Temperature characteristics of near infrared SPR sensors with Kretschmann configuration*

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The temperature characteristics of near infrared surface plasmon resonance (SPR) sensors with Kretschmann configuration are studied theoretically and experimentally. The experimental results match with the numerical simulations in the temperature range from 10 °C to 40 °C. With the increase of temperature, the resonance angle for gas increases slightly, but that for aqueous solution decreases obviously. No matter the dielectric layer is gas or aqueous solution, the resonance peaks are both broadened.

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Surface plasmon resonance (SPR) and local surface plasmon resonance (LSPR) technologies have been widely used in biomedical engineering, food safety and environmental monitoring because of their high sensitivity, real-time analysis and sample without tags[1-3]. Up to now, most of researches are concentrated in the optimization of experimental configuration and the improvement of sensitivity and accuracy in detection, but they are lack of the influence of temperature characteristics on SPR sensor.

We discuss the effect of temperature on the performance of SPR sensor in this paper. It is well known that the change of environmental temperature affects the physical characteristics of light source, prism, metal film and sample under test. The temperature fluctuation which is not large in the interior has limited influence on the test results for qualitative analysis of accuracy, but the influence is much bigger in open air, and it should not be ignored. In practical applications, the sensor suffers from the effects of environmental temperature inevitably, especially in wild environment, where the temperature is hard to control. The change of environmental temperature affects not only the dielectric constant and the thickness of the metal film but also the refractive index of medium (here referring to prism) and dielectric layer. Therefore, it is necessary to study the temperature characteristics of an SPR sensor. Most reports on this subject are based on prism type SPR sensors[4] and visible spectrum zone[5,6]. For the different ways of stimulation, metal nano-films[7-10] and nanocomposite films[11] are used instead of traditional metal film. Up to now, there is no report at the communication wavelength of 850 nm. In this paper, we discuss the temperature characteristics of an SPR sensor operating at 850 nm theoretically and experimentally.

According to the modified Drude model[12], the dielectric function of the metal layer in an SPR sensor can be described as

$$\varepsilon(\omega)=\varepsilon(\infty)-\frac{\omega_{\mathrm{p}}^{2}}{\omega(\omega+\mathrm{i}\omega_{\mathrm{c}})}, \tag{1}$$

where $\varepsilon(\infty)$ is associated with the absorption peak at high frequency ($\omega \gg \omega_c$). ω_p and ω_c refer to plasma frequency and collision frequency, respectively. The plasma frequency changing with temperature can be described as

$$\omega_{\mathrm{p}}(T)=\omega_{\mathrm{p}}(T_0)\exp\left[-\frac{1}{2}\int_{T_0}^{T}\alpha_{\mathrm{V}}(T)\mathrm{d}T\right], \tag{2}$$

where T_0 and α_V refer to the room temperature (298.15 K, 25 °C) and the thermal volume expansion coefficient of the metal, respectively. The collision frequency consists of the electron-electron scattering ω_{ce} and the phonon-electron scattering ω_{cp}, so ω_c can be described as

$$\omega_{\mathrm{ce}}(T)=\omega_{\mathrm{ce}}+\omega_{\mathrm{cp}}=$$
$$\frac{1}{6}\pi^4\frac{\Gamma\Delta}{hE_{\mathrm{F}}}\left[\left(k_{\mathrm{B}}T\right)^2+\left(\frac{h\omega}{4\pi^2}\right)^2\right]+$$
$$\omega_0\left[\frac{2}{5}+4\left(\frac{T}{T_{\mathrm{D}}}\right)^5\int_0^{T_{\mathrm{D}}/T}\frac{z^4}{\mathrm{e}^z-1}\mathrm{d}z\right], \tag{3}$$

where E_F and T_D refer to the Fermi energy of metal elec-

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trons and the Debye temperature, respectively, Γ, Δ and ω_0 are constants related to the metal material, and for Ag, Γ=0.55, Δ=0.73 and ω_0=2.034 7×10^{13} rad/s[13]. Combining Eqs.(1)–(3), we can obtain the dielectric constant of Ag changing with the temperature as shown in Fig.1.

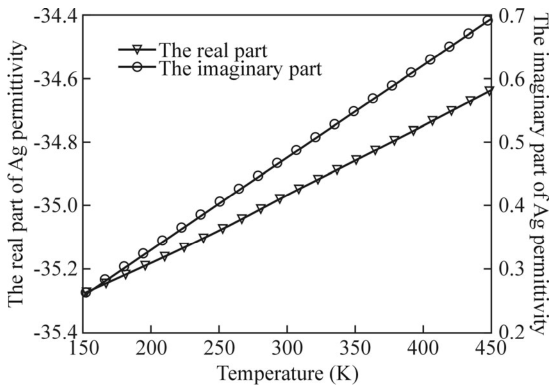


Fig.1 The real part and imaginary part of dielectric constant of Ag changing with temperature at incident wavelength of 854 nm

In addition to the influence on the dielectric constant of metal, the temperature also affects its thickness. The thickness of the metal film changing with temperature can be expressed as

$$d(T)=d_0\exp\left[\int_{T_0}^{T}\alpha_{\mathrm{L}}^{'}(T)\mathrm{d}T\right], \tag{4}$$

where d_0 is the thickness of metal film at room temperature, and $\alpha_{\mathrm{L}}^{'}(T)$ refers to the change rate of the thickness of metal with temperature, which can be written as

$$\alpha_{\mathrm{L}}^{'}(T)=\alpha_{\mathrm{L}}(T)\frac{1+\mu}{1-\mu}, \tag{5}$$

where μ is the Poisson number of the metal, for Ag, μ=0.37, and $\alpha_{\mathrm{L}}(T)=1/3\alpha_{\mathrm{V}}(T)$ is the linear thermal expansion coefficient of the metal.

The refractive indices of prism and dielectric layer vary with temperature, and can be written in the same formula of thermal coefficient as

$$n_j(T)=n_j(T_0)+(T-T_0)\times\frac{\mathrm{d}n_j}{\mathrm{d}T}\quad(j=\mathrm{p,s}), \tag{6}$$

where p and s refer to the prism and the dielectric layer, respectively, and $\mathrm{d}n_j/\mathrm{d}T$ is the thermal coefficient of the material. The prism used in experiment is made of N-BK7 glass, and water is taken as the dielectric layer. The refractive index of water can be written in an international standard formula of wavelength, temperature and density as

$$\frac{n^2-1}{n^2+2}(1/\overline{\rho})=a_0+a_1\overline{\rho}+a_2\overline{T}+$$

$$a_3\overline{\lambda}^2\overline{T}+a_4/\overline{\lambda}^2+\frac{a_5}{\overline{\lambda}^2-\overline{\lambda}_{\mathrm{UV}}^2}+\frac{a_6}{\overline{\lambda}^2-\overline{\lambda}_{\mathrm{IR}}^2}+a_7\rho^2, \tag{7}$$

where $\overline{T}=T/T^*$, $\overline{\rho}=\rho/\rho^*$, $\overline{\lambda}=\lambda/\lambda^*$, a_0–a_7, T^*, ρ^*, λ^*, $\overline{\lambda}_{\mathrm{UV}}^2$ and $\overline{\lambda}_{\mathrm{IR}}^2$ are all constants related to water.

Combining Eqs.(1)–(7) with the well-known Fresnel equations, we can obtain the simulation of the theoretical SPR curves for water at different temperatures as shown in Fig.2.

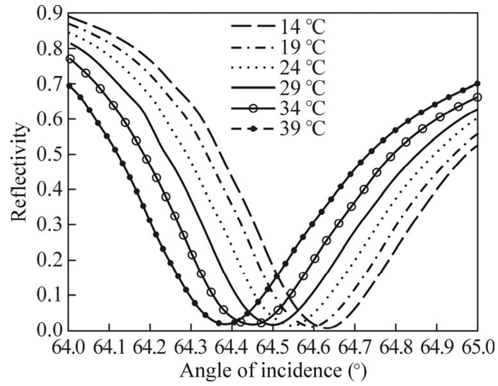


Fig.2 The theoretical SPR curves of water at different temperatures

The experimental setup is shown in Fig.3. A coaxial laser at 854 nm was employed in our system to study the temperature characteristics of the SPR sensor.

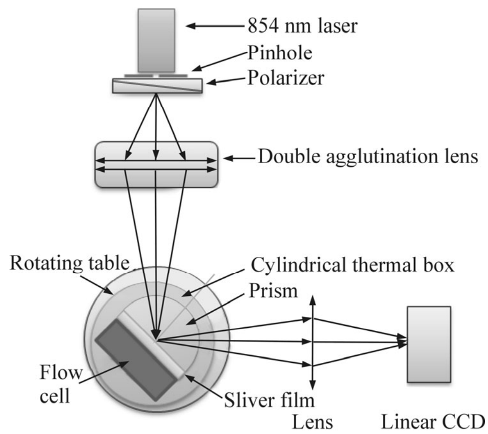
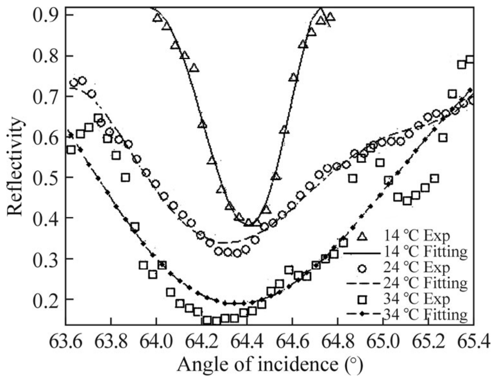
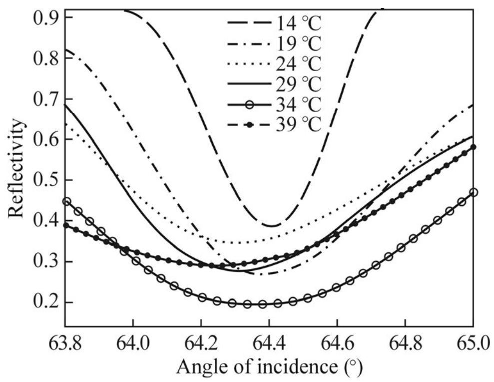


Fig.3 Schematic diagram of experimental setup

Linearly polarized beam with angular frequency of ω_0 passes through a pinhole and a polarizer. Then the beam is directed into a double agglutination lens, and reflected from the cylindrical silver-coated prism mounted on a fine tuning rotating plate. A flow cell with volume of 0.30 mL fits with the silver coating. The thickness of the silver film is 50 nm. The temperature of the sensing system is controlled by a cylindrical thermal box wound by a resistance wire and an intelligent temperature controller. A thermistor which is connected with the temperature controller is put inside the thermal box to monitor the internal temperature. The thermal box preserves the temperature inside by the resistance wire and the asbestine layer. When the internal temperature is lower than the set value, the controller connects the resistance wires to heat, otherwise drops off the power supply. We measure the reflectivity spectra with a linear charge coupled device (CCD), and carry out a series of measurements with different incident angles to obtain the SPR curves. Fig.4 shows the experimental SPR curves for water in a temperature range from 14 °C to 39 °C with the step of 5 °C.



(a) Experimental and fitting SPR curves at temperatures of 14 °C, 24 °C and 34 °



(b) The results of polynomial fitting data in temperature range from 14 °C to 39 °C with the step of 5 °C

Fig.4 Experimental SPR curves and the results of polynomial fitting data at different temperatures from 14 °C to 39 °C

Fig.5 shows the comparison of resonance angles between simulation and experiment. When the temperature increases from 14 °C to 39 °C, the resonance angle decreases.

From Fig.5, it is obvious that the resonance angles in both experiment and simulation decrease with the increase of temperature. The smaller experimental results come from the experimental system error. However, the full width half maximum (FWHM) of the SPR curve gets bigger as shown in Fig.6. The simulation values of FWHM are 0.588 1°, 0.592 0°, 0.596 2°, 0.599 5°, 0.602 8°, 0.605 2°, respectively, corresponding to 14 °C, 19 °C, 24 °C, 29 °C, 34 °C and 39 °C, which are almost the same. But the experimental value of FWHM varies with rate of 0.05°/°C. The reason might be the decreasing stability of temperature control system with the increase of temperature.

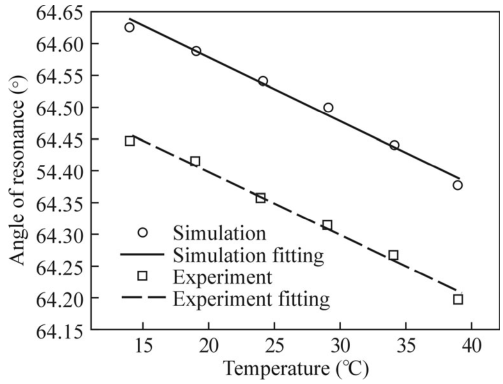


Fig.5 Resonance angle changing with temperature in experiment and simulation

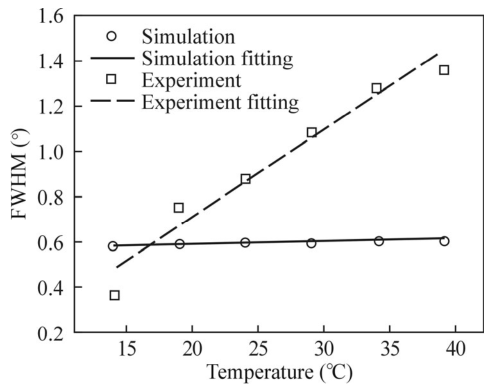


Fig.6 FWHM changing with temperature in experiment and simulation

To understand the temperature characteristics of SPR sensor, we study the SPR reflectivity spectra varying with the temperature by simulation and experiment. In both experimental and theoretical curves, we can draw the conclusion that the resonance angle decreases and the resonance pattern broadens when the temperature increases.

We take the refractive index of the sample of air as a constant (1.000 29). Then the resonance angle shift is caused by the sensor itself, that is to say, the metal film and the prism affected by temperature are the major reasons. The prism used in experiments is made of N-BK7 glass whose thermo-optic coefficient is very small (~10^{-6} /K), so the refractive index shift of prism caused by temperature is negligible. From Fig.1 we find that the real part of the dielectric constant of silver increases with the temperature, which leads to the increase of resonance angle, but it is barely distinguishable, almost remaining the same.

The thermo-optic coefficient of water is negative and much bigger (~10^{-4} /K) than that of air. Therefore, its refractive index decreasing with the increasing temperature is very obvious, as the refractive index of water at wavelength of 854 nm shown in Fig.7. The resonance angle decreases obviously with the increase of temperature in Fig.5.

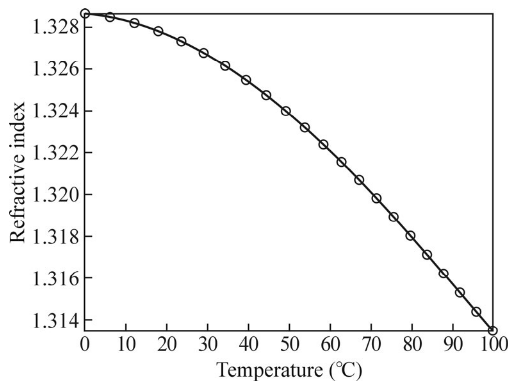


Fig.7 The refractive index of water changing with temperature at wavelength of 854 nm

The imaginary part of dielectric constant describes the absorption properties of metal for electromagnetic wave. The broadening of the resonance pattern results from the increase of the imaginary part of the dielectric constant of silver. The loss increasing with the temperature causes the resonance peak broadening.

To compare the results of experiment and simulation, we find that the match of the curves isn't perfect. There are two major reasons. Firstly, reading and adjusting the angles involve random error in our experiments, because the operations are all by hands. The oxidization of the silver film could be one of the influence factors. Secondly, the modified Drude model, the dielectric constant model we used is only accurate in low frequency band for the dielectric constant calculation, while all the beams under our investigation belong to the high frequency band.

We study the temperature characteristics of a Kretschmann configuration SPR sensor in the near infrared region theoretically and experimentally, which has a cylindrical silver-coated prism. Temperature variations change the dielectric constant of metal and the refractive indices of prism and dielectric layer, which affect the SPR sensor's performance. If the dielectric layer is gas, the impacts of the sensor itself and the dielectric layer are almost the same. For aqueous solution, the influence of the dielectric layer is much bigger than that of the sensor itself, which becomes the major factor. The resonance angle decreases when temperature increases. No matter the dielectric layer is gas or aqueous solution, the resonance peaks always broaden. For both visible and near infrared regions, the sensitivity decreases when the temperature increases for angle modulation SPR sensor. This work may lead to a better application for SPR sensor in temperature detection.

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