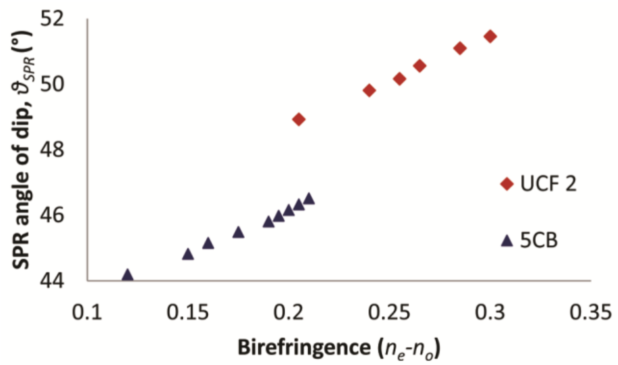

Fig. 6 — Change in the SPR angle of dip, θ_{SPR} with change in birefringence of UCF 2 and 5CB due to change in temperature.

compared to that with the SPR angle of dip as the parameter, albeit over a smaller range. The range of temperature over which the curves in Fig. 5 are linear is found to be about 6.5 K for UCF 2 and 12.5 K for 5CB. It is possible to select a SPR reflectance curve at a particular temperature and then fix the incident angle at a value close to θ_{SPR} for this curve in order to sense the temperature with a higher sensitivity in the vicinity of this temperature.

The calculated changes in the SPR angle of dip, θ_{SPR} with changes in birefringence (n_o – n_e) due to change in temperature are shown in Fig. 6. It is noted from the figure that in the anisotropic phase of the crystal, there is a more or less linear increase in θ_{SPR} with birefringence, as temperature decreases. Moreover, although the absolute values of n_o and n_e are different for both the LCs, the rate of change of θ_{SPR} with birefringence is quite close for both the materials. For a change in birefringence of 0.1 with temperature, the change in θ_{SPR} is about 2.7° for UCF 2 and 2.5° in the case of 5CB Fig. 6.

4 Conclusions

The scope of application of SPR modes excited along the interface of a silver film and two homeotropic LCs for temperature sensing has been theoretically studied. It is found that the sensors are highly sensitive using both SPR angle of dip and SPR reflectance at a fixed incident angle as parameters. The sensors are reversible but effective only in the anisotropic range of the LC. The sensitivity is higher using the LC mixture UCF 2 as compared to 5 CB. However, the range for measuring with higher sensitivity is more in the case of 5CB. The change in SPR angle of dip is found to be linear with change in birefringence as temperature varies. The data of refractive indices of the LCs below the temperatures studied in this paper may be used for further study.

Acknowledgements

The author is grateful to Prof. M. R. Shenoy, Indian Instituite of Technology, Delhi, India, for fruitful discussions.

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